MODELING OF MULTICOMPONENT MULTISTAGE LIQUID-LIQUID EXTRACTION PROCESS

By

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MODELING OF MULTICOMPONENT MULTISTAGE

LIQUID-LIQUID EXTRACTION PROCESS

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NOMENCLATURE

A	transfer area, m^2
a	activity
B	bottoms mass flow rate, kg/min
C	number of components
C_E	extract concentration, kg/m^3
C_R	raffinate concentration, kg/m^3
D	top mass flow rate, kg/min, impeller diameter, m
D_C, D_d	solute diffusivity, cm^2/sec
d	drop diameter, cm
F	number of degrees of freedom
f	fugacity, atm
G	specific Gibbs free energy, J/kg-mole
g	gravity acceleration, $(kg \cdot m)/sec^2$
H	height of liquid in the vessel, m
K_a	overall mass transfer coefficient, $kg/(m^2 \cdot sec)$
K_i	distribution coefficient for component i
k_d	dispersed phase mass transfer coefficient, $kg/(m^2 \cdot sec)$
k_c	continuous phase mass transfer coefficient, $kg/(m^2 \cdot sec)$
L_j	overall down-stream mass flow rate for stage j, kg/min
LLE	liquid-liquid equilibrium
l_i	down-stream mass flow rate of component i, kg/min

M	number of stages below feed
N	total number of stages
N_{Bo}	Bond number
N_A	mass transfer rate, $kg/(m^2 \cdot sec)$
N_{Fr}	Froude number
N_{Ga}	Galileo number
N_{Re}, Re	Reynolds number
N_{Sc}, Sc	Schmidt number
N_{Sh}, Sh	Sherwood number
n_i	number of moles of component i
P, p	pressure, atm
p_i^r	reference vapor pressure for component i, atm
Q	group area parameter
R	radius, m, or gas constant, $(m^3 \cdot atm)/(kg\text{-}mole \cdot K)$
S	specific entropy, $J/(g\text{-}mole \cdot K)$ or solvent mass flow rate, kg/min
T	temperature, K, tank diameter, m
t	time, sec
U	specific internal energy, J/g-mole
U_s	slip velocity of the drop, m/sec
u	chemical potential
V	volume, m^3
V_j	overall up-stream mass flow rate for stage j, kg/min
v_i	up-stream mass flow rate of component i, kg/min
x_i	mass fraction of component i (down-stream)
y_i	mass fraction of component i (up-stream)
z_i	mass fraction of feed for component i

Greek Letters

$\beta_{i,j}$	selectivity of species i and j
γ_i	activity coefficient of component i
$\Delta\rho$	$\lvert \rho_c - \rho_d \rvert$
ϵ	eccentricity of drop
θ,σ	interfacial tension, dyn/cm
μ	viscosity, cP
ρ_c	continuous phase density, kg/m^3
ρ_d	dispersed phase density, kg/m^3
ρ_M	$\phi\rho_d + (1-\phi)\rho_c$, kg/m^3
ϕ	volume fraction
ψ	group interaction parameter
ω	oscillation frequency

Superscript

E	extract phase
G	gas phase
L	liquid phase
R	raffinate phase
*	in equilibrium with bulk concentration in the other phase

Subscripts

c	continuous phase or circulating drops
d	dispersed phase
E	extract phase
i,j,k	component i, j, and k
j	stage j
M	mean value

o oscillating drops

R raffinate phase

s stagnent drops

CHAPTER I

INTRODUCTION

Liquid-liquid extraction is one of the important mass-transfer processes used by the chemical engineer. Solvent extraction has been established as an effective and valuable technique for the study of chemical equilibria in both aqueous and organic phases. The objective of this work was to make a computer program which can simulate multicomponent (up to 30 species) and multistage (up to 2000 stages) processes. Four basic sets of equations are used to describe this process: Material balance equations, Equilibrium relationships, Summation equations for mole fractions, and Heat balance equations. These equations are often referred to as the MESH equations, as Wang and Henke (1966) put it. In addition to these equations, correlations are needed to estimate thermodynamic equilibrium constants. Since these correlations are complicated and nonlinear, it is not possible to solve the MESH equations analytically or directly. Iterative, numerical methods are used and the convergence of such methods is not always guaranteed.

The literature survey is presented in Chapter II, and the thermodynamic correlations are discussed in Chapters III and IV. The UNIFAC activity coefficient model, which is up-to-date, is adopted in the program for estimating the distribution coefficient, K. As discussed in Chapter V, the multicomponent, multistage liquid-liquid extraction column problem can be solved by two methods: the short-cut method and stage-to-stage calculations. The one assumes that the mass flow rates of all streams vary linearly; the other solves MESH equations simultaneously using the results of the short-cut method as initial values. To account for nonideality of the fluids, composition is included as an independent variable in the model. The model is formulated by 3C + 2N + 8 independent variables. But we can assume that all stage pressures and temperatures are constant; then, the number of independent variables becomes 3C+8. The equations are linearized and solved by the summation rates method. Program source code and input file information are illustrated in Appendices A and B. The UNIFAC validation is presented in Appendix C.

Depending on the number of stages and/or components, the number of equations to be solved could be in the thousands. These equations are solved iteratively, until convergence is obtained. The computational efficiency of such large problems, when programmed in Fortran 77 in a virtual storage machine, is improved by using what are known as column-oriented algorithms.

The summation rates method needs initial estimates for the independent variables. The results of short-cut calculations can be used as good initial values. The convergence characteristics of the problem depend on these initial estimates. A 'good' initial estimate is required for the success of this method. Otherwise, there can be difficulties in obtaining a converged solution. These difficulties may be due to specifications which are very nonlinear functions of the independent variables and/or the phase behavior of the mixture which is highly non-ideal.

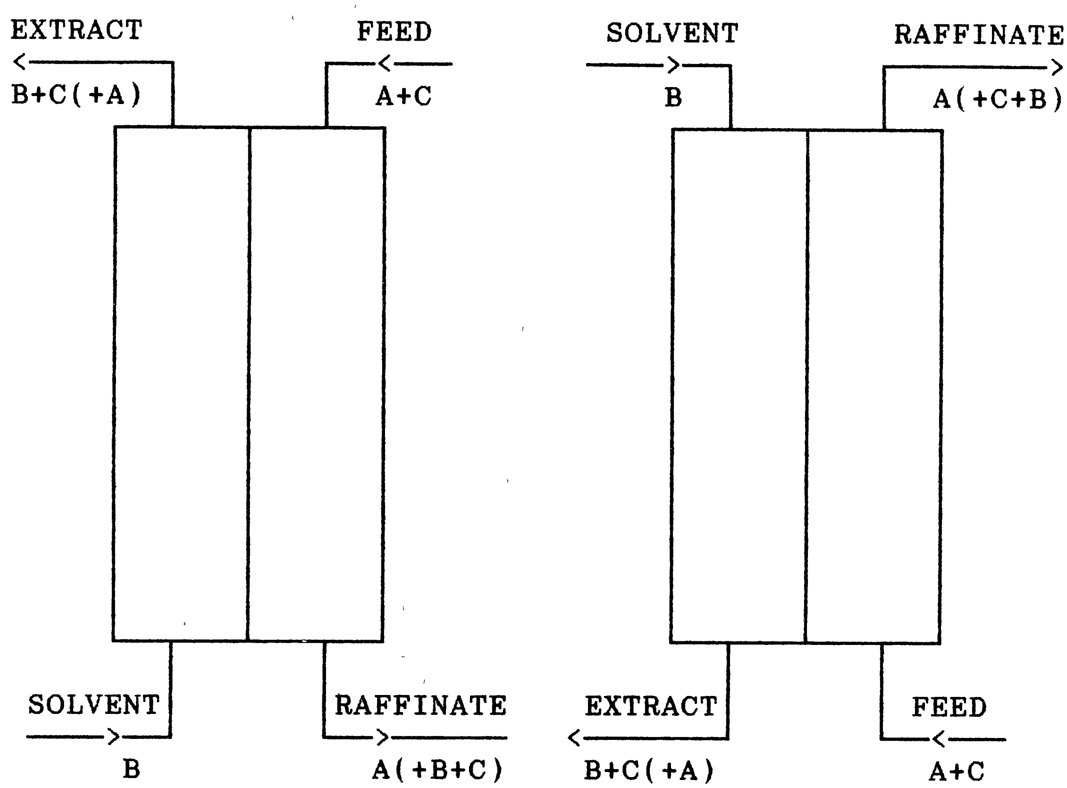
CHAPTER II

LITERATURE SURVEY

Extraction is a physical method of separation and is related to the separation by distillation, adsorption, crystallization, etc. Liquid extraction, sometimes called solvent extraction, is the separation of the constituents of a liquid solution by another insoluble liquid (Gerster, 1966).

Liquid extraction can be selective for components of a similar chemical nature, whereas distillation is selective only for components of different boiling points. Therefore, liquid extraction can separate components having similar boiling points which can only with difficulty and great expense be separated by distillation. Liquid extraction also can avoid thermal decomposition. Other advantages of liquid extraction lie in separating dilute mixtures, components that form azeotropes, etc. (Thornton, 1987). Important applications of liquid-liquid extraction are in the refining of petroleum, the processing of nuclear fuels, the purifying of vitamins and antibiotics, and the refining of vegetable oils, etc.

The basic concept of the liquid-liquid extraction is the transfer of solute from the carrier phase to the solvent



Light Solvent Heavy Solvent

A : Carrier

B : Solvent

C : Solute(Distributed Component)

Figure 1. Schematic of a Liquid-Liquid Extraction System with the Associated Nomenclature.

phase. Liquid-liquid extraction consists of four important elements: feed, solvent, extract, and raffinate. The feed is the solution which is to be extracted; the solvent is the liquid with which the feed is contacted; the extract is the solvent-rich product of the operation; and the raffinate is the residual liquid from which the solute has been removed (Dadgar, 1986).

Phase Equilibrium

The equilibrium distribution of solute between the extract phase and raffinate phase is represented by a quantity, the equilibrium ratio (distribution coefficient), K, which is analogous to that of vapor liquid systems (Alders, 1959).

$$K = \frac{g\ mole\ solute\ /\ \ell\ \ in\ the\ extract\ phase}{g\ mole\ solute\ /\ \ell\ \ in\ the\ raffinate\ phase}$$

substituting mole fractions for component C and A

$$K_C = \frac{(X_C)^E}{(X_C)^R} \quad , \qquad K_A = \frac{(X_A)^E}{(X_A)^R} \tag{2.1}$$

where, E : Extract, R : Raffinate

As in the case of vapor-liquid equilibria, numerical values of the selectivity, designated as ß, are needed, and are calculated as is the analogous property, relative volatility, for the distillation process. The selectivity ß is defined as :

$$\beta_{C,A} = \frac{K_C}{K_A} = \frac{(X_C)^E (X_A)^R}{(X_A)^E (X_C)^R} \tag{2.2}$$

and, since at equilibrium the activities of each distributed substance are the same in all phases,

$$\beta_{C,A} = \frac{(\gamma_A)^E (\gamma_C)^R}{(\gamma_C)^E (\gamma_A)^R} \tag{2.3}$$

In a system consisting of many solutes distributed between two solvents as is often found, Equations 2.2 and 2.3 can be applied to any pair of solutes.

Mass Transfer

Mass transfer between phases occurs by diffusion through the interface. The rate of diffusion of a component is dependent on, among other things, the ratio of the concentrations of this component in the two phases.

Liquid-liquid extraction can be treated as a mass transfer process, applying transport theory and the two-film concept in obtaining rate equations.

The general mass transfer equation is as follows:

$$N_A = K_A \ (\ C_E - C_R \ )_A$$

where subscript A denote species

And the mass transfer rate is correlated by Treybal (1980) as follows:

$$N_{sh,A} = \frac{k_A T}{D_A} = 0.052\ N_{Re,A}^{0.833} N_{Sc,A}^{0.5}$$

Oberg and Jones (1963) devised the rate equation(x for the raffinate phase, y for the extract phase) as follows:

$$\text{rate (Raffinate)} = k_R\ A\ (\ x - x_i\ )$$

$$\text{rate (Extract)} = k_E\ A\ (\ y_i - y\ )$$

where x and x_i denot bulk and interfacial raffinate value; y and y_i, bulk and interfacial extract value. If the transfer has reached steady state, these rates are equal; then these rate equations result in the following:

$$(y_i - y)/(x_i - x) = (-Ak_R)/(Ak_E) = -k_R/k_E$$

Mass transfer coefficient (k_d)

The rate of mass transfer of the solute(s) in liquid-liquid systems depends on the mass transfer rate during drop formation, during passage through the equipment and during coalescence. The mass transfer coefficient of the drops during passage through the equipment depends on the resistance inside the drop, at the interface and in the continuous phase. These depend on the hydrodynamic state of the liquid inside and outside the drop and principally on drop size. For stagnant drops, the Newman (1960) correlation can be used. The notation D denotes solute diffusivity in following four equations and Table I.

$$k_d = \frac{d}{6t} \ln \frac{6}{n^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-4n^2 D_d \pi^2 t}{d^2}\right), \qquad n : integer$$

For circulating drops the Kronig and Brink (1960) equation is applied.

$$k_d = \frac{17.9 D_d}{d}$$

And for oscillating drops the Rose and Kintner (1966) equation applies.

$$k_d = 0.95\, D_d^{0.5} \left(\frac{8\theta^{0.225}\, d}{d^3 (3\rho_d + 2\rho_c)}\right)^{0.25}$$

A correlation based on the concept of surface stretch, Angelo and Lightfoot (1966), is as follows:

$$k_d = \frac{4 D_d \omega (1 + t_0)}{\pi}, \qquad t_0 : initial\ time$$

The continuous phase mass transfer coefficient is generally estimated by the correlation of Garner, Foord and Bayban (1959). These have been universally accepted and are summarized in Table I.

To extend the scope of using drop mass transfer models, the drop Reynolds number ($Re = dU_s \rho_c / \mu_c$) has been suggested as a criterion for choosing the models.

Re ≤ 1.0	The stagnant drop model (Newman, 1983) is used.
50 ≥ Re ≥ 1.0	The circulating drops model (Kronig and

TABLE I

MASS TRANSFER COEFFICIENT MODELS (Jeffreys, 1987)

State of droplet	Reynolds number	Model	Equation number
		Dispersed phase coefficient	
Stagnant	Re<10	$k_{d,s} = \frac{4\pi^2 D_d}{3d_s}$ Treybal (1963)	1
Circulating	10<Re<200	$k_{d,c} = \frac{17.9 D_d}{d_c}$ Kronig and Brink (1960)	3
Oscillating	Re>200	$K_{d,o} = 0.45\ (wD_d)^{0.5}$ Rose Kintner (1966)	5
		$K_{d,o} = \frac{4wD_d(1+\epsilon_o)}{\pi}$ where $\epsilon_o = \epsilon + \frac{3}{8}\epsilon^2$ Angelo-Lightfoot (1966)	6
		Continuous phase coefficient	
Stagnant	Re<10	$Sh_{c,s} = 2.076\ (Re)^{0.5}\ (Sc)^{0.3}$ Rowe (1965)	2
Circulating	10<Re<200	$Sh_{c,c}=-126+1.8(Re)^{0.5}(Sc)^{0.42}$ Garner-Foord-Tayeban (1959)	4
Oscillating	Re>200	$Sh_{c,o}=50+0.0085(Re)(Sc)^{0.7}$ Garner-Tayeban (1960)	7

Brink) is used.

Re > 50 The oscillating drops model (Rose and Kintner) is used.

To evaluate the mass transfer coefficients of the continuous phase, the Calderbank and Moo-Young correlation (1961) for agitated vessels was used. The overall mass transfer coefficient based on dispersed phase was then obtained from the individual coefficients, k_d and k_c, by

$$\frac{1}{K_{0d}} = \frac{1}{k_d} + \frac{m}{k_c}, \qquad m = \textit{distribution ratio}$$

Solvent Selection

The choice of the appropriate solvent is the key to any successful liquid-liquid extraction process. The following are the quantities to be given consideration in making a solvent choice (Treybal, 1980).

1. <u>Selectivity</u>. This property of the solvent is defined as the ability to extract a component in the solution preferentially. The ratio of the separation factors, or selectivity, ß, is analogous to the relative volatility of distillation.

$$\beta = \frac{(\text{wt fraction C in E})/(\text{wt fraction A in E})}{(\text{wt fraction C in R})/(\text{wt fraction A in R})}$$

$$= \frac{y_B^* \ (\text{wt fraction A in R})}{x_R \ (\text{wt fraction A in E})}$$

where y_E^* is concentration of extract phase in equilibrium with bulk concentration in the other phase. For all useful extraction operations, the selectivity must exceed unity; the larger, the better. If the selectivity is unity, no separation is possible.

2. <u>Distribution coefficient</u>. This is the ratio, $k_c = (x_c)^E/(x_c)^R$, at equilibrium. While it is not necessary that the distribution coefficient be larger than 1, large values are desirable since less solvent will then be required for the extraction.

3. <u>Insolubility of solvent</u>. The mutual solubilities of solvent and solution should be low. This will aid in better solvent recovery and avoids a costly additional separation of solvent and the raffinate.

4. <u>Recoverability</u>. For economical reasons, the solvent must be recovered for reuse.

5. <u>Density</u>. A large difference in densities between the solvent and solution is necessary.

6. <u>Interfacial tension</u>. The larger the interfacial tension, the more readily coalescence of emulsions will occur but the more difficult the dispersion of one liquid in the other will be. In general, higher values of interfacial tension are preferred.

7. <u>Chemical reactivity</u>. The solvent should not change chemically.

8. <u>Viscosity, vapor pressure, and freezing point</u>. These

should be low for ease in handling and storage.

9. The solvent should be nontoxic, nonflammable and of low cost.

Typical solvents used in commercial liquid-liquid extraction process are summarized in Table II.

Equipment

Equipment used in liquid-liquid extraction is quite varied, but fortunately it can be classified according to construction and/or operational characteristics. The classification, characteristics and applications are summarized in Table III.

Selection of Equipment

Selection of a particular extractor for a separation is still largely based on experience, with some degree of risk involved. In general, it is necessary to establish the desired and/or possible solute recovery (the chemical and physical properties of the system being known) for specified flow rates. Complications arising from solids, emulsions, and easily degradable materials must be dealt with. Finally, the cost of installation, maintenance and operation must be estimated for a given extractor that most nearly meets all requirements. Advantages and disadvantages in various types of equipment are summarized in Table IV.

TABLE II

TYPICAL SOLVENTS USED IN COMMERCIAL LIQUID-LIQUID EXTRACTION PROCESS (Oberg and Jones, 1963)

Extractant	feed	solvent and remarks
CHEMICAL PROCESS EXTRACTIONS		
Isobutylene	C_4 fraction from catalytic cracker or steam cracker	Solvent:50% H_2SO_4 Remarks:Isobutylene removed from acid by distillation
Acetic acid	Submerged-fermentation liquor	Solvent:Ethyl acetate
Nickel, Cobalt	Sulfate solution	Solvent:Dinonyl-naphthalene sulfonic acid in kerosene
NUCLEAR METAL EXTRACTIONS		
Uranium from aluminum-clad spent fuel	Acid-deficient HNO_3 solution	Solvent:Methylisobutyl ketone(hexone) Remark:Redox process. $Al(NO_3)_3$ salting agent.
Uranium from ore	Sulfuric acid leach liquor	Solvent:3% dodecyl phosphoric acid (DDPA) in kerosene Remarks:HCl strips U from solvent. DDPA produced in plant.
Uranium from ore	Low quality sulfuric acid leach liquor	Solvent:Mixed secondary and tertiary amines Remarks:Amex process
PETROLEUM REFINING EXTRACTIONS		
Sulfur-containing and aromatic compounds	Diesel oil, lubricating oil, jet fuel, etc.	Solvent:Liquid SO_2 Remarks:Edelenau process. First installation in 1991; modified plants now in operation.

TABLE II (Continued)

Extractant	feed	solvent and remarks
Lubricating oil	Heavy crude residuums	Solvent:Propane Remarks:Asphaltic and resinous materials insoluble in propane.
Oil impurity	Wax-containing distillate	Solvent:Propane or mixture of ketones, benzene and toluene.
	Remarks:Solvent dewaxing process. Wax crystalizes and is filtered out.	

TABLE III

INDUSTRIAL APPLICATION OF COMMERCIAL EXTRACTORS
(Treybal, 1963)

Type of extractor	General feature	Fields of industrial Application
Unagitated columns	low capital cost, low operating and maintenance cost, simplicity in construction, handles corrosive material	petrochemical, chemical
mixer-settler	high-stage efficiency, handles wide solvent ratios, high capacity, good flexibility, reliable scale-up, handles liquids with high viscosity	petrochemical, nuclear, fertilizer, metallurgical
pulsed columns	low HETS, no internal moving parts, many stages possible	nuclear, petrochemical, metallurgical
rotary agitated columns	reasonable capacity, reasonable HETS, many stages possible, reasonable construction cost, low operating and maintenance cost	petrochemical, metallurgical, pharmaceutical, chemical
reciprocating-plate columns	high throughput, low HETS, great versatility and flexibility, simplicity in construction, handles liquid containing suspended solids, handles mixtures with emulsifying tendencies	pharmaceutical, petrochemical, metallurgical chemical
centrifugal extractors	short contacting time for unstable material, limited space required, handles easily-emulsified material, handles systems with little liquid density difference	pharmaceutical, nuclear, petrochemical

TABLE IV

ADVANTAGES AND DISADVANTAGES IN EQUIPMENT (Akell, 1966)

Equipment	Advantages	Disadvantages
Mixer-settler	1. Good contacting 2. Handles wide flow ratio 3. Low headroom 4. High efficiency 5. Many stages 6. Reliable scale-up	1. Large hold up 2. High power cost 3. High investment 4. Large floor space 5. Interstage pumping may be required
Differential contactors (Not mechanically aided)	1. Low initial cost 2. Low operating cost 3. Simplest construction	1. Limited throughput with small density difference 2. Cannot handle wide flow rate 3. High headroom 4. Sometimes low efficiency 5. Difficult scale-up
Differential contactors (Mechanically aided)	1. Good dispersion 2. Reasonable cost 3. Many stages possible 4. Relatively easy scale-up	1. Limited throughput with small gravity difference 2. Cannot handle emulsifying system 3. Cannot handle high flow rate
Centrifugal extractor	1. Handle low gravity difference 2. Low hold up volume 3. Short holdup time 4. Low space requirement 5. Small inventory of solvent	1. High initial costs 2. High operating cost 3. High maintenance cost 4. Limited number of stages in single unit

The Scale-up Problems

The scale-up problems due to the system variables in any given extractor, as shown in the following list, are the controlling factors (Treybal, 1966):

1. The chemical system, the concentration of components, and physical properties of the liquids. This includes the influence of slimes, surface active agents, and the like,
2. the total flow rate of liquids through the extractor,
3. the ratio of liquid flows,
4. the ratio of liquid flows whose liquid is continuous or dispersed,
5. the direction of extraction, either from aqueous to organic, or from dispersed to continuous phase, or vice versa.
6. the material of construction and its wetting characteristics,
7. the nature, whether rotary or pulsing, and intensity, whether fast or slow, of mechanical agitation, if any,
8. size of dispersed phase droplets and their size distribution,
9. dispersed phase hold-up,
10. intrastage recycling of liquids,
11. end effects, and
12. axial mixing, or backmixing.

Agitator Speed Effects

In the laboratory, the stirred vessel should be operated at various agitator speeds, not only to determine the effect on stage efficiency but also to determine the speed where perfect mixing occurs, for each liquid flow rate and ratio (Dickey, 1984). Dispersed-phase hold-up may be determined by quick shut-off of inlet flow and allowing the dispersion to settle out. Recycle of the smaller flow rate liquid from settler to mixer should be tried for possible enhancement of mass transfer as well as settling. Since some mass transfer occurs in the settler under conditions different from those in the mixer, an average over-all K_a for both has little significance. Therefore, a stage efficiency or K_a for the mixer alone is best determined. This may be done by the sampling of the contents through a glass or plastic (Teflon) frit, which will preferentially pass only aqueous or organic liquids, respectively, if interfacial tension is not too low or the rate of sample withdrawal is not too great. If the slope, m, of the equilibrium distribution curve is not constant, stage efficiencies should be studied at various concentration levels.

End and Backmixing Effects

End effects are probably best eliminated from the measured transfer coefficients by computing them between two levels within the packing. This may be done by withdrawing samples for analysis along the side of tower. Samples taken from the dispersed-phase inlet end for this purpose should then not be taken nearer than about 3 ft. from the inlet for the characteristic drop size to develop. Another method which has been used is to make over-all measurements (end to end) with various packed depths, but this is expensive and may lead to confusion of end effects with backmixing, which is tower-height dependent.

The effect of height on backmixing, and the end effects can presumably be eliminated on scale-up, or at least minimized, by redistributing the liquids at intervals of packed depth in the laboratory model. But the effect of tower diameter on backmixing can be eliminated only by using on the large scale a multiplicity of small-scale towers operated in parallel, which is impractical.

Minimum Agitator Speeds for Complete Liquid-Liquid Dispersion

Liquid-liquid dispersion in agitated vessels finds extensive application in mixer-settler design in extraction operations and in emulsion polymerization processes. In such work, it is necessary to ensure that the agitator speed is high enough to achieve complete dispersion of one liquid in the other. Skelland and Ramsay (1987) suggested the minimum agitator speeds for complete liquid-liquid dispersion. The few previous studies began with Nagata's (1950) work; he used an unbaffled, flat-bottomed vessel, with a centrally mounted, four-blade flat-blade turbine agitator, with T/D of 3 and a blade width of 0.06T. T denotes tank diameter, m, and D denotes impeller diameter, m, in this section. He obtained an empirical expression

$$N_{\min} = 6D^{-2/3}\left(\frac{\mu_c}{\rho_c}\right)^{1/9}\left(\frac{\Delta\rho}{\rho_c}\right)^{0.26}$$

and reported that $N_{\min}$, rev/s, minimum rotational speed of impeller for complete liquid-liquid dispersion in agitated, baffled vessels without regard to uniformity is independent of interfacial tension.

Van Heuven and Beek (1971) studied dispersion with a six-blade disk turbine in a baffled vessel. From a combination of theory and experiment, they obtained

$$N_{\min} = \frac{3.28 g^{0.83}\Delta\rho^{0.38}\mu_c^{0.08}\sigma^{0.08}(1 + 2.5\phi_{DF})^{0.90}}{D^{0.77}\rho_M^{0.54}}$$

where D/T was constant at 0.333.

The study by Skelland and Seksaria (1978) included a variety of impellers-propellers, pitched-blade turbines, flat-blade turbines, and curved-blade turbines-in a baffled vessels. They found

$$N_{\min} = C_0 D^{\alpha_0}\mu_c^{1/9}\mu_d^{-1/9}\sigma^{0.3}\Delta\rho^{0.25}$$

where H/T = 1 and ϕ = 0.5; T did not vary. The constants C_0 and a_0 are functions of the impeller type and location.

Zwietering (1958) used turbines, paddles, propellers, and vaned disks to suspend sand and sodium chloride particles in liquids in baffled vessels. He presented

$$N_{min} = C'\left(\frac{T}{D}\right)^{a'} \frac{g^{0.45}\Delta\rho^{0.45}\mu_c^{0.1}D_p^{0.2}(100R)^{0.13}}{D^{0.85}\rho_c^{0.55}}$$

where C′ and a′ : constants - shape factors

R : weight fraction of solid

D_p : particle diameter

Pavlushenko et al. (1957) used three-bladed square-pitch propellers for sand and iron suspensions to obtain

$$N_{min} = 0.105\left(\frac{T}{D}\right)^{1.9} \frac{g^{0.6}\rho_d^{0.8}D_p^{0.4}}{D^{0.6}\rho_c^{0.6}\mu_c^{0.2}}$$

Skelland and Ramsay (1987) used five common types of impellers, two generating axial flow and three radial flow, in four locations, eleven fluid systems, several tank diameters, and liquid heights, and a wide range of volume fractions of the dispersed phase. They obtained

$$(N_{Fr})_{min} = C^2\left(\frac{T}{D}\right)^{2a}\phi^{0.106}(N_{Ga}\,N_{Bo})^{-0.084}$$

where C and a are functions of the impeller type and location. The above can be rearranged to put this expression into a form similar to the other equations.

$$N_{\min} = C\left(\frac{T}{D}\right)^{a} \frac{g^{0.42}\Delta\rho^{0.42}\mu_{M}^{0.08}\sigma^{0.04}\phi^{0.05}}{D^{0.71}\rho_{M}^{0.54}}$$

where

$$\mu_{M} = \frac{\mu_{c}}{1-\phi}\left(1 + \frac{1.5\mu_{d}\,\phi}{\mu_{d}+\mu_{c}}\right)$$

Skelland and Ramsay's correlation is the best available method to predict minimum agitator speeds for complete liquid-liquid dispersion.

CHAPTER III

THERMODYNAMIC PRINCIPLES

Phase Equilibria

A number of industrially important processes, such as distillation, absorption, and extraction, bring into contact two phases which are not in equilibrium. The rate at which a species is transferred from one phase to the other depends on the departure of the system from equilibrium, and the quantitative treatment of these rate processes requires knowledge of the equilibrium states of the system (Kyle, 1984). There are two approaches to the study of phase equilibria: the phase rule and the law of distribution.

The Nature of Equilibrium

Equilibrium implies a situation in which there is no macroscopic change with respect to time. In thermodynamics, where attention is focused upon a particular quantity of material, this means no change in the properties of the material with time. Actually, a true state of equilibrium is probably never reached, not only because of continual variations in the surroundings but because of retarding resistances. Equilibrium requires a balance of all potentials that may cause a change. However, the rate of change, and hence the rate of approach to equilibrium, is proportional to the difference in potential between the actual state and the equilibrium state. Therefore, the rate of change becomes very slow as equilibrium is approached. Actually, equilibrium is assumed in scientific studies when changes can no longer be detected with the available measuring devices.

Phase Rule

There is a general rule which allows one to determine the number of independent variables that must be arbitrarily fixed so as to establish the intensive state of a system. This number is referred to as the degrees of freedom for the system, and it is given by the celebrated phase rule of J. Willard Gibbs, who deduced it by theoretical reasoning in 1875 (Smith, 1975). It is presented here without proof in the form applicable to nonreacting systems.

$$F = 2 - \pi + C \tag{3.1}$$

where, F : the number of degrees of freedom, or the number of independent variables, such as temperature, pressure, and concentration, that must be fixed to define completely a system at equilibrium.

C : the number of components, or the lowest number of independently variable constituents required to express the composition of each phase.

π : the number of phases. A phase is defined as any homogeneous part of a system, bounded by surfaces and capable of mechanical separation from the rest of the system.

The definition of these terms must be made most carefully for proper application of the rule.

Laws of Distribution

These laws attempt to synthesize the relationships among concentrations of various components in various phases of a system at equilibrium. The equilibrium stage is defined in terms of the distribution coefficient K (Storvick, 1977). The first attempt to predict K values for design purposes made use of Raoult's law.

$$K_i = \frac{y_i}{x_i} = \frac{p_i^r}{p} = \frac{(f_i^L/x_i)}{(f_i^G/y_i)} \qquad (VLE) \tag{3.2}$$

$$K_i = \frac{(x_i)_E}{(x_i)_R} = \frac{(f_i^L/x_i)_R}{(f_i^L/x_i)_E} \qquad (LLE) \tag{3.3}$$

where, subscript E : extract

R : raffinate

Fugacity and Activity

The Gibbs free energy of a pure component is defined as

$$F = H - TS = E + pV - TS \tag{3.4}$$

or, in the differentiated form,

$$dF = dE + p\,dV + V\,dp - T\,dS - S\,dT \tag{3.5}$$

Applying the first and second laws of thermodynamics, Equation 3.5 reduces to

$$dE = T\,dS - p\,dV \tag{3.6}$$

At constant temperature then

$$dF_T = V\,dp \tag{3.7}$$

where, the subscript T on dF denotes constant temperature. Using the ideal gas relation

$$V = \frac{RT}{P} \tag{3.8}$$

And substituting Equation 3.8 into 3.7, thus yields

$$dF = RT\frac{dp}{p} = RT\,d\ln p \tag{3.9}$$

The fugacity f of the substance is defined in such a manner as to preserve the form of this equation.

$$dF = RT\,d\ln f = V\,dp \tag{3.10}$$

Integrating between two conditions of pressure(p_1 and p_2) at constant temperature then gives

$$F_2 - F_1 = RT\ln\frac{f_2}{f_1} = \frac{p_2}{p_1}\,V\,dp \tag{3.11}$$

The ratio $f_2 \,/\, f_1$ is defined as the activity, a.

Activity Coefficient

The activity, a_i, of the ith component in a mixture is related to its mole fraction by the definition of the activity coefficient, γ_i, for component i (Pierotti, 1959).

$$\gamma_i = \frac{a_i}{x_i} \tag{3.12}$$

Substituting the definition of activity, then

$$\gamma_i = \frac{f_i^{L}}{f_i^{0} x_i} = \frac{f_i^{L}}{f_{i,p}^{L} x_i} \tag{3.13}$$

where $f_{i,p}^{L}(f_i^{0})$ is the fugacity of some selected reference state. Changing the form of Equation 3.13 gives

$$\frac{f_i^{L}}{x_i} = \gamma_i \, f_{i,p}^{L} \tag{3.14}$$

Equation 3.14 explains the relationship between the composition and activity coefficient.

Equilibrium Criteria

According to the second law of thermodynamics, entropy is maximum and the Gibbs free energy is minimum at the equilibrium state.

$$(dS^t)_{U^t,V^t} \geq 0 , \qquad (dG^t)_{T,P} \leq 0 \tag{3.15}$$

where, superscript t is the total property.

For every component, i, for liquid phase, E, and another liquid phase, R, the equation of equilibrium is expressed in terms of chemical potential, u_i, and the fugacity f_i :

$$u_i^E = u_i^R \tag{3.16}$$

and

$$f_i^E = f_i^R \tag{3.17}$$

When the same standard-state fugacity is used in both phases, Equation 3.17 can be written

$$(\gamma_i x_i)^E = (\gamma_i x_i)^R \qquad x_i : \textit{mole fraction} \tag{3.18}$$

Equation 3.18 is the key equation for calculation of multicomponent liquid-liquid equilibria.

<u>Gibbs-Duhem</u> <u>Equation</u>

A fundamental relation in the thermodynamics of solution is given by the Gibbs-Duhem equation :

$$S\,dT - V\,dp + \sum_{i=1}^{C} n_i\,du_i = 0 \tag{3.19}$$

Equation 3.19 related T, p, and u_i of each component present in a given phase of an heterogeneous system. At constant T and p Equation 3.19 can be written as

$$\sum_{i=1}^{C} x_i\,du_i = 0 \tag{3.20}$$

or,

$$\sum_{i=1}^{C} x_i\,d\ln\gamma_i = 0 \tag{3.21}$$

The Gibbs-Duhem equation enjoys wide application in two areas: as a basis for the development of activity coefficient models and a basis for internal consistency tests of experimental thermodynamics data.

CHAPTER IV

MODELS FOR THE ACTIVITY COEFFICIENT

Models for the activity coefficient, γ_i, must be specified in order to solve phase equilibrium problems using activity coefficients for the liquid phase behavior.

Excess Functions

Expressions for γ_i are usually derived from expressions for G^E (excess Gibbs energy) (Green, 1984). Recall

$$dG = - S\,dS + V\,dp + \sum_i u_i\,dn_i \tag{4.1}$$

also, any partial molar property, $\overline{X}$, obeys

$$\overline{X} = \sum_i x_i\,\overline{X_i} \tag{4.2}$$

so,

$$\overline{G} = \sum_i x_i\,\overline{G_i} \qquad or \qquad G = \sum_i n_i\,G_i \tag{4.3}$$

where xi denots mole fraction (from Equation 4.2 to Equation 4.8), now

$$G^E = G - G_{Ideal} \tag{4.4}$$

and

$$G^E = G_{real} - (\Sigma x_i \; G_{i(ideal)} + \Sigma x_i \ln x_i) \tag{4.5}$$

With Equation 4.3, the above equation becomes

$$G^E = \Sigma x_i \; (G_{i(real)} - G_{i(ideal)}) - \Sigma x_i \ln x_i \tag{4.6}$$

but

$$G_{i(real)} - G_{i(ideal)} = RT \ln (f_i / f_i^{\,o}) \tag{4.7}$$

so

$$G^E = RT \, \Sigma x_i \ln (f_i / f_i^{\,o} x_i) \tag{4.8}$$

or

$$G^E = RT \, \Sigma \ln \gamma_i \tag{4.9}$$

hence

$$nG^E = RT \, \Sigma n_i \ln \gamma_i \tag{4.10}$$

at T, P = constant, substituting G_i instead of u_i, Equation 4.1 becomes

$$dG = \Sigma G_i \; dn_i \tag{4.11}$$

and from Equation 4.3

$$dG = \Sigma n_i \; dG_i + \Sigma G_i \; dn_i \tag{4.12}$$

comparing Equations 4.11 and 4.12; yields

$$\sum n_i \; dG_i = 0 \qquad @ \; T, \; P \tag{4.13}$$

which can yield

$$\sum n_i \; d \ln \gamma_i = 0 \qquad @ \; T, \; P \tag{4.14}$$

Thus Equation 4.10 becomes

$$\left(\frac{\partial (nG^E)}{\partial n_k} \right)_{T,P,n_i} = RT \ln \gamma_k \tag{4.15}$$

This expression can be used for calculating the activity coefficients.

Descriptions and Comparisons of Activity Coefficient Models

Various activity coefficient models such as Van Laar, Margules, Redlich-Kister, Wilson, NRTL(The NonRandom Two-Liquid equation), UNIQUAC, UNIFAC, etc. have been developed from the nineteenth century to now. Only a few are widely used. The Van Laar, the Margules and the Redlich-Kister equations are historically important models that are not effective models now. The Wilson equation as stated in his article (1964) has several advantages; for example, it presents behavior of highly nonideal systems better than earlier models, even when they use more parameters, and it extends directly to multicomponent systems, using only binary parameters. But it cannot predict a liquid-liquid phase separation.

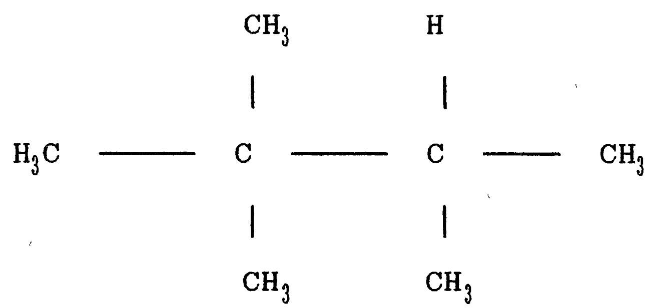
Renon (1968) explained the NRTL model based on local composition concept in his article. The advantage of this equation is that NRTL can predict the liquid-liquid phase split. This requires three parameters per binary.

Abrams (1975) suggested the UNIQUAC model based on the local composition concept in his article. The UNIQUAC equation gives good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolyte components such as hydrocarbons, ketones, esters, amines, alcohols, nitriles, water, etc. This equation is applicable also to polymer solutions. The advantage of UNIQUAC is that, for a large variety of multicomponent systems and using only two adjustable parameters per binary, reliable estimates can be made of both vapor-liquid and liquid-liquid equilibria using the same equation for the excess Gibbs energy. But this equation has a more complex form and often makes slightly poorer predictions than do the simple models for some systems (Prausnitz, 1980).

A summary of the above activity coefficient models for binary and multicomponent systems can be found in Walas's Tables 4.4 and 4.6 (Walas, 1985)

Until now, we have looked at activity coefficient models based on the local composition concept (molecules); on the other hand, there are group contribution methods.

These methods express parameters in terms of the sum of contributions from groups rather than molecules. For example,



consists of

5 - CH_3 groups

1 - CH group

1 - C group

Benzene yields six aromatic CH (ACH) groups. This method can represent very many mixtures in terms of only a few interactions. For example, "CH_3", "CH_2", and "OH" could describe all mixtures of n-paraffins and n-alcohols. The specific models for these methods are the ASOG (Analytic Solution Of Groups) method based on the Wilson equation and the UNIFAC method based on the UNIQUAC model. The UNIFAC method is probably more widely used than is the ASOG method.

The UNIFAC model was suggested by Fredenslund et al. (1975). The fundamental idea of a solution-of-groups model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. One of the main advantages of the UNIFAC method is that UNIFAC is well established to get pure group properties (Fredenslund, 1977). Another is that many of UNIFAC's parameters have been determined; in short, UNIFAC is widely applicable.

Ruiz, et al. (1986) suggested a new model for activity coefficients. This model is suggested for EGE (Excess Gibbs Energy), which is suitable for the representation of phase equilibria in chemical engineering applications and introduces a new parameter, k_{ij}, which allows a new dependence of EGE on the composition and gives an extraordinary flexibility to the model. The results obtained for the average error were always lower than those obtained by the other models such as UNIQUAC and NRTL. But few parameters have been determined; in short, the new model is not widely applicable yet.

UNIFAC Method

The fundamental idea of a solution-of-groups model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. In this method, the size and the group contributions to the activity coefficient are called the configuration; this consists of both combinatorial (C) and residual (R) contributions. The main UNIFAC equation is :

$$\ln \gamma_i = \ln \gamma_i^{C} + \ln \gamma_i^{R} \tag{4.16}$$

where

$$\ln \gamma_i^{C} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \Sigma_j x_j l_j \tag{4.17}$$

and

$$\ln \gamma_i^{R} = q_i [1 - \ln (\Sigma_j \theta_j \tau_{ji}) - \Sigma_j (\theta_j \tau_{i,j} / \Sigma_k \theta_k \tau_{kj})] \tag{4.18}$$

$$l_i = \frac{z}{2} (\gamma_i - q_i) - (\gamma_i - 1) \ ; \ z = 10 \tag{4.19}$$

$$\theta_i = \frac{q_i x_i}{\Sigma_j q_j x_j} \ ; \qquad \Phi_i = \frac{\gamma_i x_i}{\Sigma_j \gamma_j x_j} \tag{4.20}$$

and

$$\tau_{j,i} = \exp -\left(\frac{u_{j,i} - u_{i,i}}{R \ T} \right) \tag{4.21}$$

In these equations, z is lattice coordination number, a constant here set equal to ten; x_i is the mole fraction of component i, and the summations in Equations 4.17, 4.18 and 4.20 are over all components, including component i; θ_i is the area fraction, and Φ_i is the segment fraction which is similar to the volume fraction. Pure component parameters γ_i and q_i are measures of molecular van der Waals volumes and molecular surface areas. The two adjustable parameters τ_{ij} and τ_{ji} appearing in Equation 4.18 must be evaluated from experimental phase equilibrium data.

$$\gamma_i = \Sigma_k v_k^{(i)} R_k \quad and \quad q_i = \Sigma_k v_k^{(i)} Q_k \tag{4.22}$$

where $v_k^{(i)}$, always an integer, is the number of groups of type k in molecule i. R_k and Q_k are group parameters which are given by Bondi (1968).

The residual part of the activity coefficient, Equation 4.16, is replaced by the solution-of-groups concept. In Equation 4.16, we use

$$\ln \gamma_i^R = \sum_{k \atop all\ groups} v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{4.23}$$

where Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i.

The group activity coefficient, Γ_k, is found from an expression similar to Equation 4.16 :

$$\ln \Gamma_k = Q_k [1 - \ln (\Sigma_m \Theta_m \Psi_{mk}) - \Sigma_m (\Theta_m \Psi_{km} / \Sigma_n \Theta_n \Psi_{nm})] \tag{4.24}$$

where Θ_m is the area fraction of group m, and the sums are over all different groups.

$$\Theta_m = \frac{Q_m X_m}{\Sigma_n Q_n X_n} \tag{4.25}$$

where X_m is the mole fraction of group m in the mixture and Q is group area parameter. The group interaction parameter, Ψ_{mn}, are given by

$$\Psi_{mn} = \exp -\left(\frac{U_{mn} - U_{nn}}{R\ T} \right) = \exp -(a_{mn} / T) \qquad (4.26)$$

where U_{mn} is a measure of the energy of interaction between groups m and n. The group-interaction parameters, a_{mn}, (two parameters per binary mixture of groups) are the parameters which must be evaluated from experimental phase equilibrium data.

CHAPTER V

STAGED MODELING

There are two methods for stage calculations: a short-cut method and a stage-to-stage method (stripping factor method). The short-cut method calculates an approximate solution for liquid-liquid extraction problems; in this method the amounts of all streams leaving the stages are assumed to vary linearly along the vessel. On the other hand, the stage-to-stage method solves the problem while using mass and energy balances simultaneously.

Number of Variables

The general stage scheme, Figure 2. illustrates that an extraction unit with two feeds is composed essentially of two simple extraction units connected to an intermediate feed stage. The number of independent variables, F_i, associated with a feed stage has been shown to be 3C + 8. From the analysis for a simple extraction unit, F_i for the bottom section is 2C + 2M + 5 and F_i for the top section is 2C + 2(N - M - 1) + 5. These sums include the degrees of freedom necessary to specify the number of stages in each section. The combination of the three elements is

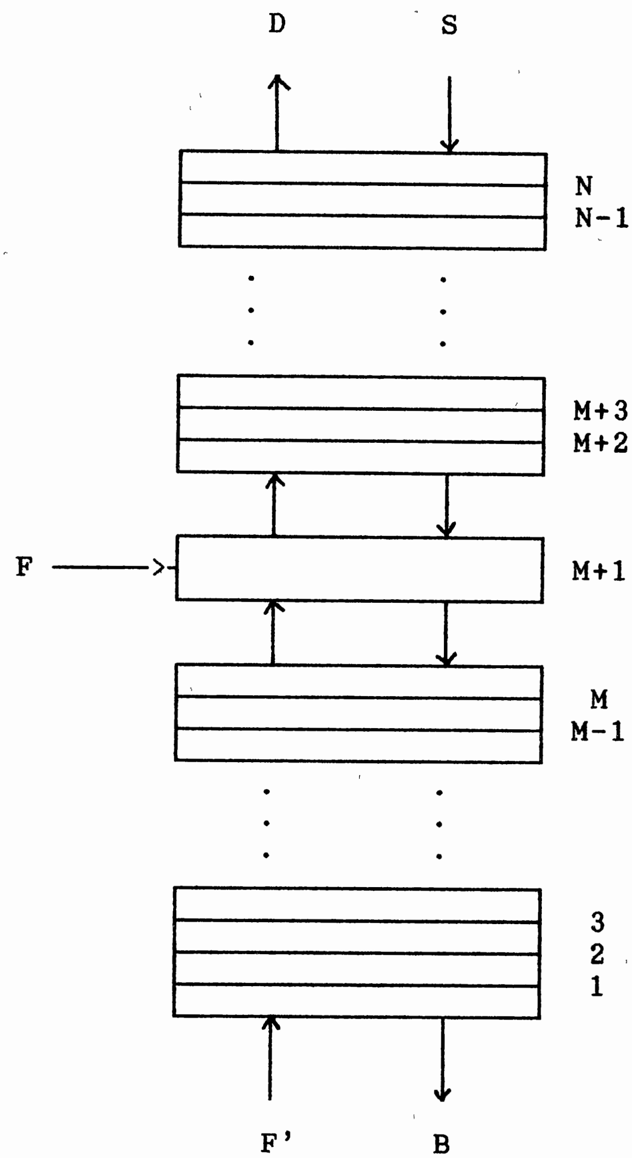


Figure 2. Extraction Unit with Two Feeds

$$F_v = (3C + 8) + (2C + 2M + 5) + [2C + 2(N - M - 1) + 5]$$
$$= 7C + 2N + 16$$

F_v : total number of independent variables

The number of restricting relationships, F_c, due to new interstreams is $4(C + 2)$ or $4C + 8$. Therefore,

$$F_i = F_v - F_c = (7C + 2N + 16) - (4C + 8)$$
$$= 3C + 2N + 8$$

The designer might specify the following variables:

Specifications	F_i
Pressure in each stage	N
Heat leak in each stage	N
S	C + 2
F	C + 2
F'	C + 2
Total number of stages, N	1
Number of stages below feed, M	1
	3C + 2N + 8

Short-Cut Method

Short-cut methods (Smith, 1960) for the approximate solution of multicomponent, multistage separation problems continue to serve useful purposes, even though electronic computers are available to provide rigorous solutions. The general short-cut equation illustrates the extraction process for two feeds and reflux at both ends as shown in Figure 3. It is a complicated case but can be solved by the short-cut method. The quantity f in Equation 5.1 represents the fraction of the component which will be recovered at the

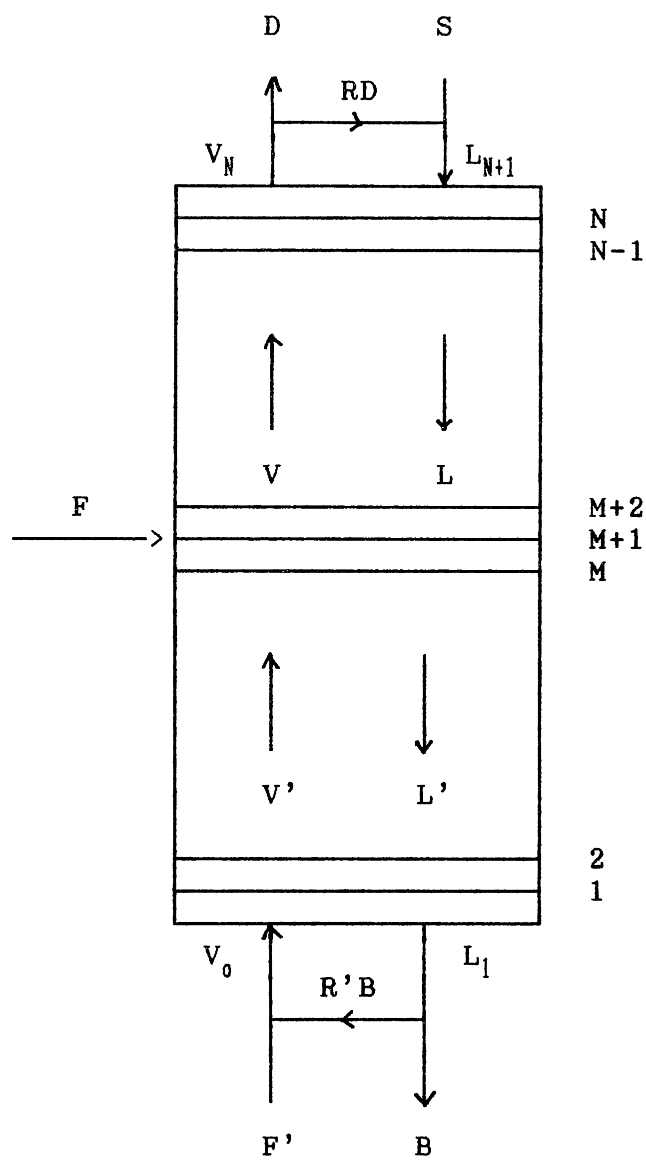


Figure 3. Extraction Process with Two Feeds and Reflux at both Ends.

lower end of the column.

$$f = \frac{(1-S_n^{N-M}) + q_s(S_n^{N-M} - S_n) + R(1-S_n) + hq_{F'}S_n^{N-M}(1-S_n^{M})}{(1-S_n^{N-M}) + hS_n^{N-M}(1-S_m^{M}) + R(1-S_n) + h[(1+R')/(1+gR')]S_m^{M}S_n^{N-M}(1-S_m)} \tag{5.1}$$

where S_n = KV/L = the average stripping factor for the component in the upper section of the column

S_m = K'V'/L' = the average stripping factor for the component in the lower section of the column.

K = the average distribution coefficient for the component in the upper section of the column

K' = the average distribution coefficient for the component in the lower section of the column

The q_s and $q_{F'}$ are the mass fractions of the component which enter in the solvent and lower feed, respectively. The R and R' are the reflux ratios at the top and bottom ends of the column, and g is the assumed recovery factor for the component in the solvent-recovery device. The value of h to be used depends upon the nature of the feed. For feeds more similar in nature to the light(vapor) or raffinate phase,

$$h = \frac{L}{L'}\left\{\frac{1 - S_n}{1 - S_m}\right\} \tag{5.2}$$

For a feed more similar to the heavy (liquid) or extract phase,

$$h = \frac{K'}{K}\,\frac{L}{L'}\left\{\frac{1 - S_n}{1 - S_m}\right\} \tag{5.3}$$

The calculation procedure for the extraction problem can be summarized as follows:

1. Average all available tie-line data to obtain component K values for the first trial. Assume that K = K' for each component if two column sections are involved.

2. Assume f's and calculate B and D with Equations 5.4 and 5.5. Use material balances to calculate any other end rates. Equations 5.6 and 5.7 are useful if extract reflux is used.

$$Bx_B + S_E x_{SE} = f(Fx_F + F'x_{F'} + Sx_S) \tag{5.4}$$

$$Dx_D = (1 - f)(Fx_F + F'x_{F'} + Sx_S) \tag{5.5}$$

$$Bx_B = \frac{1 - g}{1 + gR'} (Bx_B + S_E x_{SE}) \tag{5.6}$$

$$L_1 x_1 = \frac{1 + R'}{1 - g} Bx_B \tag{5.7}$$

where x's are mass fraction.

3. Assume the extract rate to vary linearly from L_{N+1} to L_1. (In high solvent flow rate cases allowance should be made for a possible large change in L across stage N as the solvent becomes saturated with raffinate.) Calculate the raffinate rates by material balance. Average the rates in some manner to obtain realistic average extract and raffinate rates for each section. The arithmetic means of the end values (difference of both ends over number of stages) is often sufficient.

4. Use the average rates and K values to calculate average stripping factors for each component. Use Equation 5.1 to

predict the individual recoveries.

5. Calculate the amounts of each component leaving each end of the column with Equations 5.4 and 5.5. If extract reflux is used, calculate L_1x_1 with Equations 5.6 and 5.7.

6. Use the calculated end compositions to estimate better K values. If the new K's differ appreciably from those used previously, repeat the calculations using new K's.

Stage-to-Stage Calculation

RIGOROUS METHOD

Smith (1960) suggested a rigorous method (stripping factor method) for solving multicomponent, multistage liquid-liquid extraction problems. Multicomponent extraction calculations differ from those for the vapor-liquid processes (distillation, absorption, and stripping) in several respects. First, since two liquid phases are involved, calculation of the distribution coefficient between the two liquid phases involves two liquid activity coefficients instead of one.

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L}{\gamma_i^V} \quad (5.8)$$

where y and V refer to the raffinate phase and x and L to the extract phase (Alders, 1959).

A second major difference between liquid-liquid extraction and the vapor-liquid processes lies in the nature of the temperature profile. The temperature profile in an extraction tower or train is fixed to take maximum advantage of the solubility behavior of the system. The stage temperatures are not determined by the stage compositions and cannot be calculated from the compositions by dew or bubble points. Solubilities rather than enthalpies control the phase rates, and enthalpy balances cannot be used to calculate the rate profiles.

The mass transfer between the two phases may be almost unidirectional (similar to absorption and stripping), or the transfer may be almost equal in both directions (similar to distillation).

Multistage, multicomponent calculation methods (Smith, 1960) can be considered to consist of two major parts, or loops in computer logic terms. The first loop calculates the stage compositions and the second loop calculates the phase rates which correspond to a given temperature profile. It is necessary to calculate exactly the stage compositions and phase rates which correspond to the originally specified temperature profile. The iteration variables which are assumed to start each iteration are as follows:

1. Extract product (L_1) composition,
2. Extract product (L_1) rate,
3. Linear extract rate (L) profile.

The raffinate rate, V, profile is calculated from the assumed L profile. Stage-to-stage calculations are made from the bottom up in the usual manner (alternate use of the equilibrium and material-balance relationships).

The following equations are used in stage-to-stage calculation based on Figure 3.

1. Error equation

$$e_{xN+1} = (S_1 \cdot \cdot \cdot S_N + k\phi) \frac{L_1}{L_{N+1}} e_{x1}$$

where ϕ is defined as

$$\phi = (S_2 \cdot \cdot \cdot S_N + S_3 \cdot \cdot \cdot S_N + \cdots + S_{N-1}S_N + S_N + 1)$$

and

$$k = 1 - \frac{R'}{1 + R'}$$

2. Stripping-factor equation

$$L_1x_1 = \frac{(\phi+R)F'y_{F'}+(\psi+R)Fy_F+(1+R)Sx_S}{S_1 \cdot \cdot \cdot S_N + k\phi + kR} \tag{5.9}$$

where ϕ is as defined above and ψ is

$$\psi = (S_{M+2} \cdot \cdot \cdot S_N + S_{M+3} \cdot \cdot \cdot S_N + \cdots + S_{N-1}S_N + S_N + 1)$$

3. Material-balance equations

$$B = \frac{L_1}{1 + R'} [1 - \sum_{i=1}^{C} (x_i)_i]$$

$$V_0y_0 = \frac{R'}{1 + R'} L_1x_1 + F'y_{F'}$$

$$Bx_B = \frac{1}{1 + R'} L_1x_1$$

$$L_1 = \frac{F'(y_{F'} - y_D) + F(y_F - y_D) + S(x_S - y_D)}{kx_1 - jy_D}$$

where j represents a grouping of terms as shown in the following equation:

$$j = \frac{R'}{1 + R'} [1 - \sum_{i=1}^{C} (x_1)_i] - 1.0$$

The calculation procedure for extraction problems can be summarized as follows:

1. Assume L_1 and x_1's

   The results of short-cut calculations can be used as starting values.
2. Calculate B, V_0, and D using material balance equations.
3. Calculate k, Φ, and Ψ
4. Calculate L_1x_1 using Equation 5.9 and determine L_2x_2, L_3x_3, ..., L_nx_n.

   $$V_ny_n = S_nL_nx_n$$
5. Assume the initial values of L, V, and K in each stage. The results of the short-cut calculation can be used.
6. Check the initial L and V profile using the following

equations.

$$\Sigma\, y_n = \frac{\Sigma\, V_n y_n}{\text{assumed } V_n}$$

$$\Sigma\, x_n = \frac{\Sigma\, L_n x_n}{\text{assumed } L_n}$$

where $\Sigma\, V_n y_n$ and $\Sigma\, L_n x_n$ refer to the calculated values obtained with the stripping-factor equation. Do three or four iterations and make new L and V profile.

7. Use new $L_1 = \Sigma\, L_1 x_1$

   Then repeat steps 2. to 6. till converged.

Matrix Solution

The solution of the equilibrium stage model for separation problems is obtained by finding a set of temperatures, phase rates, and compositions which satisfy all the equations of the model. The model equations may be expressed as follows:

1. The equilibrium relationship

$$y_{i,n} = K_{i,n} x_{i,n} \tag{5.10}$$

2. The component material balance around stage n

$$l_{i,n} + v_{i,n} - l_{i,n-1} - v_{i,n-1} - f_{i,n} = 0 \tag{5.11}$$

3. The energy balance around stage n (It is not required for

liquid-liquid extraction because all stages are at nearly the same temperature.)

$$L_n h_n + V_n H_n - L_{n+1} H_{n+1} - V_{n-1} H_{n-1} - F_n h_{Fn} - q_n = 0 \qquad (5.12)$$

4. The restriction on fractional concentrations

$$\sum_i x_{i,n} = 1.0 \quad \text{and} \quad \sum_i y_{i,n} = 1.0 \qquad (5.13)$$

For a general stage j (Figure 4.) between the top stage and the bottom stage, the mass balance for any component is

$$V_j y_j + L_j x_j - V_{j-1} y_{j-1} - L_{j+1} x_{j+1} = F_j z_j \qquad (5.14)$$

The unknown raffinate compositions, y_j and y_{j-1}, can be replaced using the equilibrium expressions

$$y_j = K_j x_j \qquad \text{and} \qquad y_{j-1} = K_{j-1} x_{j-1} \qquad (5.15)$$

where the K values depend on T and p. If we also replace x_j and x_{j+1} with

$$x_j = l_j \,/\, L_j\,, \qquad x_{j+1} = l_{j+1} \,/\, L_{j+1} \qquad (5.16)$$

where l_j and l_{j+1} are the extract component flow rates, we obtain

$$\left(\frac{-V_{j-1}K_{j-1}}{L_{j-1}}\right) l_{j-1} + \left(1 + \frac{V_j K_j}{L_j}\right) l_j + (-1)\, l_{j+1} = F_j z_j \qquad (5.17)$$

This equation can be written in the general form

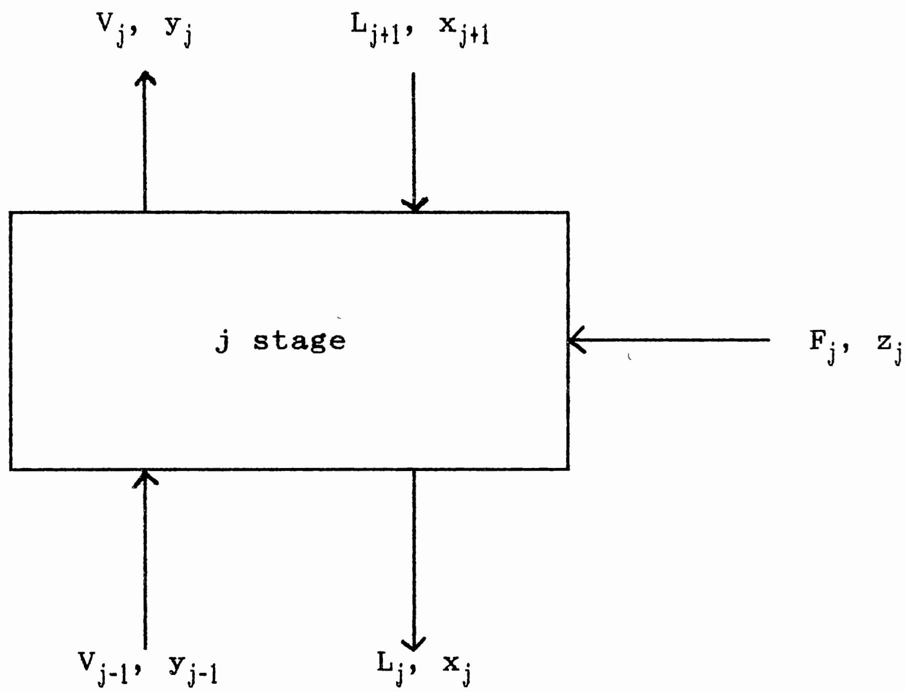


Figure 4. General Stage in Column

$$A_j l_{j-1} + B_j l_j + C_j l_{j+1} = D_j \tag{5.18}$$

The constants A_j, B_j, C_j, and D_j are easily determined by comparing Equations 5.17 and 5.18.

$$A_j = -\frac{K_{j-1} V_{j-1}}{L_{j-1}}, \; B_j = 1 + \frac{V_j K_j}{L_j}, \; C_j = -1, \; D_j = F_j z_j \tag{5.19}$$

Equation 5.18 and 5.19 are valid for all stages in the column, $2 \leq j \leq N-1$, and are repeated for each of the C components. If a stage has no feed, then $F_j = D_j = 0$.

For stage 1 the mass balance becomes

$$B_1 l_1 + C_1 l_2 = D_1 \tag{5.20}$$

where

$$B_1 = 1 + \frac{V_1 K_1}{L_1}, \quad C_1 = -1, \quad D_1 = F_1 z_1 = V_0 y_0 \tag{5.21}$$

and the component flow rates are $l_1 = L_1 x_1$ and $l_2 = L_2 x_2$. These equations are repeated for each component.

For stage N the mass balance is

$$A_n l_{N-1} + B_N l_N = D_N \tag{5.22}$$

where

$$A_N = -\frac{V_{N-1} K_{N-1}}{L_{N-1}}, \quad B_N = 1 + \frac{V_N K_N}{L_N}, \quad D_N = F_N z_N = L_{N+1} x_{N+1} \tag{5.23}$$

In matrix notation, the component mass balance and equilibrium relationships are

$$\begin{bmatrix} B_1 & C_1 & 0 & 0 & 0 & \cdot & \cdot & 0 & 0 & 0 \\ A_2 & B_2 & C_2 & 0 & 0 & \cdot & \cdot & 0 & 0 & 0 \\ 0 & A_3 & B_3 & C_3 & 0 & \cdot & \cdot & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & \cdot & \cdot & A_{N-1} & B_{N-1} & C_{N-1} \\ 0 & 0 & 0 & 0 & 0 & \cdot & \cdot & 0 & A_N & B_N \end{bmatrix} \begin{bmatrix} l_1 \\ l_2 \\ l_3 \\ \cdot \\ l_{N-1} \\ l_N \end{bmatrix} = \begin{bmatrix} D_1 \\ D_2 \\ D_3 \\ \cdot \\ D_{N-1} \\ D_N \end{bmatrix} \tag{5.24}$$

This set of simultaneous linear algebraic equations can be solved by inverting the ABC matrix. This can be done using any standard matrix inversion routine. The particular matrix form shown in Equation 5.24 is a tridiagonal matrix, which is particularly easy to invert using the Thomas algorithm (see Table V). The results are liquid component flow rates l_j, that are valid for the assumed L_j and V_j.

The next step is to use the summation equations to find new total flow rates L_j and V_j. The new extract flow rate is conveniently determined as

$$L_{j,new} = \sum_{i=1}^{C} l_{i,j} \tag{5.25}$$

The raffinate flow rates are determined by summing the component raffinate flow rates,

$$V_{j,new} = \sum_{i=1}^{C} \left[\left(\frac{K_{ij} V_j}{L_j} \right)_{old} l_{i,j} \right] \tag{5.26}$$

Convergence can be checked with

TABLE V

THOMAS ALGORITHM FOR INVERTING TRIDIAGONAL MATRICES (Riggs, 1988)

Consider solution of a matrix in the form of equation 5.24 where all A_j, B_j, C_j, and D_j are known.

1. Calculate three intermediate variables for each row of the matrix starting with j = 1. For $1 \leq j \leq N$.

$$(V1)_j = B_j - A_j(V3)_{j-1}$$
$$(V2)_j = [D_j - A_j(V2)_{j-1}] / (V1)_j$$
$$(V3)_j = C_j / (V1)_j$$

   since $A_1 \equiv 0$, $(V1)_1 = B_1$, and $(V2)_1 = D_1 / (V1)_1$.

2. Initialize $(V3)_0 = 0$ and $(V2)_0 = 0$, so you can use the general formulas.

3. Calculate all unknowns U_j (1_j in equation 5.24 and V_j in equation 5.26). Start with i = N and calculate

$$U_N = (V2)_N$$

   Then going from j = N-1 to j=1, calculate U_{N-1}, U_{N-2}, . . ., U_1 from

$$U_j = (V2)_j - (V3)_j U_{j+1}, \qquad 1 \leq j \leq N-1$$

$$\left| \frac{L_{j,old} - L_{j,new}}{L_{j,old}} \right| < \epsilon \text{ and } \left| \frac{V_{j,old} - V_{j,new}}{V_{j,old}} \right| < \epsilon \qquad (5.27)$$

for all stages. For computer calculations, an ϵ of 10^{-4} or 10^{-5} can be used. If convergence has not been reached, new extract and raffinate flow rates are determined, and we return to the component mass balances. Direct substitution ($L_j = L_{j,new}$, $V_j = V_{j,new}$) is usually adequate.

Problem Formation and Convergence

Friday (1964) suggested a method to form the right equations by six major decisions. Ishii (1973) described the general algorithm for multistage multicomponent separation calculation. He emphasized distillation and absorber calculations but not extraction. In addition, he did not touch upon how to set up the matrix. Ravi (1989) did good work but he did not deal with how he formed the matrix, either. The following is a summary of Friday's work. Friday's method of six decisions provides the idea of how to determine the new assumed values in stage-to-stage calculation.

The model equations by type may be expressed in Equations 5.10, 5.11, 5.12, and 5.13.

First Decision.

The first major decision to be made in the formulation of a solution method is concerned with the grouping of the model equation. Grouping by component type (not by stage) is the preferable second decision.

Second Decision.

The second decision involves the order to use in satisfying the four types of restrictions. The analysis for extraction is slightly different from the analysis of distillation because the energy balance restrictions (Equation 5.12) are not involved in the solution of the model equation.

Third Decision.

The third decision concerns the selection of the appropriate type of equation to provide a given variable. There are two methods such as bubble point (BP) method and summation-rates (SR) method. All extraction, washing, absorber, and stripping problems plus wide boiling distillation problems with less than ten stages would utilize the SR method. The extraction calculation can not use bubble point calculations as the equilibrium is not vapor-liquid, i.e., bubble point, but liquid-liquid with both phases probably subcooled.

Forth Decision.

The forth decision is the selection of a method of solving the C-matrix equation for the new stage concentrations or phase rates.

Fifth Decision.

The fifth decision includes the selection of a method of calculating the new T_j for whichever choice was made in the third decision. So, we do not have to consider this decision.

Sixth Decision.

The last decision is about the method of obtaining the new V_n and L_n. In the SR method, the new V_n and L_n are immediately available from following equations.

$$V_n = \sum_i v_{i,n} \quad \text{and} \quad L_n = \sum_i l_{i,n} \tag{5.28}$$

CHAPTER VI

RESULTS AND DISCUSSION

Introduction

The intent of this section is to illustrate the use and validity of the program which calculates the multicomponent, multistage liquid-liquid extraction process. Smith (1960) suggested a rigorous method for calculating multicomponent, multistage liquid extraction problems; this work, however, has been done by matrix solution for Smith's method rarely converged. Different case studies will be reviewed to show the range of applications of the program. For each case study, the assumptions used and the input variables are given.

Convergence Techniques

Friday (1964) suggested a convergence check method which checks whether the summation of x_i and y_i on all stages is 1.0 or not. But, it is very difficult to force the summation of x and of y to 1.0 at all stages. Wankat (1988) suggested a new convergence check method which compares the new calculated L and V (total flow rates) profile with the old L and V profile. When the new assumed L and V profile is input the new calculated L and V profile is entered as a new assumed value (Summation rates method). The program uses the summation-rates method so that convergence depends only slightly on the initial guess. The program uses the results of the short-cut calculation as an initial guess.

Model Verification

Each of the different elements of the program was analyzed by a series of case studies. The purpose of these case studies was to independently analyze each aspect of the program and verify its validity.

Case Study I

The first test of the program was to test a simple conventional two liquid phase and three cases of hypothetical three components (water - n-propanol as feed, n-hexane, n-heptane, and benzene as solvent) liquid-liquid extraction column. The production of oxygen-containing chemicals by oxidation of light hydrocarbons and as by-products from the synthesis of liquid fuels has become important. The use of hydrocarbon as an azeotroping agent in the separation and drying of these oxygenated chemicals has also been widely investigated. McCants (1953) showed the experimental ternary solubility data for systems involving 1-propanol and water. The object of this test was to predict which solvent is better without experimentation or running pilot plant.

All input data are the same at each calculation without solvent component at each calculation. The program solved a hypothetical column of five stages, one feed at bottom stage, and no extract reflux. The maximum iteration number was 30,000. The program first deal with short-cut calculation, and then stage-to-stage calculation using the results of short-cut calculation as initial values. After running the program, results of this case study show that benzene is the best solvent among benzene, n-hexane, and n-heptane. N-heptane is the worst solvent among the three solvents. These results agreed with McCants' work. Smith's method did not converge for any of the three trials so the results of this work can not be compared to the results of Smith's. Table VI shows the results of this work; Figure 5., 7., and 9., the extract and raffinate rate profiles; Figure 6., 8., and 10., the extract and raffinate composition profiles.

Case Study II

The second test of the program was to test a real process. Grote (1958) showed the real process results of some applications of the Udex process to the recovery of aromatics from various feedstocks. The Udex process has been applied to refinery streams to recover aromatics concentrates of high octane ratings. The development of

TABLE VI

RESULTS OF CASE STUDY I

WATER - N-PROPANOL - BENZENE SYSTEM

STAGE	DOWN STREAM	UP STREAM
5	81.52	73.50
4	78.93	55.03
3	77.64	52.43
2	77.00	51.15
1	76.49	50.51

BOTTOM OUTLET STREAM	=	76.49
BOTTOM INLET STREAM	=	50.00
TOP OUTLET STREAM	=	73.50
TOP INLET STREAM	=	100.00
FEED STREAM	=	50.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	WATER	.9971	.0036
2	N-PROPANOL	.0024	.0064
3	BENZENE	.0005	.9900

----- STAGE 2 ----

	COMPONENT	XE	XR
1	WATER	.9928	.0043
2	N-PROPANOL	.0066	.0180
3	BENZENE	.0006	.9777

----- STAGE 3 ----

	COMPONENT	XE	XR
1	WATER	.9851	.0058
2	N-PROPANOL	.0142	.0400
3	BENZENE	.0007	.9542

TABLE VI (Continued)

----- STAGE 4 ----

	COMPONENT	XE	XR
1	WATER	.9702	.0087
2	N-PROPANOL	.0289	.0804
3	BENZENE	.0009	.9109

----- STAGE 5 ----

	COMPONENT	XE	XR
1	WATER	.9414	.0507
2	N-PROPANOL	.0565	.2696
3	BENZENE	.0020	.6797

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
WATER	.9971	.0000	.0507	.8000
N-PROPANOL	.0024	.0000	.2696	.2000
BENZENE	.0005	1.0000	.6797	.0000

WATER - N-PROPANOL - N-HEXANE SYSTEM

STAGE	DOWN STREAM	UP STREAM
5	88.23	69.70
4	84.64	57.93
3	84.12	54.34
2	82.72	53.82
1	80.29	52.42

BOTTOM OUTLET STREAM	=	80.29
BOTTOM INLET STREAM	=	50.00
TOP OUTLET STREAM	=	69.70
TOP INLET STREAM	=	100.00
FEED STREAM	=	50.00

TABLE VI (Continued)

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	WATER	.9582	.0031
2	N-PROPANOL	.0414	.0427
3	N-HEXANE	.0004	.9542

----- STAGE 2 ----

	COMPONENT	XE	XR
1	WATER	.9321	.0049
2	N-PROPANOL	.0672	.0653
3	N-HEXANE	.0007	.9298

----- STAGE 3 ----

	COMPONENT	XE	XR
1	WATER	.9178	.0056
2	N-PROPANOL	.0813	.0732
3	N-HEXANE	.0009	.9212

----- STAGE 4 ----

	COMPONENT	XE	XR
1	WATER	.9126	.0135
2	N-PROPANOL	.0863	.1188
3	N-HEXANE	.0011	.8677

----- STAGE 5 ----

	COMPONENT	XE	XR
1	WATER	.8809	.0439
2	N-PROPANOL	.1157	.2392
3	N-HEXANE	.0034	.7169

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
WATER	.9582	.0000	.0439	.8000
N-PROPANOL	.0414	.0000	.2392	.2000
N-HEXANE	.0004	1.0000	.7169	.0000

TABLE VI (Continued)

WATER - N-PROPANOL - N-HEPTANE SYSTEM

STAGE	DOWN STREAM	UP STREAM
5	96.79	57.28
4	96.70	54.07
3	96.70	53.98
2	96.76	53.98
1	92.71	54.05

BOTTOM OUTLET STREAM	=	92.71
BOTTOM INLET STREAM	=	50.00
TOP OUTLET STREAM	=	57.28
TOP INLET STREAM	=	100.00
FEED STREAM	=	50.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	WATER	.8572	.0048
2	N-PROPANOL	.1415	.0684
3	N-HEPTANE	.0013	.9269

----- STAGE 2 ----

	COMPONENT	XE	XR
1	WATER	.8240	.0047
2	N-PROPANOL	.1737	.0674
3	N-HEPTANE	.0023	.9279

----- STAGE 3 ----

	COMPONENT	XE	XR
1	WATER	.8245	.0047
2	N-PROPANOL	.1732	.0674
3	N-HEPTANE	.0023	.9279

TABLE VI (Continued)

----- STAGE 4 ----

	COMPONENT	XE	XR
1	WATER	.8245	.0047
2	N-PROPANOL	.1732	.0673
3	N-HEPTANE	.0023	.9280

----- STAGE 5 ----

	COMPONENT	XE	XR
1	WATER	.8237	.0092
2	N-PROPANOL	.1731	.1202
3	N-HEPTANE	.0032	.8706

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
WATER	.8572	.0000	.0092	.8000
N-PROPANOL	.1415	.0000	.1202	.2000
N-HEPTANE	.0013	1.0000	.8706	.0000

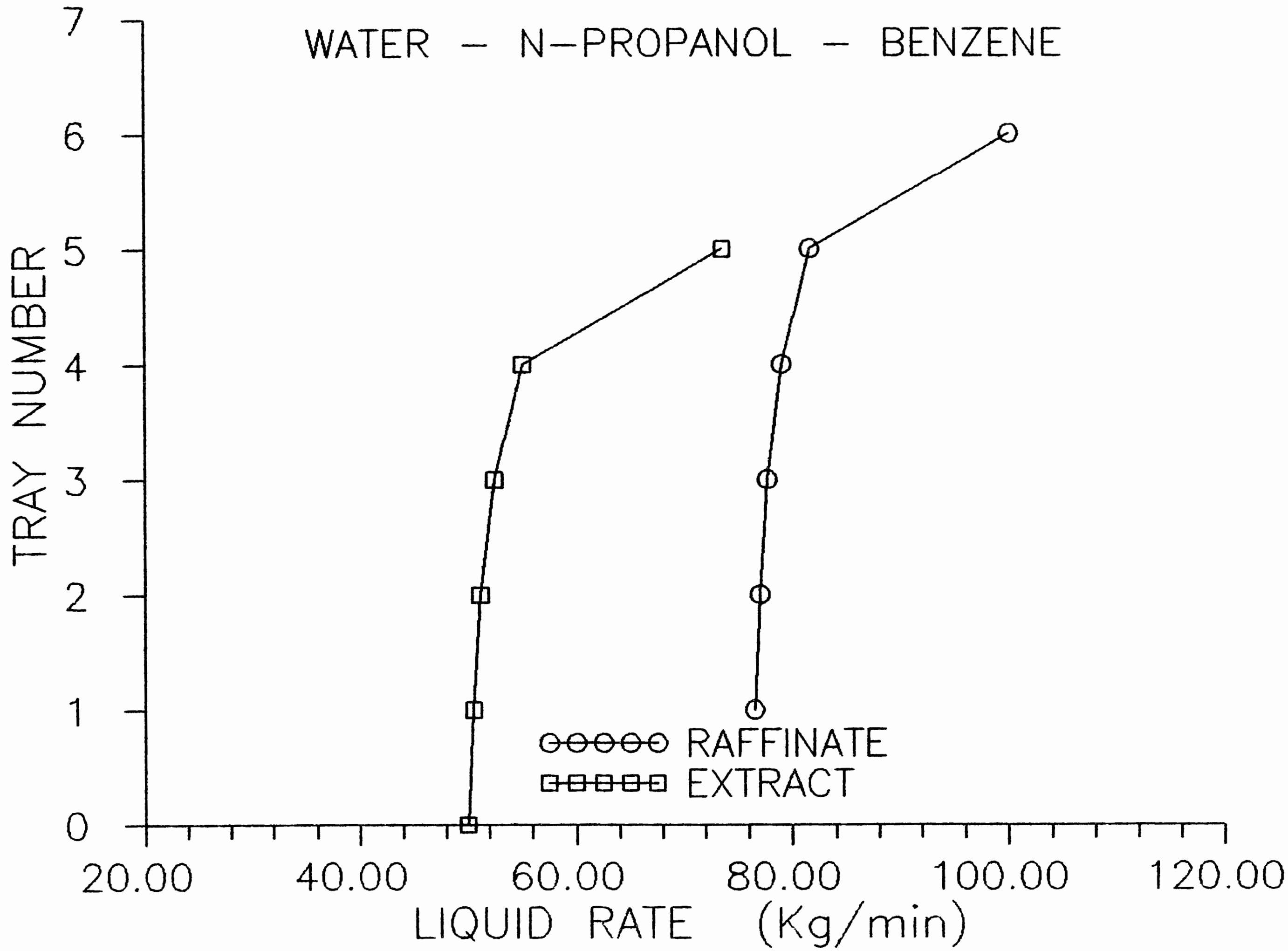


Figure 5. Case Study I-1 Flow Rate Profile

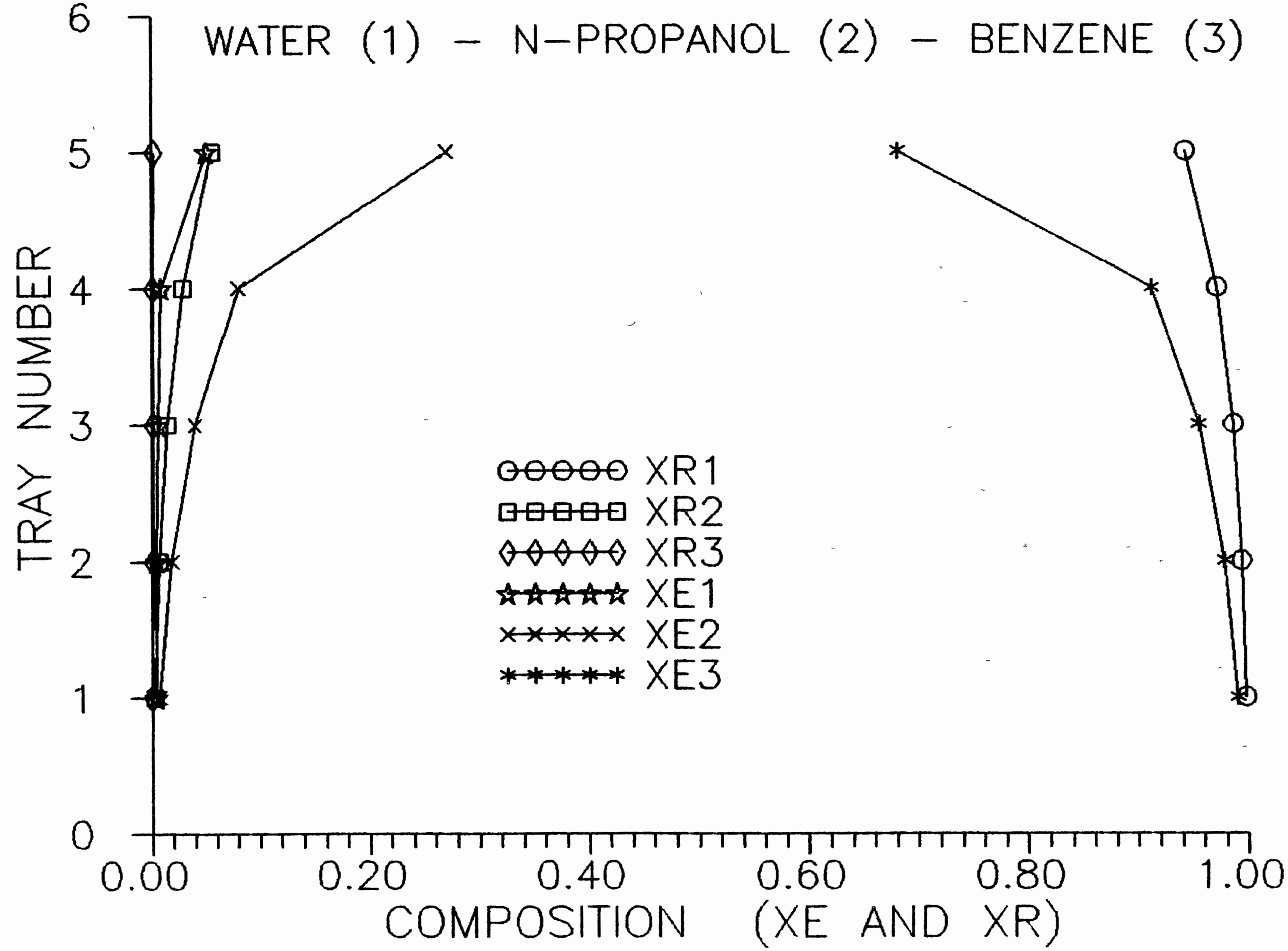


Figure 6. Case Study I-1 Composition Profile

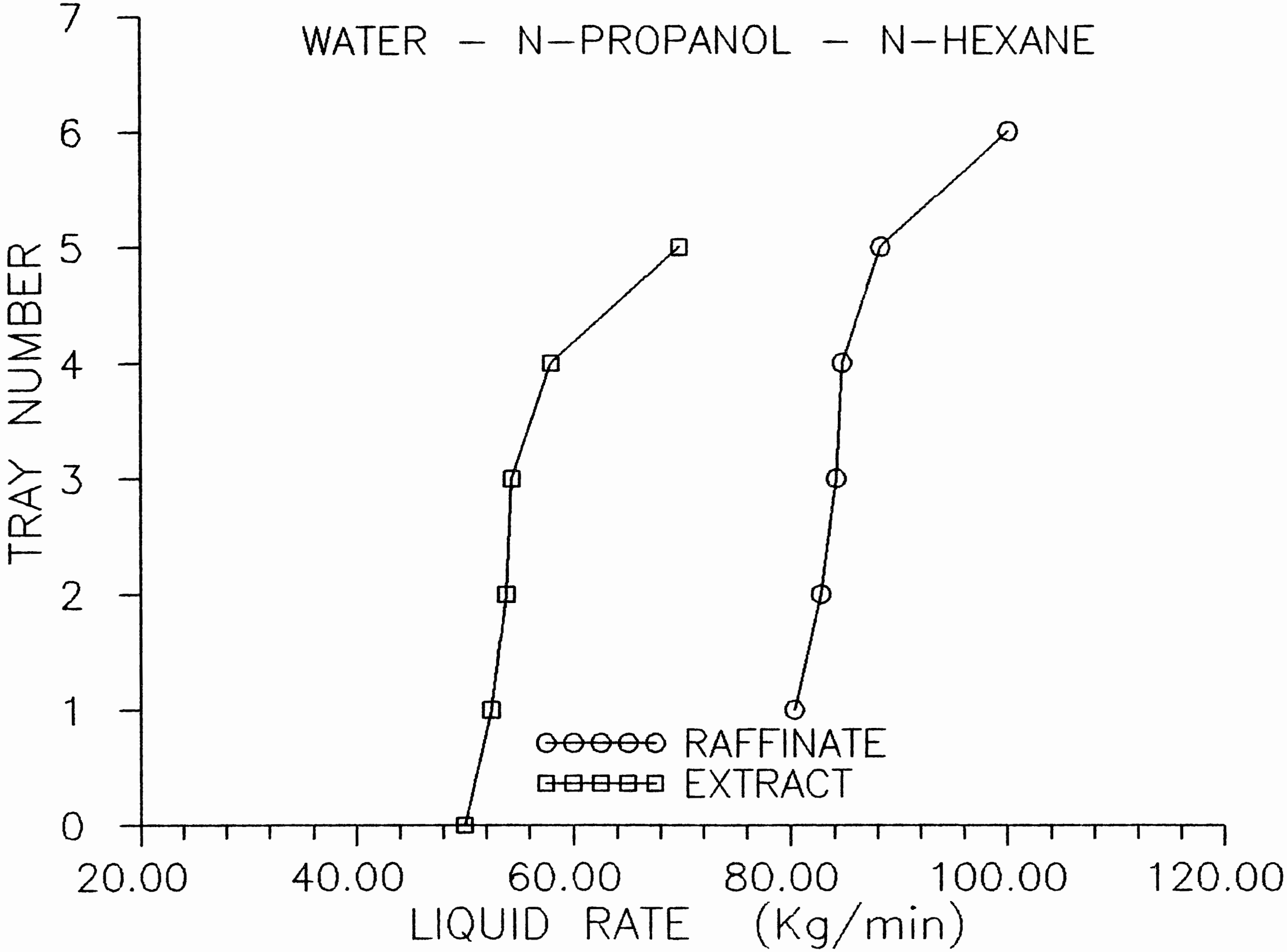


Figure 7. Case Study I-2 Flow Rate Profile

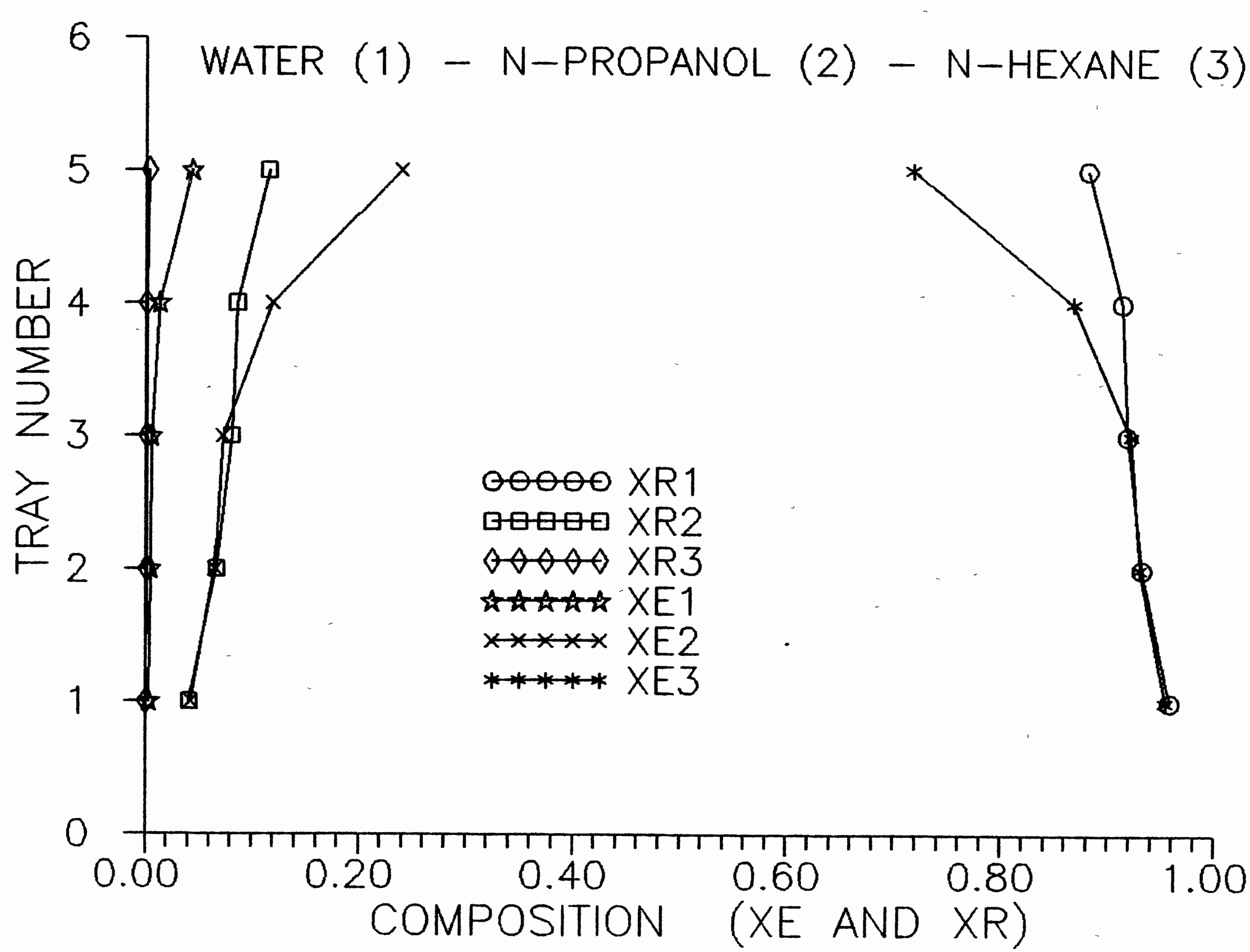


Figure 8. Case Study I-2 Composition Profile

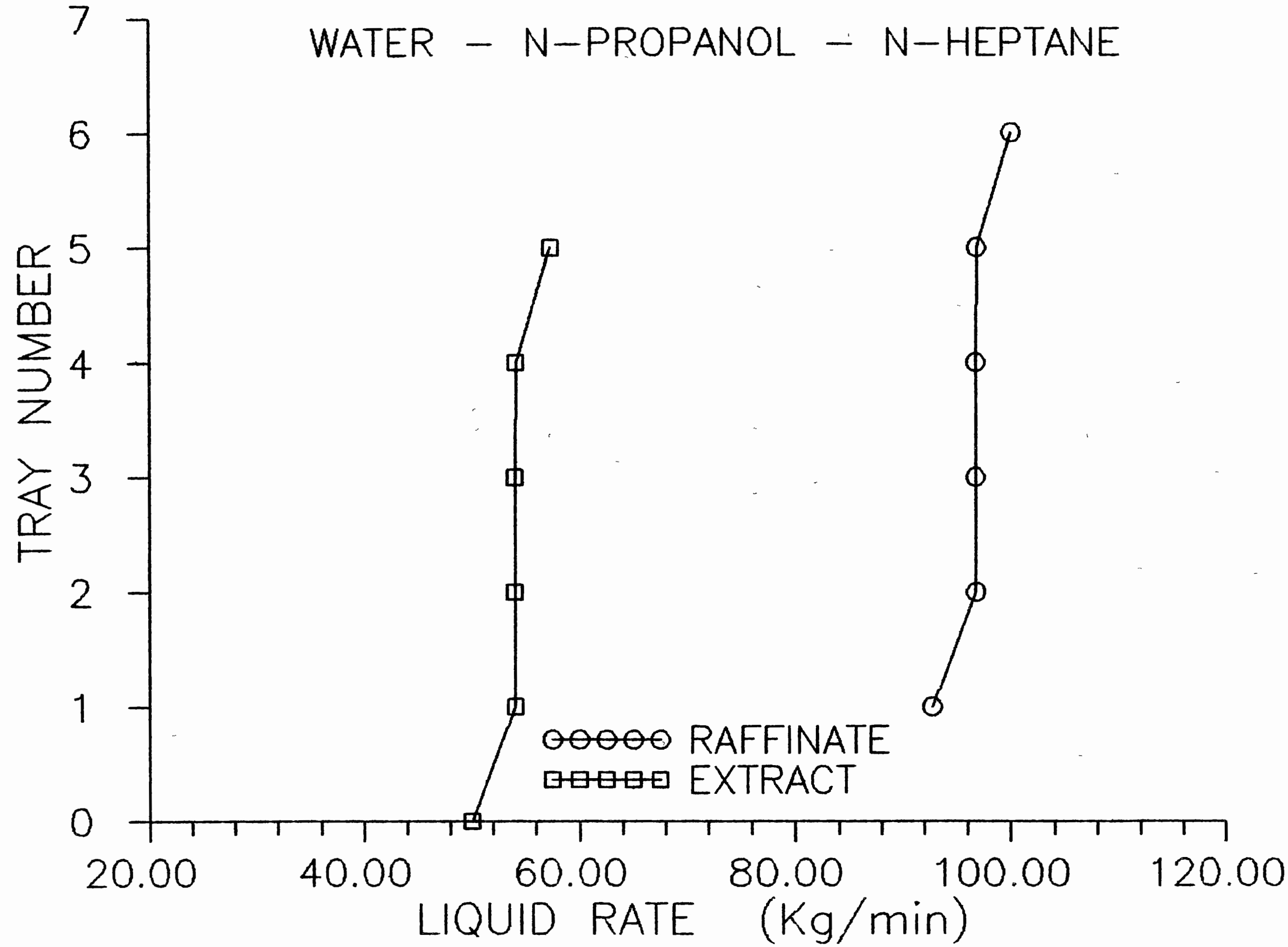


Figure 9. Case Study I-3 Flow Rate Profile

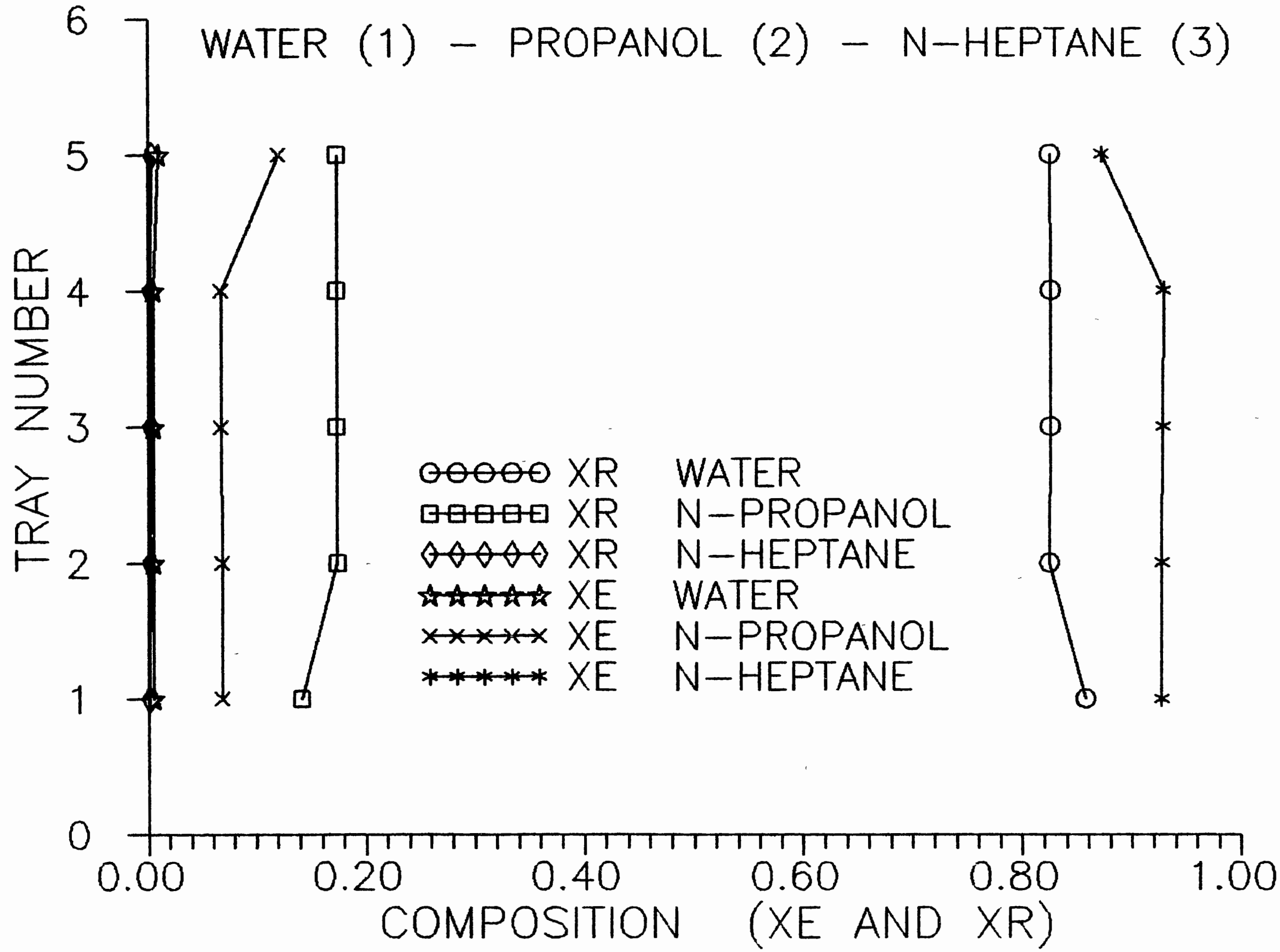


Figure 10. Case Study I-3 Composition Profile

this economical technique had made it possible for both large and small refiners to enter the petrochemical field. The objective of this case study is to predict the optimum number of stages, the graphical method for predicting the number of stages is not applicable to more than a three component mixture.

Among several mixtures, a system which consists of benzene - toluene - xylenes -n-octane mixture and diethylene glycol as solvent was selected and the number of stages is varied at each trial. All input data are the same at each trial except the number of stages. The maximum iteration number was 30,000. The number of stages of 2-20 was tested. According to the results of this work, the optimum number of stages is five. I tested dozens solvent; ethylenediamine is the best solvent among them. Ethylenediamine is a better solvent than ethylene glycol. Tables VII and VIII present the results of this work. Figures 11 and 13 show extract and raffinate flow rate profiles; Figures 12 and 14 illustrate extract and raffinate composition profiles.

Study III

The third test of the program was to examine the solvent extraction process for phenols recovery from coke plant aqueous waste. Today, economical waste water treatment has become very important for environmental pollution control. Lauer et al. (1969) suggested

TABLE VII

RESULTS OF CASE STUDY II

NUMBER OF STAGE	RAFFINATE (Kg/hr)	EXTRACT (Kg/hr)
2	5602.00	11466.84
3	5500.00	11569.27
4	5459.94	11609.35
5	5444.71	11624.92
6	5437.91	11631.38
7	5435.05	11634.25
8	5433.70	11635.59
10	5432.71	11636.58
20	5432.35	11636.94
50	5714.83	11356.11

TABLE VIII

COMPARISON OF ETHYLENE GLYCOL WITH ETHYLENEDIAMINE

DIETHYLENE GLYCOL - BENZENE - TOLUENE - XYLENES - N-OCTANE

STAGE	DOWN STREAM	UP STREAM
5	10827.87	5444.37
4	11373.30	6272.23
3	11554.38	6817.67
2	11619.21	6998.74
1	11624.92	7063.58

BOTTOM OUTLET STREAM	=	11624.92
BOTTOM INLET STREAM	=	7070.00
TOP OUTLET STREAM	=	5444.37
TOP INLET STREAM	=	10000.00
FEED STREAM	=	7070.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	DIETHYLENE GLY	.8576	.0026
2	BENZENE	.0532	.1559
3	TOLUENE	.0588	.2375
4	XYLENES	.0024	.0134
5	N-OCTANE	.0280	.5905

----- STAGE 2 ----

	COMPONENT	XE	XR
1	DIETHYLENE GLY	.8596	.0026
2	BENZENE	.0512	.1502
3	TOLUENE	.0586	.2372
4	XYLENES	.0024	.0136
5	N-OCTANE	.0281	.5964

TABLE VIII (Continued)

----- STAGE 3 ----

	COMPONENT	XE	XR
1	DIETHYLENE GLY	.8644	.0026
2	BENZENE	.0472	.1385
3	TOLUENE	.0574	.2325
4	XYLENES	.0025	.0138
5	N-OCTANE	.0286	.6127

----- STAGE 4 ----

	COMPONENT	XE	XR
1	DIETHYLENE GLY	.8781	.0023
2	BENZENE	.0385	.1135
3	TOLUENE	.0517	.2106
4	XYLENES	.0024	.0134
5	N-OCTANE	.0293	.6602

----- STAGE 5 ----

	COMPONENT	XE	XR
1	DIETHYLENE GLY	.9220	.0056
2	BENZENE	.0190	.0930
3	TOLUENE	.0300	.1831
4	XYLENES	.0016	.0122
5	N-OCTANE	.0274	.7061

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
DIETHYLENE GLY	.8576	.0000	.0056	1.0000
BENZENE	.0532	.1591	.0930	.0000
TOLUENE	.0588	.2376	.1831	.0000
XYLENES	.0024	.0134	.0122	.0000
N-OCTANE	.0280	.5899	.7061	.0000

TABLE VIII (Continued)

ETHYLENEDIAMINE - BENZENE - TOLUENE - XYLENES - N-OCTANE

STAGE	DOWN STREAM	UP STREAM
5	9211.06	5759.59
4	10313.94	4970.65
3	11144.75	6073.53
2	11994.08	6904.33
1	11309.70	7753.67

BOTTOM OUTLET STREAM	=	11309.70
BOTTOM INLET STREAM	=	7070.00
TOP OUTLET STREAM	=	5759.59
TOP INLET STREAM	=	10000.00
FEED STREAM	=	7070.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	ETHYLENEDIAMIN	.6724	.1687
2	BENZENE	.0863	.1193
3	TOLUENE	.1324	.1679
4	XYLENES	.0076	.0089
5	N-OCTANE	.1012	.5351

----- STAGE 2 ----

	COMPONENT	XE	XR
1	ETHYLENEDIAMIN	.7431	.1818
2	BENZENE	.0648	.0963
3	TOLUENE	.0934	.1290
4	XYLENES	.0050	.0065
5	N-OCTANE	.0937	.5863

----- STAGE 3 ----

	COMPONENT	XE	XR
1	ETHYLENEDIAMIN	.7950	.1837
2	BENZENE	.0464	.0721
3	TOLUENE	.0636	.0923
4	XYLENES	.0033	.0044
5	N-OCTANE	.0917	.6475

TABLE VIII (Continued)

----- STAGE 4 ----

	COMPONENT	XE	XR
1	ETHYLENEDIAMIN	.8455	.1924
2	BENZENE	.0280	.0461
3	TOLUENE	.0367	.0570
4	XYLENES	.0018	.0026
5	N-OCTANE	.0879	.7018

----- STAGE 5 ----

	COMPONENT	XE	XR
1	ETHYLENEDIAMIN	.9295	.4158
2	BENZENE	.0087	.0258
3	TOLUENE	.0110	.0316
4	XYLENES	.0005	.0014
5	N-OCTANE	.0502	.5254

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
ETHYLENEDIAMIN	.6724	.0000	.4158	1.0000
BENZENE	.0863	.1591	.0258	.0000
TOLUENE	.1324	.2376	.0316	.0000
XYLENES	.0076	.0134	.0014	.0000
N-OCTANE	.1012	.5899	.5254	.0000

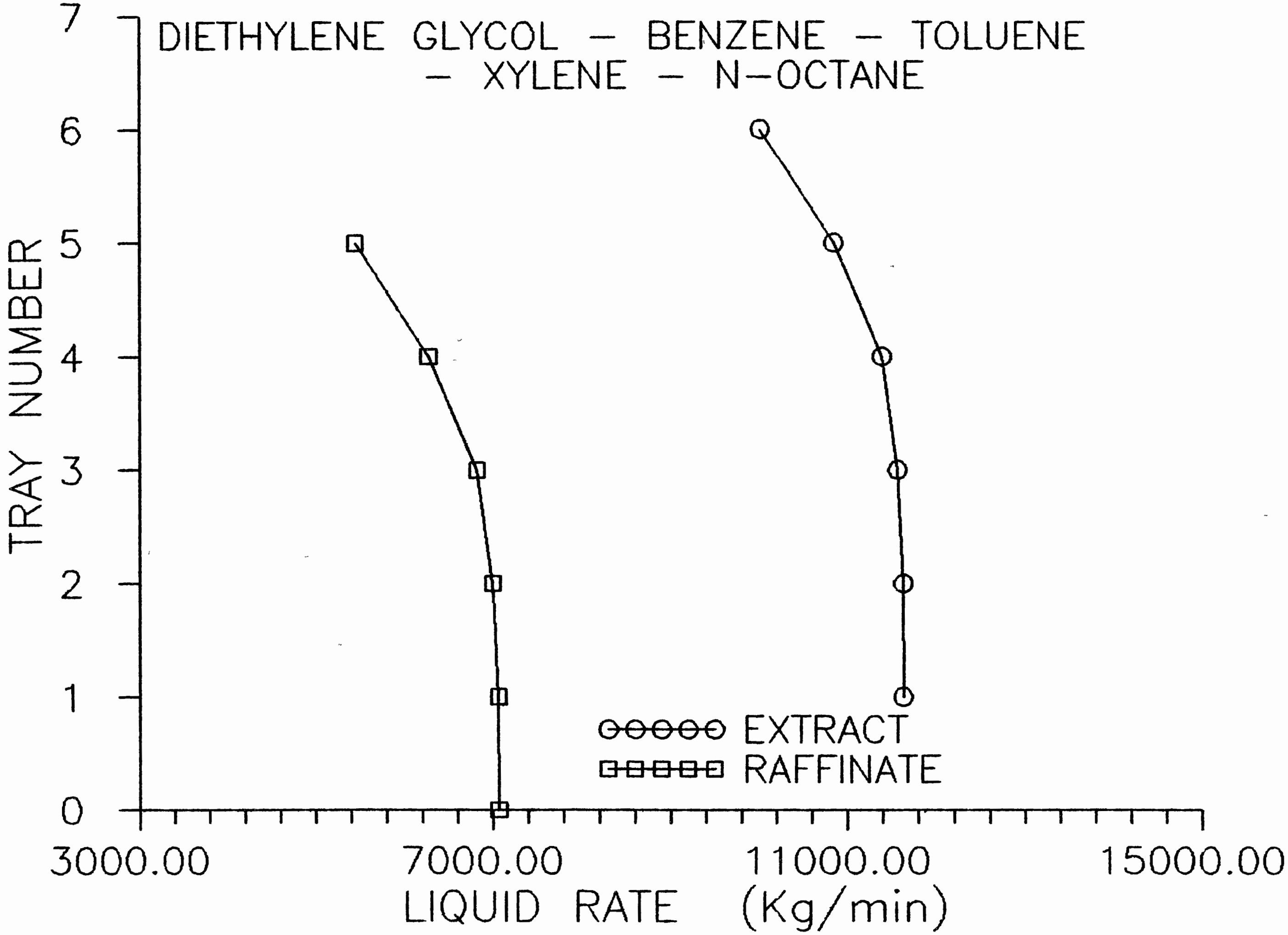


Figure 11. Case Study II-1 Flow Rate Profile

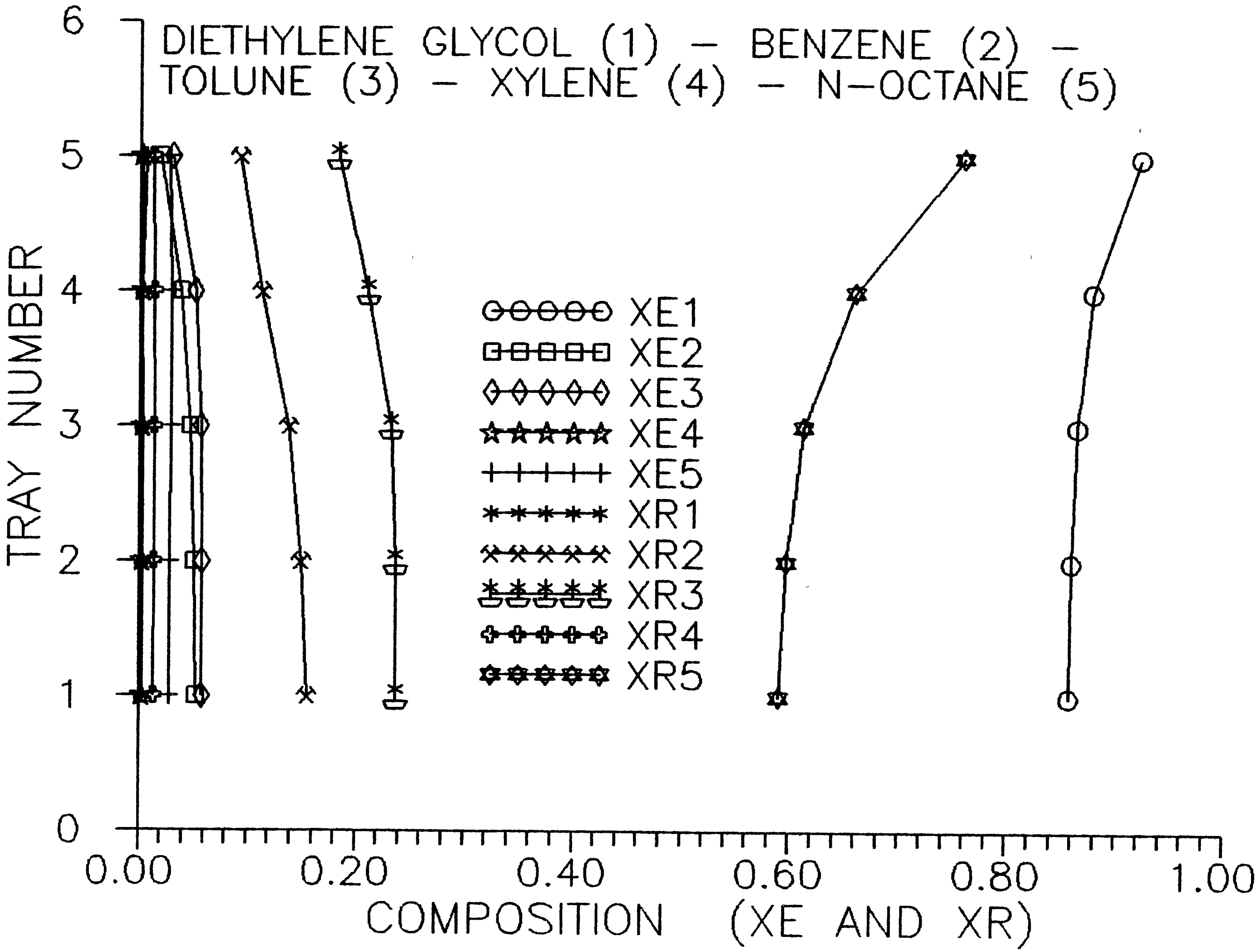


Figure 12. Case Study II-1 Composition Profile

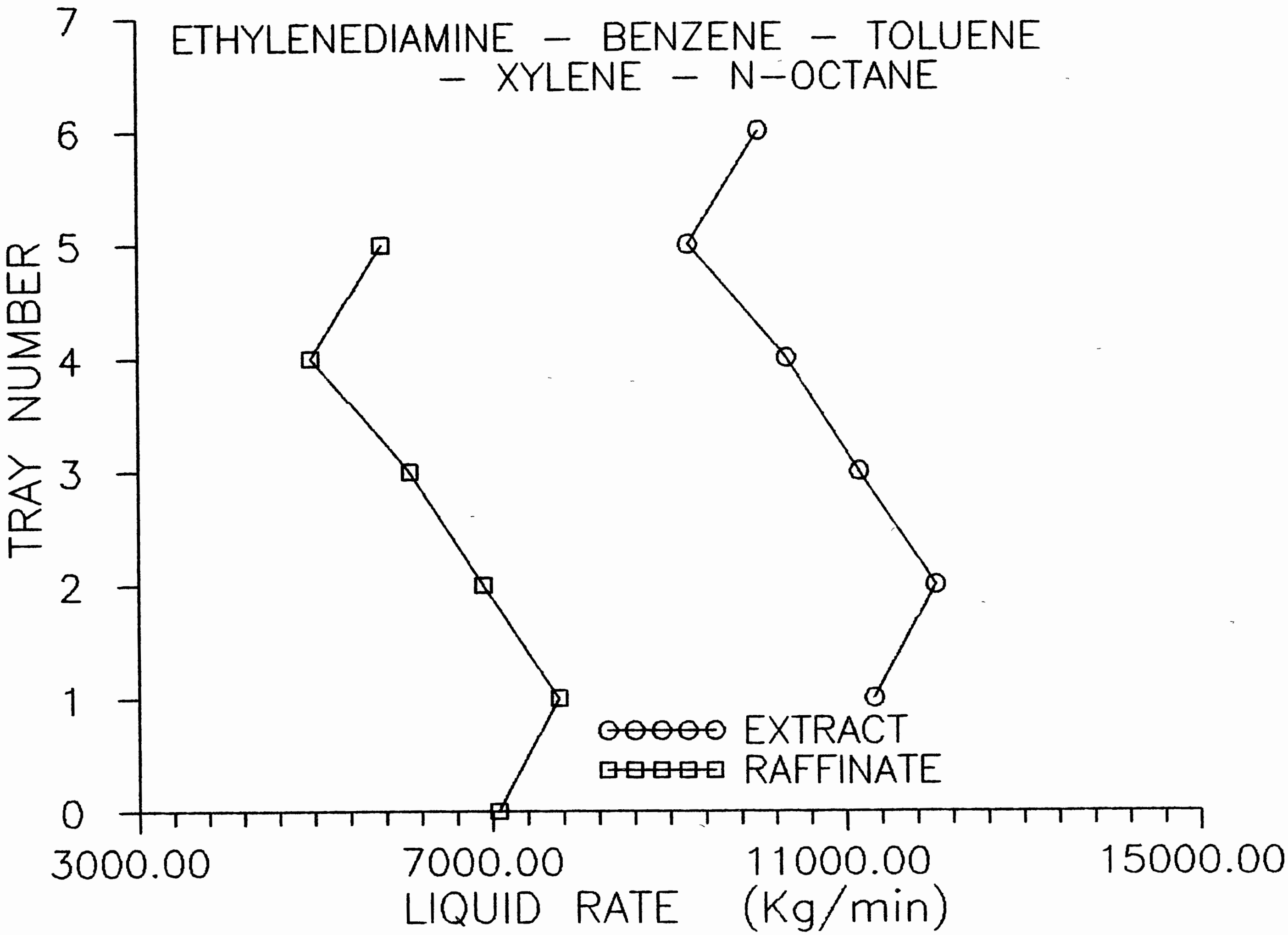


Figure 13. Case Study II-2 Flow Rate Profile

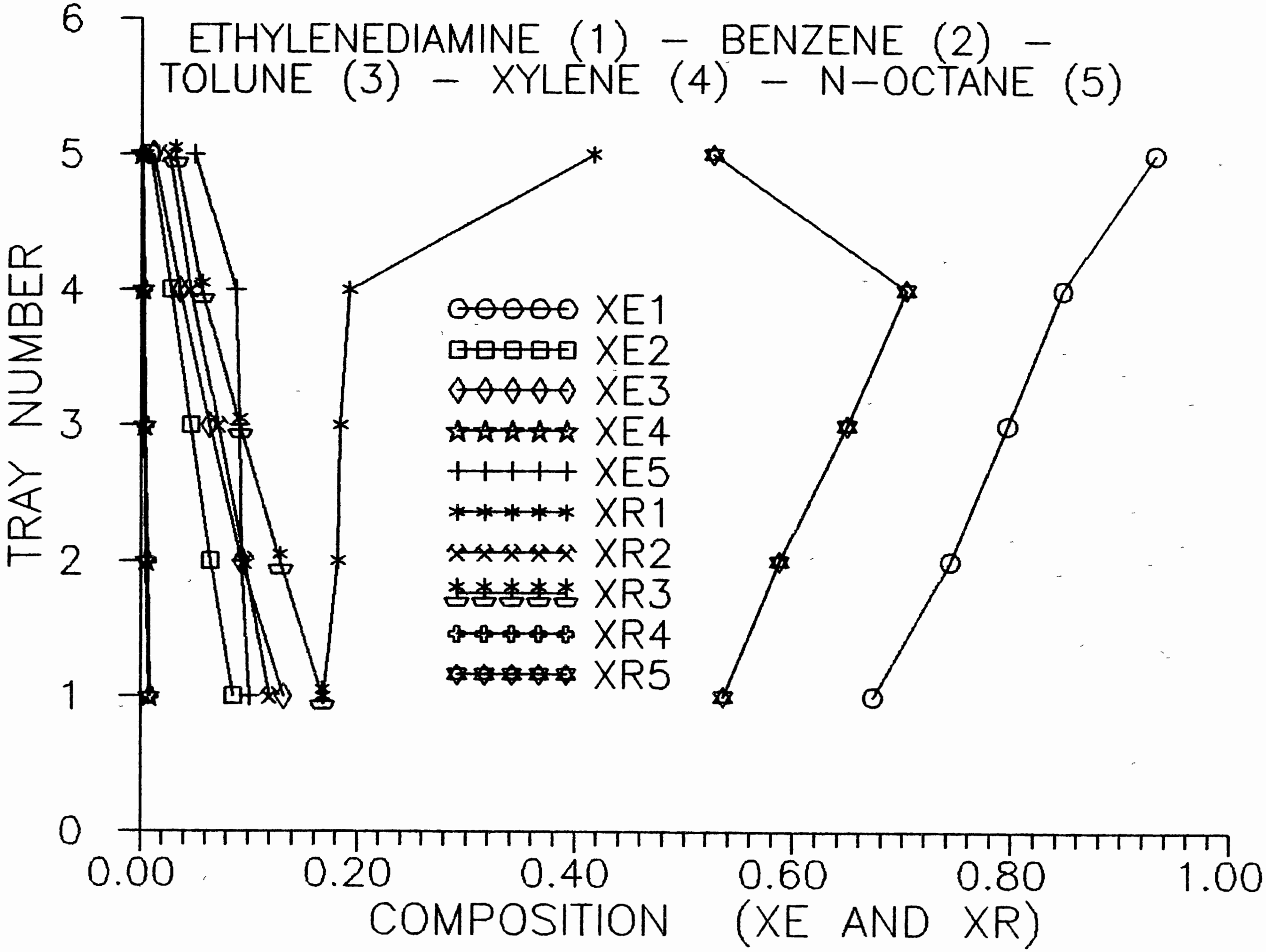


Figure 14. Case Study II-2 Composition Profile

methylnaphthalene as a good solvent for extracting phenol from a water - phenol mixture. The extraction was performed in four ideal extractor stages. The temperature was 67°C. The feed to solvent ratio was 9 to 1. According to the results, almost all phenol was extracted into the methylnaphthalene phase. This operation could achieve 99.9 percent phenols removal. According to the experimental results of Lauer et al., four actual stages could achieve 97 to 99 percent phenol removal. Table IX shows results of this work; Figure 15, the extract and raffinate flow rate profiles; and Figure 16, the extract and raffinate composition profiles.

Case Study IV

The fourth test of the program was to check a three component (styrene - ethylbenzene - diethylene glycol) system. Pyrolytic tars, particularly those produced by the manufactured gas industry, contain readily polymerizable unsaturates which are lost when conventional tar processing methods of thermal dehydration and batch distillation are used. If these tars were first fractionated cold by means of solvents and the fractions then extracted with other solvents selective for unsaturates, it might be possible to avoid thermal losses of useful products. Boobar et al. (1951) showed experimental ternary saturation-equilibrium data. Styrene and ethylbenzene were chosen as

TABLE IX

RESULTS OF CASE STUDY III

WATER - PHENOL - METHYLNAPHTHALENE SYSTEM

STAGE	DOWN STREAM	UP STREAM
4	44.48	10.86
3	44.30	5.35
2	44.28	5.16
1	44.13	5.14

BOTTOM OUTLET STREAM	=	44.14
BOTTOM INLET STREAM	=	5.00
TOP OUTLET STREAM	=	10.86
TOP INLET STREAM	=	50.00
FEED STREAM	=	5.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	WATER	1.0000	.0283
2	PHENOL	.0000	.0003
3	METHYLNAPHTHAL	.0000	.9714

----- STAGE 2 ----

	COMPONENT	XE	XR
1	WATER	1.0000	.0287
2	PHENOL	.0000	.0031
3	METHYLNAPHTHAL	.0000	.9682

----- STAGE 3 ----

	COMPONENT	XE	XR
1	WATER	.9996	.0312
2	PHENOL	.0004	.0342
3	METHYLNAPHTHAL	.0000	.9346

TABLE IX (Continued)

----- STAGE 4 ----

	COMPONENT	XE	XR
1	WATER	.9959	.0794
2	PHENOL	.0041	.4603
3	METHYLNAPHTHAL	.0000	.4603

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
WATER	1.0000	.0000	.0794	.9000
PHENOL	.0000	.0000	.4603	.1000
METHYLNAPHTHAL	.0000	1.0000	.4603	.0000

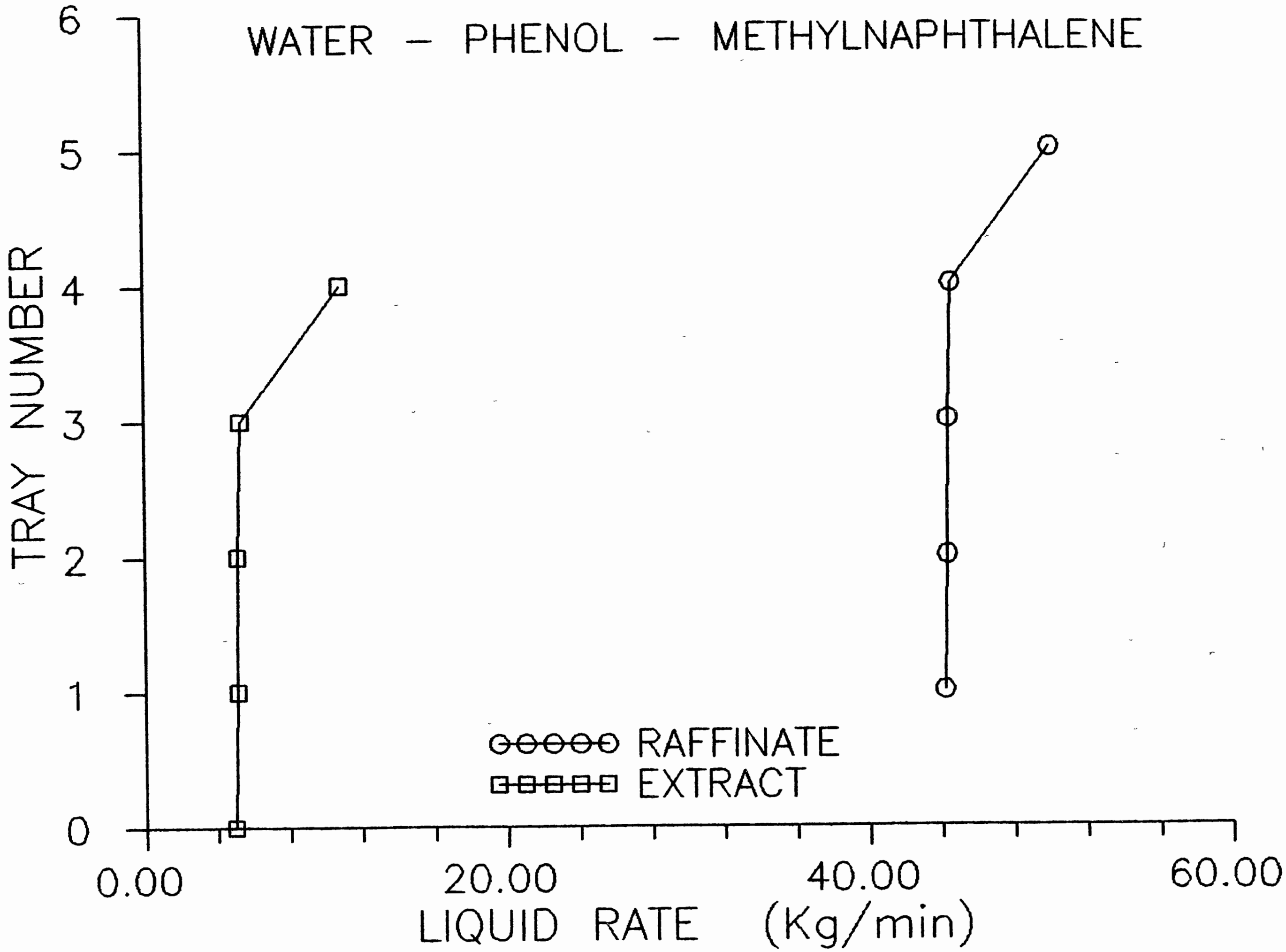


Figure 15. Case Study III Flow rate Profile

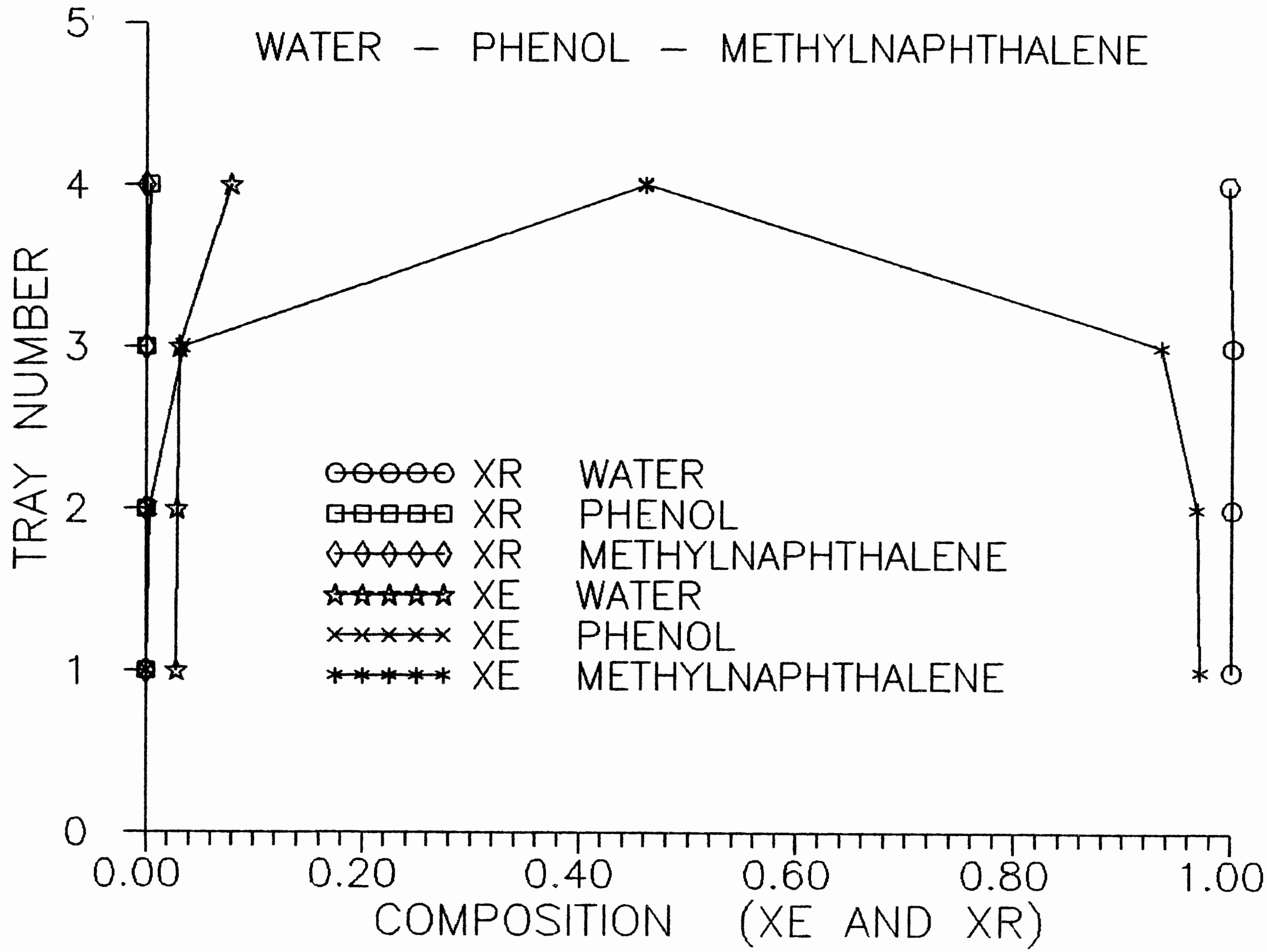


Figure 16. Case study III Composition Profile

representative examples of both heat-sensitive unsaturated hydrocarbons and the saturated hydrocarbons to be found in anarrow boiling fraction of tars. Boobar et al. presented eleven theoretical extraction stages would be required to effect an increase in the concentration of styrene from 10 percent in the feed to 90 percent in the solvent free extract phase. The temperature of this process was 25°C. According to the results of this work, styrene is extracted to diethylene glycol phase from 10 percent in the feed to 90.6 percent in the solvent free extract phase. Table X shows the results of case study IV.

Case Study V

The objective of Case Study V is to design a liquid-liquid extraction process which can reduce benzene contamination in a refinery wastewater stream from 200 ppm to less than 1 ppm before the wastewater is sent to further biological treatment. The flow rate of the wastewater stream is expected to be 4542.5 Kg/min. Because of limited information, several assumptions had to be made which apply to the liquid-liquid extraction process investigated. First, it was assumed that the contaminated wastewater was available at 1 atm and 70°F. The required flow rate of solvent (hydrocarbons) is available for use as a process stream of the refinery and the benzene extracted into the hydrocarbon stream will not cause any problems downstream of

TABLE X

RESULTS OF CASE STUDY IV

ETHYLBENZENE - STYRENE - DIETHYLENE GLYCOL SYSTEM

STAGE	DOWN STREAM	UP STREAM
11	83.11	131.81
10	83.16	114.92
9	83.16	114.98
8	83.16	114.98
7	83.16	114.98
6	83.16	114.98
5	83.16	114.98
4	83.16	114.98
3	83.16	114.98
2	83.08	114.98
1	68.18	114.89

BOTTOM OUTLET STREAM	=	68.19
BOTTOM INLET STREAM	=	100.00
TOP OUTLET STREAM	=	131.81
TOP INLET STREAM	=	100.00
FEED STREAM	=	100.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

----- STAGE 1 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8933	.0123
2	STYRENE	.1024	.1168
3	DIETHYLENE GLY	.0043	.8709

----- STAGE 2 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8946	.0122
2	STYRENE	.1011	.1175
3	DIETHYLENE GLY	.0043	.8702

TABLE X (Continued)

----- STAGE 3 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8948	.0122
2	STYRENE	.1009	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 4 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 5 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 6 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 7 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 8 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

TABLE X (Continued)

----- STAGE 9 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 10 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8949	.0122
2	STYRENE	.1008	.1176
3	DIETHYLENE GLY	.0043	.8702

----- STAGE 11 ----

	COMPONENT	XE	XR
1	ETHYLBENZENE	.8954	.0229
2	STYRENE	.1009	.2207
3	DIETHYLENE GLY	.0037	.7564

OVERALL COLUMN BALANCE, MASS FRACTIONS

COMPONENT	BOTTOM		TOP	
	OUTLET	INLET	OUTLET	INLET
ETHYLBENZENE	.8933	.0000	.0229	.9000
STYRENE	.1024	.0000	.2207	.1000
DIETHYLENE GLYCOL	.0043	1.0000	.7564	.0000

the extraction unit. The liquid-liquid extractor was designed to operate at a pressure of around 100 psia (above the saturated conditions of the solvent). Saturated hydrocarbons (n-C_4 - n-C_{10}) were tested as solvents. Table XI presents the results of the solvent tests. According to the results of dozens of trials, isobutane is the best solvent among them. Isobutane can be easily separated from extract phase. A feed to solvent ratio of 10 to 1 is applicable for one two-stage column with no recirculation of extract into feed. A simplified process flow diagram for the liquid-liquid extraction process is shown in Figure 17 and corresponding process flow information is contained in table XII.

TABLE XI

COMPARISON OF SOLVENT USE

Component	Feed Amount(Kg/min)
water	4541.59
benzene	0.91

5 stages, at 70°F, at saturated pressure.

WATER - BENZENE - BUTANE SYSTEM

BOTTOM OUTLET STREAM	=	4493.36
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	499.13
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.998E+00	.000E+00	.109E+00	.999E+00
BENZENE	.233E-22	.000E+00	.182E-02	.200E-03
BUTANE	.142E-02	.100E+01	.888E+00	.000E+00

WATER - BENZENE - ISO-BUTANE SYSTEM

BOTTOM OUTLET STREAM	=	4493.99
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	498.49
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.998E+00	.000E+00	.108E+00	.999E+00
BENZENE	.521E-11	.000E+00	.182E-02	.200E-03
ISOBUTANE	.142E-02	.100E+01	.889E+00	.000E+00

TABLE XI (Continued)

WATER - BENZENE - PENTANE SYSTEM

BOTTOM OUTLET STREAM	=	4424.35
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	568.14
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.999E+00	.000E+00	.209E+00	.999E+00
BENZENE	.628E-22	.000E+00	.159E-02	.200E-03
PENTANE	.384E-03	.100E+01	.789E+00	.000E+00

WATER - BENZENE - HEXANE SYSTEM

BOTTOM OUTLET STREAM	=	4453.41
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	539.08
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.999E+00	.000E+00	.164E+00	.999E+00
BENZENE	.294E-22	.000E+00	.168E-02	.200E-03
HEXANE	.817E-04	.100E+01	.834E+00	.000E+00

WATER - BENZENE - HEPTANE SYSTEM

BOTTOM OUTLET STREAM	=	4471.14
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	521.35
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

TABLE XI (Continued)

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.999E+00	.000E+00	.135E+00	.999E+00
BENZENE	.179E-22	.000E+00	.174E-02	.200E-03
HEPTANE	.183E-04	.100E+01	.862E+00	.000E+00

WATER - BENZENE - OCTANE SYSTEM

BOTTOM OUTLET STREAM	=	4482.86
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	509.63
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.999E+00	.000E+00	.115E+00	.999E+00
BENZENE	.121E-22	.000E+00	.178E-02	.200E-03
OCTANE	.424E-05	.100E+01	.882E+00	.000E+00

WATER - BENZENE - NONANE SYSTEM

BOTTOM OUTLET STREAM	=	4491.09
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	501.39
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.999E+00	.000E+00	.101E+00	.999E+00
BENZENE	.857E-23	.000E+00	.181E-02	.200E-03
NONANE	.100E-05	.100E+01	.897E+00	.000E+00

TABLE XI (Continued)

WATER - BENZENE - DECANE SYSTEM

BOTTOM OUTLET STREAM	=	4497.15
BOTTOM INLET STREAM	=	450.00
TOP OUTLET STREAM	=	495.34
TOP INLET STREAM	=	4542.50
FEED STREAM	=	450.00

COMPOSITION PROFILE, MASS FRACTION
EQUILIBRIUM STREAMS LEAVING STAGE

COMPONENT	BOTTOM OUTLET	BOTTOM INLET	TOP OUTLET	TOP INLET
WATER	.999E+00	.000E+00	.897E-01	.999E+00
BENZENE	.626E-23	.000E+00	.183E-02	.200E-03
DECANE	.243E-06	.100E+01	.908E+00	.000E+00

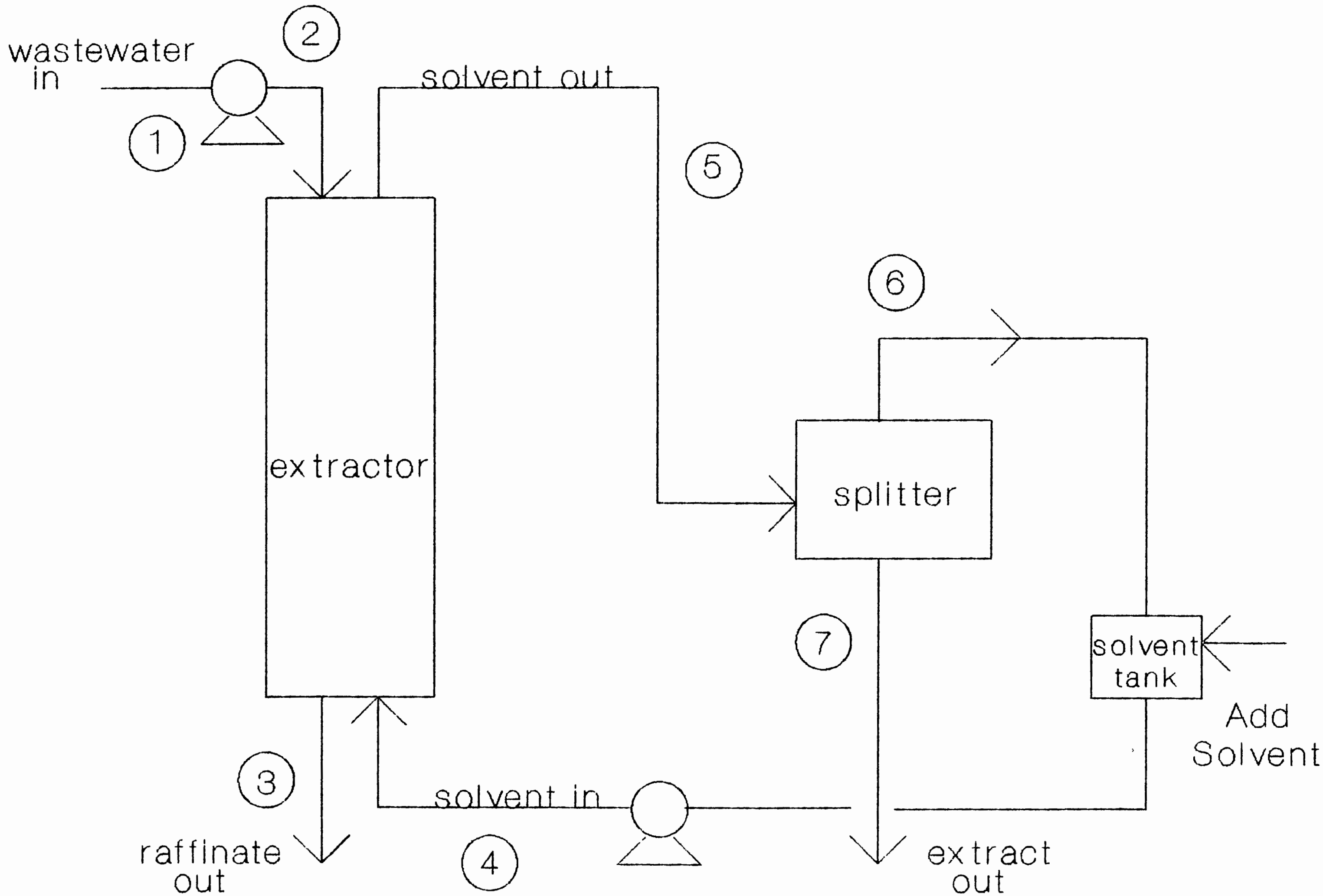


Figure 17. Simplified Process Flow Diagram for the Liquid-Liquid Extraction Scheme

TABLE XII

PROCESS FLOW INFORMATION FOR THE LIQUID-LIQUID EXTRACTION PROCESS

Stream #	Pressure, psia	Flow, Kg/min	Benzene content
1	14.7	4541.5860	200 ppm
2	108.5	4541.5860	200 ppm
3	14.7	4493.8100	5.2×10^{-4} ppm
4	100.0	450.0000	0 %
5	100.0	498.6856	.182 %
6	14.7	443.5808	0 %
7	14.7	55.1048	1.649 %

CHAPTER VII

CONCLUSION AND RECOMMENDATION

Conclusion

A liquid-liquid extraction simulator has been developed for the purpose of modeling steady state liquid-liquid extraction behavior. The program runs by batch input. An algorithm was included to allow for hypothetical components and extractor stages. The program can estimate equilibrium data without experimental equilibrium data input. The user may either specify initial temperature and extract rate profiles or use the program to calculate them on the basis of top and bottoms estimates. An extensive printout of the program results may be requested when solution is complete. The printout includes the description of system input values and availability of the UNIFAC data. It also includes streams around the both top and bottom leaving streams. The output also includes a tray-by-tray listing of extract and raffinate flow rates and extract and raffinate composition profiles.

The model was checked for each aspect of the program using a series of case studies. In each of these case studies, the accuracy of the model largely depends on the UNIFAC model. If given components do not have the UNIFAC interaction parameter, the UNIFAC methodology cannot be used to calculate the distribution coefficient. For the lack of information on existing plants, several sample systems have been tested in this work. According to the results of Case Study I, benzene is the best solvent among three tested solvents, hence the program can be used to select a good solvent component. As you see the results of Case Study II, optimum number of stages is five, so the program can be used to determine the optimum number of theoretical stages. The results of Case Study III show that phenol is easily separated from the water contaminated by phenol. Case Study IV proves that the program can be used to solve both aqueous and organic component systems. According to Case Study V, this work can be used to design a liquid-liquid extraction process. Smith's method (rigorous method) was not converged in all four case studies; Smith's method program did not calculate K (distribution coefficients) value while running the program in Case II and IV, and it diverged in Case Study I and III (both raffinate and extract rates made overflow). The outcome of this work greatly depends on distribution coefficient estimation. Grote (1958) presented that up to 97 percent recovery was indicated, according to the results of Case Study II, aromatics recovery is up to 55 percent using diethylene glycol as solvent, as far as I am concerned, the difference between Grote results and this work results are caused by using different equipment. I used one extract column, on the other hand, Udex process used complex equipment. Aromatics recovery is up to 86.7 percent using ethylenediamine as solvent at one five-stage column.

Recommendation

The author realizes that no simulation is without fault and that there is always room for improvement. The following recommendations represent some of the areas in which the author feels this simulation can be improved.

The input section of the program can be improved so that the user can input by either key-board or file, and can save input data after inputting by key-board. The output section of the program should be printed out results which are necessary, otherwise, the output file will be too big to manage.

UNIFAC interaction parameters have been developed; the UNIFAC interaction parameter data in this work are the newest data. More updated UNIFAC interaction parameters will offer a means of more accurate and wider estimation of distribution coefficient K. So far the UNIFAC is the most powerful model when experimental data are not available, but the results will be better, if program adopt the better γ_i model which doesn't exist yet.

The model assumed that temperature is constant at any place in the liquid-liquid extraction column. But heat effects caused by mixing, agitating, and transferring to/from surroundings can be considered for more accurate results.

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APPENDICES

APPENDIX A

FORTRAN SOURCE CODE FOR THE MULTICOMPONENT MULTISTAGE LIQUID-LIQUID EXTRACTION PROCESS CALCULATION PROGRAM

```
$DEBUG
C234567
C .............................................................
C .....
C .....
C     ....  SHORT CUT AND STAGE TO STAGE CALCULATION
C
C
      IMPLICIT REAL(A-H,L,O-Z)
      CHARACTER FILE1*30
C
      WRITE(*,11)
   11 FORMAT(//,5X,'ENTER THE INPUT FILE NAME')
      READ(*,21)FILE1
   21 FORMAT(30A)
C
      OPEN(UNIT=8,FILE=FILE1,STATUS='UNKNOWN')
      OPEN(UNIT=9,FILE='MAIN1.OUT',STATUS='UNKNOWN')
C
      WRITE(*,31)
   31 FORMAT(//,3X,'ENTER THE NUMBER YOU WANT',////,
     &         5X,'1. ONLY SHORT CUT METHOD',//,
     &         5X,'2. ONLY STAGE TO STAGE CALCULATION',//,
     &         5X,'3. BOTH SHORT CUT AND STAGE TO STAGE CALCULATION',/
     &         //,5X,'--------------->')
C
      READ(*,*)MODE
C
      GOTO (10,20,30),MODE
C
   10 CALL SC
      GOTO 999
C
   20 CALL STS(MODE)
      GOTO 999
C
   30 CALL SC
      CALL STS(MODE)
C
  999 CONTINUE
      STOP
      END
C
C
$DEBUG
C234567
C .............................................................
C .....
C .....
C ******************************************************************
C ****    SUBROUTINE SHORT CUT METHOD                           ****
C ****    THIS PROGRAM CALCULATE UP TO 2000 STAGES, 30 COMPONENT  ****
C ****    REFERENCE :  Smith, D. B., "Design of Equilibrium     ****
C ****               Stage Processes", McGraw-Hill, N.Y., 1963. ****
C ******************************************************************
C
C ******************************************************************
C     INPUT
C     TEXT = IDENTIFICATION OF THE SYSTEM
C     NC   = NUMBER OF COMPONENT
C     NG   = NUMBER OF DIFFERENT GROUPS
C     ITAB = THE NUMBER OF GROUPS OF TYPE K IN MOLECULE I
C            UNIFAC SPECIFICATION OF GROUPS
C            COMPONENT I = ID NUMBER OF COMPONENT I
C            COMPONENT J = THE NUMBER OF JTH GROUPS
C     T    = TEMPERATURE IN K
C     Z(I) = TOTAL MOLES OF COMP. I IN THE MIXTURE, ALL I
C
      SUBROUTINE SC(CNAME)
```

```
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      COMMON /MM/   MO
      CHARACTER TEXT*80,A*5,CNAME(30)*30,UNIT*25
C
C     INPUT DATA (FOR K VALUES))
C
      NT=57
      MO=0
C
C     TEXT
C
      READ(8,1001) TEXT
      WRITE(6,1001) TEXT
      WRITE(9,1001)TEXT
 1001 FORMAT(75A)
C
C     NC, NG
C
      READ(8,1002) NC,NG,NITAB
      WRITE(6,1002)NC,NG,NITAB
      WRITE(9,1002)NC,NG,NITAB
 1002 FORMAT(10X,3I5)
C
C     CNAME(I)
C
      DO K=1,NC
        READ(8,1003)CNAME(K)
        WRITE(6,1003)CNAME(K)
        WRITE(9,1003)CNAME(K)
 1003   FORMAT(10X,35A)
      END DO
C
C     ITAB(I,J)
C
      DO 60 I=1,NC
        DO 60 J=1,NT
           ITAB(I,J) = 0.0
   60 CONTINUE
C
      DO 10 K=1,NITAB
           READ(8,1004)ID,ID1,ITAB(ID,ID1)
           WRITE(6,1004)ID,ID1,ITAB(ID,ID1)
           WRITE(9,1004)ID,ID1,ITAB(ID,ID1)
           IF(ID .EQ. 0) GOTO 11
 1004      FORMAT(10X,3I5)
   10 CONTINUE
C
C     TOTAL MOLES OF COMP. I  Z(I)
C
   11 CONTINUE
C
      DO 15 K=1,NC
         READ(8,1005) Z(K),UNIT
         WRITE(6,1005)Z(K),UNIT
         WRITE(9,1005)Z(K),UNIT
 1005    FORMAT(10X,F10.4,30A)
   15 CONTINUE
C
C     NFEED, F1, F2, SOL
```

```
 C
       READ(8,1006) NFEED,F1,F2,SOL
       WRITE(6,1006)NFEED,F1,F2,SOL
       WRITE(9,1006)NFEED,F1,F2,SOL
  1006 FORMAT(10X,I5,3F10.4)
 C
 C     REFLUX, REFLUX1
 C
       READ(8,1007) REFLUX,REFLX1
       WRITE(6,1007)REFLUX,REFLX1
       WRITE(9,1007)REFLUX,REFLX1
  1007 FORMAT(10X,2F10.4)
 C
       WRITE(6,30)
       WRITE(9,30)
    30 FORMAT(//,5X,'***  IDENTIFICATION OF SYSTEM  ***')
       WRITE(9,40) TEXT
    40 FORMAT(//,3X,A74)
       WRITE(6,50) NC,NG
       WRITE(9,50) NC,NG
   50 FORMAT(//,5X,'NUMBER OF COMPONENTS IS',I3,//,5X,
     &       'NUMBER OF DIFFERENT GROUPS IS',I3,//)
      IF (NC.EQ.0) THEN
      WRITE(6,*)'   THE NUMBER OF COMPONENT IS 0.0,  PROGRAM TERMINATED'
      WRITE(9,51)
   51 FORMAT(/,3X,'THE NUMBER OF COMPONENT IS 0.0,  PROGRAM TERMINATED')
      STOP
      END IF
      NR=0
C
C     XXS(I),YF1(I),YF2(I)
C
      DO I=1,NC
        READ(8,1009) XXS(I),YF1(I),YF2(I)
        WRITE(6,1009)XXS(I),YF1(I),YF2(I)
        WRITE(9,1009)XXS(I),YF1(I),YF2(I)
 1009   FORMAT(10X,3F10.8)
      END DO
C
      DO 113 I=1,NC
         SS(I)=SOL*XXS(I)
         L(NSTAGE+1)=SOL
         LX(NSTAGE+1,I)=SS(I)
  113 CONTINUE
C
C     END TEMPERATURE
C
      READ(8,1010) T
      WRITE(6,1010)T
      WRITE(9,1010)T
 1010 FORMAT(10X,2F10.4)
C
C     NSTAGE, JSTAGE
C
      READ(8,1011) NSTAGE,MSTAGE
      WRITE(6,1011)NSTAGE,MSTAGE
      WRITE(9,1011)NSTAGE,MSTAGE
 1011 FORMAT(10X,2I5)
C
C
C
C  ********************************************************************
      CALL KCAL
C  ********************************************************************
C
      WRITE(6,130)
      WRITE(9,130)
  130 FORMAT(//,11X,'NAME',16X,'K')
      DO 140 I=1,NC
```

```
      WRITE(9,150) CNAME(I),CAY(I)
 140  WRITE(6,150) CNAME(I),CAY(I)
 150  FORMAT(10X,A15,F10.4)
C
C     ASSUME K=K'  IF TWO COLUMN SECTION ARE INVOLVED
C
C     TWO COLUMN .. Y
C     ONE COLUMN .. N
C
      READ(8,68) A
  68  FORMAT(10X,5A)
      IF(A .EQ. 'Y') THEN
       DO 160 I=1,NC
        ACAY(I)=CAY(I)
 160    ACAY1(I)=CAY(I)
      END IF
C
      DO 170 I=1,NC
        ACAY(I)=CAY(I)
        ACAY1(I)=ACAY(I)
 170  CONTINUE
 171  CONTINUE
C
C     ASSUME  B AND D
C
      READ(8,173) B,D
 173  FORMAT(10X,2F10.4)
      WRITE(9,1101)B,D
1101  FORMAT(/,10X,'B  =',F15.4,/,10X,'D  =',F15.4)
C
      V(0)=REFLX1*B+F2
      IF(MSTAGE.EQ.0) THEN
        V(0)=REFLX1*B+F1
      END IF
C
C     USE MATERIAL BALANCE TO CALCULATE ANY OTHER END RATES
C
      L(1)=B+(V(0)-F2)
C
C     ASSUME THE EXTRACT RATE TO VARY LINEARLY FROM L(N+1) TO L(1)
C         AND VN TO V0
C
      LCH=ABS(SOL-L(1))/(NSTAGE)
      DO 180 I=1,NSTAGE
        IF(L(1).GT.SOL) THEN
          L(I)=L(1)-(I-1)*LCH
        ELSE
          L(I)=L(1)+(I-1)*LCH
        END IF
 180  CONTINUE
C
      L1SUM=0.0
      L2SUM=0.0
C
      DO 181 I=MSTAGE+1,NSTAGE
 181    L1SUM=L1SUM+L(I)
C
      LLL1=L1SUM/(NSTAGE-MSTAGE)
C
      DO 182 I=1,MSTAGE
 182    L2SUM=L(I)+L2SUM
C
      IF(MSTAGE.EQ.0) THEN
       LLL2=LLL1
      ELSE
       LLL2=L2SUM/MSTAGE
      END IF
C
      VCH=ABS((D-V(0))/(NSTAGE))
```

```
C
      IF(V(0) .GE. D) THEN
        DO 185 I=1,NSTAGE
          V(I)=V(0)-I*VCH
  185   CONTINUE
      ELSE
        DO 188 I=1,NSTAGE
  188     V(I)=V(0)+I*VCH
      END IF
C
      V1SUM=0.0
      V2SUM=0.0
C
      DO 191 I=MSTAGE+1,NSTAGE
  191   V1SUM=V1SUM+V(I)
C
      VVV1=V1SUM/(NSTAGE-MSTAGE)
C
      DO 192 I=1,MSTAGE
  192   V2SUM=V2SUM+V(I)
C
      IF(MSTAGE.EQ.0) THEN
        VVV2=VVV1
      ELSE
        VVV2=V2SUM/MSTAGE
      END IF
C
C     USE EQS. TO PREDICT THE INDIVIDUAL RECOVERIES
C
C     ITMAX : THE MAXIMUM ITERATION NUMBER
C
      READ(8,200) ITMAX
  200 FORMAT(10X,I5)
      WRITE(9,*)
      WRITE(6,*)'     MAXIMUM NO. OF ITERATION IS = ',ITMAX
      WRITE(9,*)'     MAXIMUM NO. OF ITERATION IS = ',ITMAX
C
      NNN=1
C
      DO 220 M=1,ITMAX
C
      TEMP=REAL(M/10.)
      IF((TEMP-INT(TEMP)).EQ.0.0) THEN
        WRITE(6,230) M
        WRITE(9,230) M
  230   FORMAT(/,3X,'********   TRIAL',3X,I3,2X,'********')
      END IF
C
      DO 115 I=1,NC
        IF(CAY(I).LE.(0.0)) THEN
          WRITE(6,110)
          WRITE(9,110)
  110     FORMAT(//,3X,' **** CANNOT CALCULATE K VALUE IN THIS SYSTEM',
     &             //,5X,'THIS SYSTEM BECOME ONE PHASE OR DOES NOT HAVE',
     &                1X,'INTERACTION PARAMETERS',/,5X,'CHECK INTERACTION'
     &                1X,'PARAMETER IN OUTPUT FILE',/,5X,'OR CHANGE',1X,
     &                   'SOLVENT TO FEED RATIO')
          STOP
       END IF
  115 CONTINUE
C
C  ******************************************************************
      CALL RECAL(LLL1,LLL2,VVV1,VVV2)
C  ******************************************************************
C
C     CALCULATE THE AMOUNT OF EACH COMPONENT LEAVING EACH END OF THE
C      COLUMN WITH EQ.
C
C  *******************************************************************
```

```
      CALL LACAL(LLL1,LLL2,VVV1,VVV2,SDYD,SL1X1,SBXB,NNN,M)
C  *******************************************************************
C
C
      DO 235 I=1,NC
        ACAY(I)=SUMC(I)
  235   ACAY1(I)=SUMCC(I)
      IF(MSTAGE.EQ.0) THEN
        DO I=1,NC
          ACAY1(I)=ACAY(I)
        END DO
      END IF
C
  220 CONTINUE
C
C     OUT PUT OF FINAL RESULT
C
      WRITE(6,240)
      WRITE(9,240)
  240 FORMAT(//,3X,'****  FINAL  RESULTS  ****',//,5X,'BOTTOM OUTLET',
     & 3X,'TOP OUTLET',3X,'BOTTOM INLET')
C
      WRITE(6,250)SBXB,SDYD,SL1X1,UNIT
      WRITE(9,250)SBXB,SDYD,SL1X1,UNIT
  250 FORMAT(6X,F10.4,5X,F10.4,4X,F10.4,/,5X,'UNIT =  ',A20)
C
C
      WRITE(9,290)
      WRITE(6,290)
  290 FORMAT(//,10X,'LV PROFILE',/,3X,'STAGE',8X,'DOWN STREAM',5X,'UP ST
     &REAM')
C
      DO I=1,NSTAGE
        WRITE(9,300)I,L(I),V(I)
        WRITE(6,300)I,L(I),V(I)
  300   FORMAT(3X,I3,5X,2F15.4)
      END DO
C
      RETURN
      END
C
C ....................................................................
C
C *********************************************************************
      SUBROUTINE RECAL(LLL1,LLL2,VVV1,VVV2)
C *********************************************************************
C
C *********************************************************************
C     THIS SUBROUTINE CALCULATE THE AVERAGE STRIPPING FACTORS FOR EACH
C      COMPONENT USING THE AVERAGE RATES AND K VALUES AND CALCULATE f.
C *********************************************************************
C
C
      IMPLICIT REAL (A-H,L,O-Z)
      REAL*8 SA
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      COMMON /MM/   MO
      DIMENSION H(30),SN(30),SM(30),QQSS(30),QF(30)
C
C     USE THE AVERAGE RATES AND K VALUE TO CALCULATE AVERAGE STRIPPING
C     FACTORS FOR EACH COMPONENT,  SN AND SM
```

```
C
      DO 5 I=1,NC
         SN(I)=ACAY(I)*VVV1/LLL1
         SM(I)=ACAY1(I)*VVV2/LLL2
         IF(MSTAGE.EQ.0) SM(I)=SN(I)
C
C     CALCULATION OF H
C
         H(I)=(ACAY1(I)/ACAY(I))*(LLL1/LLL2)*(1-SN(I))/(1-SM(I))
C
C     CALCULATION OF f
C
      QQSS(I)=XXS(I)/(XXS(I)+YF1(I)+YF2(I))
      QF(I)=YF2(I)/(YF2(I)+YF1(I)+XXS(I))
      IF(MO.EQ.1) THEN
         SA=2.**30
      ELSE
         SA=SN(I)**(NSTAGE-MSTAGE)
      END IF
      TEMP=0.0
      IF(SA.NE.0.0) TEMP=REAL(DLOG(SA))
      IF(TEMP.GE.(ALOG(2)*30.)) MO=1
C
      IF(QQSS(I).EQ.0.0.AND.MSTAGE.EQ.0) THEN
         F(I)=(1.-SA)/(1.-SA*SN(I))
      ELSE
         IF(QQSS(I).EQ.1.0 .AND. MSTAGE.EQ.0) THEN
           F(I)=(1.-SN(I))/(1.-SA*SN(I))
           ELSE
      F(I)=((1.-SA)+QQSS(I)*(SA-SN(I))+REFLUX*(1-SN(I))+H(I)*QF(I)*SA*
     &     (1-SM(I)**MSTAGE))/((1-SA)+H(I)*SA*(1-SM(I)**MSTAGE)+REFLUX*
     &     (1-SN(I))+H(I)*((1+REFLX1)/(1+G(I)*REFLX1))*(SM(I)**MSTAGE)*
     &     SA*(1-SM(I)))
         END IF
      END IF
C
    5 CONTINUE
      RETURN
      END
C
C ...................................................................
C
C ***********************************************************************
      SUBROUTINE LACAL(LLL1,LLL2,VVV1,VVV2,SDYD,SL1X1,SBXB,
     & NNN,KK)
C ***********************************************************************
C
C
C ***********************************************************************
C     THIS SUBROUTINE CALCULATE THE AMOUNT OF EACH COMPONENT LEAVING
C      EACH END OF THE COLUMN.
C ***********************************************************************
C
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION BS(30),DYD(0:30),BXB(30),L1X1(30),YD(30),
     &          CAYY(30),CAYYY(30),YO(30),VCH(30),LCH(30)
C
C     BS(I)=B*XB(I)+SE*XSE(I)
C     IF SE=0.0 BXB=BS
```

```
C     DYD(I)=D*YD(I)
C     BXB(I)=B*XB(I)
C     L1X1(I)=L1*X1(I)
C
      SBS = 0.
      SDYD = 0.
      SBXB = 0.
      SL1X1 = 0.
      BO=B
      DO=D
C
C
      DO 10 I=1,NC
         BS(I)=(F(I))*(((F1*YF1(I))+(F2*YF2(I))+SS(I)))
         DYD(I)=(1-F(I))*(((F1*YF1(I))+(F2*YF2(I))+SS(I)))
         IF(SE .EQ. 0.0 .AND. REFLX1 .EQ. 0.0) THEN
           BXB(I)=BS(I)
           L1X1(I)=BXB(I)
         ELSE
           BXB(I)=((1-G(I))/(1+G(I)*REFLX1))*(BS(I))
           L1X1(I)=((1+REFLX1)/(1-G(I)))*(BXB(I))
         END IF
C
         SBS=SBS+BS(I)
         SDYD=SDYD+DYD(I)
         SBXB=SBXB+BXB(I)
         SL1X1=SL1X1+L1X1(I)
   10 CONTINUE
      SE=SBS-SBXB
      TEMP=REAL(KK/10.)
      IF((TEMP-INT(TEMP)).EQ.0.0) THEN
        WRITE(6,17)
        WRITE(9,17)
   17   FORMAT(/,11X,'BOTTOM OUTLET',8X,'TOP OUTLET')
C
        B=SBXB
        D=SDYD
C
        IF((ABS(B-BO)/BO).LT.1.E-4.AND.(ABS(DO-D)/DO).LT.1.E-4) KK=ITMAX
     &+1
C
        WRITE(6,20)B,D
        WRITE(9,20)B,D
   20   FORMAT(6X,F16.4,4X,F16.4)
      END IF
C
      SUM1=0.0
      SUM2=0.0
C
      DO 30 I=1,NC
        X1(I)=L1X1(I)/SL1X1
        YD(I)=DYD(I)/SDYD
        SUM1=SUM1+X1(I)
        SUM2=SUM2+YD(I)
   30 CONTINUE
C
      IF(NNN .GE. ITMAX) GOTO 999
C
      DO 100 J=1,NSTAGE
C
C     ***RAFFINATE CHANGE
C
        IF(MSTAGE.EQ.0) THEN
          V(0)=SBXB*REFLX1+F1
        ELSE
          V(0)=SBXB*REFLX1+F2
        END IF
C
        DO 50 I=1,NC
```

```
        IF(MSTAGE.EQ.0) THEN
          ZZ(I)=REFLX1*SBXB*X1(I)+F1
        ELSE
          ZZ(I)=REFLX1*SBXB*X1(I)+F2
        END IF
        YO(I)=(ZZ(I))/V(0)
   50   VCH(I)=ABS((V(0)*YO(I)-DYD(I))/(NSTAGE))
C
C     ***EXTRACT CHANGE
C
       DO 70 I=1,NC
         LCH(I)=ABS((L1X1(I)-SS(I))/(NSTAGE))
   70  CONTINUE
       DO 80 I=1,NC
         IF(SS(I).LE.L1X1(I)) THEN
           ZL=(SS(I)+LCH(I)*(NSTAGE-J))
         ELSE
           ZL=(SS(I)-LCH(I)*(NSTAGE-J))
         END IF
C
         IF(DYD(I).LE.ZZ(I)) THEN
           ZV=(ZZ(I)-VCH(I)*(J-1))
         ELSE
           ZV=(ZZ(I)+VCH(I)*(J-1))
         END IF
C
         Z(I)=ZL+ZV
   80  CONTINUE
C
C   *******************************************************************
      CALL KCAL
C   *******************************************************************
C
       DO 90 I=1,NC
         CCAY(J,I)=CAY(I)
   90  CONTINUE
  100 CONTINUE
C
      DO 130 J=1,NC
       DO 120 I=1,NC
         SUMC(I)=0.0
         DO 110 K=NSTAGE,MSTAGE+1,-1
           CAYY(I)=CCAY(K,I)
           SUMC(I)=SUMC(I)+CAYY(I)
  110    CONTINUE
         SUMC(I)=SUMC(I)/(NSTAGE-MSTAGE)
C
         SUMCC(I)=0.0
         DO 115 K=1,MSTAGE+1
           CAYYY(I)=CCAY(K,I)
           SUMCC(I)=SUMCC(I)+CAYYY(I)
  115    CONTINUE
         IF(MSTAGE.EQ.0) THEN
           SUMCC(I)=SUMC(I)
         ELSE
           SUMCC(I)=SUMCC(I)/(MSTAGE+1.)
         END IF
  120  CONTINUE
C
  130 CONTINUE
C
C     *** RAFFINATE LEAVING UPPER PART AND LOWER PART
C
      VVCH=ABS(V(0)-SDYD)/NSTAGE
      V1SUM=0.0
      V2SUM=0.0
      IF(V(0) .GE. SDYD) THEN
        DO 52 I=1,NSTAGE
   52     V(I)=V(0)-VVCH*I
```

```
      ELSE
        DO 53 I=1,NSTAGE
   53     V(I)=V(0)+VVCH*I
      END IF
C
      DO 54 I=MSTAGE+1,NSTAGE
   54   V1SUM=V1SUM+V(I)
C
      VVV1=V1SUM/(NSTAGE-MSTAGE)
C
      DO 55 I=1,MSTAGE
   55   V2SUM=V2SUM+V(I)
C
      IF(MSTAGE.EQ.0) THEN
        VVV2=VVV1
      ELSE
        VVV2=V2SUM/MSTAGE
      END IF
C
C     *** EXTRACT LEAVING UPPER PART AND LOWER PART
C
      LLCH=ABS(SL1X1-SOL)/NSTAGE
C
      L(1)=SL1X1
      L(NSTAGE)=SOL
      DO 72 I=2,NSTAGE
        IF(SOL.LT.SL1X1) THEN
          L(I)=SL1X1-LLCH*(I-1)
        ELSE
          L(I)=SL1X1+LLCH*(I-1)
        END IF
   72 CONTINUE
C
      L1SUM=0.0
      L2SUM=0.0
C
      DO 74 I=MSTAGE+1,NSTAGE
   74   L1SUM=L1SUM+L(I)
C
      LLL1=L1SUM/(NSTAGE-MSTAGE)
C
      DO 76 I=1,MSTAGE
   76   L2SUM=L2SUM+L(I)
C
      IF(MSTAGE.EQ.0) THEN
        LLL2=LLL1
      ELSE
        LLL2=L2SUM/MSTAGE
      END IF
C
  999 NNN=NNN+1
C
      RETURN
      END
C
C
$DEBUG
C234567
C ..................................................................
C.....
C.....  MAIN SUBPROGRAM OF STAGE TO STAGE CALCULATION
C
C
C ..................................................................
C
      SUBROUTINE STS(MODE,CNAME)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),Q(30),XXS(30),SOL,
```

```
     &               ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &               F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/   CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &               L(200),V(0:200),LX(200,30),VY(0:200,30),
     &               X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &               CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/  NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &               PARB(76,76),XL(30)
      COMMON /CMB/   AA(200,30),BB(200,30),CC(200,30),DD(200,30),
     &               FZ(0:200,30)
      CHARACTER TEXT*80,CNAME(30)*30,UNIT*25
C
C
      IF(MODE.EQ.3) GOTO 4
C
C
      CALL INPUT(TEXT,CNAME,UNIT,MODE)
C
C
    4 CONTINUE
C
      WRITE(9,1)
      WRITE(6,1)
    1 FORMAT(////,5X,'***  STAGE - TO - STAGE CALCULATION  ***',//,)
C
      NITER=1
C
    3 CONTINUE
C
      IF(NITER.EQ.1) THEN
      READ(8,6) RD
    6 FORMAT(10X,F10.4)
      END IF
C
      TEMP=REAL(NITER/RD)
      IF(ABS(TEMP-INT(TEMP)).EQ.0.0) THEN
        WRITE(6,5)NITER
        WRITE(9,5)NITER
    5 FORMAT(/,3X'*************  TRIAL NUMBER ,',I5,3X,'*************',
     &/)
      END IF
C
C
      CALL SCAL
C
C
      CALL CMBEE
C
C
      CALL LVCAL
C
C
C .... CALCULATION OF K VALUES AT EACH STAGE
C
C
      DO 30 I=1,NSTAGE
        DO 20 J=1,NC
          Z(J)=LX(I+1,J)+VY(I-1,J)
   20 CONTINUE
C
C
          CALL KCAL
C
C
          DO J=1,NC
            SCAY(I,J)=CAY(J)
          END DO
   30 CONTINUE
C
```

```
C
      CALL CONV(ICON,NITER,RD)
C
C
      IF(ICON.EQ.1) THEN
        NITER=NITER+1
        GOTO 3
      END IF
C
C
      CALL OUTPUT(NITER,CNAME)
C
C
      RETURN
      END
C
C
C ......................................................................
C .....
C ****   SUBROUTINE INPUT
C .....
C
C234567
C
      SUBROUTINE INPUT(TEXT,CNAME,UNIT,MODE)
C
C     INPUT VARIABLE
C
C     USE THE RESULTS OF SHORT-CUT CALCULATION
C
C     TEXT - IDENTIFICATION OF SYSTEM
C     NFEED - THE NUMBER OF FEED
C     REFLX1 - EXTRACT REFLUX
C     REFLUX - RAFFINATE REFLUX
C     NC - THE NUMBER OF COMPONENTS
C     NG - THE NUMBER OF DIFFERENT GROUPS
C     CNAME(I) - COMPONENT NAME
C     ITAB(I,J) - UNIFAC SPECIFICATION OF GROUPS
C     Z(I) - TOTAL MOLES OF COMP. I IN THE MIXTURE ALL I
C     UNIT - THE UNIT OF Z(I)
C     F1 - MOLES OF FEED 1
C     F2 - MOLES OF FEED 2
C     SOL - MOLES OF SOLVENT
C     XXS(I) - MOLE FRACTION OF COMP. I IN SOLVENT
C     YF1(I) - MOLE FRACTION OF COMP. I IN FEED 1
C     YF2(I) - MOLE FRACTION OF COMP. I IN FEED 2
C     G(I) - RECOVERY OF COMP. I IN SE
C     T1 - TEMPERATURE AT THE TOP
C     T2 - TEMPERATURE AT THE BOTTOM
C     NSTAGE - THE NUMBER OF STAGE
C     JSTAGE - FEED STAGE LOCATION FROM THE TOP
C
C     INPUT OF ASSUMED VALUE
C
C     X(I,J) - ASSUMED MOLE FRACTION OF COMP.I IN EXTRACT PRODUCT (L1(I))
C     LX(I,J) - ASSUMED RATE OF EXTRACT PRODUCT (L1)
C     L(I) - ASSUMED RATE OF LINEAR EXTACT (L) PROFILE
C     CCAY(I,J) - ASSUMED K PROFILE I=STAGE, J=COMPONENT
C         --- USE RESULTS OF SHORT CUT METHOD
C     ITMAX - THE MAXIXMUM NUMBER OF ITERATION
C
C
C.........................
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
```

```
     &               L(200),V(0:200),LX(200,30),VY(0:200,30),
     &               X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &               CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &               PARB(76,76),XL(30)
      CHARACTER TEXT*80,CNAME(30)*20,UNIT*25
C
C     INPUT DATA (FOR K VALUES))
C
      NT=57
C
      IF(MODE.EQ.3) GOTO 999
C
C     TEXT
C
      READ(8,1001) TEXT
      WRITE(6,1001)TEXT
      WRITE(9,1001)TEXT
 1001 FORMAT(75A)
C
C     NC, NG
C
      READ(8,1002) NC,NG,NITAB
      WRITE(6,1002)NC,NG,NITAB
      WRITE(9,1002)NC,NG,NITAB
 1002 FORMAT(10X,3I5)
C
C     CNAME(I)
C
      DO K=1,NC
        READ(8,1003)CNAME(K)
        WRITE(6,1003)CNAME(K)
        WRITE(9,1003)CNAME(K)
 1003   FORMAT(10X,35A)
      END DO
C
C     ITAB(I,J)
C
      DO 60 I=1,NC
        DO 60 J=1,NT
           ITAB(I,J) = 0.0
   60 CONTINUE
C
      DO 10 K=1,NITAB
           READ(8,1004)ID,ID1,ITAB(ID,ID1)
           WRITE(6,1004)ID,ID1,ITAB(ID,ID1)
           WRITE(9,1004)ID,ID1,ITAB(ID,ID1)
           IF(ID .EQ. 0) GOTO 11
 1004      FORMAT(10X,3I5)
   10 CONTINUE
C
C     TOTAL MOLES OF COMP. I  Z(I)
C
   11 CONTINUE
C
      DO 15 K=1,NC
         READ(8,1005) Z(K),UNIT
         WRITE(6,1005)Z(K),UNIT
         WRITE(9,1005)Z(K),UNIT
 1005    FORMAT(10X,F10.4,30A)
   15 CONTINUE
C
C     NFEED, F1, F2, SOL
C
      READ(8,1006) NFEED,F1,F2,SOL
      WRITE(6,1006)NFEED,F1,F2,SOL
      WRITE(9,1006)NFEED,F1,F2,SOL
 1006 FORMAT(10X,I5,3F10.4)
C
```

```
C     REFLUX, REFLUX1
C
      READ(8,1007) REFLUX,REFLX1
      WRITE(6,1007)REFLUX,REFLX1
      WRITE(9,1007)REFLUX,REFLX1
 1007 FORMAT(10X,2F10.4)
C
      WRITE(6,30)
      WRITE(9,30)
   30 FORMAT(//,5X,'***  IDENTIFICATION OF SYSTEM  ***')
      WRITE(9,40) TEXT
   40 FORMAT(//,3X,A74)
      WRITE(6,50) NC,NG
   50 FORMAT(//,5X,'NUMBER OF COMPONENTS IS',I3,//,5X,
     &       'NUMBER OF DIFFERENT GROUPS IS',I3,//)
      IF (NC.EQ.0) THEN
      WRITE(6,*)'   THE NUMBER OF COMPONENT IS 0.0,  PROGRAM TERMINATED'
      WRITE(9,*)'   THE NUMBER OF COMPONENT IS 0.0,  PROGRAM TERMINATED'
      STOP
      END IF
      NR=0
C
C     XXS(I),YF1(I),YF2(I),G(I)
C
      DO I=1,NC
        READ(8,1009) XXS(I),YF1(I),YF2(I)
        WRITE(6,1009)XXS(I),YF1(I),YF2(I)
        WRITE(9,1009)XXS(I),YF1(I),YF2(I)
 1009   FORMAT(10X,3F10.4)
      END DO
C
      DO 113 I=1,NC
         SSX(I)=SOL*XXS(I)
  113 CONTINUE
C
C     TEMPERATURE
C
      READ(8,1010) T
      WRITE(6,1010)T
      WRITE(9,1010)T
 1010 FORMAT(10X,F10.4)
C
C     NSTAGE, JSTAGE
C
      READ(8,1011) NSTAGE,MSTAGE
      WRITE(6,1011)NSTAGE,MSTAGE
      WRITE(9,1011)NSTAGE,MSTAGE
 1011 FORMAT(10X,2I5)
C
C
      DO 125 I=1,NC
        READ(8,1012) X(1,I)
        WRITE(6,1012)X(1,I)
        WRITE(9,1012)X(1,I)
  125 CONTINUE
 1012 FORMAT(10X,F10.4)
C
C
      READ(8,1013) L(1)
      WRITE(6,1013)L(1)
      WRITE(9,1013)L(1)
 1013 FORMAT(10X,F10.4)
C
      DO 138 I=1,NC
  138   LX(1,I)=L(1)*X(1,I)
C
      DO 140 I=2,NSTAGE+1
        READ(8,1014) L(I)
        WRITE(6,1014)L(I)
```

```
      WRITE(9,1014)L(I)
 1014   FORMAT(10X,F10.4)
 140 CONTINUE
C
    DO 170 I=1,NSTAGE
      DO 160 J=1,NC
        READ(8,1015) SCAY(I,J)
        WRITE(6,1015)SCAY(I,J)
        WRITE(9,1015)SCAY(I,J)
 1015     FORMAT(10X,F10.4)
  160   CONTINUE
  170 CONTINUE
C
      READ(8,1016) ITMAX
      WRITE(6,1016)ITMAX
      WRITE(9,1016)ITMAX
 1016 FORMAT(10X,I5)
      GOTO 9999
C
  999 CONTINUE
C
      DO 500 I=1,NSTAGE
          X(1,I)=X1(I)
        DO 490 J=1,NC
          SCAY(I,J)=CCAY(I,J)
  490   CONTINUE
  500 CONTINUE
C
 9999 CONTINUE
C
      RETURN
      END

C
C.....................................................................
C .....
C .....
C
C234567
      SUBROUTINE CONV(ICON,NITER,RD)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION LN(200),VN(0:200)
C
C     NEW L(I) AND V(I) PROFILE
C
      DO 10 I=1,NSTAGE
        ASUM=0.0
        BSUM=0.0
          DO 20 J=1,NC
            BSUM=BSUM+VY(I,J)
   20       ASUM=ASUM+LX(I,J)
        VN(I)=BSUM
        LN(I)=ASUM
   10 CONTINUE
C
      TEMP=REAL(NITER/RD)
      IF(ABS(TEMP-INT(TEMP)).EQ.0.0) THEN
C
        WRITE(9,*)'  STAGE    DOWN STREAM      UP STREAM'
```

```
        WRITE(6,*)'  STAGE    DOWN STREAM      UP STREAM'
C
        DO 30 I=1,NSTAGE
          WRITE(9,40)I,LN(I),VN(I)
          WRITE(6,40)I,LN(I),VN(I)
   40     FORMAT(3X,I3,2X,2F15.5)
   30   CONTINUE
      END IF
C
C     CONVERGE CRITERIA
C
      IF(NITER.EQ.1) THEN
        READ(8,35) EPSYL
   35   FORMAT(10X,F10.8)
        WRITE(9,36)EPSYL
        WRITE(6,36)EPSYL
   36   FORMAT(10X,'TOLERANCE =',F10.8)
      END IF
C

C
      DO 50 I=1,NSTAGE
         TEMP1=ABS((L(I)-LN(I))/L(I))
         TEMP2=ABS((V(I)-VN(I))/V(I))
           IF(TEMP1 .GT. EPSYL .OR. TEMP2 .GT. EPSYL) THEN
                ICON=1
             IF(I.EQ.NSTAGE.AND.(VN(NSTAGE)-V(NSTAGE)).LE.(-0.0001).OR.
     &          NITER.GE.ITMAX) ICON=0
               GOTO 99
           END IF
   50 CONTINUE
C
      ICON=0
C
   99 CONTINUE
C
      DO 60 I=1,NSTAGE
        L(I)=LN(I)
   60   V(I)=VN(I)
C
      RETURN
      END
C
C ....................................................................
C .....
C .....
C
C ......   SUBROUTINE LVCAL
C .....    CALCULATION OF L AND V PORFILE
C
C234567
      SUBROUTINE LVCAL
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      COMMON /CMB/  AA(200,30),BB(200,30),CC(200,30),DD(200,30),
     &              FZ(0:200,30)
      DIMENSION BETA(200,30),GAM(200,30)
C
C     USING THOMAS METHOD
C
```

```
      DO 10 I=1,NC
        BETA(1,I)=BB(1,I)
        GAM(1,I)=DD(1,I)/BETA(1,I)
        LX(NSTAGE+1,I)=SS(I)
        IF(MSTAGE.EQ.0) VY(0,I)=F1*YF1(I)
          DO 20 J=2,NSTAGE
            BETA(J,I)=BB(J,I)-AA(J,I)*CC(J,I)/BETA(J-1,I)
            GAM(J,I)=(DD(J,I)-AA(J,I)*GAM(J-1,I))/BETA(J,I)
   20     CONTINUE
C
            LX(NSTAGE,I)=GAM(NSTAGE,I)
C
          DO 30 J=2,NSTAGE
            K=NSTAGE-J+1
   30       LX(K,I)=GAM(K,I)-CC(K,I)*LX(K+1,I)/BETA(K,I)
C
          DO 40 J=1,NSTAGE
            VY(J,I)=VY(J-1,I)+LX(J+1,I)-LX(J,I)
   40     CONTINUE
   10 CONTINUE
C
      RETURN
      END
C
C ..................................................................
C .....
C .....
C
C .......  SUBROUTINE SCAL
C ......   CALCULATION OF STRIPPING FACTOR AT EACH STAGE
C          CALCULATION OF PARAMETER K, PI AND PSI
C
C234567
      SUBROUTINE SCAL
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),PS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76).XL(30)
C
      DO 10 I=1,NSTAGF
        DO 10 J=1,NC
         S(I,J)=SCAY(I,J)*V(I)/L(I)
   10 CONTINUE
C
      RETURN
      END
C
C ..................................................................
C .....
C .....
C
C234567
      SUBROUTINE CMBEE
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
```

```
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      COMMON /CMB/  AA(200,30),BB(200,30),CC(200,30),DD(200,30),
     &              FZ(0:200,30)
C
      DO 10 I=1,NC
        DO 20 J=1,NSTAGE
   20     FZ(J,I)=0.0
        FZ(MSTAGE,I)=F1*YF1(I)
   10 CONTINUE
C
      DO 30 I=1,NC
        S(0,I)=0.0
        DO 40 J=2,NSTAGE-1
          AA(J,I)=-S(J-1,I)
          BB(J,I)=1.+S(J,I)
          CC(J,I)=-1.
          DD(J,I)=FZ(J,I)
   40   CONTINUE
   30 CONTINUE
C
      DO 50 I=1,NC
        AA(1,I)=0.0
        BB(1,I)=1+S(1,I)
        CC(1,I)=-1.
        DD(1,I)=VY(0,I)
   50 CONTINUE
C
      DO 60 I=1,NC
        AA(NSTAGE,I)=-S(NSTAGE-1,I)
        BB(NSTAGE,I)=1.+S(NSTAGE,I)
        CC(NSTAGE,I)=0.0
        DD(NSTAGE,I)=SS(I)
   60 CONTINUE
C
      RETURN
      END
C
C ......................................................................
C .....
C .....
C
C ......    SUBROUTINE OUTPUT
C ....      OUTPUT OF STAGE-TO-STAGE CALCULATION
C
C234567
      SUBROUTINE OUTPUT(ITER,CNAME)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(200,30),
     &              L(200),V(0:200),LX(200,30),VY(0:200,30),
     &              X(200,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(200,30),F(30),SUMC(30),S(0:200,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION BXB(30),XB(30),SEXSE(30),XSE(30),Y(0:200,30),XSUM(200),
     &          YSUM(0:200)
      CHARACTER*30 CNAME(30)
C
      DO 1 I=1,NSTAGE
           XSUM(I)=0.0
           YSUM(I)=0.0
        DO 2 J=1,NC
           X(I,J)=LX(I,J)/L(I)
           Y(I,J)=VY(I,J)/V(I)
           XSUM(I)=XSUM(I)+X(I,J)
```

```
          YSUM(I)=YSUM(I)+Y(I,J)
    2   CONTINUE
    1 CONTINUE
C
C     NORMALIZE COMPOSITION
C
      DO 3 I=1,NSTAGE
        DO 4 J=1,NC
          X(I,J)=X(I,J)/XSUM(I)
          Y(I,J)=Y(I,J)/YSUM(I)
    4   CONTINUE
    3 CONTINUE
C
      WRITE(6,10)
      WRITE(9,10)
   10 FORMAT(/////,5X,'******  FINAL RESULTS  **********',
     &//,5X,'STAGE',5X,'DOWN STREAM',6X,'UP STREAM')
      DO I=NSTAGE,1,-1
         WRITE(6,20)I,L(I),V(I)
         WRITE(9,20)I,L(I),V(I)
   20    FORMAT(3X,I5,1X,2F16.4)
      END DO
C
C     B, SE AND V(0)
C
      GSUM=0.0
      DO 21 I=1,NC
        GSUM=GSUM+G(I)*X(1,I)
   21 CONTINUE
      B=L(1)/(1+REFLX1)*(1-GSUM)
C
      BSUM=0.0
      DO 22 I=1,NC
        BXB(I)=(1-G(I))/(1+REFLX1)*LX(1,I)
        XB(I)=BXB(I)/B
        BSUM=BSUM+XB(I)
   22 CONTINUE
C
      DO I=1,NC
        XB(I)=XB(I)/BSUM
      END DO
C
      SE=L(1)-(1+REFLX1)*B
C
      IF(SE.EQ.0) GOTO 25
C
      SSUM=0.0
      DO 23 I=1,NC
       SEXSE(I)=G(I)*LX(1,I)
       XSE(I)=SEXSE(I)/SE
       SSUM=SSUM+XSE(I)
   23 CONTINUE
C
      DO I=1,NC
        XSE(I)=XSE(I)/SSUM
      END DO
C
   25 CONTINUE
C
      IF(MSTAGE.EQ.0) THEN
        V(0)=REFLX1*B+F1
      ELSE
        V(0)=REFLX1*B+F2
      END IF
C
      YSUM(0)=0.0
      DO 24 I=1,NC
        IF(MSTAGE.EQ.0) THEN
          VY(0,I)=REFLX1*(1-G(I))/(1+REFLX1)*LX(1,I)+F1*YF1(I)
```

```
          Y(0,I)=VY(0,I)/V(0)
          YSUM(0)=YSUM(0)+Y(0,I)
        ELSE
          VY(0,I)=REFLX1*(1-G(I))/(1+REFLX1)*LX(1,I)+F2*YF2(I)
          Y(0,I)=VY(0,I)/V(0)
          YSUM(0)=YSUM(0)+Y(0,I)
        END IF
   24 CONTINUE
C
      DO I=1,NC
        Y(0,I)=Y(0,I)/YSUM(0)
      END DO
C
      WRITE(6,30)B,V(0),V(NSTAGE),SOL,F1
      WRITE(9,30)B,V(0),V(NSTAGE),SOL,F1
   30 FORMAT(//,5X,'BOTTOM OUTLET STREAM =',F15.4,/,5X,'BOTTOM INLET STR
     &EAM  =',F15.4,/,5X,'TOP OUTLET STREAM    =',F15.4,/,5X,'TOP INLET
     &STREAM     =',F15.4,/,5X,'FEED STREAM          =',F15.4)
C
      WRITE(9,44)
      WRITE(6,44)
   44 FORMAT(//,10X,'----  COMPOSITION PROFILE  ----',/)
C
      DO 41 I=1,NSTAGE
        WRITE(9,31)I
        WRITE(6,31)I
   31   FORMAT(/,5X,' -----   STAGE ',I4,2X,'----',//,3X,'COMPONENT',
     &         12X,'XE',8X,'XR')
        DO 42 J=1,NC
          WRITE(9,32)CNAME(J),X(I,J),Y(I,J)
          WRITE(6,32)CNAME(J),X(I,J),Y(I,J)
   32     FORMAT(2X,A15,2F10.4)
   42   CONTINUE
   41 CONTINUE
C
      WRITE(9,103)
      WRITE(6,103)
  103 FORMAT(/,2X,'COMPONENT',6X,'BOTTOM OUTLET',3X,'BOTTOM INLET',
     &3X,'TOP OUTLET',3X,'TOP INLET',3X,'FEED',/)
C
      DO 33 I=1,NC
        WRITE(9,104)CNAME(I),XB(I),Y(0,I),Y(NSTAGE,I),XXS(I),YF1(I)
        WRITE(6,104)CNAME(I),XB(I),Y(0,I),Y(NSTAGE,I),XXS(I),YF1(I)
  104   FORMAT(1X,A15,F10.4,6X,F10.4,3X,F10.4,3X,F10.4,F9.4)
   33 CONTINUE
C
      IF(ITER.GT.ITMAX) THEN
        WRITE(6,35)ITER
        WRITE(9,35)ITER
   35   FORMAT(//,3X,'THE METHOD IS NOT CONVERGED IN',I5,1X,
     &  'ITERATIONS')
      ELSE
        WRITE(6,40) (ITER-1)
        WRITE(9,40) (ITER-1)
   40   FORMAT(//,3X,'THE METHOD CONVERGED IN',I4,2X,'ITERATIONS')
      END IF
C
      RETURN
      END
C
C234567
C ......................................................................
C .....
C .....
C .....   PREDICTION OF LIQUID-LIQUED EQUILIBRIUM COMPOSITIONS
C
      SUBROUTINE KCAL
C
C ***********************************************************************
```

```
C **  THIS SUBROUTINE CALCULATES THE LIQUED - LIQUED EQUILBRIUM      **
C **  COMPOSITIONS AND THE AMOUNTS OF THE TWO LIQUED PHASES FOR A     **
C **  SYSTEM CONTAINING UP TO 30 COMPONENTS. THE SAMPLE INPUT TO THE **
C **  PROGRAM IS A SPECIFICATION OF THE COMPONENTS AND THE TOTAL      **
C **  COMPOSITION OF THE SYSTEM. THE UNIFAC METHOD IS USED TO         **
C **  CALCULATE THE ACTIVITY  COEFFICIENTS.                           **
C *********************************************************************
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /VAR/  CAY(30),ACAY(30),ACAY1(30),CKAY(30),SCAY(2000,30),
     &              L(2000),V(0:2000),LX(2000,30),VY(0:2000,30),
     &              X(2000,30),SSX(30),X1(30),ZZ(30),SS(30),SUMCC(30),
     &              CCAY(2000,30),F(30),SUMC(30),S(0:2000,30)
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION FD(30),FDD(30),XD(30),XDD(30),GAMD(30),GAMDD(30),
     &          XDN(30),XDDN(30)
C
  102 FORMAT(////,80A1,//,4X,'MOLE FRACTIONS',26X,
     &       'ACTIVITY COEFFICIENTS',/)
  104 FORMAT(/,3X,'THE UNIFAC METHOD IS UNABLE TO PREDICT',1X,
     &      'THE PHASE SPLIT',/,3X,' THE COMPOSITION IS',/,5X,'X(',I3,
     &      ') = ',F10.4)
C
      DELTA1=.001
      DELTA2=.0001
C
      DO 10 I=1,NC
       FD(I)=0.0
   10 CONTINUE
      S11=0.
C
      DO 40 I=1,NC
   40   S11=S11+Z(I)
C
      DO 45 I=2,NC-1,1
   45   FD(I)=.5*Z(I)
C
      FD(1)=.9*Z(1)
      FD(NC)=.1*Z(NC)
      SFD=0.
      SFDD=0.
C
      DO 50 I=1,NC
        FDD(I)=Z(I)-FD(I)
        SFD=SFD+FD(I)
        SFDD=SFDD+FDD(I)
   50 CONTINUE
C
      DO 55 I=1,NC
        IF(FD(I).EQ.0.0.AND.SFD.EQ.0.0) THEN
          WRITE(*,*)'  CAN NOT CALCULATE K VALUE'
          STOP
        END IF
        IF(FDD(I).EQ.0.0.AND.SFDD.EQ.0.0) THEN
          WRITE(*,*)'  CAN NOT CALCULATE K VALUE'
          STOP
        END IF
        XD(I)=FD(I)/SFD
        XDD(I)=FDD(I)/SFDD
   55 CONTINUE
C
   60 CONTINUE
C
C
        CALL UNIFA(XD,GAMD)
```

```
C
C
      NR=NR+1
C
C
        CALL UNIFA(XDD,GAMDD)
C
C
      TSFD=0.
      TSFDD=0.
C
      DO 65 I=1,NC
        FD(I)=Z(I)/(1.+SFDD*GAMD(I)/SFD/GAMDD(I))
        FDD(I)=Z(I)-FD(I)
        TSFD=TSFD+FD(I)
        TSFDD=TSFDD+FDD(I)
   65 CONTINUE
C
      DO 70 I=1,NC
        XDN(I)=FD(I)/TSFD
   70   XDDN(I)=FDD(I)/TSFDD
C
      DO 75 I=1,NC
        IF(ABS(XD(I)-XDN(I)).GT.DELTA1) GO TO 80
        GO TO 90
   75 CONTINUE
C
      IF(ABS(TSFD-SFD).GT.DELTA2) GO TO 80
      GO TO 90
C
   80 DO 85 I=1,NC
        XD(I)=XDN(I)
   85   XDD(I)=XDDN(I)
C
      SFD=TSFD
      SFDD=TSFDD
C
      IF(NR.GT.9999) GO TO 90
      GO TO 60
C
   90 IF(ABS(XD(1)-XDD(1)).LE..01) THEN
        DO 95 I=1,NC
          WRITE(6,104) I, XD(I)
   95   CONTINUE
        GOTO 99
      ENDIF
C
      DO 93 I=1,NC
C
C ******      GAMD : EXTRACT        GAMDD : RAFFINATE
C
      CAY(I)=GAMD(I)/GAMDD(I)
C
   93 CONTINUE
C
      DO 115 I=1,NC
        IF(CAY(I).LE.(0.0)) THEN
          WRITE(6,110)
          WRITE(9,110)
  110     FORMAT(//,3X,' **** CANNOT CALCULATE K VALUE IN THIS SYSTEM',
     &           //,5X,'THIS SYSTEM BECOME ONE PHASE OR DOES NOT HAVE',
     &              1X,'INTERACTION PARAMETERS',/,5X,'CHECK INTERACTION'
     &              1X,'PARAMETER IN OUTPUT FILE',/,5X,'OR CHANGE',1X,
     &                 'SOLVENT TO FEED RATIO')
          STOP
       END IF
  115 CONTINUE
C
   99 RETURN
```

```
      END
C
C
C ..................................................................
C ......
C ......
C *******************************************************************
C **  SUBROUTINE UNIFA(X,XA)                                       **
C *******************************************************************
C     UNIFA GIVES THE ACTIVITY COEFFICIENT (THE VECTOR XA) FOR GIVEN
C      VALUES OF TEMPERATURE T (IN K) AND COMPOSITION X (MOLE FRACTION)
C
C     PARA CONTAINS THE A(I,J) GROUP INTERACTION PARAMETERS NEEDED
C      FOR THE PARTICULAR MIXTURE. PARB = EXP(-PARA/T)
C
C     GAMC IS THE COMBINATORIAL ACTIVITY COEFFICIENT
C     GAMRF IS THE RESIDUAL ACTIVITY COEFFICIENT STEMMING FROM THE PURE
C      COMPONENT.
C     GAMR IS THE RESIDUAL ACTIVITY COEFFICIENT  MINUS GAMRF.
C     NG IS THE NUMBER OF DIFFERENT FUNCTIONAL GROUPS IN THE MIXTURE.
C     ITAB IS THE NUMBER OF GROUPS OF TYPE K IN MOLECULE I.
C     K IS AN INTEGER BETWEEN 1 AND 76 ACCORDING TO THE GROUPE
C      DEFINITION.
C     NY(I,J) IS THE COMPACTED MATRIX, WHICH ON THE BASIS OF THE
C      INFORMATION STORED IN THE MATRIX ITAB GIVES THE NUMBER OF GROUPS
C      OF KIND I IN  MOLECULE J, I = 1,NG AND J = 1,NC.
C     RS IS THE MOLECULAR VOLUMES.
C     QS IS THE SURFACE AREAS.
C     XL IS LOWER CASE L, A COMBINATION OF RS AND QS.
C
C     NR MUST BE ZERO THE FIRST TIME UNIFA IS CALLED FOR A MIXTURE OF
C      GIVEN COMPONENTS, IN SUBSEQUENT CALLS FOR MIXTURES WITH THE SAME
C      COMPONENTS, NR SHOULD BE GREATER THAN ZERO.
C
      SUBROUTINE UNIFA(X,XA)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION GAMC(30),GAMRF(30),GAMR(76),X(30),XA(30)
C
      IF(NR.NE.0) GO TO 10
C
C
        CALL SYSTM
C
C
   10 CONTINUE
C
C
        CALL GREF(GAMRF)
C
C
        CALL GRES (X,GAMR)
C
C
        CALL GCOMB(X,GAMC)
C
C
      DO 20 J=1,NC
   20   XA(J)=GAMC(J)*GAMR(J)/GAMRF(J)
C
      RETURN
      END
C
C ..................................................................
```

```
C ......
C ......
C ******************************************************************
C **  SUBROUTINE SYSTM                                            **
C ******************************************************************
C
C ******************************************************************
C     THE FOLLOWING DATA HAVE BEEN TAKEN FROM THE REFERENCE :
C      WALAS, M. S., 'PHASE EQUILIBRIA IN CHEMICAL ENGINEERING',
C      BUTTERWORTH PUBLISHERS, MA, 1985.
C ******************************************************************
C
C     FORMATION OF 'THE COMPACTED PARAMETER MATRIX' FORM THE LARGE
C     UNIFAC PARAMETER TABLE ON THE BASIS OF INFORMATION STORED IN ITAB
C
C     THE SUBGROUPS ARE
C     1 = CH3, 2 = CH2, 3 = CH, 4 = C, 5 = CH=CH2, 6 = CH=CH, 7 = CH2=C,
C     8 = CH=C, 9 = C=C, 10 = ACH, 11 = AC, 12 = ACCH3, 13 = ACCH2,
C     14 = ACCH, 15 = OH, 16 = CH3OH, 17 = H2O, 18 = ACOH, 19 = CH3CO,
C     20 = CH2CO, 21 = CHO, 22 = CH3COO, 23 = CH2COO, 24 = HCOO,
C     25 = CH3O, 26 = CH2O, 27 = CH-O, 28 = FCH2O, 29 = CH3NH2,
C     30 = CH2NH2, 31 = CHNH2, 32 = CH3NH, 33 = CH2NH, 34 = CHNH,
C     35 = CH3N, 36 = CH2N, 37 = ACNH2, 38 = C5H5N, 39 = C5H4N,
C     40 = C5H3N, 41 = CH3CN, 42 = CH2CN, 43 = COOH, 44 = HCOOH,
C     45 = CH2CL, 46 = CHCL, 47 = CCL, 48 = CH2CL2, 49 = CHCL2,
C     50 = CCL2, 51 = CHCL3, 52 = CCL3, 53 = CCL4, 54 = ACCL,
C     55 = CH3NO2, 56 = CH2NO2, 57 = CHNO2, 58 = ACNO2, 59 = CS2,
C     60 = CH3SH, 61 = CH2SH, 62 = FURFURAL, 63 = (CH2OH)2, 64 = I,
C     65 = Br, 66 = CH_C, 67 = CC_C, 68 = Me2SO, 69 = ACRY,
C     70 = CL(C=C), 71 = ACF, 72 = DMF-1, 73 = DMF-2, 74 = CF3,
C     75 = CF2, 76 = CF
C
      SUBROUTINE SYSTM
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
C
      DIMENSION ARR(40,40),RR(76),QQ(76),KTAB(30),NKTAB(76)
      DIMENSION AA1(40),AA2(40),AA3(40),AA4(40),AA5(40),AA6(40),AA7(40),
     *AA8(40),AA9(40),AA10(40),AA11(40),AA12(40),AA13(40),AA14(40),AA15(
     *40),AA16(40),AA17(40),AA18(40),AA19(40),AA20(40),AA21(40),AA22(40)
     *,AA23(40),AA24(40),AA25(40),AA26(40),AA27(40),AA28(40),AA29(40),AA
     *30(40),AA31(40),AA32(40),AA33(40),AA34(40),AA35(40),AA36(40),AA37(
     *40),AA38(40),AA39(40),AA40(40)
C
      DATA NKTAB/4*1,5*2,2*3,3*4,5,6,7,8,2*9,10,2*11,12,4*13,3*14,3*15,2
     **16,17,3*18,2*19,2*20,3*21,3*22,2*23,24,25,3*26,27,28,2*29,30,31,3
     *2,33,2*34,35,36,37,38,2*39,3*40/
C
      DATA RR/.9011,.6744,.4469,.2195,1.3454,1.1167,1.1173,.8886,.6605,.
     *5313,.3652,1.2663,1.0396,.8121,1.,1.4311,.92,.8952,1.6724,1.4457,.
     *9980,1.9031,1.6764,1.242,1.145,.9183,.6908,.9183,1.5959,1.3692,1.1
     *417,1.4337,1.2070,.9795,1.1865,.9597,1.06,2.9993,2.8332,2.667,1.87
     *01,1.6434,1.3013,1.5280,1.4654,1.238,1.006,2.2564,2.0606,1.8016,2.
     *87,2.6401,3.39,1.1562,2.0086,1.7818,1.5544,1.4199,2.057,1.877,1.65
     *1,3.168,2.4088,1.264,.9492,1.292,1.0613,2.8266,2.3144,.791,.6948,3
     *.0856,2.6322,1.406,1.0105,.615/
C
      DATA QQ/.848,.540,.228,.000,1.176,.867,.988,.676,.485,.400,.120,.9
     *68,.660,.348,1.200,1.432,1.40,.680,1.488,1.180,.948,1.728,1.420,1.
     *188,1.088,.780,.468,1.1,1.544,1.236,.924,1.244,.936,.624,.940,.632
     *,.816,2.113,1.833,1.553,1.724,1.416,1.224,1.532,1.264,.952,.724,1.
     *988,1.684,1.448,2.410,2.184,2.910,.844,1.868,1.560,1.248,1.104,1.6
     *5,1.676,1.368,2.481,2.248,.992,.832,1.088,.784,2.472,2.052,.724,.5
     *24,2.736,2.120,1.380,.920,.460/
```

```
C
C     THE MAIN GROUPS ARE
C     1 = CH2, 2 = C=C, 3 = ACH, 4 = ACCH2, 5 = OH, 6 = CH3OH, 7 = CH3OH
C     , 8 = ACOH, 9 = CH2CO, 10 = CHO, 11 = CCOO, 12 = HCOO, 13 = CH2O,
C     14 = CNH2, 15 = CNH, 16 = (C)3N, 17 = ACNH2, 18 = PYRIDINE,
C     19 = CCN, 20 = COOH, 21 = CCL, 22 = CCL2, 23 = CCL3, 24 = CCL4,
C     25 = ACCL, 26 = CNO2, 27 = ACNO2, 28 = CS2, 29 = CH3SH,
C     30 = FURFURAL, 31 = (CH2OH)2, 32 = I, 33 = Br, 34 = C_C,
C     35 = Me2SO, 36 = ACRY, 37 = CLCC, 38 = ACF, 39 = DMF, 40 = CF2,
C
C     ************************** W A R N I N G ************************
C     AN OFF-DIAGONAL ZERO IN THE A-PARAMETER MATRIX MEANS THAT THE
C     PARAMETER IN QUESTION IS NOT AVAILABLE
C     *****************************************************************
C
      DATA                AA1/0.,-200.0,61.13,76.50,986.5,697.2,1318.0,13
     *33.0,476.4,677.0,232.1,741.4,251.5,391.5,255.7,206.6,1245.0,287.7,
     *597.0,663.5,35.93,53.76,24.90,104.3,321.5,661.5,543.0,153.6,184.4,
     *354.5,3025.0,335.8,479.5,298.9,526.5,689.0,-.505,125.8,485.3,-2.85
     *9/
C
      DATA                AA2/2520.0,0.,340.7,4102.0,693.9,1509.0,634.2,5
     *47.4,524.5,000.00,71.23,468.7,289.3,396.0,273.6,658.8,000.00,000.0
     *0,405.9,730.4,99.61,337.1,4584.0,5831.0,959.7,542.1,000.00,76.30,0
     *00.00,000.00,000.00,000.00,000.00,523.6,000.00,000.00,237.3,000.00
     *,320.4,000.00/
C
      DATA                AA3/-11.12,-94.78,0.,167.0,636.1,637.3,903.8,13
     *29.0,25.77,000.00,5.994,000.00,32.14,161.7,122.8,90.49,668.2,-4.44
     *9,212.5,537.4,-18.81,-144.4,-231.9,3.000,538.2,168.0,194.9,52.07,-
     *10.43,-64.69,210.4,113.3,-13.59,000.00,169.9,000.00,69.11,389.3,24
     *5.6,000.00/
C
      DATA                AA4/-69.70,-269.7,-146.8,0.,803.2,603.2,5695.0,
     *884.9,-52.10,000.00,5688.0,000.00,213.1,000.00,-49.29,23.50,764.7,
     *52.80,6096.0,603.8,-114.1,000.00,-12.14,-141.3,-126.9,3629.0,4448.
     *0,-9.451,000.00,-20.36,4975.0,000.00,-171.3,000.00,4284.0,000.00,0
     *00.00,101.4,5629.0,000.00/
C
      DATA                AA5/156.4,8694.0,89.60,25.82,0.,-137.1,353.5,-2
     *59.7,84.00,441.8,101.1,193.1,28.06,83.02,42.70,-323.0,-348.2,170.0
     *,6.712,199.0,75.62,-112.1,-98.12,143.1,287.8,61.11,157.1,477.0,147
     *.5,-120.5,-318.9,313.5,133.4,000.00,-202.1,000.00,253.9,44.78,-143
     *.9,000.00/
C
      DATA                AA6/16.51,-52.39,-50.00,-44.50,249.1,0.,-181.0,
     *-101.7,23.39,306.4,-10.72,193.4,-180.6,359.3,266.0,53.90,335.5,580
     *.5,36.23,-289.5,-38.32,-102.5,-139.4,-67.80,17.12,75.14,000.00,-31
     *.09,37.84,000.00,000.00,000.00,000.00,000.00,-399.3,000.00,-21.22,
     *-48.25,-172.4,000.00/
C
      DATA                AA7/300.0,692.7,362.3,377.6,-229.1,289.6,0.,324
     *.5,-195.4,-257.3,14.42,000.00,540.5,48.89,168.0,304.0,213.0,459.0,
     *112.6,-14.09,325.4,370.4,353.7,497.5,678.2,220.6,399.5,887.1,000.0
     *0,188.0,0.,000.00,000.00,000.00,-139.0,160.8,000.00,000.00,319.0,0
     *00.00/
C
      DATA                AA8/275.8,1665.0,25.34,244.2,-451.6,-265.2,-601
     *.8,0.,-356.1,000.00,-449.4,000.00,000.00,000.00,000.00,000.00,000.
     *00,-305.5,000.00,000.00,000.00,000.00,000.00,1827.0,000.00,000.00,
     *000.00,000.00,000.00,000.00,-687.1,000.00,000.00,000.00,000.00,000
     *.00,000.00,000.00,000.00,000.00/
C
      DATA                AA9/26.76,-82.92,140.1,365.8,164.5,108.7,472.5,
     *-133.1,0.,-37.36,-213.7,000.00,5.202,000.00,000.00,000.00,937.9,16
     *5.1,481.7,669.4,-191.7,-284.0,-354.6,-39.20,174.5,137.5,000.00,216
     *.1,-46.28,-163.7,000.00,53.59,245.2,-246.6,-44.58,000.00,-44.42,00
     *0.00,-61.70,000.00/
C
```

```
      DATA             AA10/505.7,000.00,000.00,000.00,-404.8,-340.2,2
     *32.7,000.00,128.0,0.,000.00,000.00,304.1,000.00,000.00,000.00,000.
     *00,000.00,000.00,000.00,751.9,000.00,000.00,000.00,000.00,000.00,0
     *00.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,000.00,000.00/
C
      DATA             AA11/114.8,269.3,85.84,-170.0,245.4,249.6,10000
     *.0,-36.72,372.2,000.00,0.,372.9,-235.7,000.00,-73.50,000.00,000.00
     *,000.00,494.6,660.2,000.00,108.9,-209.7,54.47,629.0,000.00,000.00,
     *183.0,000.00,202.3,-101.7,148.3,000.00,000.00,52.08,000.00,-23.30,
     *000.00,000.00,000.00/
C
      DATA             AA12/90.49,91.65,000.00,000.00,191.2,155.7,000.
     *00,000.00,000.00,000.00,-261.1,0.,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,-356.3,000.00,000.00,-287.2,000.00,000.00,000.00,
     *000.00,000.00,4.339,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,000.00,000.00/
C
      DATA             AA13/83.36,76.44,52.13,65.69,237.7,339.7,-314.7
     *,000.00,52.38,-7.838,461.3,000.00,0.,000.00,141.7,000.00,000.00,00
     *0.00,000.00,664.6,301.1,137.8,-154.3,47.67,000.00,95.18,000.00,140
     *.9,-8.538,000.00,-20.11,-149.5,-202.3,000.00,172.1,000.00,145.6,00
     *0.00,254.8,000.00/
C
      DATA             AA14/-30.48,79.40,-44.85,000.00,-164.0,-481.7,-
     *330.4,000.00,000.00,000.00,000.00,000.00,000.00,0.,63.72,-41.11,00
     *0.00,000.00,000.00,000.00,000.00,000.00,000.00,-99.81,68.81,000.00
     *,000.00,000.00,-70.14,000.00,000.00,000.00,000.00,000.00,000.00,00
     *0.00,000.00,000.00,000.00,000.00/
C
      DATA             AA15/65.33,-41.32,-22.31,223.0,-150.0,-500.4,-4
     *48.2,000.00,000.00,000.00,136.0,000.00,-49.30,108.8,0.,-189.2,000.
     *00,000.00,000.00,000.00,000.00,000.00,000.00,71.23,4350.0,000.00,0
     *00.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,000.00,000.00/
C
      DATA             AA16/-83.98,-188.0,-223.9,109.0,28.60,-406.8,-5
     *98.8,000.00,000.00,000.00,000.00,000.00,000.00,38.89,865.9,0.,000.
     *00,000.00,000.00,000.00,000.00,-73.85,-352.9,-8.283,-86.36,000.00,
     *000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000
     *.00,000.00,000.00,000.00,000.00/
C
      DATA             AA17/5339.0,000.00,650.4,979.8,529.0,5.182,-339
     *.5,000.00,-399.1,000.00,000.00,000.00,000.00,000.00,000.00,000.00,
     *0.,000.00,-216.8,000.00,000.00,000.00,000.00,8455.0,699.1,000.00,-
     *62.73,000.00,000.00,000.00,125.3,000.00,000.00,000.00,000.00,000.0
     *0,000.00,000.00,-293.1,000.00/
C
      DATA             AA18/-101.6,000.00,31.87,49.80,-132.3,-378.2,-3
     *32.9,-341.6,-51.54,000.00,000.00,000.00,000.00,000.00,000.00,000.0
     *0,000.00,0.,-169.7,-153.7,000.00,-351.6,-114.7,-165.1,000.00,000.0
     *0,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,0
     *00.00,000.00,000.00,000.00,000.00/
C
      DATA             AA19/24.82,34.78,-22.97,-138.4,185.4,157.8,242.
     *8,000.00,-287.5,000.00,-266.6,000.00,000.00,000.00,000.00,000.00,6
     *17.1,134.3,0.,000.00,000.00,000.00,-15.62,-54.86,52.31,000.00,000.
     *00,230.9,21.37,000.00,000.00,000.00,000.00,-203.0,000.00,81.57,-19
     *.14,000.00,000.00,000.00/
C
      DATA             AA20/315.3,349.2,62.32,268.2,-151.0,1020.0,-66.
     *17,000.00,-297.8,000.00,-256.3,312.5,-338.5,000.00,000.00,000.00,0
     *00.00,-313.5,000.00,0.,44.42,-183.4,76.75,212.7,000.00,000.00,000.
     *00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,
     *-90.87,000.00,000.00,000.00/
C
      DATA             AA21/91.46,-24.36,4.680,122.9,562.2,529.0,698.2
     *,000.00,286.3,-47.51,000.00,000.00,225.4,000.00,000.00,000.00,000.
     *00,000.00,000.00,326.4,0.,108.3,249.2,62.42,464.4,000.00,000.00,45
```

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     *0.1,59.02,000.00,000.00,000.00,-125.9,000.00,000.00,000.00,-58.77,
     *000.00,000.00,000.00/
C
      DATA            AA22/34.01,-52.71,121.3,000.00,747.7,669.9,708.
     *7,000.00,423.2,000.00,-132.9,000.00,-197.7,000.00,000.00,-141.4,00
     *0.00,587.3,000.00,1821.0,-84.53,0.,0.,56.33,000.00,000.00,000.00,0
     *00.00,000.00,000.00,000.00,177.6,000.00,000.00,215.0,000.00,000.00
     *,000.00,000.00,000.00/
C
      DATA            AA23/36.70,-185.1,288.5,33.61,742.1,649.1,826.7
     *,000.00,552.1,000.00,176.5,488.9,-20.93,000.00,000.00,-293.7,000.0
     *0,18.98,74.04,1346.0,-157.1,0.,0.,-30.10,000.00,000.00,000.00,116.
     *6,000.00,-64.38,000.00,86.40,000.00,000.00,363.7,000.00,-79.54,000
     *.00,000.00,000.00/
C
      DATA            AA24/-78.45,-293.7,-4.700,134.7,856.3,860.1,120
     *1.0,10000.,372.0,000.00,129.5,000.00,113.9,261.1,91.13,-126.0,1301
     *.0,309.2,492.0,689.0,11.80,17.97,51.90,0.,475.8,490.9,534.7,132.2,
     *000.00,546.7,000.00,247.8,41.94,000.00,337.7,000.00,-86.85,215.2,4
     *98.6,000.00/
C
      DATA            AA25/-141.3,-203.2,-237.7,375.5,246.9,661.6,920
     *.4,000.00,128.1,000.00,-246.3,000.00,000.00,203.5,-108.4,1088.0,32
     *3.3,000.00,356.9,000.00,-314.9,000.00,000.00,-255.4,0.,-154.5,000.
     *00,000.00,000.00,000.00,000.00,000.00,-60.70,000.00,000.00,000.00,
     *000.00,000.00,000.00,000.00/
C
      DATA            AA26/-32.69,-49.92,10.38,-97.05,341.7,252.6,417
     *.9,000.00,-142.6,000.00,000.00,000.00,-94.49,000.00,000.00,000.00,
     *000.00,000.00,000.00,000.00,000.00,000.00,000.00,-34.68,794.4,0.,5
     *33.2,000.00,000.00,000.00,139.8,304.3,10.17,-27.70,000.00,000.00,4
     *8.40,000.00,000.00,000.00/
C
      DATA            AA27/5541.0,000.00,1824.0,-127.8,561.6,000.00,3
     *60.7,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.0
     *0,5250.0,000.00,000.00,000.00,000.00,000.00,000.00,514.6,000.00,-8
     *5.12,0.,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,00
     *0.00,000.00,000.00,000.00,000.00/
C
      DATA            AA28/-52.65,16.62,21.50,40.68,823.5,914.2,1081.
     *0,000.00,303.7,000.00,243.8,000.00,112.4,000.00,000.00,000.00,000.
     *00,000.00,335.7,000.00,-73.09,000.00,-26.06,-60.71,000.00,000.00,0
     *00.00,0.,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,-
     *47.37,000.00,000.00,000.00/
C
      DATA            AA29/-7.481,000.00,28.41,000.00,461.6,382.8,000
     *.00,000.00,160.6,000.00,000.00,239.8,63.71,106.7,000.00,000.00,000
     *.00,000.00,125.7,000.00,-27.94,000.00,000.00,000.00,000.00,000.00,
     *000.00,000.00,0.,000.00,000.00,000.00,000.00,000.00,31.66,000.00,0
     *00.00,000.00,78.92,000.00/
C
      DATA            AA30/-25.31,000.00,157.3,404.3,521.6,000.00,23.
     *48,000.00,317.5,000.00,-146.3,000.00,000.00,000.00,000.00,000.00,0
     *00.00,000.00,000.00,000.00,000.00,000.00,48.48,-133.1,000.00,000.0
     *0,000.00,000.00,000.00,0.,000.00,000.00,000.00,000.00,000.00,000.0
     *0,000.00,000.00,000.00,000.00/
C
      DATA            AA31/140.0,000.00,221.4,150.6,267.6,000.00,0.,8
     *38.4,000.00,000.00,152.0,000.00,9.207,000.00,000.00,000.00,164.4,0
     *00.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,481.3,000.0
     *0,000.00,000.00,000.00,0.,000.00,000.00,000.00,-417.2,000.00,000.0
     *0,000.00,302.2,000.00/
C
      DATA            AA32/128.0,000.00,58.68,000.00,501.3,000.00,000
     *.00,000.00,138.0,000.00,21.92,000.00,476.6,000.00,000.00,000.00,00
     *0.00,000.00,000.00,000.00,000.00,-40.82,21.76,48.49,000.00,64.28,0
     *00.00,000.00,000.00,000.00,000.00,0.,000.00,000.00,000.00,000.00,0
     *00.00,000.00,000.00,000.00/
C
```

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      DATA                 AA33/-31.52,000.00,155.6,291.1,721.9,000.00,000
     *.00,000.00,-142.6,000.00,000.00,000.00,736.4,000.00,000.00,000.00,
     *000.00,000.00,000.00,000.00,1169.0,000.00,000.00,225.8,224.0,125.3
     *,000.00,000.00,000.00,000.00,000.00,000.00,0.,000.00,000.00,000.00
     *,000.00,000.00,000.00,000.00/
C
      DATA                 AA34/-72.88,-184.4,000.00,000.00,000.00,000.00,
     *000.00,000.00,443.6,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,329.1,000.00,000.00,000.00,000.00,000.00,000.00,1
     *74.4,000.00,000.00,000.00,000.00,000.00,000.00,000.00,0.,000.00,00
     *0.00,000.00,000.00,-119.8,000.00/
C
      DATA                 AA35/50.49,000.00,-2.504,-143.2,-25.87,695.0,-2
     *40.0,000.00,110.4,000.00,41.57,000.00,-122.1,000.00,000.00,000.00,
     *000.00,000.00,000.00,000.00,000.00,-215.0,-343.6,-58.43,000.00,000
     *.00,000.00,000.00,85.70,000.00,535.8,000.00,000.00,000.00,0.,000.0
     *0,000.00,000.00,-97.71,000.00/
C
      DATA                 AA36/-165.9,000.00,000.00,000.00,000.00,000.00,
     *386.6,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,-42.31,000.00,000.00,000.00,000.00,000.00,000.00,
     *000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000
     *.00,0.,000.00,000.00,000.00,000.00/
C
      DATA                 AA37/41.90,-3.167,-75.67,000.00,640.9,726.7,000
     *.00,000.00,-8.671,000.00,-18.87,000.00,-209.3,000.00,000.00,000.00
     *,000.00,000.00,298.4,2344.0,201.7,000.00,85.32,143.2,000.00,313.8,
     *000.00,167.9,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,0.,000.00,000.00,000.00/
C
      DATA                 AA38/-5.132,000.00,-237.2,-157.3,649.7,645.9,00
     *0.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.0
     *0,000.00,000.00,000.00,000.00,000.00,000.00,000.00,-124.6,000.00,0
     *00.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,0.,000.00,000.00/
C
      DATA                 AA39/-31.95,37.70,-133.9,-240.2,64.16,172.2,-28
     *7.1,000.00,97.04,000.00,000.00,000.00,-158.2,000.00,000.00,000.00,
     *335.6,000.00,000.00,000.00,000.00,000.00,000.00,-186.7,000.00,000.
     *00,000.00,000.00,-71.00,000.00,-191.7,000.00,000.00,6.699,136.6,00
     *0.00,000.00,000.00,0.,000.00/
C
      DATA                 AA40/147.3,000.00,000.00,000.00,000.00,000.00,0
     *00.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.
     *00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,
     *000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000.00,000
     *.00,000.00,000.00,000.00,000.00,0./
C
      DO 99 J=1,32
      ARR(1,J)=AA1(J)
      ARR(2,J)=AA2(J)
      ARR(3,J)=AA3(J)
      ARR(4,J)=AA4(J)
      ARR(5,J)=AA5(J)
      ARR(6,J)=AA6(J)
      ARR(7,J)=AA7(J)
      ARR(8,J)=AA8(J)
      ARR(9,J)=AA9(J)
      ARR(10,J)=AA10(J)
      ARR(11,J)=AA11(J)
      ARR(12,J)=AA12(J)
      ARR(13,J)=AA13(J)
      ARR(14,J)=AA14(J)
      ARR(15,J)=AA15(J)
      ARR(16,J)=AA16(J)
      ARR(17,J)=AA17(J)
      ARR(18,J)=AA18(J)
      ARR(19,J)=AA19(J)
      ARR(20,J)=AA20(J)
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      ARR(21,J)=AA21(J)
      ARR(22,J)=AA22(J)
      ARR(23,J)=AA23(J)
      ARR(24,J)=AA24(J)
      ARR(25,J)=AA25(J)
      ARR(26,J)=AA26(J)
      ARR(27,J)=AA27(J)
      ARR(28,J)=AA28(J)
      ARR(29,J)=AA29(J)
      ARR(30,J)=AA30(J)
      ARR(31,J)=AA31(J)
      ARR(32,J)=AA32(J)
      ARR(33,J)=AA33(J)
      ARR(34,J)=AA34(J)
      ARR(35,J)=AA35(J)
      ARR(36,J)=AA36(J)
      ARR(37,J)=AA37(J)
      ARR(38,J)=AA38(J)
      ARR(39,J)=AA39(J)
      ARR(40,J)=AA40(J)
   99 CONTINUE
C
      NT=57
      NM=32
      M=0
C
      DO 15 J=1,NT
        JJ=0
          DO 16 I=1,NC
   16       JJ=JJ+ITAB(I,J)
              IF (JJ) 15,15,17
   17          M=M+1
               KTAB(M)=J
   15 CONTINUE
C
      NG=M
C
      DO 20 J=1,NG
         JJ=KTAB(J)
         R(J)=RR(JJ)
         Q(J)=QQ(JJ)
           DO 20 I=1,NC
   20         NY(I,J)=ITAB(I,JJ)
C
      DO 30 I=1,NM
         DO 35 J=1,NG
           J1=KTAB(J)
           J1=NKTAB(J1)
           IF (J1-I) 35,36,35
   36         DO 37 L=1,NG
                 L1=KTAB(L)
                 L1=NKTAB(L1)
   37            PARA(J,L)=ARR(I,L1)
   35      CONTINUE
   30 CONTINUE
C
      DO 40 I=1,NC
         RS(I)=0.
         QS(I)=0.
           DO 41 J=1,NG
             RS(I)=RS(I)+NY(I,J)*R(J)
   41        QS(I)=QS(I)+NY(I,J)*Q(J)
         XL(I)=5.*(RS(I)-QS(I))-RS(I)+1.
   40     CONTINUE
C
      IF(NR) 34,34,39
   34 WRITE(6,80)
      WRITE(9,80)
   80 FORMAT (//,' GROUP CONSTANTS AND INTERACTION PARAMETERS (R,Q, AND
```

```
     &A(I,J)) ',/)
C
      DO 81 I=1,NG
        WRITE(6,82) I,I,R(I),Q(I)
        WRITE(9,82) I,I,R(I),Q(I)
      DO 83 J=1,NG
        WRITE(9,84)I,J,PARA(I,J)
   83   WRITE(6,84)I,J,PARA(I,J)
   81 CONTINUE
C
   82 FORMAT (3X,'PARAMETER R(',I2,') AND Q(',I2,') ARE',2F10.4)
   84 FORMAT(3X,'A(',I2,',','I2,') IS',F10.4)
      WRITE(6,85)
      WRITE(9,85)
   85 FORMAT(///,3X,'MOLECULAR FUNCTIONAL GROUPS'//)
C
      DO 86 I=1,NC
        DO 86 J=1,NG
        WRITE(9,87) I,J,NY(I,J)
   86   WRITE(6,87) I,J,NY(I,J)
   87   FORMAT(3X,'NY(',I3,I3,') =',I3)
C
   39 RETURN
      END
C
C ..................................................................
C .....
C .....
C *****************************************************************
C **   SUBROUTINE GREF(GAM)                                       **
C *****************************************************************
C
C
C     CALCULATION OF RESIDUAL REFERENCE ACTIVITY COEFFICIENT
C
      SUBROUTINE GREF(GAM)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION X(30),GAMX(30),GAM(30)
C
      IF(NR .GT. 3) GO TO 15
C
      DO 10 I=1,NG
         DO 10 J=1,NG
           PARB(I,J)=EXP(-((PARA(I,J))/T))
   10    CONTINUE
C
   15    CONTINUE
C
      DO 20 I=1,NC
           DO 21 J=1,NC
   21        X(J)=0.
C
      X(I)=1.
C
C
        CALL GRES(X,GAMX)
C
C
   20 GAM(I)=GAMX(I)
C
      RETURN
      END
C
```

```
C ..................................................................
C .....
C .....
C ******************************************************************
C **  SUBROUTINE GRES (X,GAM)                                     **
C ******************************************************************
C
C
C CALCULATION OF RESDIUAL ACTIVITY COEFFICIENTS LESS THE REFERENCE
C PART STEMMING FROM GRROUP K IN PURE COMPONENT I (THE LATTER IS
C CACULATED IN GREF).
C
      SUBROUTINE GRES (X,GAM)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION GAM(30),S1(76),XG(76),S4(76),TH(76),GAML(76),X(30)
C
      S3=0.
      S2=0.
C
      DO 10 K=1,NG
        S1(K)=0.
          DO 11 I=1,NC
   11       S1(K)=S1(K)+NY(I,K)*X(I)
   10   S2=S2+S1(K)
C
      DO 13 K=1,NG
        IF(S2 .EQ. 0.0) THEN
          XG(K)=0.0
          S3=1.0
        ELSE
          XG(K)=S1(K)/S2
          S3=S3+Q(K)*XG(K)
        ENDIF
   13 CONTINUE
C
      DO 15 K=1,NG
        S4(K)=0.
   15   TH(K)=Q(K)*XG(K)/S3
C
      DO 16 K=1,NG
        DO 16 I=1,NG
   16     S4(K)=TH(I)*PARB(I,K)+S4(K)
C
      DO 20 K=1,NG
        IF(S4(K).LE.0.) THEN
          WRITE(*,*)' CANNOT CALCULATE K VALUE'
          WRITE(9,*)' CANNOT CALCULATE K VALUE'
          STOP
        END IF
        GG=1.-ALOG(S4(K))
          DO 21 I=1,NG
   21       GG=GG-TH(I)*PARB(K,I)/S4(I)
   20    GAML(K)=Q(K)*GG
C
      DO 30 I=1,NC
        GG=0.
          DO 31 J=1,NG
   31       GG=NY(I,J)*GAML(J)+GG
   30    GAM(I)=EXP(GG)
C
      RETURN
      END
C
```

```
C ..............................................................
C .....
C .....
C ***************************************************************
C **  SUBROUTINE GCOMB(X,GAMMA)                                **
C ***************************************************************
C
C     CALCULATION OF COMBINATORIAL PART
C
      SUBROUTINE GCOMB(X,GAMMA)
C
      IMPLICIT REAL (A-H,L,O-Z)
      COMMON /DATA/ NC,NG,Z(30),YF1(30),YF2(30),G(30),XXS(30),SOL,
     &              ITAB(30,76),NSTAGE,MSTAGE,REFLUX,REFLX1,SE,D,B,
     &              F1,F2,T,NFEED,NT,ITMAX
      COMMON /PARA/ NY(76,30),R(76),Q(76),RS(76),QS(76),NR,PARA(76,76),
     &              PARB(76,76),XL(30)
      DIMENSION X(30),GAMMA(30)
C
      QSS=0.
      RSS=0.
      XLS=0.
C
      DO 10 I=1,NC
        QSS=QSS+QS(I)*X(I)
        RSS=RSS+RS(I)*X(I)
   10   XLS=XLS+XL(I)*X(I)
C
      DO 20 I=1,NC
        A=5.*QS(I)*ALOG(QS(I)/QSS*RSS/RS(I))+XL(I)-RS(I)/RSS*XLS
        GAMMA(I)=RS(I)/RSS*EXP(A)
   20 CONTINUE
C
      RETURN
      END
```

APPENDIX B

INPUT FILE INFORMATION

The input section is part of the main program and consists of two sections: one is input data for main calculation and the other is input data for UNIFAC subroutine which estimates distribution coefficient K_i. To enter the data, the user must create a data file. The format of the file is given so that the user may make changes. This data file name must be entered into the program. The sample input data format of the file is given in Table X, where the variables are listed. The values of those variables should be used in the program. The file is set up to allow the user to input his own physical and thermodynamic properties instead of those calculated by the program. This approach increases the flexibility of the program and is very useful when working with hypothetical components.

TABLE XIII

SAMPLE INPUT DATA FILE FORMAT

```
   WATER - N-PROPANOL - BENZENE  SYSTEM  (TITLE)
              3    5    5          NC, NG, NITAB
CNAME(1)   WATER
CNAME(2)   N-PROPANOL
CNAME(3)   BENZENE
              1   17    1                 I,J,ITAB(I,J)
              2    1    1
              2    2    2
              2   15    1
              3   10    6
Z(1)       80.
Z(2)       20.
Z(3)       50.        kg/min
              1     50.    0.        100.      NFEED,F1,F2,S
           0.         0.                       REFLUX,REFLX1
           0.8        0.          0.           XXS,YF1,YF2  1
           0.2        0.          0.                        2
           0.         1.          0.                        3
           310.67                              TEMPERATURE
              5    0                           NSTAGE,MSTAGE
              N                                LOWER SECTION?
             80.       70.                     B,D
           30000                               ITERMAX
             10.                               RD
           0.000001                            EPSYLON
END OF DATA
```

APPENDIX C

UNIFAC VALIDATION

The distribution coefficient model chosen largely affects equilibrium calculation. The UNIFAC model is the most powerful method available at this time when experimental data are not available. The UNIFAC, however, gives a wrong value in some cases. Table XI shows the predicted activity coefficient value and experimental value. As the results show, the UNIFAC gives slightly different values from experimental values; deviations of UNIFAC are 0.3 to 0.001. Generally, UNIFAC is effective in equilibrium calculations when experimental values are not available.

TABLE XIV

ACTIVITY COEFFICIENT IN THE UNIFAC VALUE AND IN EXPERIMENTAL VALUE

T (K)	x_1	γ_1 UNIFAC	γ_1 Exp.	Deviation	γ_2 UNIFAC	γ_2 Exp.	Deviation
Vinyl Acetate - Propyl Bromide							
343.4	.079	.9272	1.3308	.4036	.9968	0.9994	.0026
343.2	.109	.9486	1.3109	.3623	.9944	1.0013	.0069
343.2	.137	.9661	1.2892	.3231	.9918	1.0036	.0118
342.6	.206	.9979	1.2377	.2398	.9850	1.0076	.0226
342.5	.243	1.0102	1.2034	.1932	.9815	1.0206	.0391
342.4	.268	1.0168	1.1902	.1734	.9792	1.0251	.0459
342.3	.326	1.0275	1.1612	.1337	.9748	1.0361	.0613
342.2	.361	1.0314	1.1407	.1093	.9729	1.0466	.0737
342.2	.374	1.0323	1.1336	.1013	.9723	1.0537	.0814
342.3	.479	1.0343	1.0863	.0520	.9713	1.0863	.1150
342.3	.504	1.0334	1.0972	.0638	.9722	1.0754	.1032
342.4	.532	1.0320	1.0834	.0514	.9737	1.0880	.1143
342.5	.581	1.0287	1.0621	.0334	.9779	1.1170	.1391
342.6	.607	1.0266	1.0463	.0197	.9809	1.1395	.1586
343.0	.700	1.0183	1.0292	.0109	.9970	1.1534	.1564
343.0	.690	1.0193	1.0438	.0245	.9950	1.1469	.1519
343.3	.758	1.0130	1.0263	.0133	1.0118	1.1770	.1652
343.5	.777	1.0021	1.0165	.0144	1.0054	1.2257	.2203
343.8	.847	1.0059	1.0097	.0038	1.0430	1.2646	.2216
344.0	.869	1.0045	1.0112	.0067	1.0528	1.3213	.2685
344.3	.902	1.0026	1.0115	.0089	1.0691	1.3341	.2650
344.6	.933	1.0013	1.0129	.0116	1.0864	1.3476	.2612
344.8	.942	1.0009	1.0101	.0101	1.0920	1.3822	.2902
345.0	.973	1.0002	0.9976	.0026	1.1119	1.4523	.3404
345.1	.985	1.0001	0.9968	.0033	1.1205	1.4693	.3488
Benzene - Toluene							
383.9	.008	2.3158	1.098	1.2178	1.0001	1.000	.0001
383.2	.022	2.2433	1.076	1.1673	1.0005	1.000	.0005
380.5	.077	1.9973	1.069	.9283	1.0067	1.001	.0057
379.9	.088	1.9545	1.068	.8865	1.0087	1.001	.0077
379.6	.230	1.5376	1.045	.4926	1.0549	1.004	.0509
369.5	.352	1.3273	1.035	.2923	1.1229	1.010	.1129
366.4	.449	1.2123	1.025	.1873	1.1941	1.017	.1771

TABLE XIV (Continued)

T (K)	x_1	γ_1 UNIFAC	γ_1 Exp.	Deviation	γ_2 UNIFAC	γ_2 Exp.	Deviation
364.4	.519	1.0251	1.019	.0061	.9845	1.022	.0375
366.4	.449	1.2123	1.025	.1873	1.1941	1.017	.1771
364.4	.519	1.0251	1.019	.0061	.9845	1.022	.0375
362.2	.599	1.0976	1.014	.0836	1.3339	1.030	.3039
	Benzene - m-Xylene						
397.9	.102	.9323	1.246	.3137	.9993	1.003	.0037
392.1	.175	.9396	1.203	.2634	.9979	1.010	.0121
388.6	.214	.9434	1.182	.2386	.9967	1.015	.0183
385.5	.284	.9506	1.147	.1964	.9940	1.026	.0320
379.5	.340	.9558	1.123	.1672	.9911	1.037	.0459
375.2	.427	.9644	1.088	.1236	.9851	1.058	.0729
372.3	.494	.9707	1.067	.0963	.9792	1.077	.0978
369.8	.595	.9798	1.041	.0612	.9678	1.111	.1432
364.0	.681	.9865	1.025	.0385	.9551	1.144	.1889
	Toluene - m-Xylene						
406.3	.111	.9859	1.728	.7421	.9998	1.014	.0142
403.0	.186	.9684	1.533	.5646	.9799	1.036	.0561
392.8	.523	.9953	1.116	.1207	.9951	1.228	.2329
391.7	.561	.9960	1.094	.0980	.9943	1.258	.2637
391.1	.593	.9965	1.079	.0825	.9935	1.283	.2895
390.5	.625	.9970	1.065	.0680	.9928	1.309	.3162
389.5	.677	.9978	1.046	.0482	.9914	1.355	.3636
389.5	.688	.9979	1.042	.0441	.9911	1.365	.3739
389.1	.698	.9980	1.039	.0410	.9908	1.374	.3832
388.5	.736	.9985	1.029	.0305	.9896	1.409	.4194
	Acetone - Methanol						
328.8	.675	1.0921	1.050	.0421	1.5085	1.271	.2375
328.9	.625	1.1251	1.068	.0571	1.4270	1.231	.1960
329.1	.594	1.1487	1.081	.0677	1.3813	1.209	.1723
329.5	.515	1.2210	1.120	.1010	1.2794	1.156	.1234
330.2	.424	1.3297	1.176	.1537	1.1855	1.107	.0785
330.5	.386	1.3849	1.205	.1799	1.1528	1.088	.0648
331.0	.332	1.4749	1.250	.2249	1.1124	1.066	.0464
331.1	.314	1.5083	1.268	.2403	1.1004	1.059	.0414

TABLE XIV (Continued)

T (K)	x_1	γ_1 UNIFAC	γ_1 Exp.	Deviation	γ_2 UNIFAC	γ_2 Exp.	Deviation
332.0	.257	1.6266	1.325	.3016	1.0671	1.039	.0281
332.1	.245	1.6543	1.338	.3163	1.0610	1.036	.0250
332.7	.206	1.7515	1.384	.3675	1.0432	1.026	.0172
333.3	.168	1.8582	1.435	.4232	1.0288	1.017	.0118
333.9	.135	1.9616	1.482	.4796	1.0186	1.011	.0076
	Methanol - 1-Propanol						
365.5	.092	1.0583	0.977	.0813	1.0004	0.999	.0014
362.0	.180	1.0509	0.982	.0689	1.0015	0.999	.0025
357.1	.280	1.0426	0.988	.0546	1.0040	0.997	.0070
355.7	.320	1.0393	0.990	.0493	1.0055	0.996	.0095
353.4	.380	1.0343	0.993	.0413	1.0081	0.995	.0131
351.3	.459	1.0280	0.996	.0320	1.0127	0.993	.0197
347.6	.581	1.0188	0.999	.0198	1.0229	0.989	.0339
347.4	.583	1.0187	0.999	.0197	1.0232	0.989	.0342
344.4	.680	1.0121	1.001	.0111	1.0349	0.988	.0469
342.5	.764	1.0071	1.001	.0061	1.0484	0.987	.0614
341.5	.822	1.0043	1.001	.0033	1.0599	0.988	.0719
340.2	.862	1.0027	1.001	.0017	1.0691	0.991	.0781

VITA

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