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Li, Meng-Hui

APPLICATION OF THE LOCAL-COMPOSITION MODEL TO A GENERALIZED
EQUATION OF STATE FOR REPRESENTING VAPOR-LIQUID EQUILIBRIA OF
NONIDEAL MIXTURES

The University of Oklahoma

Ph.D. 1984

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APPLICATION OF THE LOCAL-COMPOSITION MODEL TO A GENERALIZED
EQUATION OF STATE FOR REPRESENTING VAPOR-LIQUID
EQUILIBRIA OF NONIDEAL MIXTURES

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

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MENG-HUI LI
Norman, Oklahoma
1984

APPLICATION OF THE LOCAL-COMPOSITION MODEL TO A GENERALIZED
EQUATION OF STATE FOR REPRESENTING VAPOR-LIQUID
EQUILIBRIA OF NONIDEAL MIXTURES

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MENG-HUI LI

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ABSTRACT

The statistical-mechanical local composition model has been applied to describe the composition dependence of a recently developed equation of state for use in vapor-liquid equilibria calculations. The composition-dependence for the mixture properties is derived from a local composition model expression for the Helmholtz free energy. The local composition mixing rules have been tested for a wide variety of binary mixtures: mixtures containing carbon dioxide, acetone, hydrogen sulfide, ammonia, methanol, ethanol, 1-propanol, water, etc. When compared with the conventional conformal solution model, a significant improvement is obtained for vapor-liquid equilibria predictions for strongly nonideal mixtures. This local composition model can be used to extend any corresponding-states type equation of state to mixtures.

APPLICATION OF THE LOCAL-COMPOSITION MODEL TO A GENERALIZED
EQUATION OF STATE FOR REPRESENTING VAPOR-LIQUID
EQUILIBRIA OF NONIDEAL MIXTURES

CHAPTER I.

INTRODUCTION

Many engineering processes involve vapor-liquid separation processes such as flash separation, distillation, absorption, etc. Knowledge of phase equilibria is necessary for understanding these separation processes and efficient design of the separation process units requires quantitative information on the phase equilibria of mixtures.

The thermodynamic methods for calculating vapor-liquid equilibria (VLE) usually are based on use of an expression for activity coefficients for the liquid phase along with the use of an equation of state for vapor fugacity coefficients or use of fugacity coefficients from an equation of state for both liquid and vapor phases. The activity coefficient approach works well at low reduced temperatures where the liquid phase is relatively incompressible and up to moderate pressures. However, when supercritical components are involved in the mixture, it is

necessary to use a hypothetical reference state for each of the supercritical components, which makes the calculations cumbersome. Also, the mixture critical region cannot be accurately described. The approach of using an equation of state for both the liquid and vapor phases, mixture containing supercritical components does not require the use of hypothetical standard states. Also, because the vapor and liquid phases are both described by the same equation of state, accurate descriptions of vapor liquid equilibrium at state conditions nearer the mixture critical point are possible.

The conventional method for equation of state prediction of mixture properties is based on the van der Waals one-fluid mixing rules, or the so-called Conformal Solution Model (CSM). It is supposed in the CSM that the properties of a mixture at temperature T , and pressure P , and composition x are the same as those of a hypothetical pure fluid (at the same T and P) whose characteristic parameters are functions of the composition x . These functions, called mixing rules, are quadratic in mole fraction. This model has been shown to work well for mixtures of nonpolar and slightly polar substances (Starling et al., 1977; Peng et al., 1976; Robinson et al., 1977). One of the reasons that the conventional mixing rules do not work well for polar fluids is that the quadratic mole-fraction mixing rule for parameters does not hold at liquid

densities for non-simple mixtures (Whiting and Prausnitz, 1982).

Since the presentation of the local-composition concept (Wilson, 1964), this concept has been widely applied to develop models for liquid activity coefficients. The activity coefficient approach based on the local composition model has been tested for a wide variety of fluid mixtures including strongly nonideal liquid mixtures (Renon and Prausnitz, 1968; Bruin, 1970, 1971; Abrams and Prausnitz, 1975; Fredenslund et al., 1975).

Due to the successful applications of the local composition model to the activity coefficient approach in prediction of vapor-liquid equilibria, some attempts have been made to bridge the gap between the equation of state approach and the activity coefficient approach by using the local composition concept in equations of state. Huron and Vidal (1979) have introduced the excess Gibbs free energy formulation by Renon and Prausnitz (1968) into the energy parameter 'a' in the Redlich-Kwong equation of state. Vachhani and Anderson (1982) have applied the local composition formalism to the attractive part of the Soave-Redlich-Kwong equation of state and empirically introduced density dependence into the mixing rules. Whiting and Prausnitz (1982) have developed local composition density-dependent mixing rules for the attractive part of the van

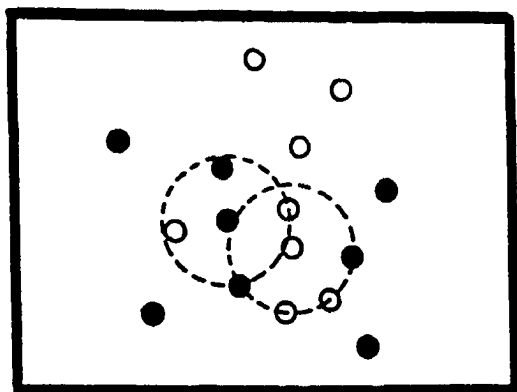
der Waals equation of state. Mathias and Copeman (1983) have developed density-dependent local composition mixing rules to extend the Peng-Robinson equation of state to highly nonideal mixtures.

It is the purpose of this study to apply the local composition model to a recently developed equation of state for vapor-liquid equilibria prediction for strongly nonideal liquid mixtures.

CHAPTER II

LOCAL COMPOSITION MODEL

The local composition concept originates from the quasi-chemical theory of Guggenheim (1935, 1952 and 1966) for lattice gases. It is believed that the motion, position and orientation of a given molecule are strongly affected, due to intermolecular forces, by its neighborhood molecules. The neighborhood molecules are, in turn, affected by the given (central) molecule. When different types of molecules coexist in a mixture, a given (central) molecule may "prefer" to surround itself with one type of molecule rather than another type of molecule. Due to this preference, the molecules distribute non-randomly in the mixture. To visualize the physical meaning of the local composition model, we consider two representative fluid regions in a binary mixture as shown in Fig. 1. These two fluid regions have a type 'A' molecule and a type 'B' molecule as the center molecule, respectively. The local composition of the fluid region with a type 'A' molecule as the center, is different from that of the fluid region with a type 'B' molecule as the center.



Type 1 Region

Type 2 Region

Center

Center

A ○

B ●

The Number of Nearest Neighbors

$$n_{BA} = 3$$

$$n_{AB} = 3$$

$$n_{AA} = 3$$

$$n_{BB} = 2$$

Coordination Number

Z_A

Z_B

$$n_{BA} + n_{AA} = 6$$

$$n_{AB} + n_{BB} = 5$$

Local Compositions

$$x_{BA} = \frac{n_{BA}}{Z_A} = \frac{3}{6}$$

$$x_{AB} = \frac{n_{AB}}{Z_B} = \frac{3}{5}$$

$$x_{AA} = \frac{n_{AA}}{Z_A} = \frac{3}{6}$$

$$x_{BB} = \frac{n_{BB}}{Z_B} = \frac{2}{5}$$

Figure 1. Local Composition Model.

STATISTICAL MECHANICAL INTERPRETATION OF LOCAL COMPOSITION

A statistical mechanical interpretation of the local composition model has been given by Lee, et al. (1983). For a binary mixture of N_A molecules of type A and N_B molecules of type B, the expression for the number of neighborhood molecules surrounding a central molecule is given by the distribution functions (for simplicity a spherically symmetrical pair potential is assumed here), $g(r)$

$$n_{AA}(L_{AA}) = \rho_A \int_0^{L_{AA}} dr \, 4\pi r^2 g_{AA}(r) \quad (2.1)$$

$$n_{BA}(L_{BA}) = \rho_B \int_0^{L_{BA}} dr \, 4\pi r^2 g_{BA}(r) \quad (2.2)$$

$$n_{AB}(L_{AB}) = \rho_A \int_0^{L_{AB}} dr \, 4\pi r^2 g_{AB}(r) \quad (2.3)$$

$$n_{BB}(L_{BB}) = \rho_B \int_0^{L_{BB}} dr \, 4\pi r^2 g_{BB}(r) \quad (2.4)$$

where n_{ij} is the number of i molecules surrounding one central j molecule with a spherical volume of radius L_{ij} , which is the radius appropriate for finding the first neighbors of a central molecule. Only the nearest-neighbor interactions are taken into account in the local composition model.

Applying the potential of mean force (according to Kirkwood, 1935), eqn. (2.1) becomes

$$\begin{aligned}
 n_{AA}(L_{AA}) &= \rho_A \int_0^{L_{AA}} dr \, 4\pi r^2 g_{AA}(r) \\
 &= \rho_A \int_0^{L_{AA}} dr \, 4\pi r^2 \exp \left[-\beta W_{AA}(r) \right] \\
 &= \rho_A \, V_{AA} \exp \left[-\beta \bar{W}_{AA} \right]
 \end{aligned} \tag{2.5}$$

and eqn. (2.2) becomes

$$\begin{aligned}
 n_{BA}(L_{BA}) &= \rho_B \int_0^{L_{BA}} dr \, 4\pi r^2 g_{BA}(r) \\
 &= \rho_B \int_0^{L_{BA}} dr \, 4\pi r^2 \exp \left[-\beta W_{BA}(r) \right] \\
 &= \rho_B \, V_{BA} \exp \left[-\beta \bar{W}_{BA} \right]
 \end{aligned} \tag{2.6}$$

where V_{AA} is the spherical volume $\frac{4}{3} \pi L_{AA}^3$, and $V_{BA} = \frac{4}{3} \pi L_{BA}^3$. The latter equalities are obtained using the mean-value theorem of calculus, i.e., the potential of mean force W_{ij} is evaluated at some mean location in the region of integration to obtain $\bar{W}_{ij}$. β is $1/kT$ and k is the Boltzmann constant. Similar expressions can be obtained for eqns. (2.3) and (2.4).

The local compositions are defined as follows:

$$x_{AA} = \frac{n_{AA}}{n_{AA} + n_{BA}} \quad (2.7)$$

$$x_{BA} = \frac{n_{BA}}{n_{AA} + n_{BA}} \quad (2.8)$$

Combining the eqns. (2.5)-(2.8), the local compositions have the following forms,

$$x_{AA} = \frac{z_A}{z_A + z_B \Lambda_{BA}} \quad (2.9)$$

$$x_{BA} = \frac{z_B \Lambda_{BA}}{z_A + z_B \Lambda_{BA}} \quad (2.10)$$

where Λ_{BA} is

$$\Lambda_{BA} = \frac{v_{BA} \exp(-\beta \bar{w}_{BA})}{v_{AA} \exp(-\beta \bar{w}_{AA})} = F_{BA} \frac{\exp(-N_{av} \bar{w}_{BA}/RT)}{\exp(-N_{av} \bar{w}_{AA}/RT)} \quad (2.11)$$

where F_{BA} is the ratio of v_{BA} to v_{AA} , and N_{av} is the Avogadro's number.

Thus, the local compositions are proportional to both the bulk composition and the Boltzmann factor whose argument characterizes the interaction of molecule pairs.

CONFIGURATIONAL HELMHOLTZ FREE ENERGY FROM LOCAL COMPOSITION

Assuming additivity, the total configurational internal energy of the binary fluid mixture can be obtained from the contributions of two types of regions. The total configurational internal energy U' ($U' = U - U_{\text{ideal gas}}$) is determined (Whiting and Prausnitz, 1982) by

$$\frac{U'}{N} = x_1 (x_{11}u'_{11} + x_{21}u'_{21}) + x_2 (x_{12}u'_{12} + x_{22}u'_{22}) \quad (2.12)$$

where u'_{ij} is the molar configurational internal energy of a fluid whose molecules interact according to ij potential and N is the total number of moles. Substituting the local composition, x_{ij} , into the eqn. (2.12), we have

$$\frac{U'}{N} = \sum_i x_i \frac{\sum_j x_j F_{ji} u'_{ji} \exp(-N_{av} \bar{w}_{ji}/RT)}{\sum_j x_j F_{ji} \exp(-N_{av} \bar{w}_{ji}/RT)} \quad (2.13)$$

A relation for the configurational Helmholtz free energy which is consistent with the thermodynamic relation between the configurational Helmholtz free energy and the configurational internal energy,

$$\left. \frac{\partial \left(\frac{A'}{NRT} \right)}{\partial \left(\frac{1}{RT} \right)} \right|_{V,n} = - \frac{U'}{N} \quad (2.14)$$

is (Lee, et al., 1983)

$$-\frac{\alpha'A'}{NRT} = \sum_i x_i \ln \sum_j x_j F_{ji} \exp(-N_{av} \bar{W}_{ji}/RT) \quad (2.15)$$

In eqn. (2.15) α' is a proportionality factor which relates the mean potential of mean force and the configurational internal energy,

$$u'_{ji} = \frac{1}{\alpha'} \left[\frac{\partial (N_{av} \bar{W}_{ji}/RT)}{\partial (1/RT)} \right] \quad (2.16)$$

CHAPTER III

MIXING RULES FROM THE LOCAL COMPOSITION MODEL

The composition dependence for equation of state calculations of mixture properties (VLE, PVT, etc.) can be derived from the local composition model expression for the Helmholtz free energy.

LOCAL COMPOSITION MIXING RULES

The form of the configurational Helmholtz free energy A' used in this study is (Lee, et al., 1983)

$$-\frac{\alpha' A'}{NRT} = \sum_i x_i \ln \sum_j x_j F_{ji} \exp(-N_{av} \bar{w}_{ji}/RT) \quad (3.1)$$

where $\bar{w}_{ji}$ is the mean potential of mean force for a pair molecules of types j and i . F_{ji} is the volume ratio given by the following relation:

$$F_{ji} = \frac{v_{ji}}{v_{ii}} = \frac{\int_0^{L_{ji}} 4\pi r^2 dr}{\int_0^{L_{ii}} 4\pi r^2 dr} \quad (3.2)$$

where L_{ji} is the radius appropriate for selection of first-neighborhood coordination. For equally sized molecules, $L_{ji}=L_{jj}=L_{ii}$, and F_{ji} is equal to unity. Therefore, F_{ji} is equal to 1 for pure fluids.

The configurational Helmholtz free energy and the mean potential of mean force can be related by considering a pure fluid. For a pure fluid, eqn. (3.1) becomes

$$N_{av} \bar{W}_{ii} = \frac{\alpha' A'_{ii}}{N_i} \quad (3.3)$$

Therefore, α' is a proportionality factor between the mean potential of mean force and the configurational Helmholtz free energy per mole.

Combining eqns. (3.1) and (3.3), the configurational Helmholtz free energy has the following form:

$$- \frac{\alpha' A'}{RT} = \sum_i x_i \ln \sum_j x_j F_{ji} \exp\left(- \frac{\alpha' A'_{ji}}{RT}\right) \quad (3.4)$$

where A'_{ji} is the molar configurational Helmholtz free energy of a system of molecules which have j-i interactions only.

The Helmholtz free energy and the internal energy follow the relation,

$$\left. \frac{\partial \left(\frac{A'}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right|_{V,n} = \underline{U'} \quad (3.5)$$

Thus, differentiating eqn. (3.4) with respect to $1/T$ yields the molar configurational internal energy (assuming that F_{ji} is independent of temperature)

$$\bar{U}' = \sum_i x_i \frac{\sum_j x_j F_{ji} \bar{U}'_{ji} \exp\left(-\frac{\alpha' A'_{ji}}{RT}\right)}{\sum_j x_j F_{ji} \exp\left(-\frac{\alpha' A'_{ji}}{RT}\right)} \quad (3.6)$$

where $\bar{U}'_{ji}$ is the molar configurational internal energy of a system of molecules with j-i interactions.

The expression for the configurational Helmholtz free energy, eqn. (3.4), with addition of the ideal gas part, can be differentiated with respect to volume to obtain the equation of state

$$P = \sum_i x_i \frac{\sum_j x_j F_{ji} P_{ji} \exp\left(-\frac{\alpha' A'_{ji}}{RT}\right)}{\sum_j x_j F_{ji} \exp\left(-\frac{\alpha' A'_{ji}}{RT}\right)} \quad (3.7)$$

A'_{ji} , $\bar{U}'_{ji}$, and P_{ji} in eqns. (3.4) - (3.7) are the properties of a system of molecules with j-i interactions and are calculated using the equation of state for pure substances. The equation of state for pure fluids used herein is a recently developed generalized equation of state for polar fluids [Khan, et al., 1983]. The equation of state has been tested for different groups of substances,

including normal paraffins(C2-nC20), ring compounds, and polar compounds(CO2, H2S, etc.), and polar and associating compounds(NH3, water, and alcohols, etc.). The results using the pure fluid equation of state are accurate enough for engineering design calculations. The equation of state and the pure fluid parameters are given in Appendix A.

REDUCED TEMPERATURE AND DENSITY

For the equation of state used herein, A'_{ij} , U'_{ij} , and P_{ij} are functions of the reduced temperature, T_{ij}^* , the reduced density, ρ_{ij}^* and the structure parameter, λ_{ij} (see Appendix A). Herein the relations used for T_{ij}^* and ρ_{ij}^* are

$$T_{ij}^* = kT / \epsilon_{ij} \quad (3.8)$$

$$\rho_{ij}^* = \rho V_x^* \quad (3.9)$$

where

$$V_x^* = \sum_m \sum_n x_m x_n V_{mn}^* \quad (3.10)$$

The use of the above relation for T_{ij}^* corresponds to a multifluid model, while the use of the above relation for ρ_{ij}^* corresponds to a one fluid model. Appendix C presents results using a multifluid model for ρ_{ij}^* ($= \rho V_{ij}^*$), which yields exceptionally good results for mixtures of similarly sized molecules. Unfortunately, the multifluid model for

ρ_{ij}^* cannot be used for large molecular size differences. The one fluid model for ρ_{ij}^* was chosen for use herein so that the problems encountered using the multifluid model for ρ_{ij}^* for mixtures with large molecular size differences are not encountered (see Appendices D and E). It should be noted that by virtue of the choices for the relations for T_{ij}^* and ρ_{ij}^* used herein, the present formulation of the local composition model has characteristics of both one fluid and multifluid models. Because the present formulation can be applied regardless of mixture component molecular sizes, it is the most broadly applicable method considered.

THE COMBINING RULES

The pair characterization parameters, λ_{ij} , v_{ij}^* , and ϵ_{ij} are functions of the corresponding pure fluid characterization parameters for components i and j, and are calculated herein using the following combining rules:

$$\lambda_{ij} = \frac{\lambda_{ii} + \lambda_{jj}}{2} \quad (3.11)$$

$$v_{ij}^* = \xi^3 (v_{ii}^* v_{jj}^*)^{1/2} \quad (3.12)$$

$$\epsilon_{ij}^0 = \zeta (\epsilon_{ii}^0 \epsilon_{jj}^0)^{1/2} \quad (3.13)$$

$$D_{ij} = \frac{D_{ii} + D_{jj}}{2} \quad (3.14)$$

$$\epsilon_{ij} / k = \epsilon_{ij}^0 / k + \frac{D_{ij}}{T} \quad (3.15)$$

where the subscripts ii and jj refer to the pure component parameters for components i and j , respectively, and ξ and ζ are binary interaction parameters. It would be more logical theoretically to base the relation for D_{ij} on known rules for dipole moments (geometric mean) than the arbitrary arithmetic rule; however, it is necessary to estimate the induced polar effect for a mixture of nonpolar and polar fluid if the geometric mean for D_{ij} is used. For the sake of simplicity, an arbitrary arithmetic rule, eqn. (3.14), is chosen. The values of characterization parameters for $j-i$ interactions are set equal to those for $i-j$ interactions.

COMPONENT FUGACITY

When dealing with phase equilibria problems, the fugacity coefficients for the components in solution must be evaluated. By applying the thermodynamic relation

$$\ln \left(\frac{\hat{f}_i}{x_i P} \right) = \int_V^\infty \left[\frac{\partial nZ}{\partial n_i} \bigg|_{T, V, n_{j \neq i}} - 1 \right] \frac{dV}{V} - \ln(Z) \quad (3.16)$$

The fugacity of ith component in solution has the following form:

$$\begin{aligned} \ln \frac{\hat{f}_i}{x_i} = & - \frac{1}{\alpha'} \left[\ln \sum_k x_k F_{ki} \exp\left(-\frac{\alpha' A_{ki}}{RT}\right) - 1 + \sum_j x_j \frac{F_{ij} \exp\left(-\frac{\alpha' A_{ij}}{RT}\right)}{\sum_k x_k F_{kj} \exp\left(-\frac{\alpha' A_{kj}}{RT}\right)} \right] \\ & + \frac{1}{\alpha'} \left[\ln \sum_k x_k F_{ki} - 1 + \sum_j x_j \frac{F_{ij}}{\sum_k x_k F_{kj}} \right] \\ & + (z - 1) \left[1 + \bar{R}_i \right] \end{aligned} \quad (3.17)$$

The derivative $\bar{R}_i$ in eqn. (3.17) is:

$$\bar{R}_i = \frac{1}{v_x^*} \left. \frac{\partial v_x^*}{\partial n_i} \right|_{T, V, n_{j \neq i}} = 2 \left[\frac{\sum_j x_j v_{ij}^*}{v_x^*} - 1 \right] \quad (3.18)$$

CHAPTER IV

RESULTS AND DISCUSSION

For purposes of comparison, vapor-liquid equilibria calculations were performed using both local composition and conformal solution mixing rules. The conformal solution model assumes that the mixture properties are the same as those of a hypothetical pure fluid characterized by equation of state characterization parameters(V^* , ϵ , and λ) which are functions of composition. In Appendix B the conformal solution mixing rules for V^* , ϵ and λ are given, along with relations for pertinent derived properties.

The value of α' in eqn. (3.4), is related to the coordination number, and is the proportionality factor between the mean potential of mean force and the configurational Helmholtz free energy. In the quasichemical theory [Guggenheim, 1952], for a lattice gas at low densities,

$$\alpha' = \frac{2}{Z} \quad (4.1)$$

where Z is the coordination number. For a simple cubic lattice $Z=6$, for a body-centred cubic lattice $Z=8$, and for a face-centred cubic lattice $Z=12$. If the coordination number in a dense fluid is approximately 8, the value of α' should be around 0.25. In the original work of Wilson (1964), the

value $\alpha' = 1$ was used. In the work of Renon and Prausnitz (1968), α' is an empirical parameter which varies between 0.3 and 0.47. Abrams and Prausnitz (1975) used $\alpha' = 1$. It has been stated by Whiting and Prausnitz (1982) that α' should be an universal constant, otherwise the local composition model cannot be extended to multicomponent mixtures, and they use $\alpha' = 0.5$ in their work. We also choose α' equal to 0.5 in this work, the value used by Whiting and Prausnitz.

The quantity F_{ij} is the ratio of V_{ij} to V_{jj} , where V_{ij} is the volume appropriate for the selection of first-neighborhood coordination.

$$F_{ij} = \frac{V_{ij}}{V_{jj}} \quad (4.2)$$

For mixtures of equal sized molecules, the F_{ij} would be unity. To account for the value F_{ij} ($i \neq j$) the binary interaction parameter δ is introduced, where $V_{ij} = \delta^3 (V_{ii} V_{jj})^{1/2}$. Herein it is assumed that the first-neighborhood volume, V_{ii} , is proportional to the molar covolume parameter, V_{ii}^* , so that

$$F_{ij} = \delta^3 \left(\frac{V_{ii}^*}{V_{jj}^*} \right)^{1/2} \quad (4.3)$$

Hereafter, We refer to the two mixing rules under study as CSM (conformal solution mixing rules) and LCM (local composition mixing rules).

The number of parameters used in the mixing rules generally affects the results in vapor-liquid equilibria calculations. The more binary interaction parameters are used, the more accurate results are expected. The mixture of methanol-CO₂ was selected to test the effects of choosing varying numbers of binary interaction parameters used in the CSM and LCM. The experimental vapor-liquid equilibria data ranges used in this study are given in Table 1. In Table 2 results calculated from both the CSM and the LCM are given. The numbers of binary interaction parameters for the CSM are two, three, and four, and for the LCM are two, and three. Even with four binary interaction parameters, the CSM still cannot work well for the methanol-CO₂ system (see Table 2). This indicates the composition dependence deficiency of the CSM for strongly nonideal mixtures. However, the LCM greatly improves on the CSM for vapor-liquid equilibria calculations for the methanol-CO₂ system. The improvement in the fit of the methanol-CO₂ data by use of the LCM is dramatical good using either two or three binary interaction parameters. In Fig. 2 the comparisons of results from the CSM with four binary interaction parameters and from the LCM with two and three binary interaction parameters are shown to illustrate the above remarks.

Based on multiproperty analysis (Starling, et al., 1971), it is believed that a reasonable mixing rule, in principle, should describe not only vapor-liquid equilibria

Table 1. Vapor-liquid equilibria and density data
used in this study

System	Prop- erty	Reference	No. of data pts	Temper- ature C	Pressure range atm
-----	-----	-----	-----	-----	-----
Ethane- n-Butane	VLE den.	Mehra, 1965 Kay, 1940	19 49	65-121 0-140	32-55 5-55
Methane- n-Decane	VLE den.	Sebastian, 1979 Reamer, 1942	12 36	270-310 37-238	30-125 136-612
Methane- CO ₂	VLE	Mraw, 1978	20	-54 -63	6-63
CO ₂ - n-Hexane	VLE	Ohgaki, 1976	10	25	4-51
CO ₂ - Benzene	VLE	Ohgaki, 1976	17	25-40	8-76
CO ₂ - n-Decane	VLE	Sebastian, 1980	16	189-310	14-51
CO ₂ - n-Hexadecane	VLE	Sebastian, 1980	16	189-390	19-50
Ethane- Acetone	VLE	Katayama, 1976	8	25	4.7-39
Propane- Acetone	VLE	Thodos, 1978b	8	77	3.4-27
n-Pentane- Acetone	VLE	Karr, 1962	11	31-49	1
Acetone- Benzene	VLE	Tasic, 1978	11	25	.15-.30
Acetone- n-Heptane	VLE	Ratcliff, 1972	8	65	.76-1.35

Table 1. (Continued)

System	Prop- erty	Reference	No. of data pts	Temper- ature C	Pressure range atm
Ethane- Methanol	VLE	Katayama, 1976	5	25	11-41
Methanol- Benzene	VLE den.	Nagata, 1969 Sumer, 1967	18 15	58-76 20-40	1 1
Propane- Ethanol	VLE	Todos, 1978a	16	127-151	6.8-54
Benzene- Ethanol	VLE	Smith, 1970	9	25	.11-.16
Ethanol- n-Decane	VLE	Ellis, 1961	11	80-160	1
n-Hexane- 1-Propanol	VLE	Prabhu, 1963	8	66-89	1
Benzene- 1-Propanol	VLE	Tojo, 1973	50	77-96	1
1-Propanol- n-Decane	VLE	Ellis, 1960	10	75-98	0.39
Methane- Water	VLE	Culberson, 1951	10	171	13-204
Ethane- Water	VLE	Culberson, 1950	10	171	13-204
Acetone- CO2	VLE	Katayama, 1975	11	25	4-55
Methanol- CO2	VLE	Katayama, 1975	13	25	2-60

Table 1. (Continued)

System	Property	Reference	No. of data pts	Temperature C	Pressure range atm
Acetone-Ethanol	VLE	Amer, 1956	9	57-76	1
Acetone-Water	VLE	Griswold, 1952	25	200	18-29
	den.	Noda, 1982	9	25	1
	den.	Thomas, 1957	34	20-80	1
Methanol-1-Propanol	VLE	Schmidt, 1926	9	50	.16-.51
Methanol-water	VLE	Griswold, 1952	9	150	5.3-13.2
	den.	Mikhail, 1961	25	25-50	1
Ethanol-1-Propanol	VLE	Kojima, 1969	9	80-94	1
Ethanol-Water	VLE	Paul, 1976	12	78-96	1
CO ₂ -Water	VLE	Takenouchi, 1961	9	275	99-690
H ₂ S-Water	VLE	Selleck, 1952	11	171	13-170
Ammonia-Water	VLE	Clifford, 1933	20	10-170	1-10

Table 2. Vapor-liquid equilibria calculations using
local composition and conformal solution
mixing rules for methanol-CO₂ at 25 C

Mixing Rules	No. of BIPs	Binary Interaction Parameters ^a					A.A.D. $\bar{x}$ ^c	
		ξ	ζ	ν	τ	δ	K1	K2
CSM	2	0.9634	1.0969	--	--	--	22.7	27.8
CSM	3	0.9614	1.1239	0.9498	--	--	22.7	26.6
CSM	4	0.9823	1.0835	0.8882	1.0532	--	37.9	9.78
LCM	^b 2	0.7815	0.9531	--	--	--	18.7	5.72
LCM	3	0.9997	0.9404	--	--	1.0722	9.13	3.24

a :

$$v_{ij}^* = \xi^3 (v_{ii}^* v_{jj}^*)^{1/2}$$

$$\epsilon_{ij}^0 = \zeta (\epsilon_{ii}^0 \epsilon_{jj}^0)^{1/2}$$

$$\lambda_{ij} = \nu \left(\frac{\lambda_{ii} + \lambda_{jj}}{2} \right)$$

$$D_{ij} = \tau \left(\frac{D_{ii} + D_{jj}}{2} \right)$$

b : set $F_{ij} = 1$

$$c : \text{A.A.D. } \bar{x} = \frac{1}{NP} \sum_{i=1}^{NP} \left| \frac{k_{\text{exp}} - k_{\text{cal}}}{k_{\text{exp}}} \right| \times 100$$

NP: number of data points

METHANOL(1)-CO₂(2)

TEMPERATURE : 25 C

* + : DATA OF KATAYAMA, 1975

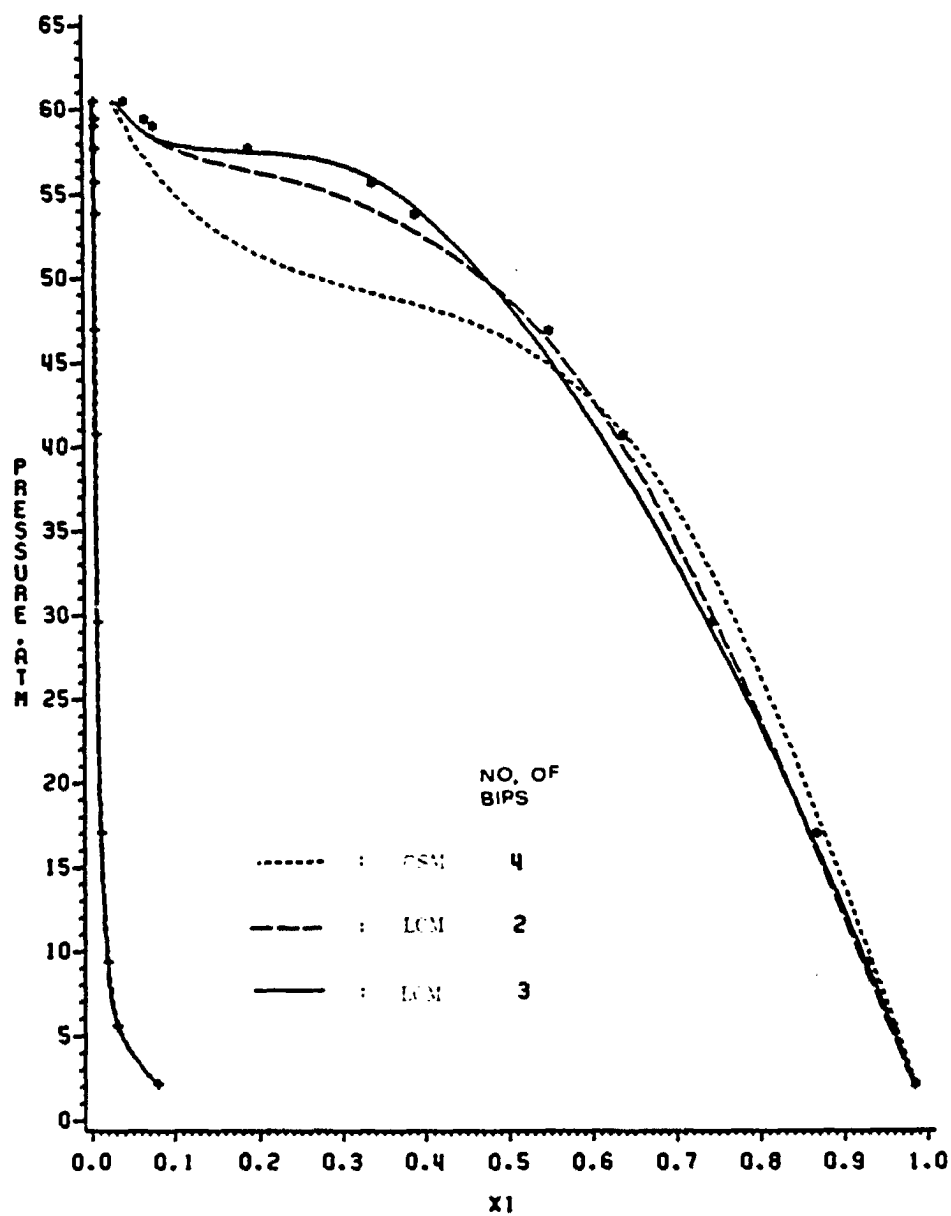


FIGURE 2. PRESSURE-COMPOSITION DIAGRAM

but also bulk properties, such as mixture density. Therefore, both vapor-liquid equilibria and mixture density data can be used to test the mixing rules. Five systems, ethane-n-butane, methane-n-decane, acetone-water, methanol-benzene, and methanol-water were selected in the test. The vapor-liquid equilibria and the mixture density data were used simultaneously in multiproperty regression analysis to determine the optimal values of the binary interaction parameters for each system. A summary of the results is given in Table 3.

For mixtures of ethane-n-butane, and methane-n-decane, although both the CSM and the LCM fit the VLE and the mixture density data reasonably well, the LCM calculates mixture density slightly better. For mixtures of acetone-water, the CSM shows its poor results for both the VLE and the mixture density. For mixture density, the average absolute deviation percentage from the CSM is 7.9 % and from the LCM is 2.3 %. Fig. 3 is a plot of percentage deviation of calculated density versus density for the acetone-water system. As shown in Fig. 4, the acetone-water system forms a maximum pressure azeotrope at 200 C. The CSM gives very poor results for VLE near the azeotrope region; similar results were noted by Huron and Vidal (1979). The LCM gives quite accurate results near the azeotrope region, as shown in Fig. 4.

Table 3. Vapor-liquid equilibria and density calculations using
local composition and conformal solution mixing
rules for five binary systems

System	Mixing rules	ξ	ζ	δ	den.	K1	K2	x1	x2	y1	y2

A.A.D. %											
Ethane- n-Butane	CSM	1.0006	0.9992	--	2.15	1.35	2.19	2.28	2.07	1.91	3.80
	LCM	1.0047	0.9843	1.0283	1.96	1.69	2.29	2.94	3.03	2.06	4.57
Methane- n-Decane	CSM	1.0741	1.1163	--	1.07	4.97	4.28	4.33	2.13	3.07	4.56
	LCM	1.0884	0.5675	0.6281	1.04	4.05	2.35	4.94	1.98	1.18	3.29
Acetone- Water	CSM	0.9797	1.0012	--	7.90	--	--	--	--	--	--
	LCM	1.0862	0.8850	1.1613	2.26	--	--	--	--	--	--
Methanol -Benzene	CSM	1.0027	0.9210	--	3.10	--	--	--	--	--	--
	LCM	0.9954	0.7943	0.7570	2.20	--	--	--	--	--	--
Methanol -Water	CSM	1.0174	1.0094	--	3.18	5.75	5.54	4.44	4.59	3.00	1.99
	LCM	1.0184	0.9825	1.0934	2.83	4.34	5.43	3.45	1.55	3.58	4.39

CSM : Conformal Solution Mixing Rules											
LCM : Local Composition Mixing Rules											

ACETONE(1)-WATER(2)

TEMPERATURE : 20-80 C

DATA SOURCES: NODA,1982, AND THOMAS, 1957

Y : CSM

+ : LCM

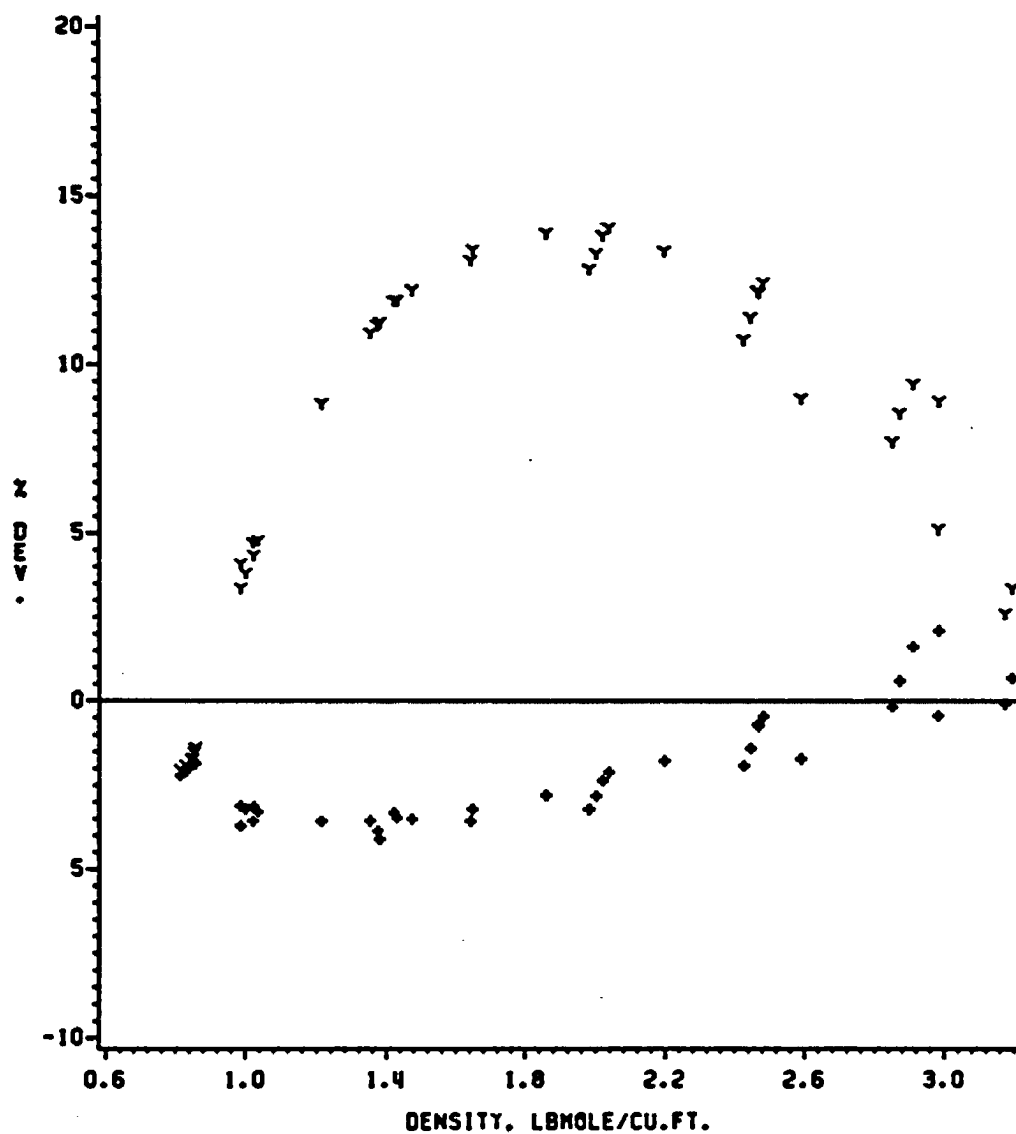


FIGURE 3. THE DEV. OF DENSITY PREDICTIONS VS. DENSITY

ACETONE(1)-WATER(2)

TEMPERATURE : 200 C
 * + : DATA OF GRISWOLD, 1952
 - - - : CSM
 - - - : LCM

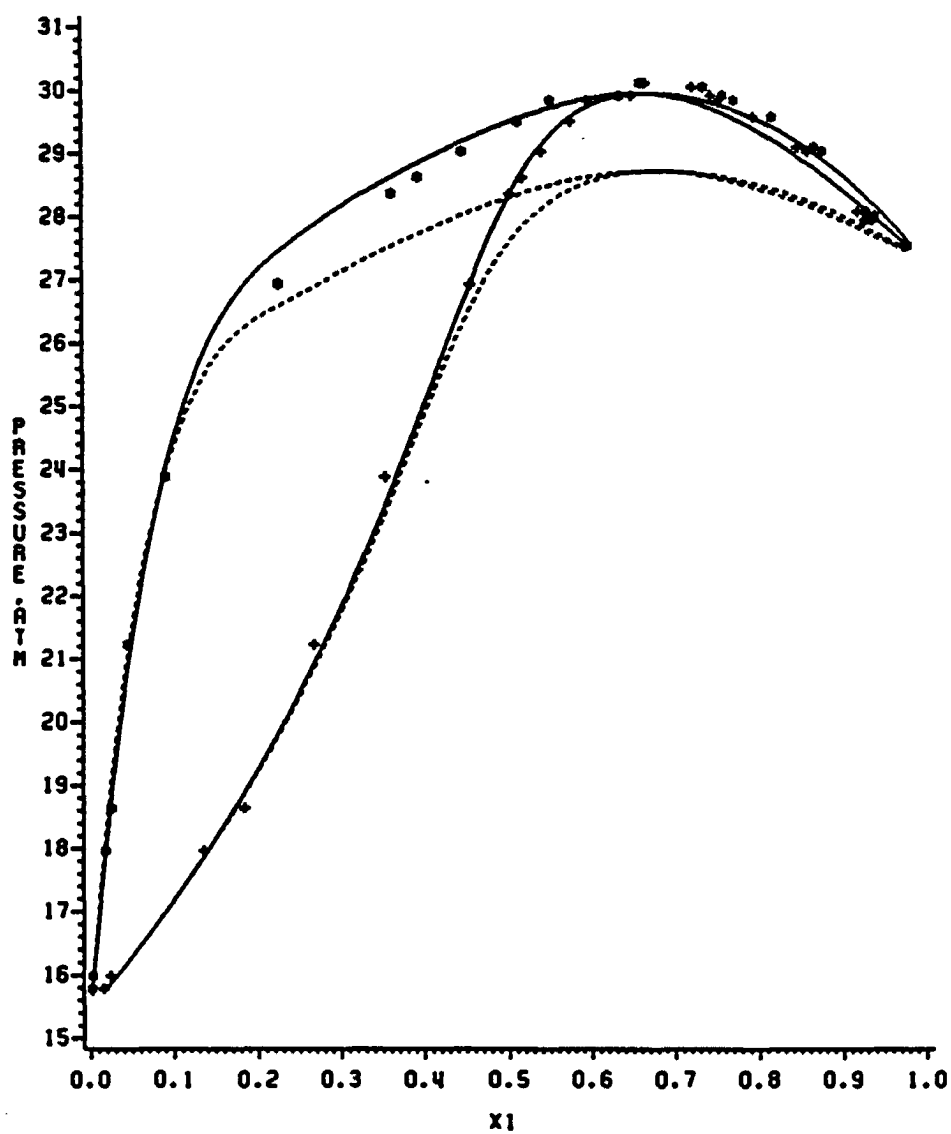


FIGURE 4. PRESSURE-COMPOSITION DIAGRAM

For the methanol-benzene system, the CSM gives a reasonable fit to mixture density data; however, the CSM calculates the VLE very poorly (see Fig. 5). The LCM calculates the VLE quite well except in the high methanol concentration range. The pure fluid equation of state predicts the boiling point (at one atmosphere) of methanol with an error of 2.4 C (experimental, 64.7 C; predicted, 62.3 C). The inaccurate pure component boiling point prediction for methanol from the equation of state artificially distorts the VLE calculations near the range of pure methanol. In order to prove this point, one of the equation of state parameters for methanol, λ , was redetermined to match the experimental boiling point at one atmosphere. The redetermined λ is 2.1495, which gives the corresponding boiling point 64.71 C. Using this new λ for pure methanol, both the CSM and the LCM binary interaction parameters for the methanol-benzene system were redetermined and are given in Table 4. As is shown in Fig. 6, the LCM VLE results have been greatly improved in the high methanol concentration range. This test demonstrates that the accuracy of the equation of state predictions of pure fluid properties is of great importance for calculations of mixture properties.

Even though methanol and water are both polar and associating substances, the methanol-water system is not a strongly nonideal system in terms of the activity

METHANOL(1)-BENZENE(2)

PRESSURE : 1 ATM
• + : DATA OF NAGATA, 1969
- - - : CSM
— : LCM

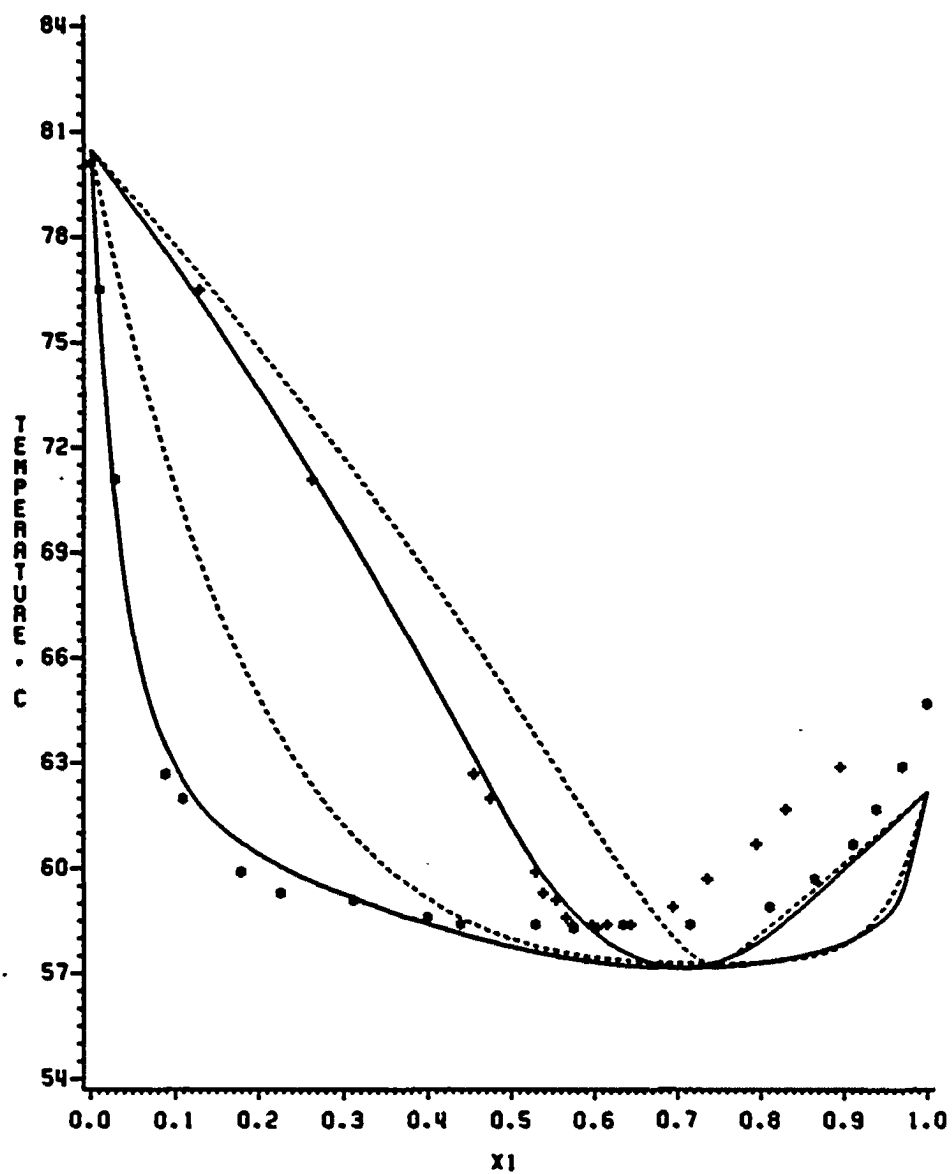


FIGURE 5. TEMPERATURE-COMPOSITION DIAGRAM

Table 4. The redetermined binary interaction parameters
for methanol-benzene system at one atm using
the redetermined λ for methanol

Mixing Rules	Binary Interaction Parameters		
	ξ	ζ	δ
-----	-----	-----	-----
CSM	0.9722	0.9165	--
LCM	1.1736	0.7456	0.9144

note: The redetermined λ for methanol is 2.1495

METHANOL(1)-BENZENE(2)

PRESSURE : 1 ATM
• + : DATA OF NAGATA, 1969
- - - : CSM
— : LCM

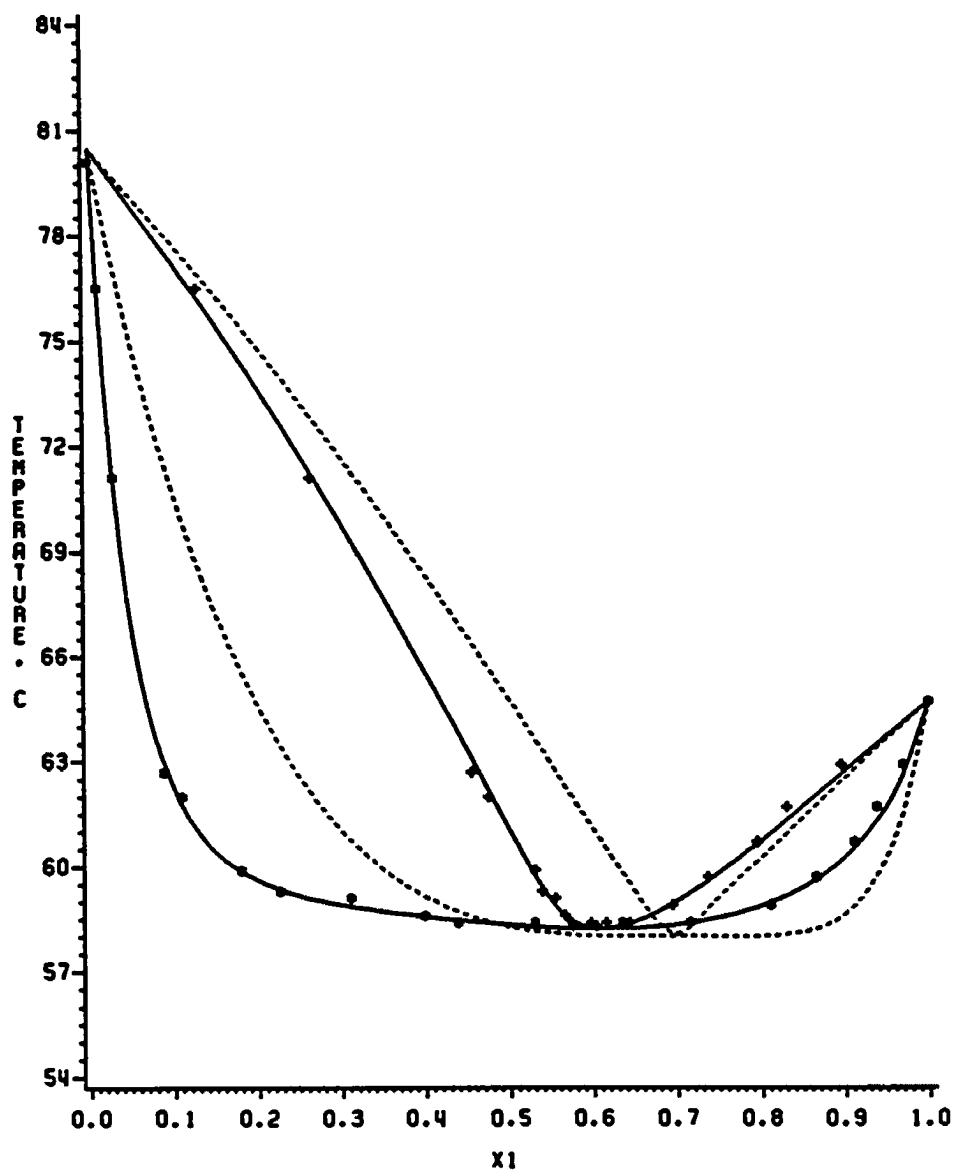


FIGURE 6. TEMPERATURE-COMPOSITION DIAGRAM

coefficients. The activity coefficients at dilute compositions at 150 C are 2.6 and 1.6 for methanol and water, respectively (Griswold, 1953). The CSM gives good results for both mixture density and VLE for the methanol-water system (see Table 3). The LCM yields slightly better VLE results than the CSM for the methanol-water system, as shown in Fig. 7.

Overall, for nonpolar mixtures such as ethane-n-butane, and methane-n-decane, the LCM gives as good or slightly better results than the CSM. For strongly nonideal mixtures such as acetone-water, methanol-benzene, and methanol-carbon dioxide, the LCM is obviously superior to the CSM.

The applicability of the LCM has also been tested for other polar mixtures, including systems containing carbon dioxide, acetone, methanol, ethanol, 1-propanol, water, ammonia, and hydrogen sulfide.

For mixtures of carbon dioxide with hydrocarbons, five systems, methane-carbon dioxide, carbon dioxide-n-hexane, carbon dioxide-benzene, carbon dioxide-n-decane, and carbon dioxide-n-hexadecane were selected for test. A summary of the results is given in Table 5. The LCM gives quite good results as shown in Figs. 8-14. For system of carbon dioxide-benzene, the improvements in the calculations of the liquid composition by use of the LCM are shown in

METHANOL(1)-WATER(2)

TEMPERATURE : 150 C
 • + : DATA OF GRISWOLD, 1952
 - - - : CSM
 — : LCM

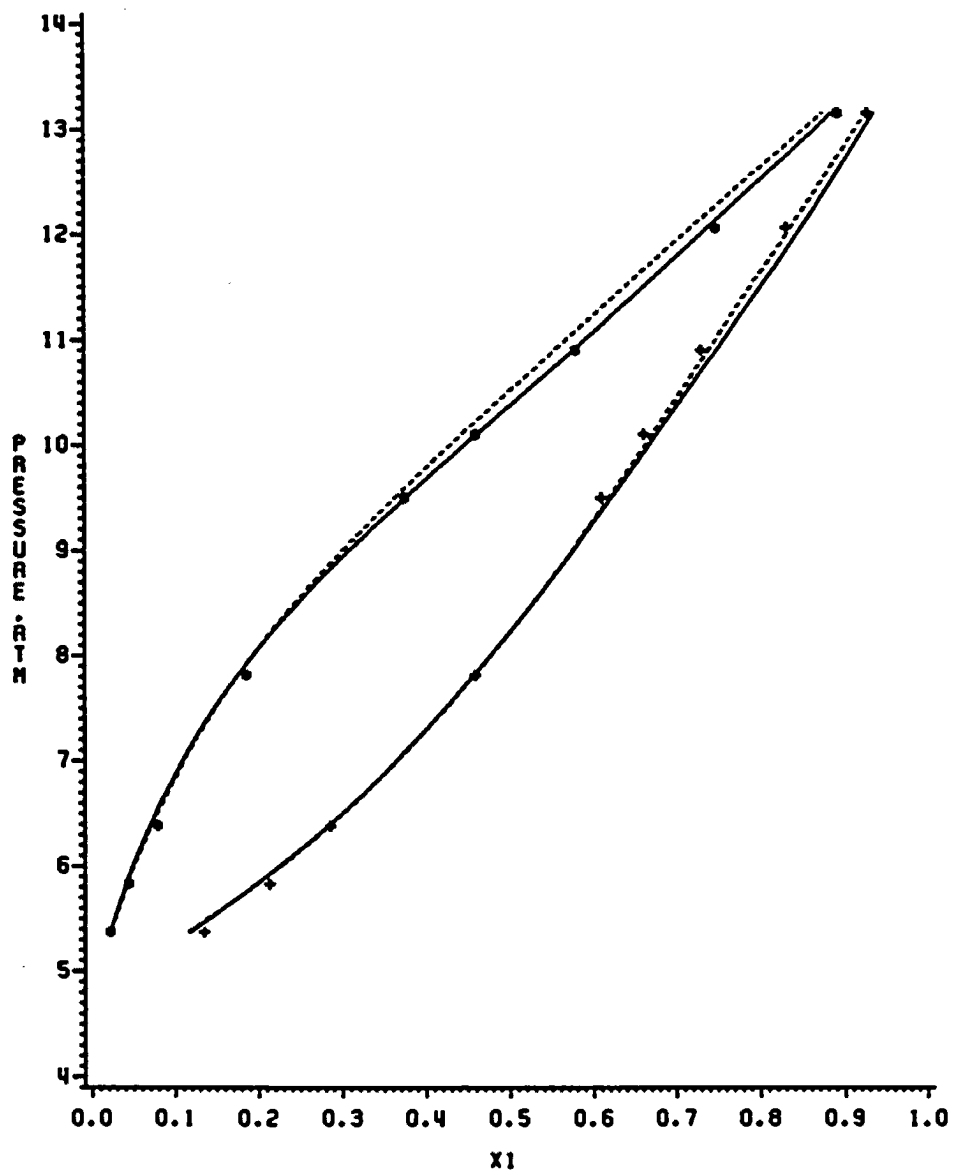


FIGURE 7. PRESSURE-COMPOSITION DIAGRAM

Table 5. Vapor-liquid equilibria calculations using
local composition and conformal solution
mixing rules for CO₂ binary mixtures

System	Mixing rules	ξ	ζ	δ	K1	K2	x1	x2	y1	y2
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
A.A.D. %										
Methane- CO ₂	CSM	0.9867	0.9718	--	3.71	5.00	3.34	4.30	2.25	6.91
	LCM	1.0429	0.8459	1.1320	3.45	3.25	2.90	2.91	1.45	2.99
CO ₂ - n-Hexane	CSM	1.0430	0.8723	--	8.93	15.4	9.73	9.09	0.45	22.9
	LCM	1.1736	0.7819	1.1824	4.34	12.3	4.85	4.75	0.33	13.7
CO ₂ - Benzene	CSM	1.0286	0.9405	--	7.70	15.2	8.07	12.1	0.29	24.1
	LCM	1.2044	0.7870	1.1369	1.65	13.7	1.64	5.70	0.11	9.18
CO ₂ - n-Decane	CSM	1.0539	0.9082	--	8.58	5.41	6.24	1.18	2.52	4.34
	LCM	1.2433	0.7511	1.1255	3.76	2.66	3.10	0.50	1.24	2.44
CO ₂ - n-Hexa- decane	CSM	1.0799	0.9051	--	12.9	8.92	12.5	2.72	1.19	8.14
	LCM	1.3504	0.7200	1.1274	10.2	9.81	10.8	2.32	1.72	10.2

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

METHANE(1)-CO2(2)

TEMPERATURE : -53.9 C

* + : DATA OF MRAW, 1978

- - - : CSM

— : LCM

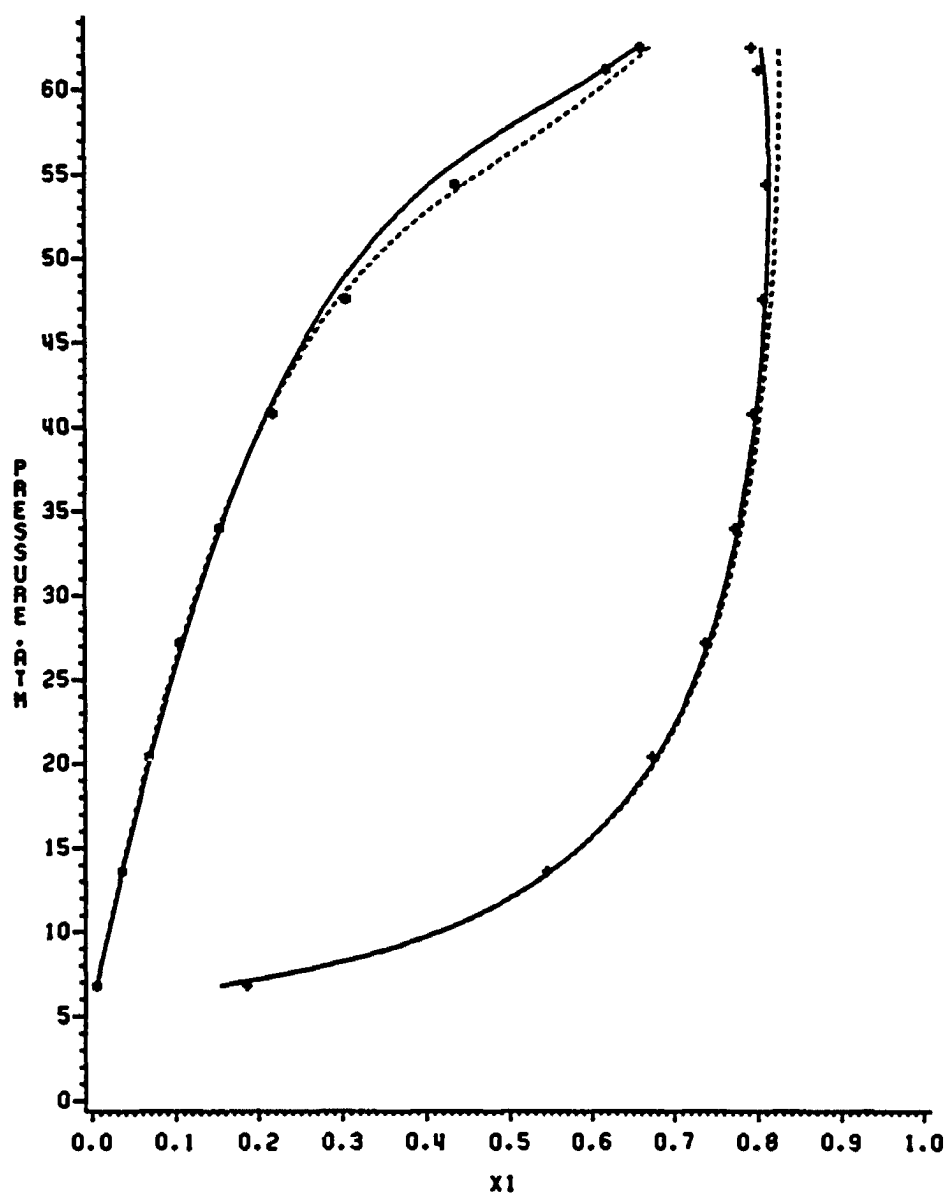


FIGURE 8. PRESSURE-COMPOSITION DIAGRAM

METHANE(1)-CO2(2)

TEMPERATURE : -63 C

* + : DATA OF MRAW, 1978

- - - - : CSM

— : LCM

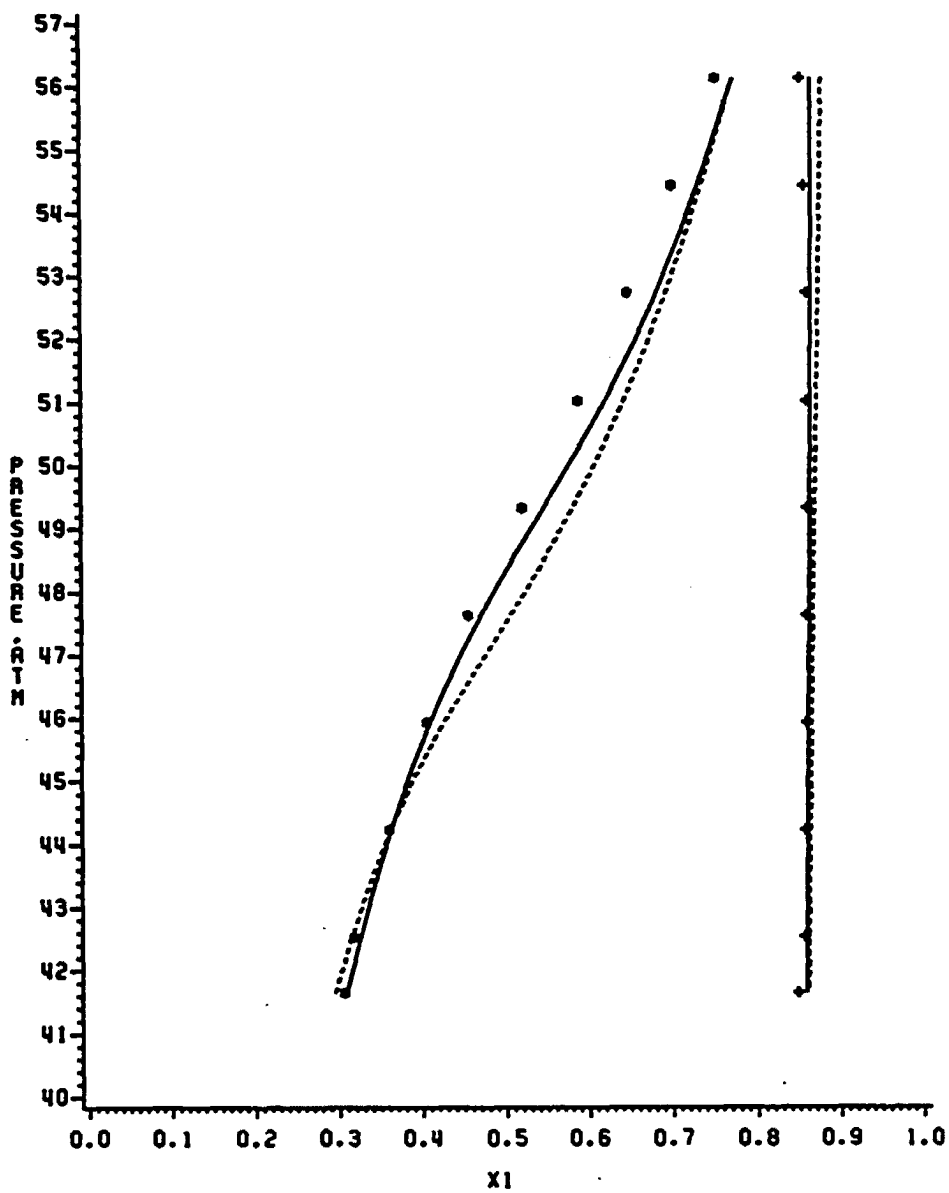


FIGURE 9. PRESSURE-COMPOSITION DIAGRAM

CO₂(1)-N-HEXANE(2)

TEMPERATURE : 25 C

* + : DATA OF OHGAKI, 1976

- - - : CSM

— : LCM

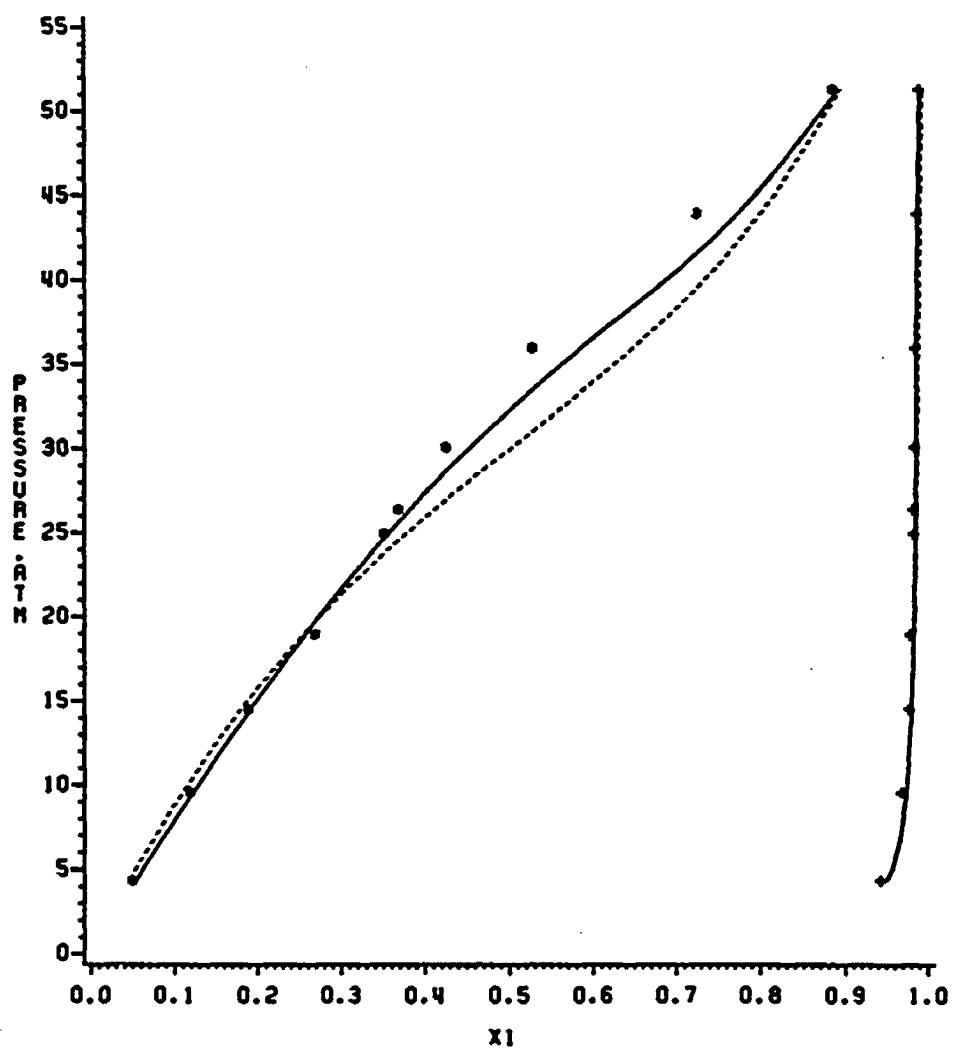


FIGURE 10. PRESSURE-COMPOSITION DIAGRAM

C02(1)-BENZENE(2)

TEMPERATURE : 25 C

* + : DATA OF OHGAKI, 1976

- - - - : CSM

— : LCM

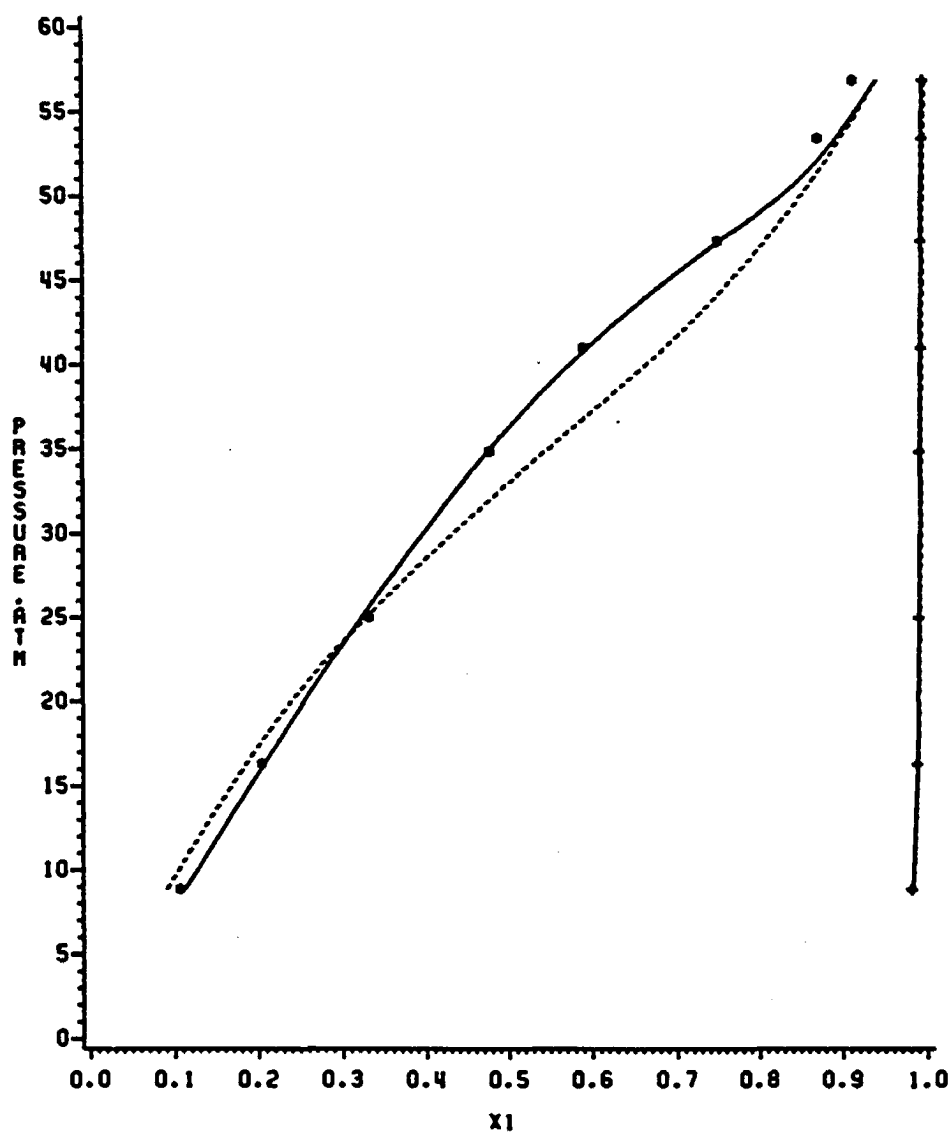


FIGURE 11. PRESSURE-COMPOSITION DIAGRAM

C02(1)-BENZENE(2)

TEMPERATURE : 40 C

* + : DATA OF OHGAKI, 1976

- - - : CSM

— : LCM

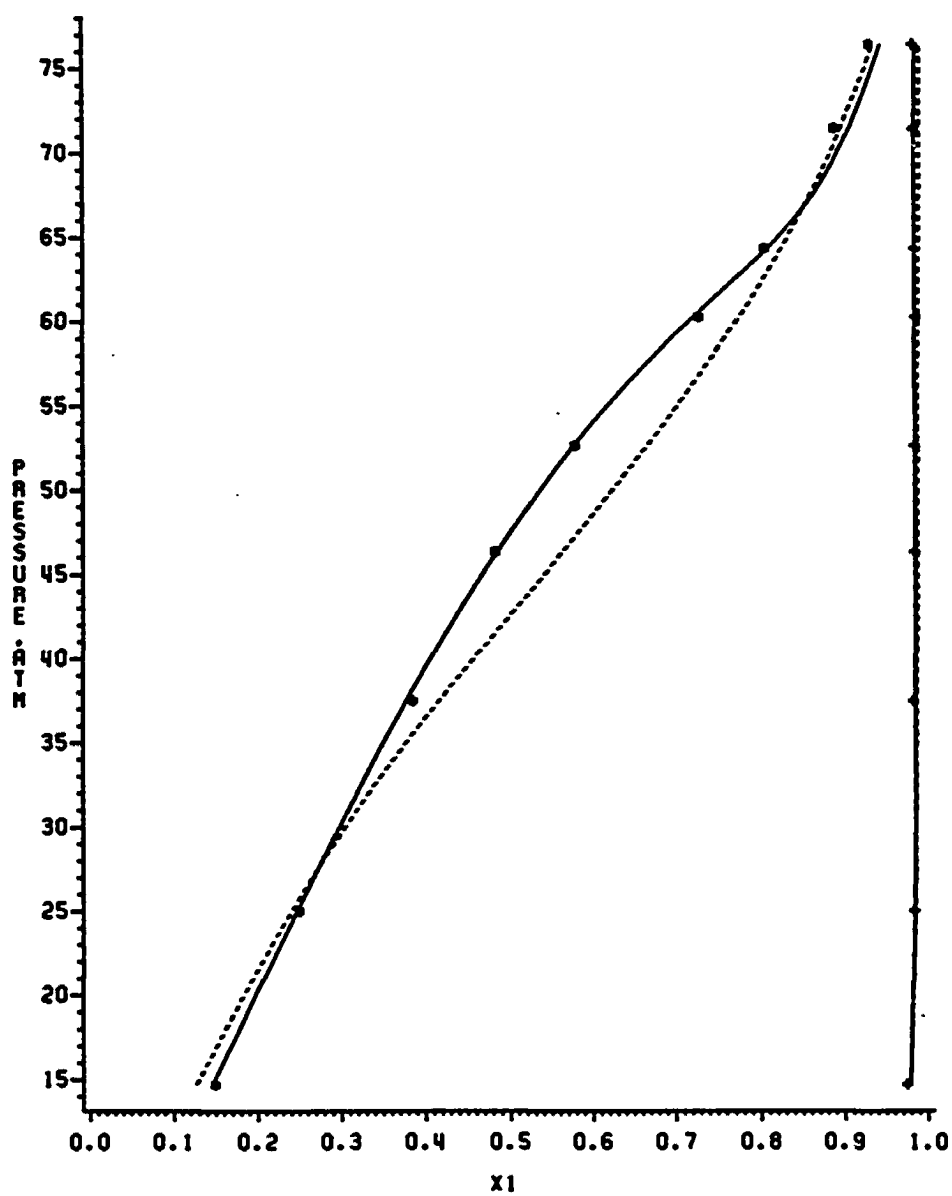


FIGURE 12. PRESSURE-COMPOSITION DIAGRAM

CO₂(1)-N-DECANE(2)

TEMPERATURE : 189.4 C

* + : DATA OF SEBASTIAN, 1980

----- : CSM

————— : LCM

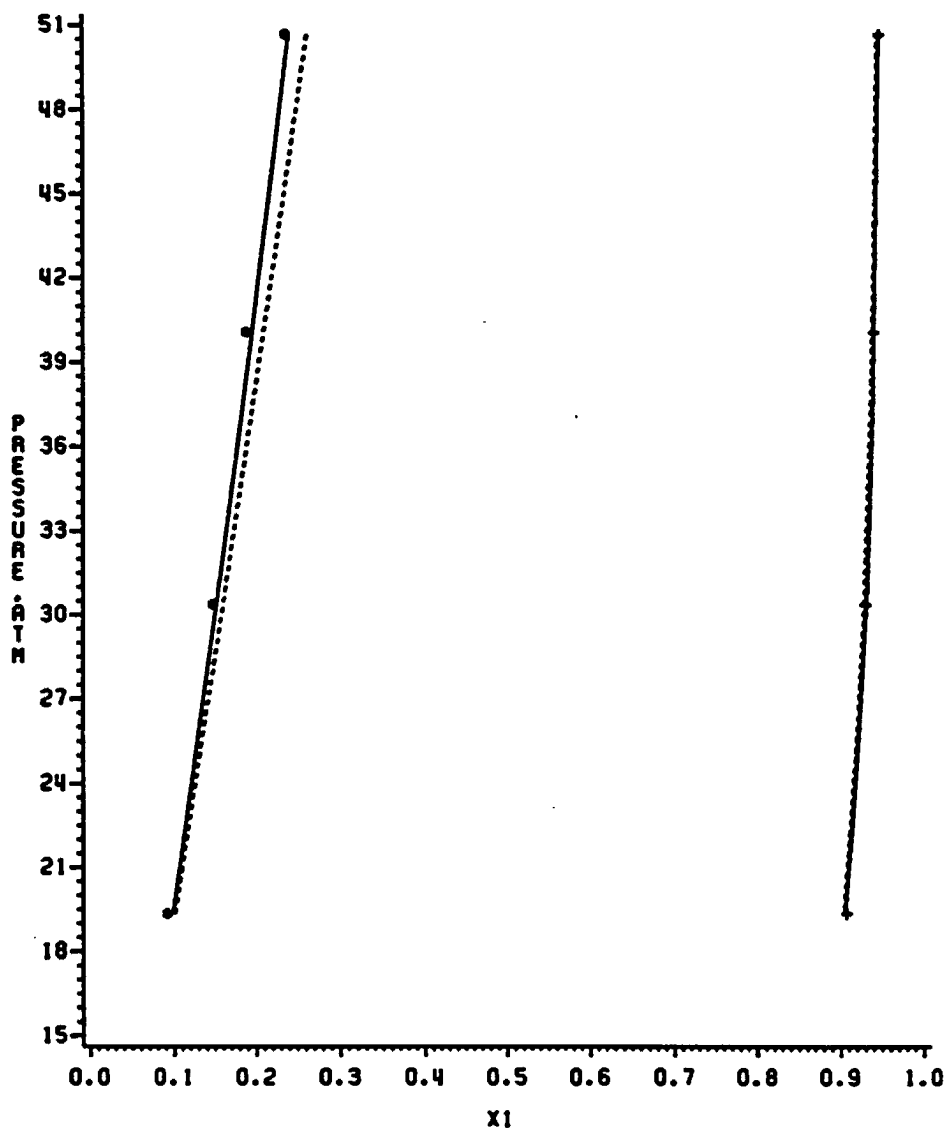


FIGURE 13. PRESSURE-COMPOSITION DIAGRAM

CO₂(1)-N-HEXADECANE(2)

TEMPERATURE : 390.6 C

* + : DATA OF SEBASTIAN, 1980

----- : CSM

————— : LCM

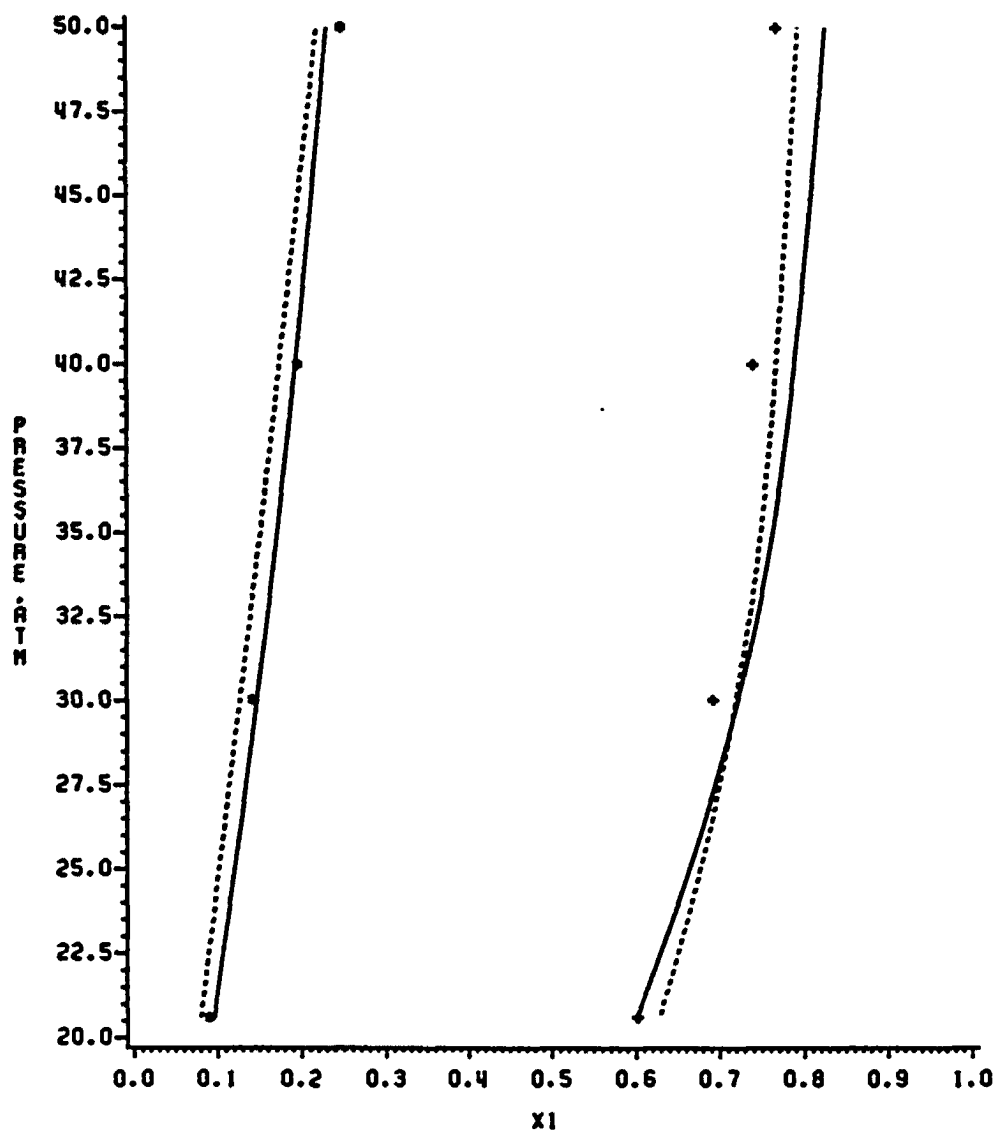


FIGURE 14. PRESSURE-COMPOSITION DIAGRAM

Figs. 11-12. For the carbon dioxide-n-hexadecane system, the ratio of the V^* is 7.6 : 1 (v^* are 0.21, and 1.59 for carbon dioxide and n-hexadecane, respectively). The LCM and the CSM have similar results for carbon dioxide-n-hexadecane system.

For mixtures of acetone and hydrocarbons, five systems, ethane-acetone, propane-acetone, n-pentane-acetone, acetone-benzene, and acetone-n-heptane were selected to test the model. In Table 6 a summary of the results for mixtures of acetone and hydrocarbons is given. For the ethane-acetone system, the LCM yields accurate results for the liquid compositions as shown in Fig. 15. Fig. 17 shows results for the n-pentane-acetone system, having a minimum azeotrope temperature. The phase behavior of the n-pentane-acetone system is very well represented by the LCM.

For mixtures of alcohols and hydrocarbons, seven systems, ethane-methanol, propane-ethanol, benzene-ethanol, ethanol-n-decane, n-hexane-1-propanol, benzene-1-propanol, and 1-propanol-n-decane were selected to test the model. For mixtures of water with hydrocarbons, methane-water, and ethane-water were selected for test. In Table 7 a summary of the results for these nine systems is given. The systems of alcohol-hydrocarbon are typically difficult to fit. For the ethane-methanol system, the LCM greatly improves results for liquid phase compositions, compared to the CSM as shown

Table 6. Vapor-liquid equilibria calculations using
conformal solution and local composition
mixing rules for acetone binary mixtures

System	Mixing rules	ξ	ζ	δ	K1	K2	x1	x2	y1	y2
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
A. A. D. %										
Ethane- Acetone	CSM	0.9588	0.9644	--	19.6	38.4	27.3	25.5	0.36	18.9
	LCM	0.8993	0.8914	1.0497	9.95	13.5	11.7	15.6	0.40	21.2
Propane- Acetone	CSM	--	--	--	--	--	--	--	--	--
	LCM	1.1227	0.9218	1.0981	4.30	5.82	7.35	13.1	2.75	16.5
n-Pentane Acetone	CSM	--	--	--	--	--	--	--	--	--
	LCM	1.1459	0.8048	0.9510	--	--	--	--	--	--
Acetone- Benzene	CSM	0.9888	0.9767	--	--	--	--	--	--	--
	LCM	0.9677	0.9820	0.9886	--	--	--	--	--	--
Acetone- n-Heptane	CSM	0.9480	0.8919	--	--	--	--	--	--	--
	LCM	1.2544	0.6902	0.8997	2.85	5.01	3.81	7.96	1.39	5.94

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

ETHANE(1)-ACETONE(2)

TEMPERATURE : 25 C

* + : DATA OF OHGAKI, 1976

----- : CSM

————— : LCM

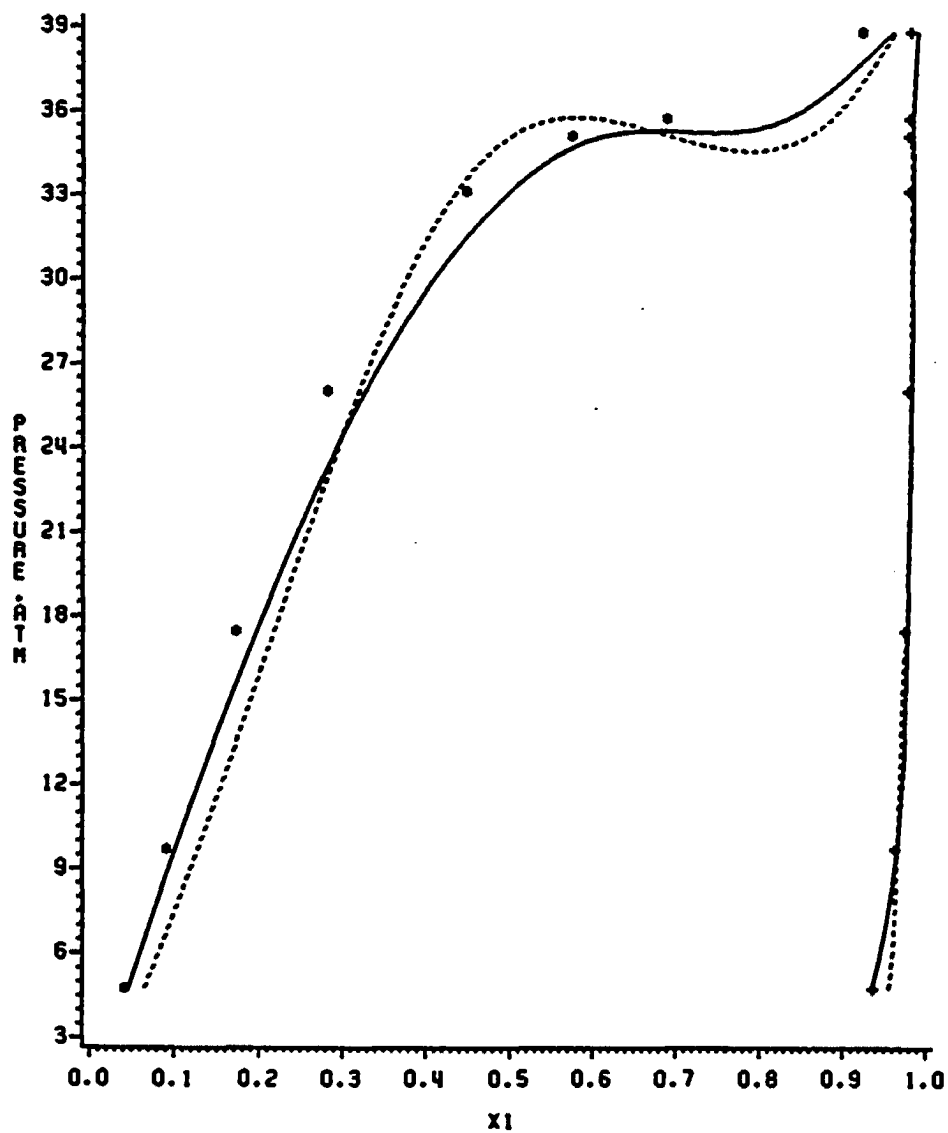


FIGURE 15. PRESSURE-COMPOSITION DIAGRAM

PROPANE(1)-ACETONE(2)

TEMPERATURE : 76.9 C

* + : DATA OF THODOS, 1978

— : LCM

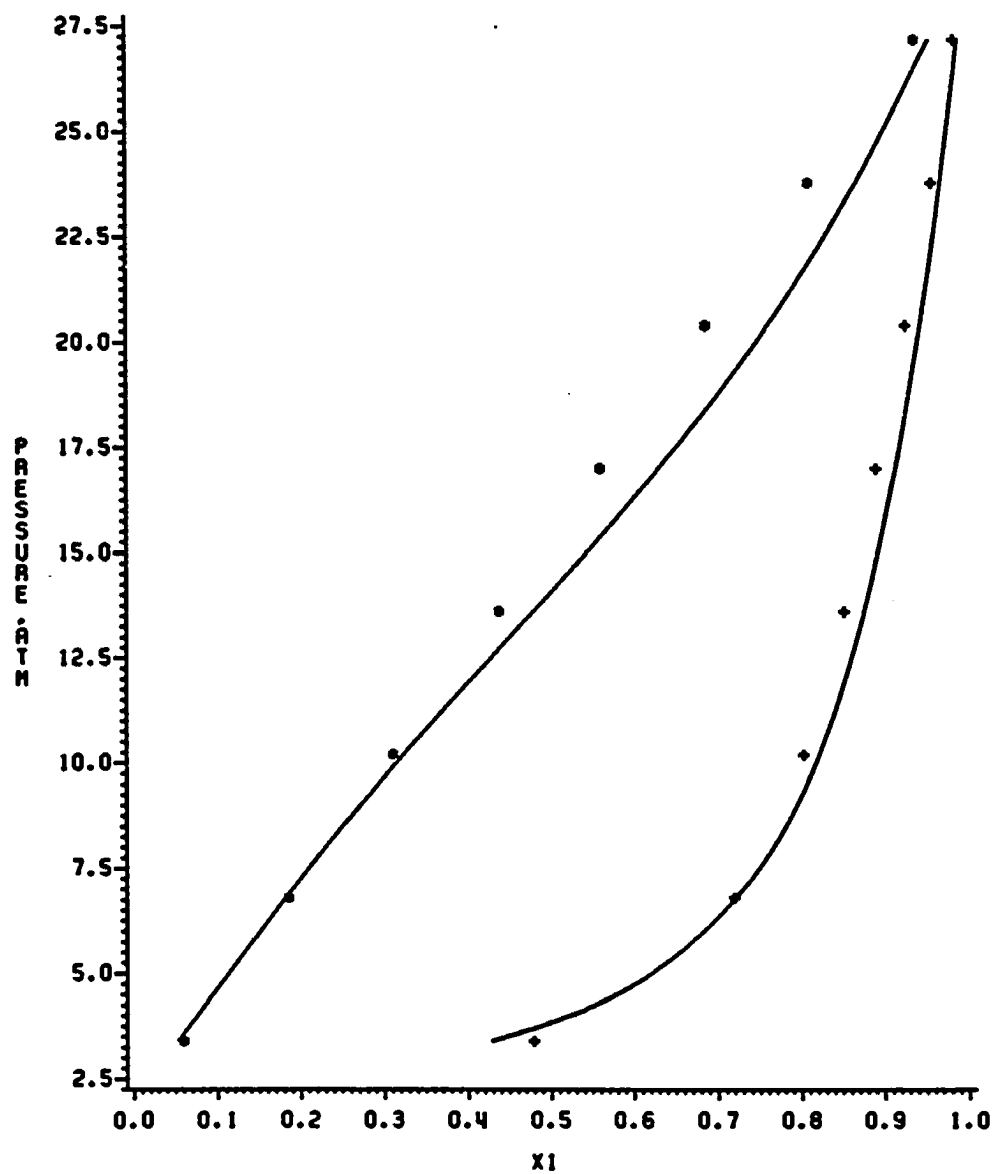


FIGURE 16. PRESSURE-COMPOSITION DIAGRAM

N-PENTANE(1)-ACETONE(2)

PRESSURE : 1 ATM
• + : DATA OF KARR, 1962
— : LCM

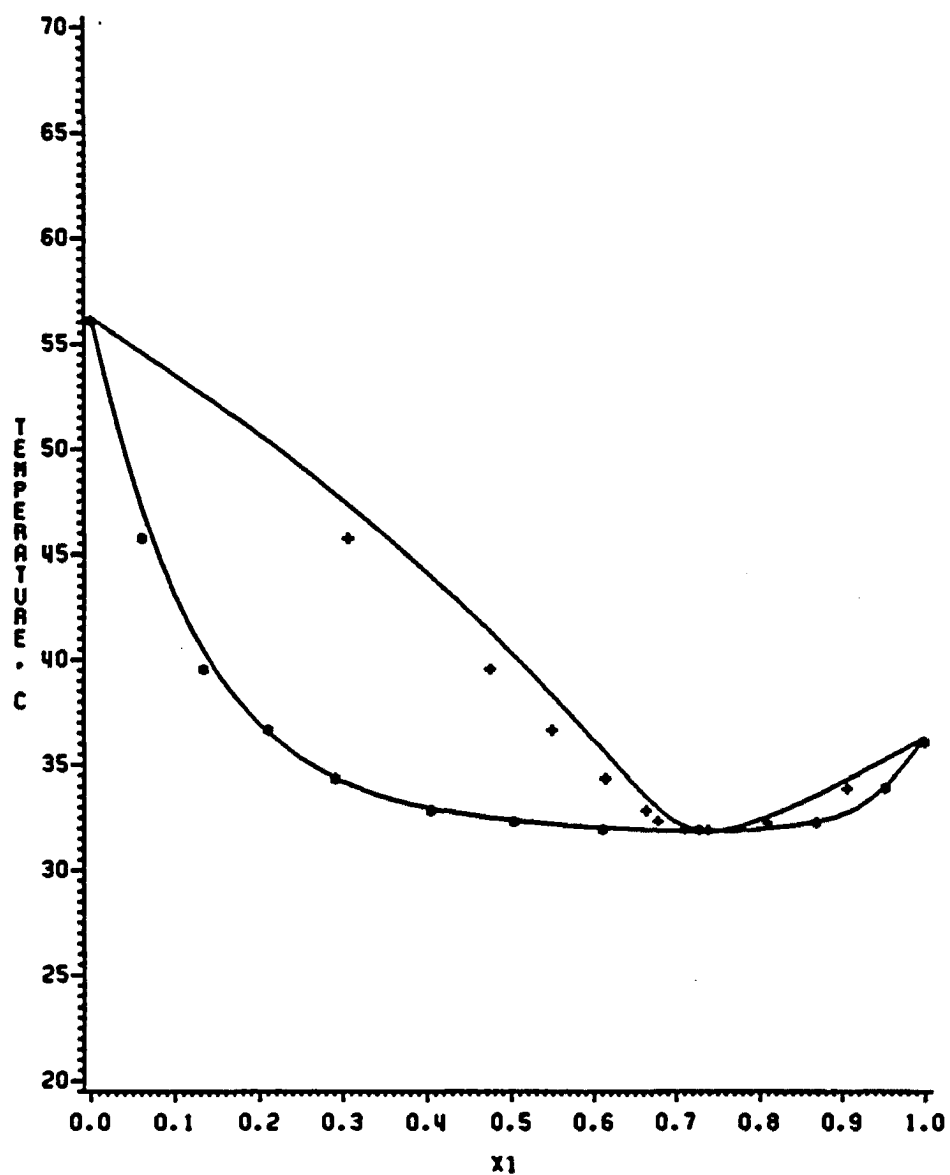


FIGURE 17. TEMPERATURE-COMPOSITION DIAGRAM

ACETONE(1)-BENZENE(2)

TEMPERATURE : 25 C
 • + : DATA OF TASIC, 1978
 - - - : CSM
 — : LCM

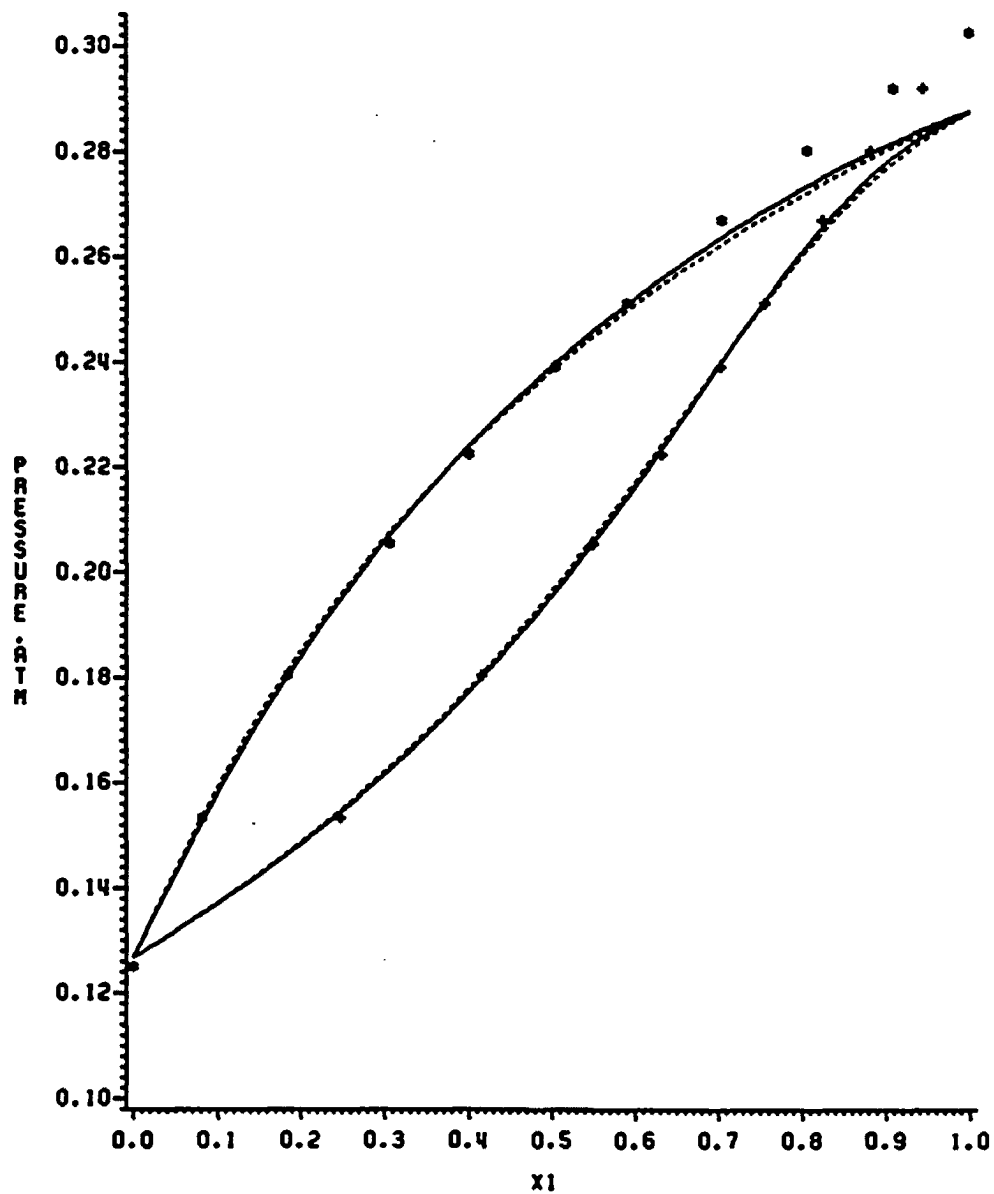


FIGURE 18. PRESSURE-COMPOSITION DIAGRAM

ACETONE(1)-HEPTANE(2)

TEMPERATURE : 65 C
 * + : DATA OF RATCLIFF, 1972
 - - - - : CSM
 ——— : LCM

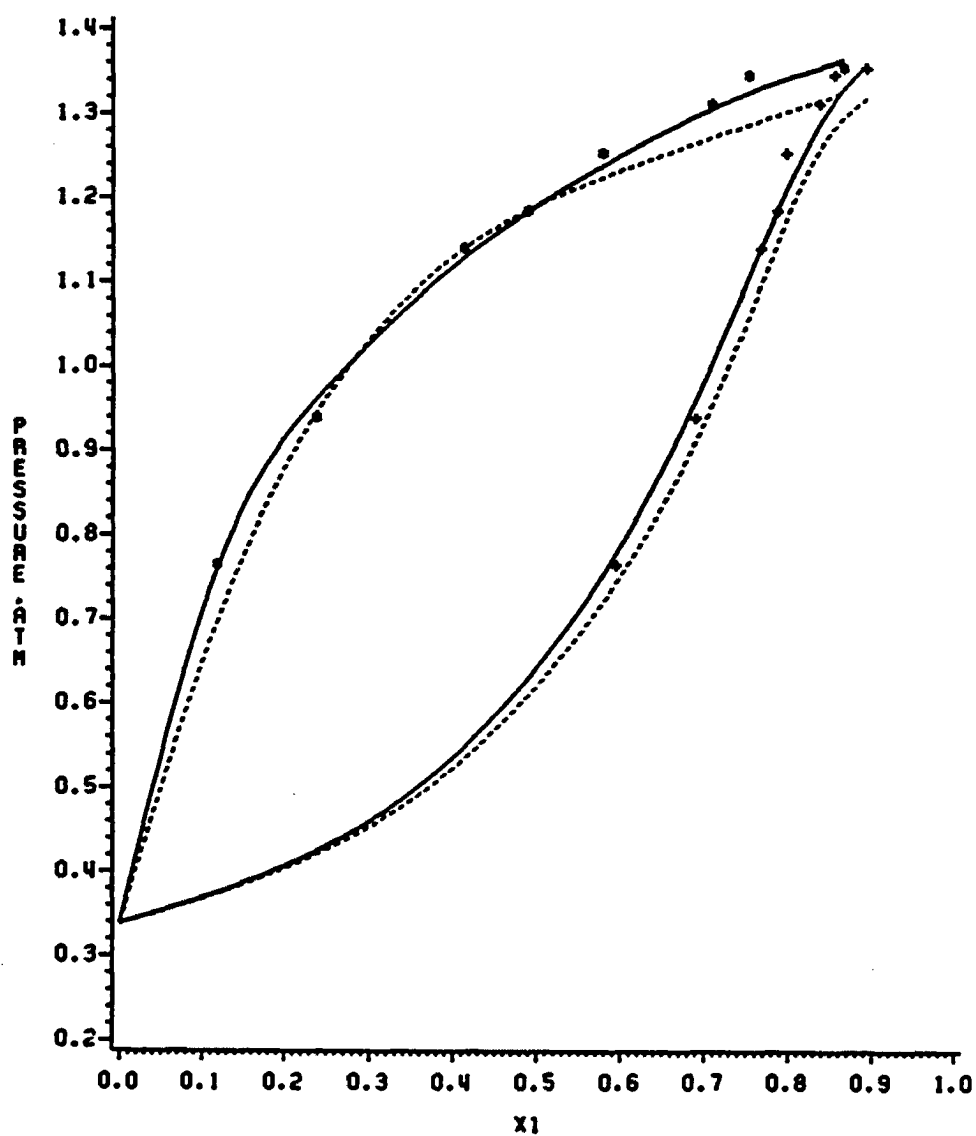


FIGURE 19. PRESSURE-COMPOSITION DIAGRAM

Table 7. Vapor-liquid equilibria calculations using
local composition and conformal solution
mixing rules for nine binary mixtures

System	Mixing rules	ξ	ζ	δ	K1	K2	x1	x2	y1	y2

A.A.D. %										
Ethane- Methanol	CSM	0.9448	1.0879	--	35.8	9.63	62.3	7.95	0.12	14.3
	LCM	0.7210	0.9322	1.0226	16.7	4.16	19.3	3.55	0.06	7.41
Propane- Ethanol	CSM	0.9921	1.0328	--	6.47	5.62	8.35	4.83	4.88	8.91
	LCM	1.1193	0.8505	1.0284	5.16	3.47	4.89	3.50	2.96	5.57
Benzene- Ethanol	CSM	--	--	--	--	--	--	--	--	--
	LCM	1.3106	0.6930	0.9401	--	--	--	--	--	--
Ethanol- n-Decane	CSM	1.1086	0.8429	--	19.9	5.21	20.7	3.56	1.82	5.64
	LCM	1.3027	0.6152	0.9710	10.3	3.73	11.4	1.27	1.67	3.85
n-Hexane- Propanol	CSM	--	--	--	--	--	--	--	--	--
	LCM	0.9090	0.9305	0.9614	11.8	6.64	12.8	4.59	4.55	10.6

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

Table 7. (Continued)

System	Mixing rules	ξ	ζ	δ	K1	K2	x1	x2	y1	y2
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
A.A.D. %										
Benzene- Propanol	CSM	--	--	--	--	--	--	--	--	--
	LCM	1.1644	0.8373	0.9327	--	--	--	--	--	--
Propanol- n-Decane	CSM	1.1232	0.8840	--	6.90	10.5	7.42	15.6	0.91	9.19
	LCM	1.2883	0.7440	0.9935	5.39	9.00	6.23	9.64	0.93	8.47
Methane- Water	CSM	0.8323	0.9969	--	1.96	0.90	2.39	0.01	0.50	0.90
	LCM	0.9523	0.5952	1.1666	2.27	1.40	2.83	0.01	0.69	1.40
Ethane- Water	CSM	0.8169	0.7889	--	4.32	1.69	4.88	0.01	0.62	1.69
	LCM	1.0321	0.6198	1.2492	1.97	2.27	2.00	0.01	0.93	2.27

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

in Fig. 20. Mixtures of benzene-ethanol and benzene-1-propanol form azeotropes, as shown in Figs. 22, and 25. The LCM describes behavior reasonably well for the benzene-ethanol, and benzene-1-propanol systems.

For polar mixtures, eight systems, acetone-carbon dioxide, acetone-ethanol, methanol-1-propanol, ethanol-1-propanol, ethanol-water, carbon dioxide-water, hydrogen sulfide-water, and ammonia-water were selected to test the model. A summary of the results is given in Table 8. Comparisons of the experimental and the predicted compositions for these eight systems are shown in Figs. 29-37. The LCM generally provides a better fit to the experimental values than the CSM.

ETHANE(1)-METHANOL(2)

TEMPERATURE : 25 C
• + : DATA OF OHGAKI, 1976
- - - : CSM
— : LCM

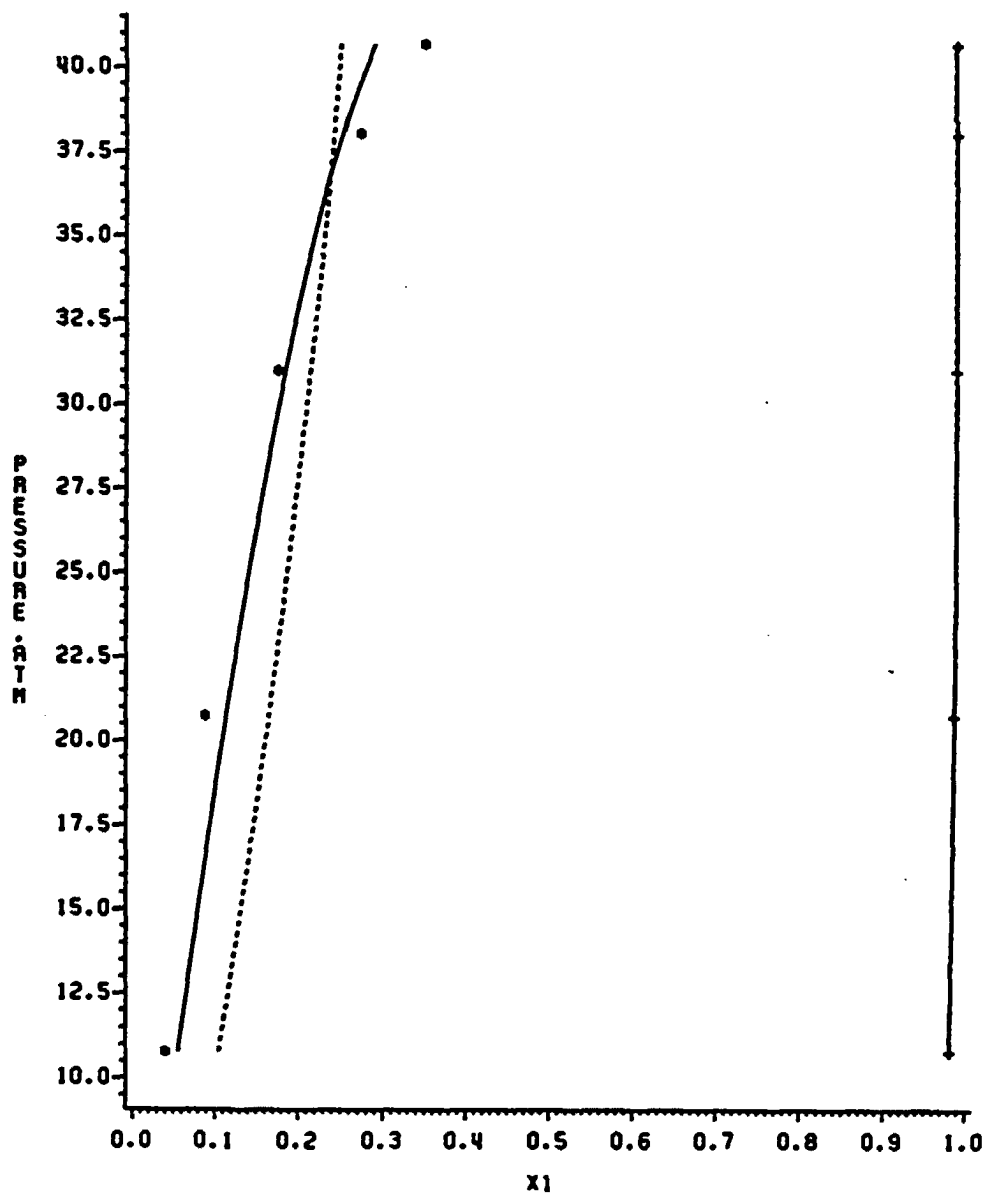


FIGURE 20. PRESSURE-COMPOSITION DIAGRAM

PROPANE(1)-ETHANOL(2)

TEMPERATURE : 127 C
• + : DATA OF THODOS, 1978
- - - : CSM
— : LCM

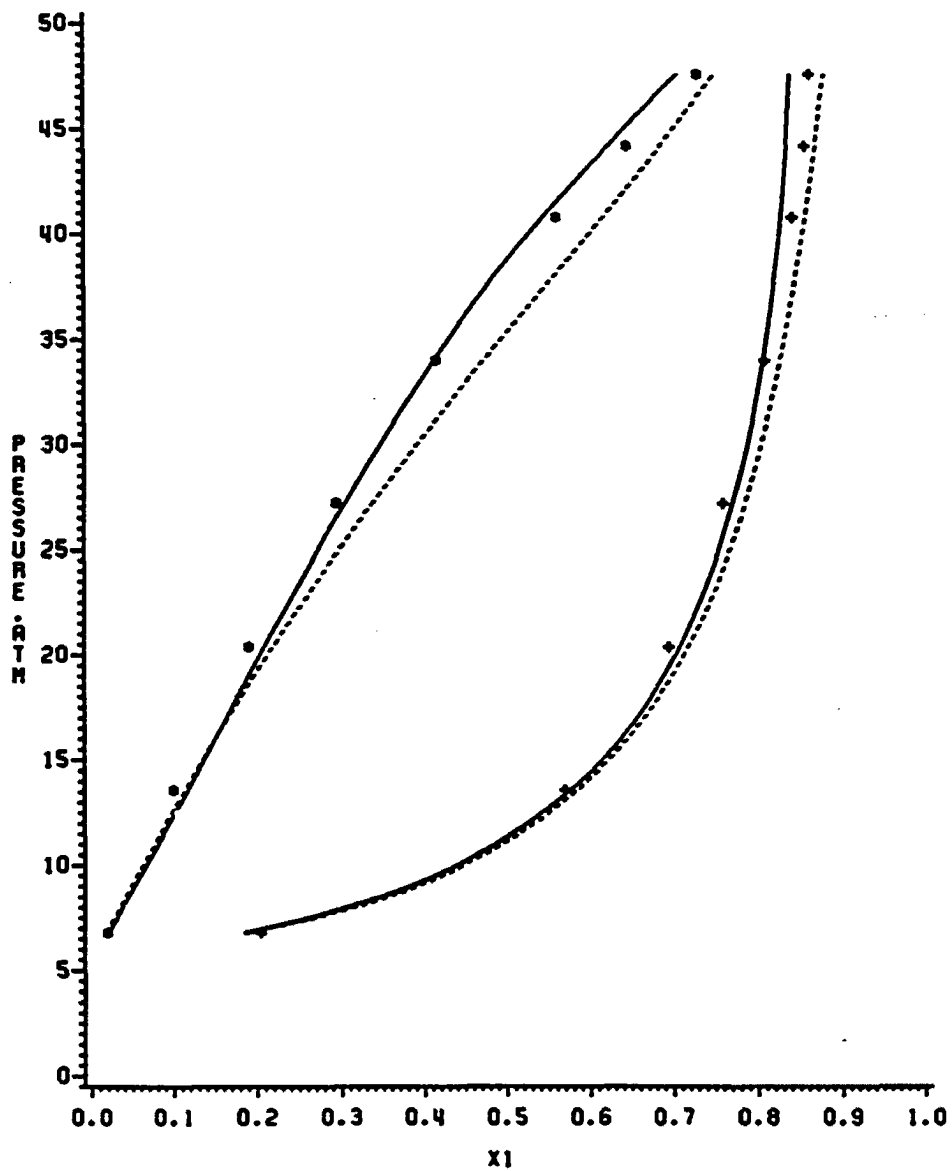


FIGURE 21. PRESSURE-COMPOSITION DIAGRAM

BENZENE(1)-ETHANOL(2)

TEMPERATURE : 25 C

• + : DATA OF SMITH, 1970

— : LCM

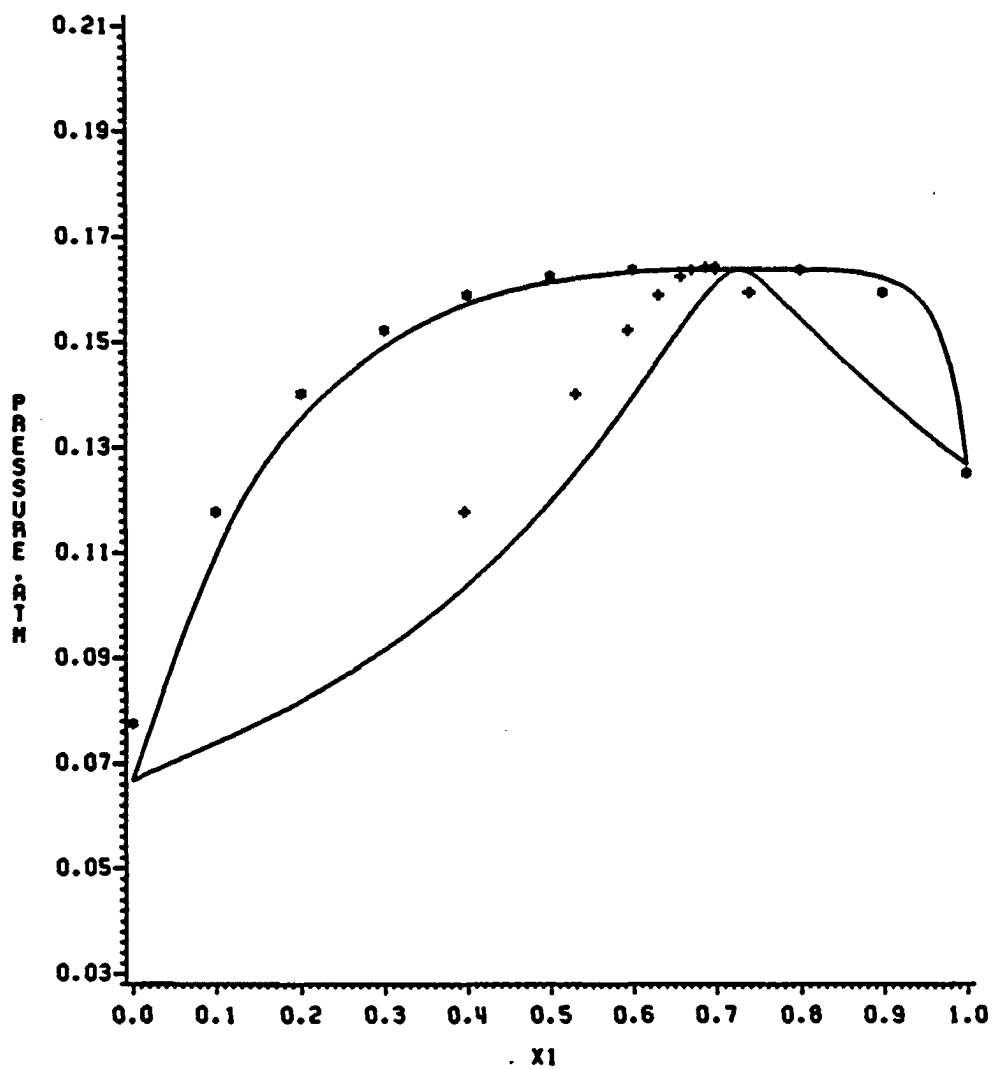


FIGURE 22. PRESSURE-COMPOSITION DIAGRAM

ETHANOL(1)-N-DECANE(2)

PRESSURE : 1 ATM

* + : DATA OF ELLIS, 1961

- - - : CSM

— : LCM

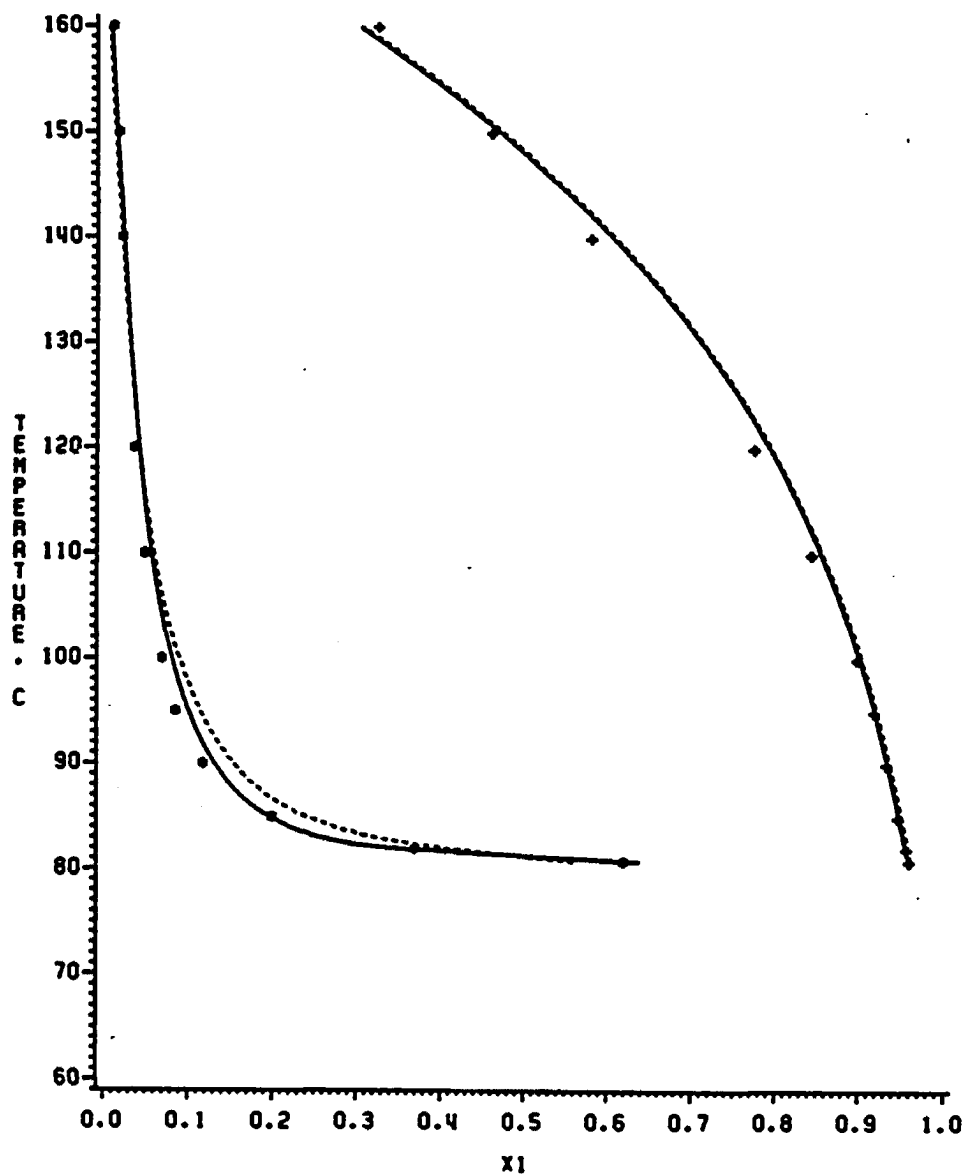


FIGURE 23. TEMPERATURE-COMPOSITION DIAGRAM

N-HEXANE(1)-PROPANOL(2)

PRESSURE : 1 ATM

• + : DATA OF PRABHU, 1963

— : LCM

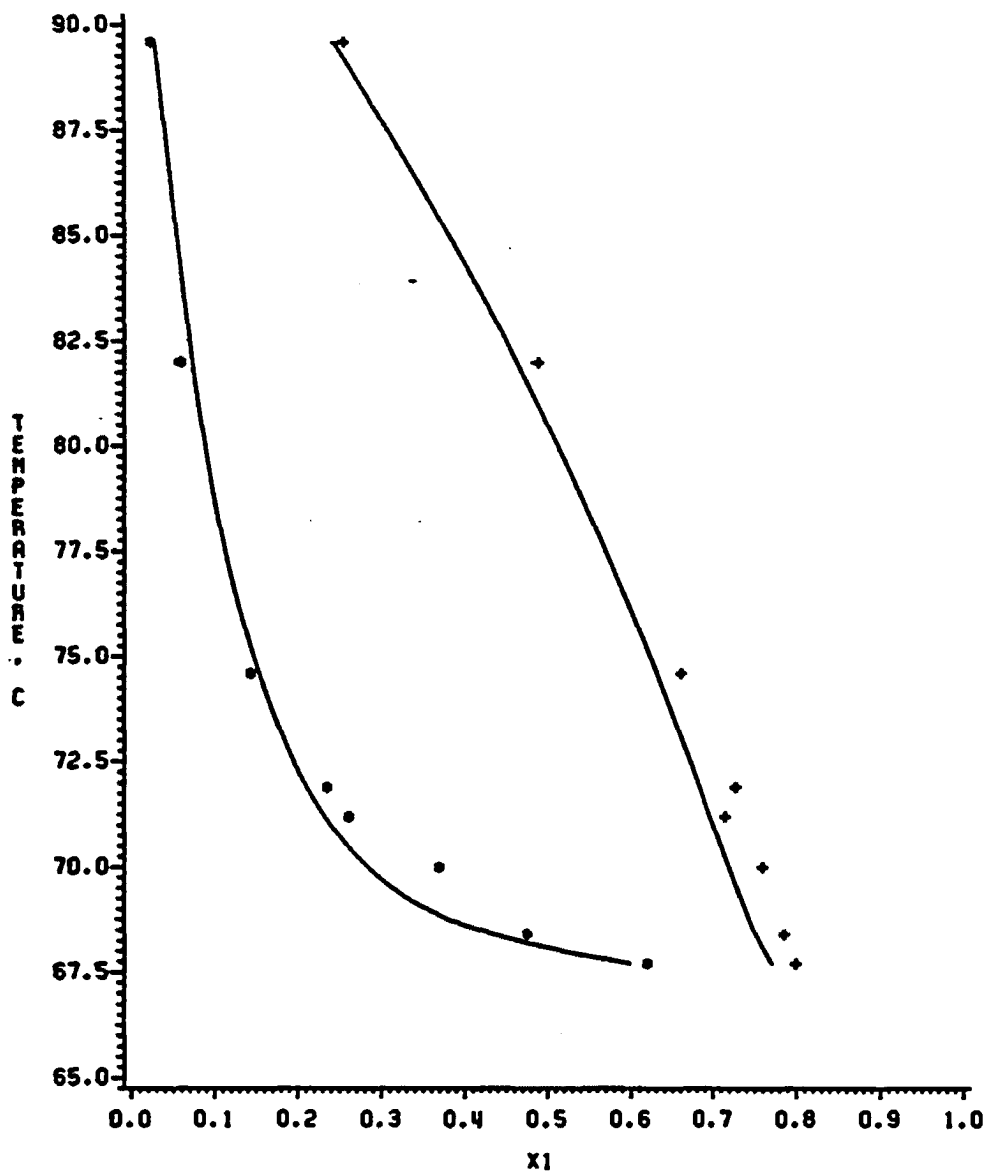


FIGURE 24. TEMPERATURE-COMPOSITION DIAGRAM

BENZENE(1)-PROPANOL(2)

PRESSURE : 1 ATM
+ : DATA OF TOJO, 1973
— : LCM

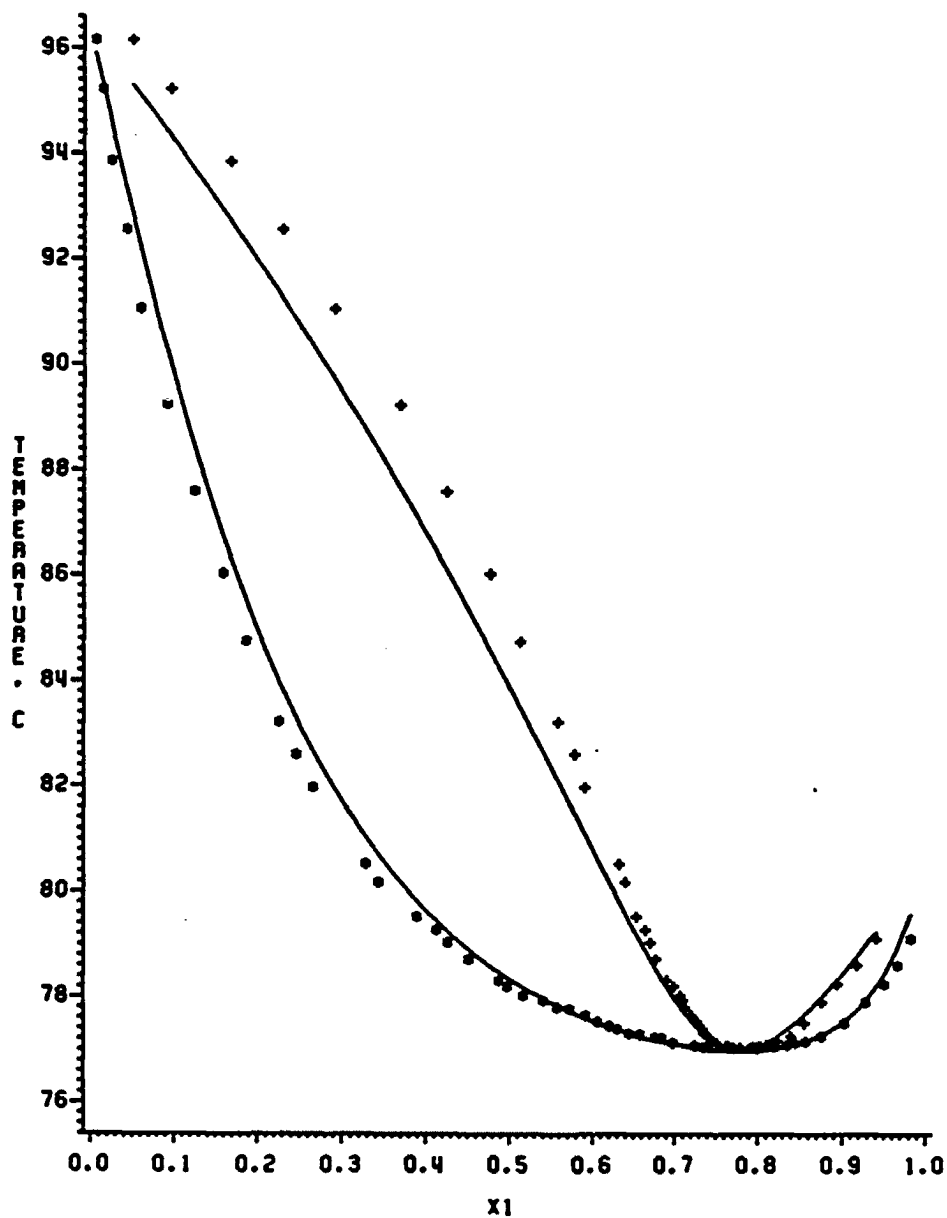


FIGURE 25. TEMPERATURE-COMPOSITION DIAGRAM

PROPANOL(1)-N-DECANE(2)

PRESSURE : 0.395 ATM

* + : DATA OF ELLIS, 1960

- - - - - : CSM

— : LCM

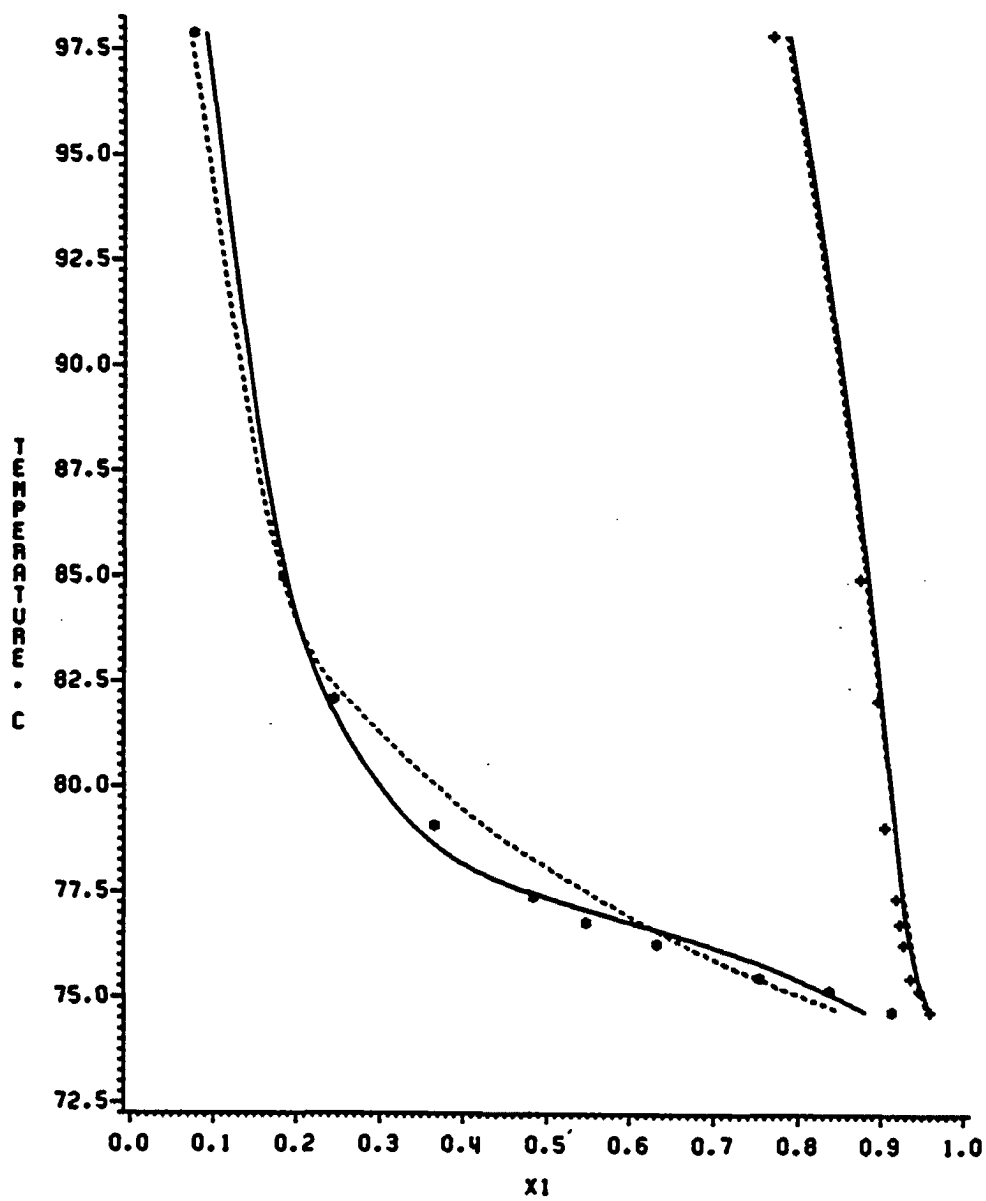


FIGURE 26. TEMPERATURE-COMPOSITION DIAGRAM

METHANE(1)-WATER(2)

TEMPERATURE : 171 C

* + : DATA OF CULBERSON, 1951

----- : CSM

————— : LCM

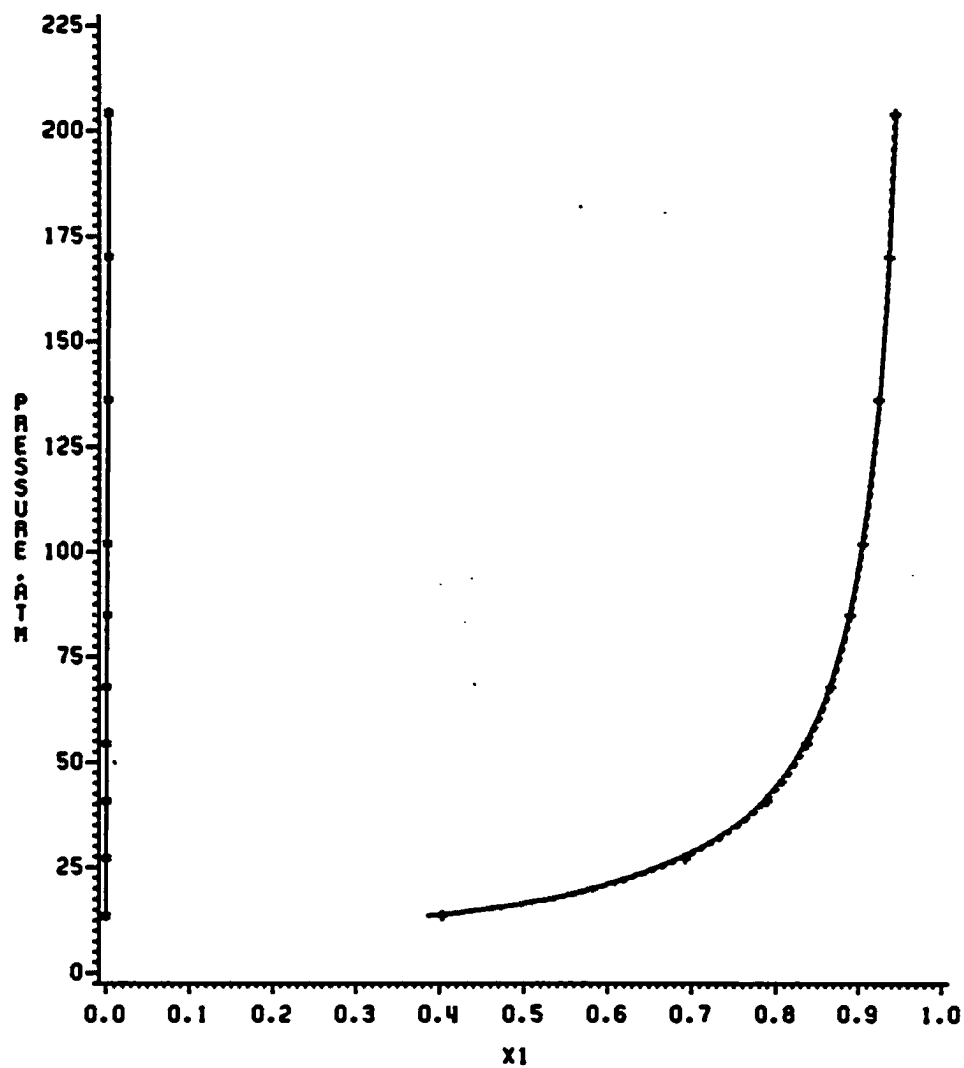


FIGURE 27. PRESSURE-COMPOSITION DIAGRAM

ETHANE(1)-WATER(2)

TEMPERATURE : 171 C

* + : DATA OF CULBERSON, 1950

----- : CSM

————— : LCM

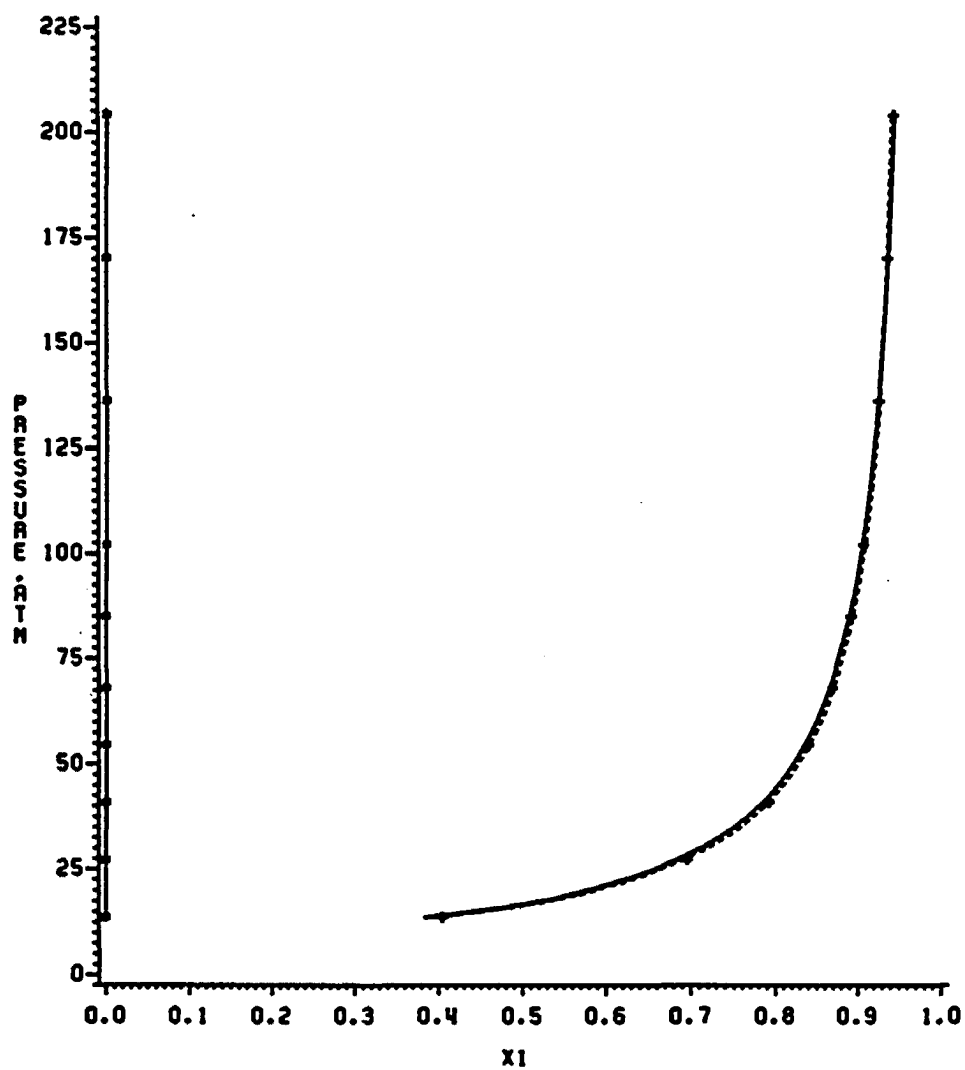


FIGURE 28. PRESSURE-COMPOSITION DIAGRAM

Table 8. Vapor-liquid equilibria calculations using
local composition and conformal solution
mixing rules for polar binary mixtures

System	Mixing rules	ξ	ζ	δ	K1	K2	x1	x2	y1	y2
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
A.A.D. %										
Acetone- CO2	CSM	1.0268	0.9644	--	19.8	6.17	4.54	5.43	21.8	0.30
	LCM	1.2054	0.8265	1.0986	9.02	2.57	6.38	2.70	10.6	0.19
Acetone- Ethanol	CSM	0.9857	0.9819	--	--	--	--	--	--	--
	LCM	0.8655	1.0133	0.7857	7.89	6.10	10.7	5.75	5.24	3.46
Methanol- Propanol	CSM	0.9948	0.9851	--	3.98	5.62	6.60	16.2	4.29	19.8
	LCM	0.7969	1.0379	0.9858	3.97	5.12	5.10	12.2	3.64	15.6
Ethanol- Propanol	CSM	1.0126	0.9954	--	3.41	3.32	9.74	11.1	8.39	12.6
	LCM	1.1817	0.9368	1.0744	3.03	2.95	6.84	9.77	6.53	12.4
Ethanol- Water	CSM	--	--	--	--	--	--	--	--	--
	LCM	0.8655	1.0133	0.9950	3.20	3.70	5.75	2.28	5.02	3.29

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

Table 8. (Continued)

System	Mixing rules	ξ	ζ	δ	K1	K2	x1	x2	y1	y2

A.A.D. %										
CO2- Water	CSM	0.6735	0.8434	--	54.9	51.4	44.1	1.94	54.4	51.7
	LCM	1.0615	0.9289	1.2397	10.6	6.92	14.6	0.74	10.2	7.46
H2S- Water	CSM	0.9757	1.0798	--	10.4	3.12	10.6	0.37	1.06	3.02
	LCM	0.7939	0.9455	1.0507	4.12	2.47	4.57	0.15	0.62	2.60
Ammonia- Water	CSM	1.0641	1.1797	--	12.5	9.80	17.0	3.83	3.71	10.5
	LCM	1.0216	1.0876	0.9318	5.26	11.1	7.52	1.87	3.10	11.4

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

ACETONE(1)-CO₂(2)

TEMPERATURE : 25 C
• + : DATA OF KATAYAMA, 1975
- - - : CSM
— : LCM

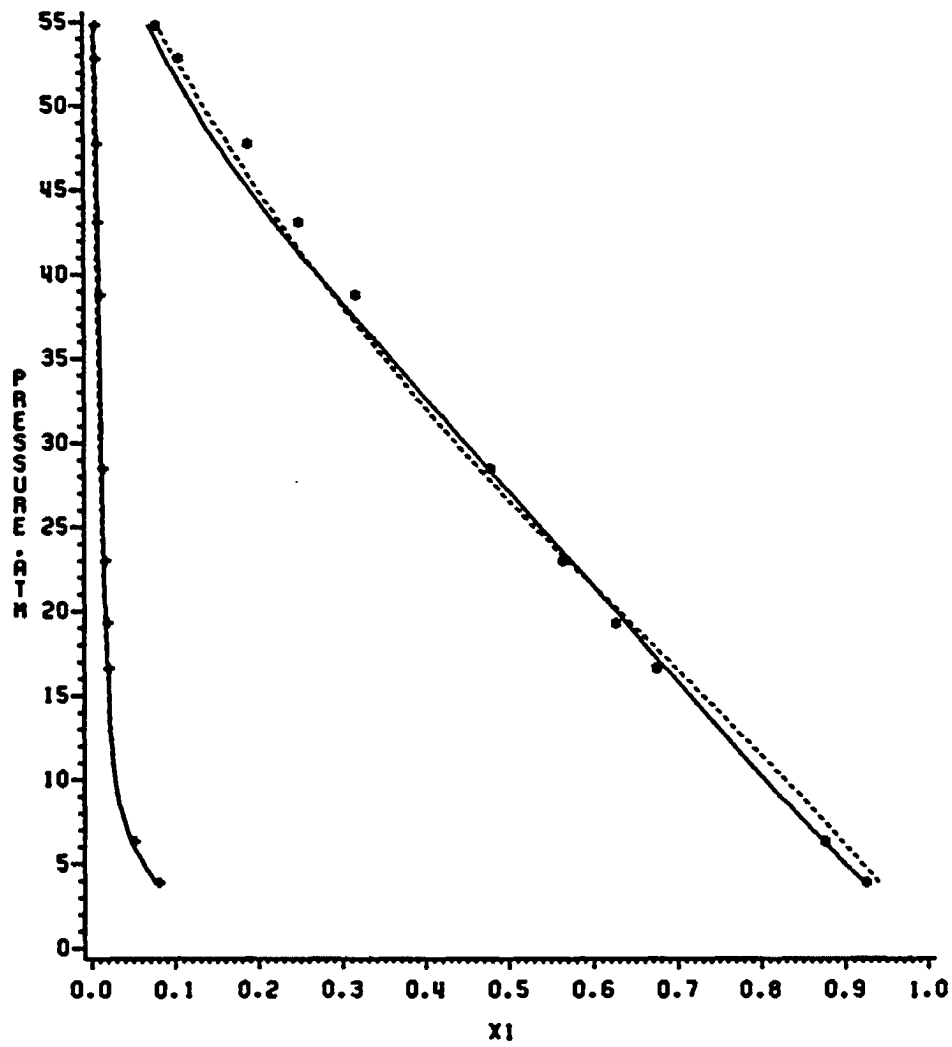


FIGURE 29. PRESSURE-COMPOSITION DIAGRAM

ACETONE(1)-ETHANOL(2)

PRESSURE : 1 ATM

* + : DATA OF AMER. 1956

----- : CSM

————— : LCM

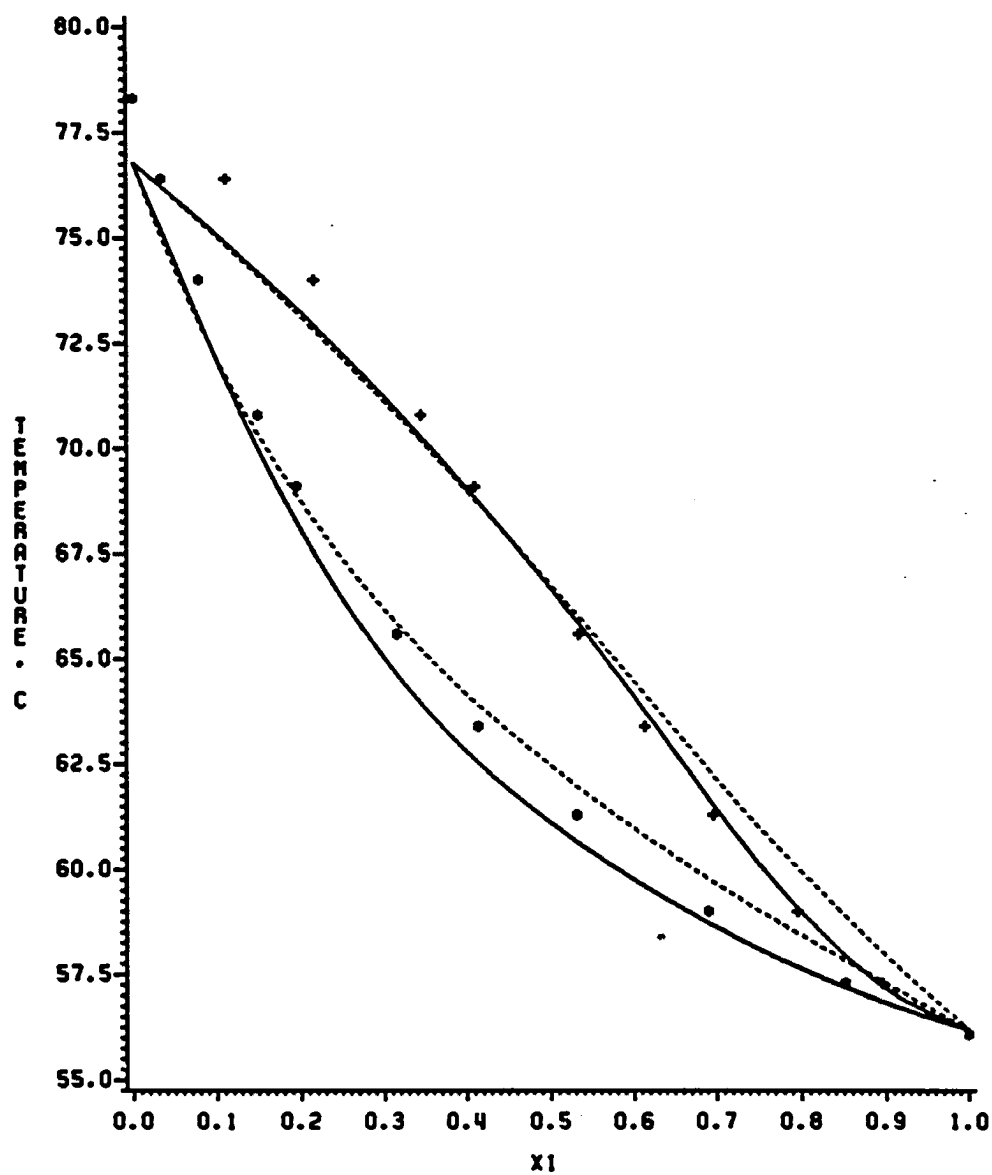


FIGURE 30. TEMPERATURE-COMPOSITION DIAGRAM

METHANOL(1)-PROPANOL(2)

TEMPERATURE : 50 C

* + : DATA OF SCHMIDT, 1926

- - - - : CSM

— : LCM

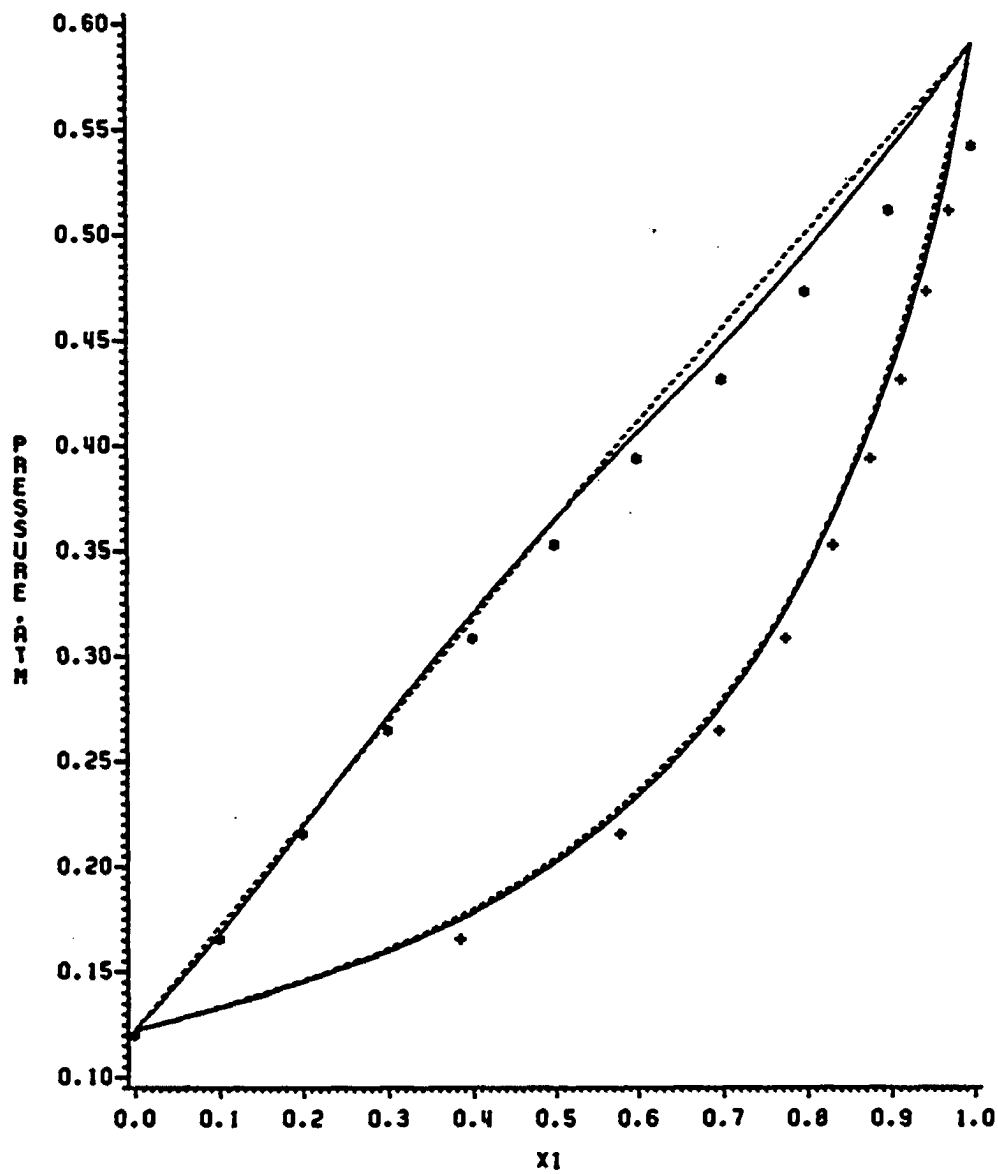


FIGURE 31. PRESSURE-COMPOSITION DIAGRAM

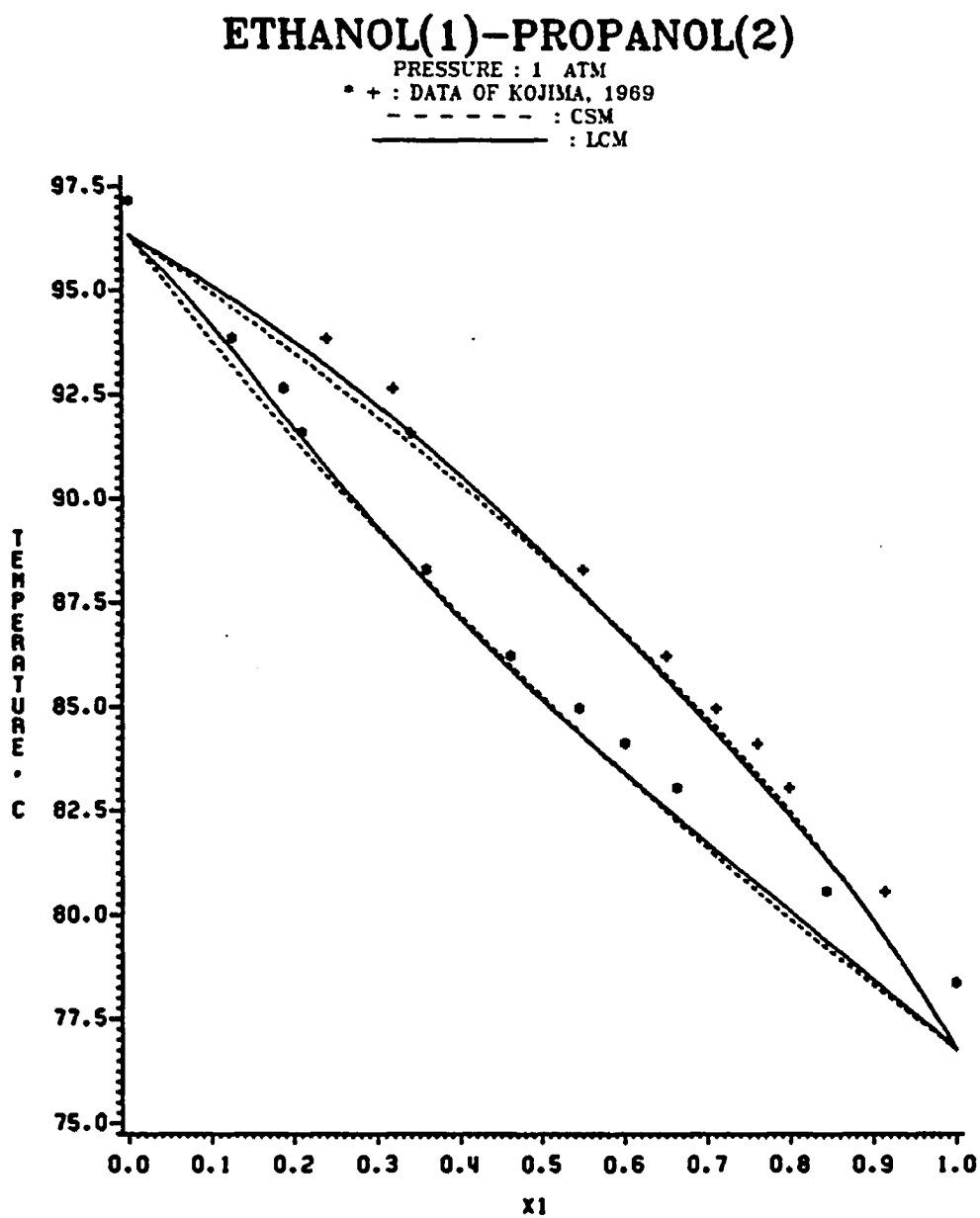


FIGURE 32. TEMPERATURE-COMPOSITION DIAGRAM

ETHANOL(1)-WATER(2)

PRESSURE : 1 ATM
* + : DATA OF PAUL, 1976
— : LCM

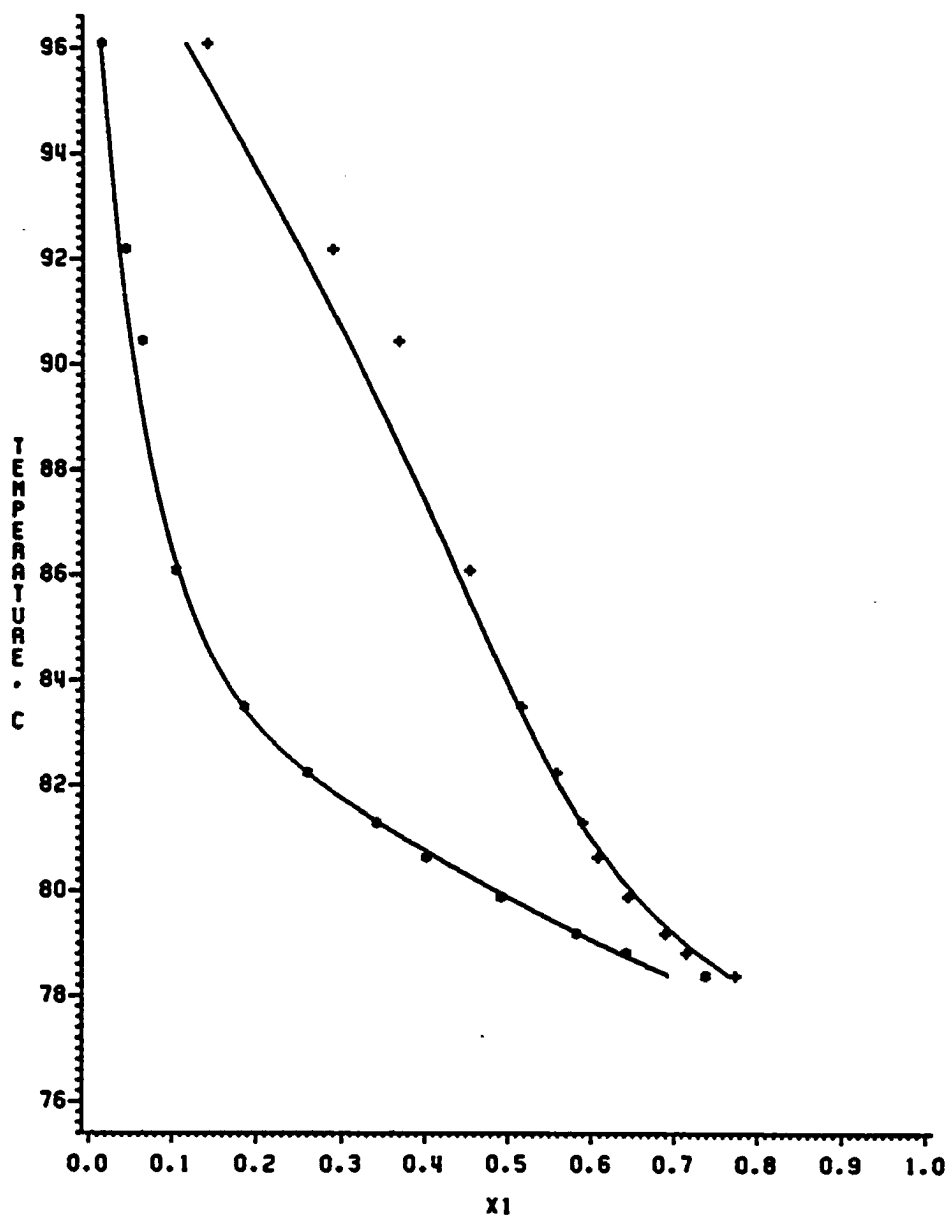


FIGURE 33. TEMPERATURE-COMPOSITION DIAGRAM

CO₂(1)-WATER(2)

TEMPERATURE : 275 C
 * + : DATA OF TAKENOUCHI, 1961
 - - - - : CSM
 ——— : LCM

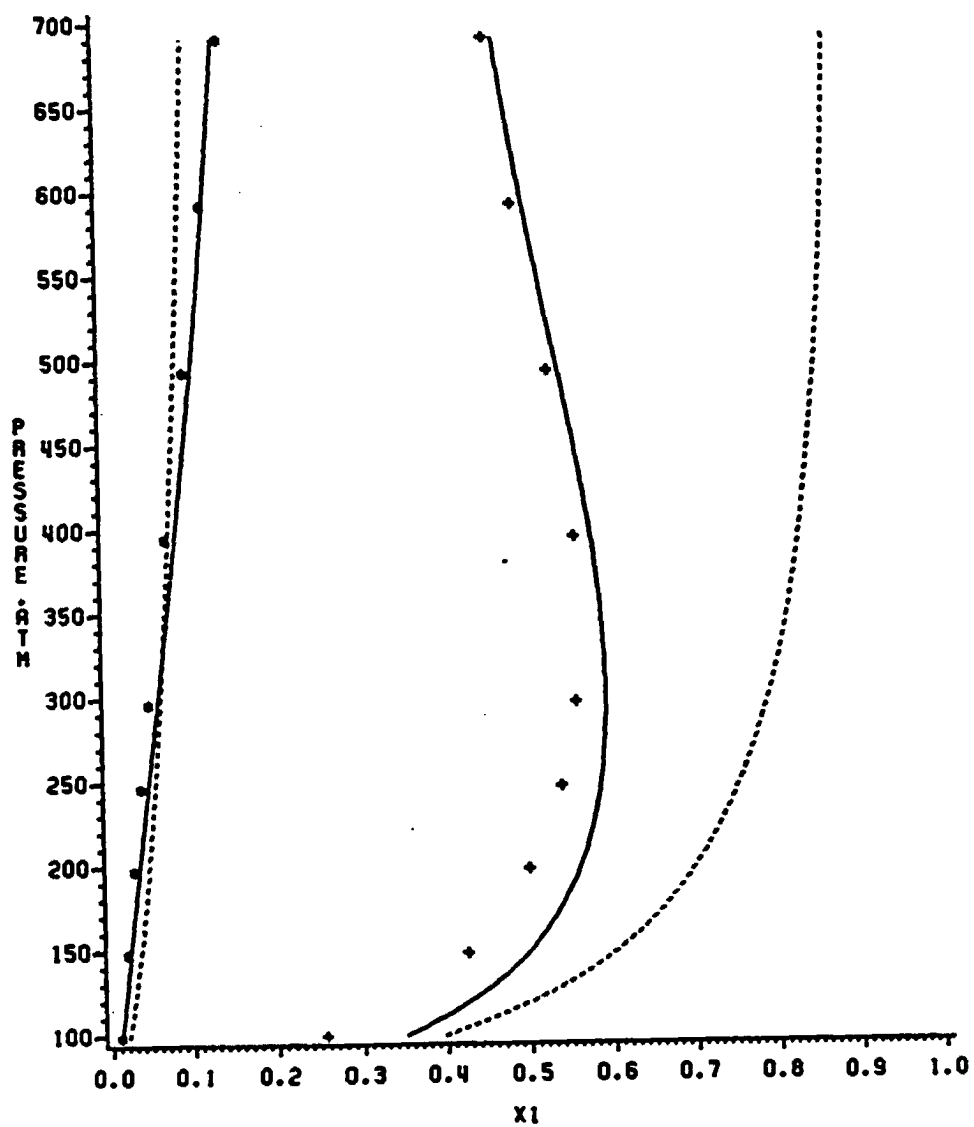


FIGURE 34. PRESSURE-COMPOSITION DIAGRAM

H₂S(1)-WATER(2)

TEMPERATURE : 171.3 C

* + : DATA OF SELLECK, 1952

- - - - : CSM

— : LCM

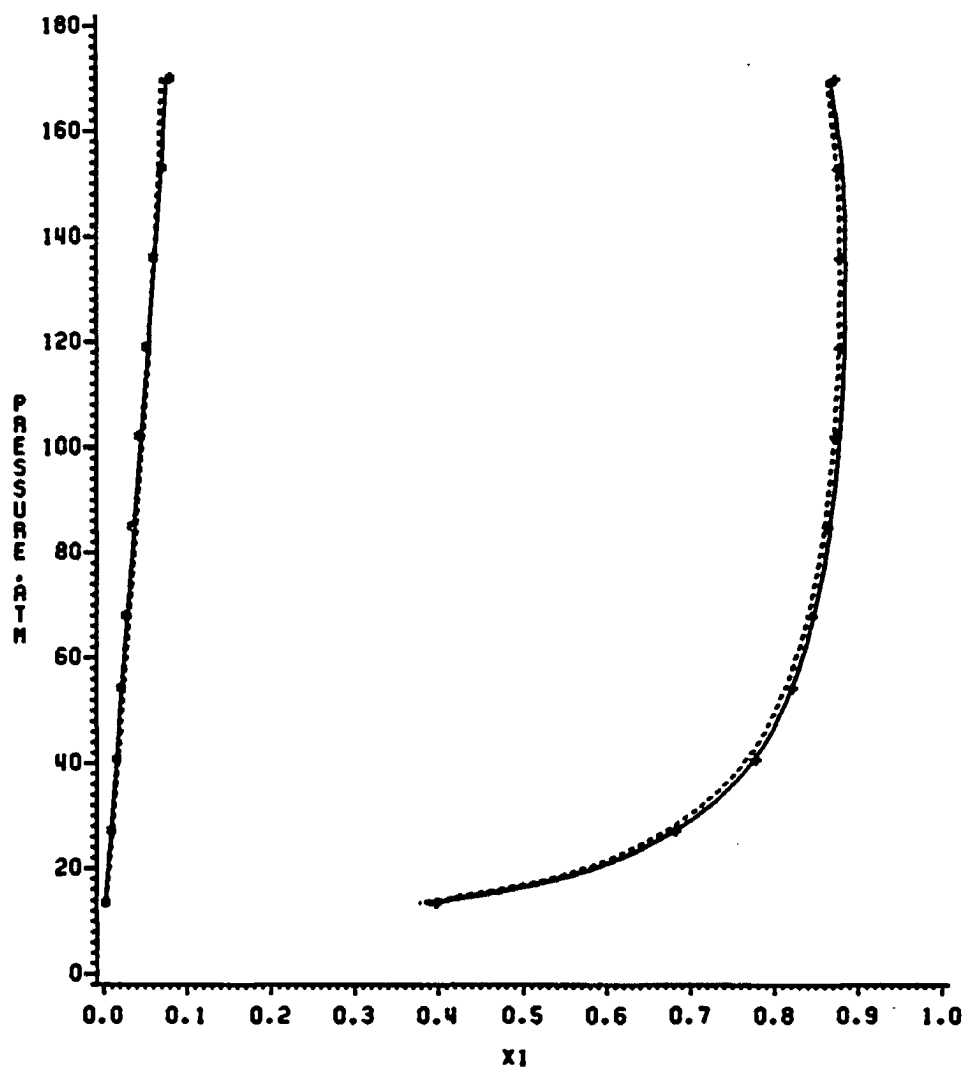


FIGURE 35. PRESSURE-COMPOSITION DIAGRAM

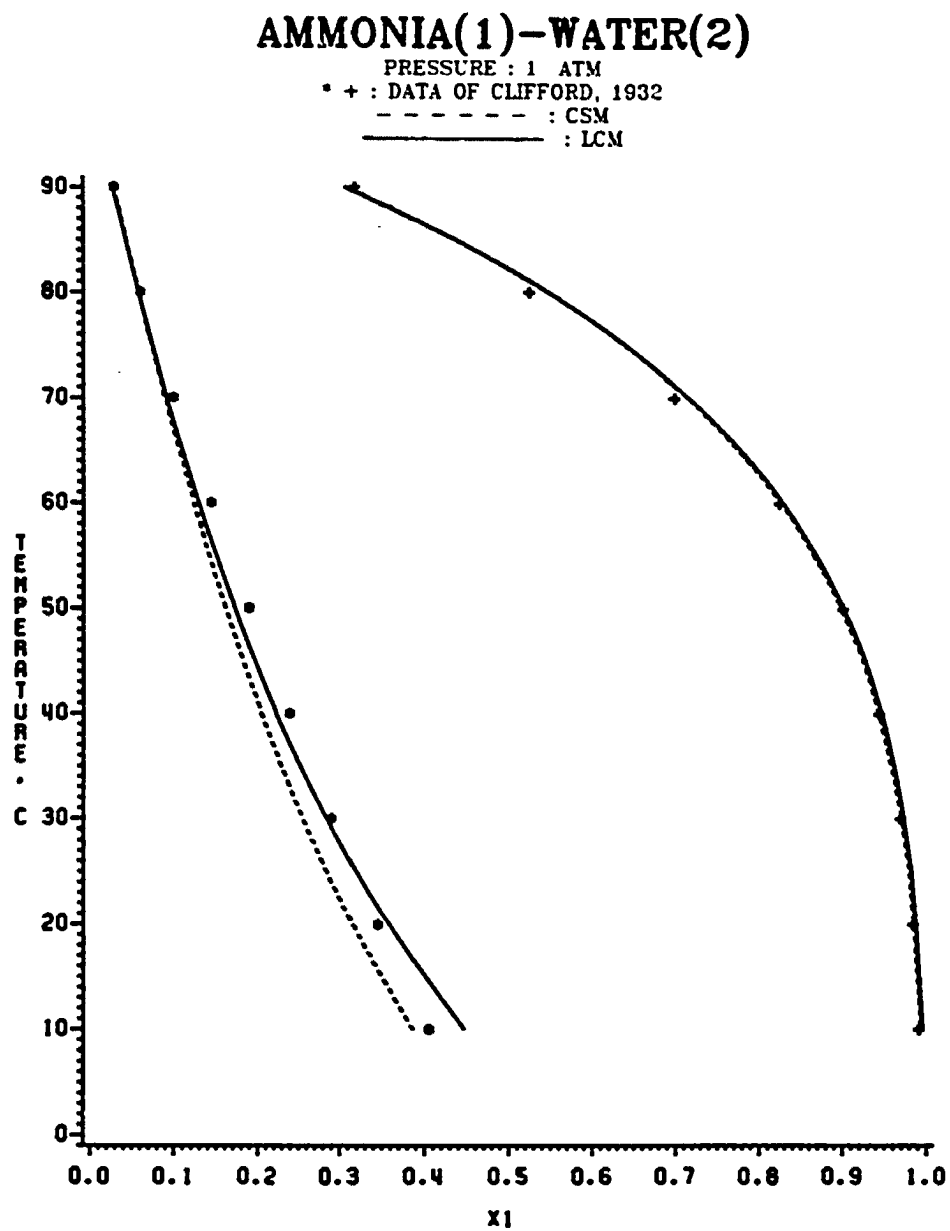


FIGURE 36. TEMPERATURE-COMPOSITION DIAGRAM

AMMONIA(1)-WATER(2)

PRESSURE : 10 ATM
• + : DATA OF CLIFFORD, 1932
- - - : CSM
— : LCM

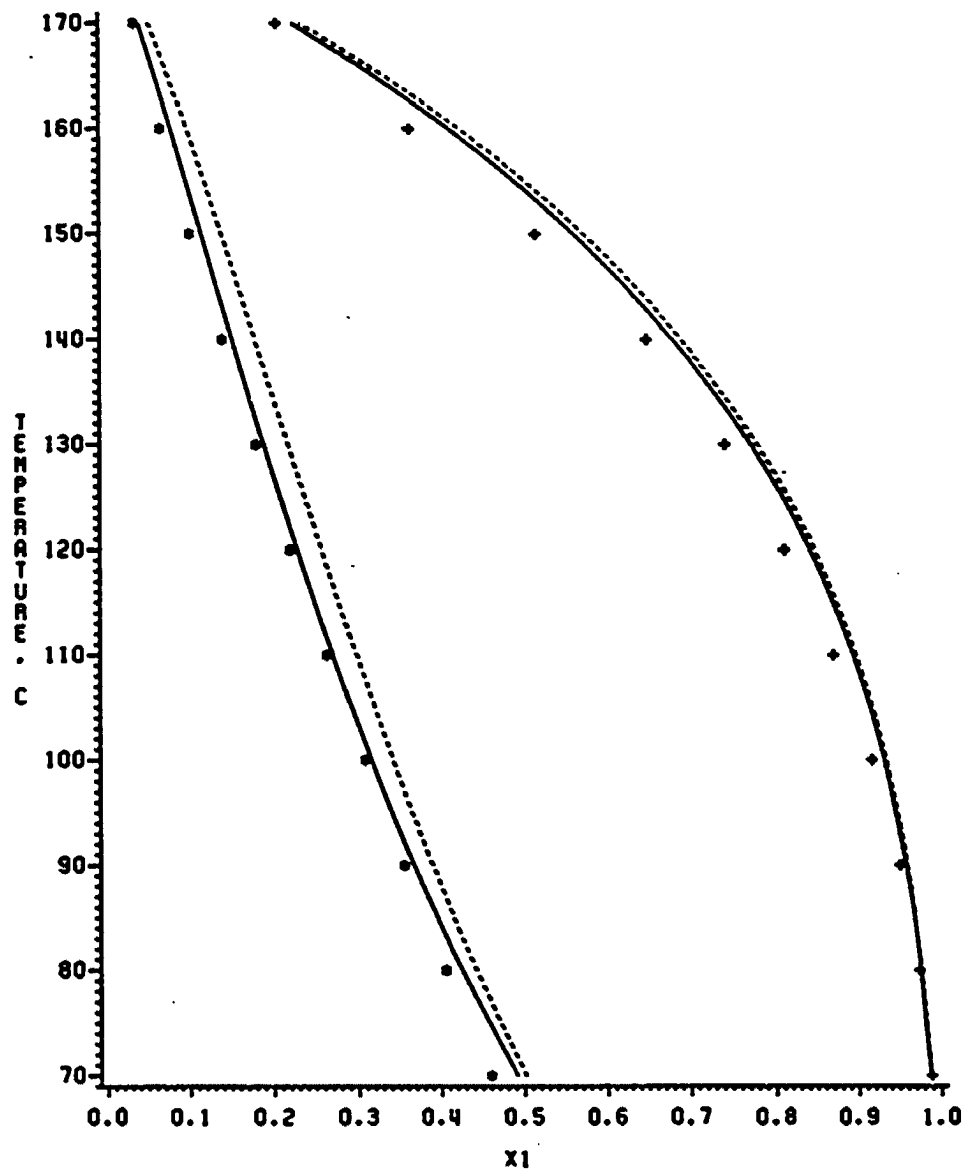


FIGURE 37. TEMPERATURE-COMPOSITION DIAGRAM

CHAPTER V

CONCLUSIONS

A local composition model has been applied to describe the composition dependence of mixture thermodynamic properties. The method has been applied using a recently developed equation of state for use in vapor-liquid equilibria and mixture density calculations. The equation of state utilizes reduced temperature and reduced density as the independent variables for calculation of all dependent variables, such as pressure, Helmholtz free energy, etc. The composition dependence for the equation of state mixture properties is derived from the local composition model expression for the Helmholtz free energy, which is, in essence, a multifluid model for the thermodynamic properties of mixtures.

In this work, a multifluid model is adopted for the reduced temperature and a one fluid model is adopted for the reduced density. Choosing these relations for the reduced temperature and reduced density, the present formulation of the local composition model has characteristics of both one-fluid and multifluid models.

It is demonstrated that if multifluid models are adopted for both the reduced temperature and the reduced density, the local composition model expression used for the mixture pressure can become infinite when component molecular size differences are sufficiently large (even at conditions where the real fluid mixture is known to exist at finite pressure). On the other hand, it is shown that the present formulation, in which a one fluid model is used for the reduced density, works well even for mixtures whose component molecules differ appreciably in size, i.e., the CO₂-n-hexadecane and acetone-water systems. In fact, the present formulation can be applied to any mixture regardless of the mixture component molecular sizes.

For strongly nonideal mixtures, such as acetone-water and methanol-benzene, the present formulation describes vapor-liquid equilibrium behavior accurately. On the other hand, it is demonstrated that the conformal solution model, which is a totally one fluid model does not work well for these strongly nonideal mixtures.

It should be noted that the present local composition mixing rules can be applied to extend virtually any corresponding-states type equation of state to mixtures.

As a summary, the present formulation of the local composition model has the following desirable characteristics:

- 1). The method works well for both mixture density

and vapor-liquid equilibria.

- 2). The method works for mixtures in which components differ appreciably in size.
- 3). The method works well for a wide variety of fluid mixtures, ranging from nonpolar to highly polar fluids.
- 4). The method can be applied to extend any corresponding-states type equation of state to mixtures.

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NOMENCLATURE

A'	total configurational Helmholtz free energy
$\underline{A}'$	molar configurational Helmholtz free energy
A_i	equation of state constants
$B_i^{(0)}$	equation of state universal constants, isotropic reference
$B_i^{(p)}$	equation of state universal constants, perturbation contribution
c	equation of state constant in eqn. (A2)
D	equation of state characterization polar parameter
$\hat{f}_i$	component fugacity in solution
g	radial distribution function
$\underline{H}_i - \underline{H}_i^0$	molar enthalpy departure
k	Boltzmann's constant
K	equilibrium constant
L_{BA}	radius of sphere appropriate for finding first-neighborhood molecules
N_{av}	Avogadro's number
P	pressure
r	radius of sphere
R	gas constant
$\underline{S}_i - \underline{S}_i^0$	molar entropy departure
T	temperature

$\underline{U}_i - \underline{U}_i^0$	molar internal departure
V^*	equation of state characterization volume parameter
V_{ji}	first neighborhood volume
W_{ji}	potential of mean force
$\bar{W}_{ji}$	mean potential of mean force
x_i	mole fraction of component i
x_{ji}	local composition of j molecules around a i molecule
Z	compressibility factor
α'	a proportionality factor between $\bar{W}_{ii}$ and A'_{ii}
β	$1/kT$
δ	a binary interaction parameter in F_{ji}
ϵ^0	equation of state characterization parameter, nonpolar
ϵ	equation of state characterization energy parameter
ζ	a binary interaction parameter
λ	equation of state characterization structure parameter
ν	a binary interaction parameter
ξ	a binary interaction parameter
ρ	density
τ	a binary interaction parameter

Appendix A

EQUATION OF STATE FOR PURE SUBSTANCES

The equation of state for pure fluids used herein is a recently developed generalized equation of state for polar fluids (Khan, et al., 1983), i.e.

$$Z = 1 + \lambda Z_{\text{conf}}^{(0)} + (\lambda - 1) Z_{\text{conf}}^{(p)} \quad (\text{A1})$$

where $Z^{(0)}$ and $Z^{(p)}$ are configurational compressibility factors: the isotropic reference and the perturbation contributions, respectively. The quantity λ is a structural parameter which characterizes the steric effects of structured molecules. Both $Z^{(0)}$ and $Z^{(p)}$ are assumed to have the same functional form

$$\begin{aligned} Z_{\text{conf.}} = & \left(A_1 + \frac{A_2}{T^*} + \frac{A_3}{T^{*2}} + \frac{A_4}{T^{*3}} + \frac{A_5}{T^{*5}} \right) \rho^* + \left(A_6 + \frac{A_7}{T^*} \right) \rho^{*2} + A_8 \rho^{*3} \\ & + \left(\frac{A_9}{T^{*3}} + \frac{A_{10}}{T^{*4}} + \frac{A_{11}}{T^{*5}} \right) \rho^{*2} \exp(-c\rho^{*2}) \\ & + \left(\frac{A_{12}}{T^{*3}} + \frac{A_{13}}{T^{*4}} + \frac{A_{14}}{T^{*5}} \right) \rho^{*4} \exp(-c\rho^{*2}) + \frac{A_{15}}{T^*} \rho^{*5} \end{aligned} \quad (\text{A2})$$

where $\rho^* = \rho V^*$, $T^* = kT/\epsilon$, and V^* and ϵ are characteristic volume and energy parameters, respectively. Note that the

constant 'c' in eqn. (A2) is equal to 31.67113. The other constants A_i are given in Table A1.

The energy parameter for polar and associating substances is assumed to be temperature dependent

$$\epsilon/k = \epsilon^0/k + \frac{D}{T} \quad (A3)$$

where ϵ^0 corresponds to the energy parameter for nonpolar contributions, and D is a polar parameter which characterizes multipolar and associating effects.

The equation of state parameters for pure substances are given in Table A2.

The configurational Helmholtz free energy is given by the following relation

$$\begin{aligned} \frac{A'}{RT} &= \int_0^{\rho} (Z - 1) \frac{\partial \rho}{\rho} + \ln(\rho RT) \\ &= \ln(\rho RT) + (A_1 + \frac{A_2}{T^*} + \frac{A_3}{T^{*2}} + \frac{A_4}{T^{*3}} + \frac{A_5}{T^{*5}}) \rho^* \\ &\quad + \frac{1}{2} (A_6 + \frac{A_7}{T^*}) \rho^{*2} + \frac{1}{3} A_8 \rho^{*3} + \frac{1}{2c} (\frac{A_9}{T^{*3}} + \frac{A_{10}}{T^{*4}} + \frac{A_{11}}{T^{*5}}) (1 - \exp(-c \rho^{*2})) \\ &\quad + \frac{1}{2c^2} (\frac{A_{12}}{T^{*3}} + \frac{A_{13}}{T^{*4}} + \frac{A_{14}}{T^{*5}}) \left[(1 - (1 + c \rho^{*2}) \cdot \exp(-c \rho^{*2})) \right] \\ &\quad + \frac{1}{5} (\frac{A_{15}}{T^*}) \rho^{*5} \end{aligned} \quad (A4)$$

Table A1.
 Universal constants $B_i^{(0)}$ and $B_i^{(p)}$ to be used
 in eqn. A1

$$A_i = \lambda B_i^{(0)} + (\lambda - 1) B_i^{(p)}$$

i	$B_i^{(0)}$	$B_i^{(p)}$
1	2.502374	0.52182
2	-7.269612	-0.7378
3	-4.530912	-2.5604
4	-1.5257331	-5.2527
5	0.3796055	-0.12
6	5.3624275	-3.3753
7	-2.8683227	17.1053
8	15.288658	-19.274
9	20.989132	79.29
10	24.738498	6.8475
11	-36.289745	15.57
12	-207.76901	-104.
13	1152.7599	-453.804
14	246.49642	149.091
15	229.89942	850.

Table A2. Pure-component parameters for eqn. (A1)

Component	ϵ/k R	V^* cu.ft./lbmole	λ	D R^2
Methane	270.8	0.2591	1.0333	0
Ethane	390.3	0.3359	1.4097	0
Propane	449.8	0.4252	1.6470	0
n-Butane	501.9	0.5145	1.8190	0
n-Pentane	534.2	0.6039	2.0582	0
n-Hexane	556.5	0.6932	2.3028	0
n-Heptane	573.6	0.7826	2.5514	0
n-Decane	619.6	1.0506	3.1904	0
n-Hexadecane	655.2	1.5855	4.6499	0
Benzene	669.3	0.5066	1.8279	0
CO ₂	358.9	0.2090	1.3665	21287.5
H ₂ S	498.5	0.2544	1.0250	24570.7
Acetone	599.1	0.4485	1.6208	40498.6
Ammonia	492.1	0.1536	1.6566	10909.5
Methanol	525.8	0.2673	2.1111	59193.7
Ethanol	476.3	0.3330	2.1563	99107.9
1-Propanol	506.0	0.4042	2.4794	73636.1
Water	789.4	0.1088	1.8376	15847.9

The equation of state has been tested for different groups of substances, including normal paraffins(C₂-nC₂₀), ring compounds, and polar compounds (CO₂, H₂S, etc.), and polar and associating compounds (NH₃, water, and alcohols, etc.). The results are accurate enough for engineering design calculations.

Appendix B

CONFORMAL SOLUTION MIXING RULES

The conformal solution mixing rules, a so called 'one-fluid model', assume that the mixture properties are the same as those of a hypothetical pure fluid characterized by equation of state characterization parameters which are functions of composition. The following mixing rules are used to obtain mixture characterization parameters as functions of composition (Lee et al., 1977):

$$V_x^* = \sum_i \sum_j x_i x_j V_{ij}^* \quad (B1)$$

$$\epsilon_x V_x^* = \sum_i \sum_j x_i x_j \epsilon_{ij} V_{ij}^* \quad (B2)$$

along with the mixing rule

$$\lambda_x V_x^* = \sum_i \sum_j x_i x_j \lambda_{ij} V_{ij}^* \quad (B3)$$

The subscript x represents the mixture characterization parameters for the hypothetical pure fluid. The combining rules used to calculate the pair characterization parameters are the same rules as eqns. (3.11) - (3.15).

The reduced density and the reduced temperature are evaluated as follows:

$$T^* = k T / \epsilon_x \quad (B4)$$

$$\rho^* = \rho V_x^* \quad (B5)$$

By substituting the values of λ_x , T^* , and ρ^* into eqn. (A1), the equation of state for mixtures is obtained.

The expressions for enthalpy departure and entropy departure involve the derivative of compressibility factor with respect to temperature. Since the energy parameter for polar fluids is temperature dependent, the derivative of the compressibility factor of mixtures with respect to temperature is the following relation,

$$T \left(\frac{\partial Z}{\partial T} \right)_\rho = T^* \left(\frac{\partial Z}{\partial T^*} \right)_{\rho^*} \left[1 - T^* \left(\frac{\partial \epsilon_x}{\partial T} \right)_{\rho^*} \right] \quad (B6)$$

where $\frac{\partial \epsilon_x}{\partial T}$ is

$$\left(\frac{\partial \epsilon_x}{\partial T} \right)_{\rho^*} = - \frac{\sum_i \sum_j x_i x_j V_{ij}^* \frac{D_{ij}}{T^2}}{V_x^*} \quad (B7)$$

The internal energy departure is related to the equation of state by the following equation:

$$\frac{U - U^0}{R T} = - \int_0^{\rho} T \left(\frac{\partial Z}{\partial T} \right)_{\rho} \frac{d\rho}{\rho} \quad (B8)$$

Combining eqns. (A1), and (B6)-(B8), the internal energy departure has the form,

$$\begin{aligned} \frac{U - U^0}{R T} &= \left[1 - T^* \left(\frac{\partial \epsilon_x}{\partial T} \right)_{\rho^*} \right] \times \left[- \int_0^{\rho^*} T^* \left(\frac{\partial Z}{\partial T^*} \right)_{\rho^*} \frac{d \rho^*}{\rho^*} \right] \\ &= \left[1 - T^* \left(\frac{\partial \epsilon_x}{\partial T} \right)_{\rho^*} \right] \times \\ &\quad \left\{ \left(\frac{A_2}{T^*} + \frac{2 A_3}{T^{*2}} + \frac{3 A_4}{T^{*3}} + \frac{5 A_5}{T^{*5}} \right) \rho^* \right. \\ &\quad + 0.5 \frac{A_7}{T^*} \rho^{*2} + \frac{1}{2c} \left(\frac{3A_9}{T^{*3}} + \frac{4A_{10}}{T^{*4}} + \frac{5A_{11}}{T^{*5}} \right) [1 - \exp(-c\rho^{*2})] \\ &\quad + \frac{1}{2c^2} \left(\frac{3A_{12}}{T^{*3}} + \frac{4A_{13}}{T^{*4}} + \frac{5A_{14}}{T^{*5}} \right) [1 - (1+c\rho^{*2}) \exp(-c\rho^{*2})] \\ &\quad \left. + \frac{1}{5} \frac{A_{15}}{T^*} \rho^{*5} \right\} \quad (B9) \end{aligned}$$

The enthalpy departure can be obtained as follows,

$$\frac{H - H^0}{R T} = (Z - 1) + \frac{U - U^0}{R T} \quad (B10)$$

The entropy departure can be obtained using

$$\frac{S - S^0}{R} = \frac{U - U^0}{R T} - \frac{A - A^0}{R T} \quad (B11)$$

where the Helmholtz free energy departure can be obtained from eqn. (A4).

The fugacity, $\hat{f}_i$, of the i th component in a mixture is:

$$\ln \left(\frac{\hat{f}_i}{x_i P} \right) = \int_V^\infty \left[\frac{\partial nZ}{\partial n_i} \bigg|_{T, V, n_{j \neq i}} - 1 \right] \frac{dV}{V} - \ln(Z) \quad (B12)$$

Combining the eqns. (A1), and (B1)-(B3), the fugacity of i th component in solution has the following form:

$$\begin{aligned} \ln \left(\frac{\hat{f}_i}{x_i} \right) = & \bar{R}_1 (Z - 1) + \left(\frac{H - H^0}{RT} - \frac{S - S^0}{RT} \right) \\ & + \bar{E}_1 \left[\frac{H - H^0}{RT} - (Z - 1) \right] / \left[1 - T^* \frac{\partial \epsilon_x}{\partial T} \right] \\ & + \bar{L}_1 \int_0^{\rho^*} \frac{\partial Z}{\partial \lambda_x} \frac{d\rho^*}{\rho^*} \end{aligned} \quad (B13)$$

The integral function in eqn. (B13) is:

$$\begin{aligned} \int_0^{\rho^*} \frac{\partial Z}{\partial \lambda_x} \frac{d\rho^*}{\rho^*} = & \left(C_1 + \frac{C_2}{T^*} + \frac{C_3}{T^{*2}} + \frac{C_4}{T^{*3}} + \frac{C_5}{T^{*5}} \right) \rho^* \\ & + \left(C_6 + \frac{C_7}{T^*} \right) \rho^{*2} + C_8 \frac{\rho^{*3}}{3} \\ & + \left(\frac{C_9}{T^{*3}} + \frac{C_{10}}{T^{*4}} + \frac{C_{11}}{T^{*5}} \right) \frac{1}{2c} \left[1 - \exp(-c\rho^{*2}) \right] \\ & + \left(\frac{C_{12}}{T^{*3}} + \frac{C_{13}}{T^{*4}} + \frac{C_{14}}{T^{*5}} \right) \frac{1}{2c^2} \left[1 - (1+c\rho^{*2}) \exp(-c\rho^{*2}) \right] \\ & + \frac{1}{5} \frac{C_{15}}{T^*} \rho^{*5} \end{aligned} \quad (B14)$$

$$\text{where } C_i = B_i^{(0)} + B_i^{(p)} \quad i = 1, 15 \quad (B15)$$

The derivatives in eqn. (B13) are:

$$\bar{R}_1 = \left. \frac{1}{V_x^*} \frac{\partial V_x^*}{\partial n_1} \right|_{T, V, n_{k \neq 1}} = 2 \left[\frac{\sum_j x_j V_{1j}^*}{V_x^*} - 1 \right] \quad (B16)$$

$$\bar{E}_1 = \left. \epsilon_x \frac{\partial \epsilon_x}{\partial n_1} \right|_{T, V, n_{k \neq 1}} = 2 \left[\frac{\sum_j x_j \epsilon_{1j} V_{1j}^*}{\epsilon_x V_x^*} - 1 \right] - \bar{R}_1 \quad (B17)$$

$$\bar{L}_1 = \left. \frac{\partial \lambda_x}{\partial n_1} \right|_{T, V, n_{k \neq 1}} = \lambda_x \left\{ 2 \left[\frac{\sum_j x_j \lambda_{1j} V_{1j}^*}{\lambda_x V_x^*} - 1 \right] - \bar{R}_1 \right\} \quad (B18)$$

Appendix C

LCM RESULTS USING A MULTIFLUID MODEL FOR REDUCED DENSITY

This appendix is devoted to the LCM, using a multifluid model for reduced density, ρ_{ij}^* ($= \rho v_{ij}^*$), for mixtures of similarly sized molecules. The fugacity coefficients for the components in solution has the following form,

$$\ln \frac{\hat{f}_i}{x_i} = -\frac{1}{\alpha'} \left[\ln \sum_k x_k F_{ki} \exp\left(-\frac{\alpha' A'_{ki}}{RT}\right) - 1 + \sum_j x_j \frac{F_{ij} \exp\left(-\frac{\alpha' A'_{ij}}{RT}\right)}{\sum_k x_k F_{kj} \exp\left(-\frac{\alpha' A'_{kj}}{RT}\right)} \right] \\ + \frac{1}{\alpha'} \left[\ln \sum_k x_k F_{ki} - 1 + \sum_j x_j \frac{F_{ij}}{\sum_k x_k F_{kj}} \right] \\ + (Z - 1) \quad (C1)$$

where A'_{ji} is the molar configurational Helmholtz free energy of a system of molecules which have j-i interactions only.

The value of α' in eqn. (3.4), is related to the coordination number, and is chosen to be 0.5 in this work. The F_{ij} values are calculated using eqn. (4.3). The δ is introduced as a binary interaction parameter for each binary mixture.

Five binary systems, methane-carbon dioxide, carbon dioxide-n-Hexane, acetone-carbon dioxide, ethane-acetone, and methanol-carbon dioxide were selected in the test. In Table C1 a summary of the results is given. Figs. C1 to C5 are plots of pressures versus experimental and calculated compositions.

Overall, the results calculated from the LCM are better than those from the CSM. For the methane-CO2 system, (V^* for methane is 0.26 and for CO2 is 0.21), both the CSM and the LCM calculate the VLE reasonably well, as shown in Fig. C1. For mixtures in which components differ in size, such as the CO2-n-Hexane (V^* for CO2 is 0.21, and for n-hexane is 0.69), the LCM yields accurate calculations for the liquid phase compositions, as shown in Fig. C2. For the acetone-CO2 system, a significant improvement is obtained in k-value calculations by use of the LCM (see Table C1). Both the ethane-acetone and the methanol-carbon dioxide are strongly non-ideal mixtures. The CSM apparently does not work well for these two strongly nonideal systems (see Figs. C4, and C5). However, the LCM greatly improves on the CSM for vapor-liquid equilibria calculations for these two strongly nonideal systems.

At this point, a conclusion can be drawn that for strongly nonideal mixtures of similarly sized components (V_1^*/V_j^* less than 3.3), the LCM, using a multifluid model for reduced density, is obviously superior to the CSM.

Table C1. Vapor-liquid equilibria calculations using
local composition and conformal solution
mixing rules for five binary mixtures

System	Mixing rules	ξ	ζ	δ	K1	K2	κ_1	κ_2	y1	y2
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
A.A.D. %										
Methane- CO2	CSM	0.9867	0.9718	--	3.71	5.00	3.84	4.30	2.25	6.91
	LCM	1.0325	0.8638	0.9804	3.26	3.11	3.40	2.03	1.60	3.91
CO2 n-Hexane	CSM	1.0430	0.8723	--	8.93	15.4	9.73	9.09	0.45	22.9
	LCM	1.2752	0.6485	0.8721	2.22	11.8	2.43	1.05	0.29	12.0
Acetone CO2	CSM	1.0272	0.9647	--	19.8	6.17	4.54	5.43	21.8	0.30
	LCM	1.1029	0.8232	1.0414	5.70	1.03	4.87	1.19	10.0	0.16
Ethane Acetone	CSM	0.9588	0.9644	--	19.6	38.4	27.3	25.5	0.36	18.9
	LCM	1.0460	0.7906	1.0733	4.09	5.27	4.44	7.79	0.13	5.56
Methanol CO2	CSM	0.9634	1.0968	--	22.7	27.8	27.9	60.7	33.8	0.31
	LCM	1.0503	0.7931	1.0498	2.33	2.17	4.82	2.26	5.14	0.05

CSM : Conformal Solution Mixing Rules

LCM : Local Composition Mixing Rules

METHANE(1)-CO2(2)

TEMPERATURE : -54 C
 * + : DATA OF MRAW, 1978
 - - - : CSM
 — : LCM

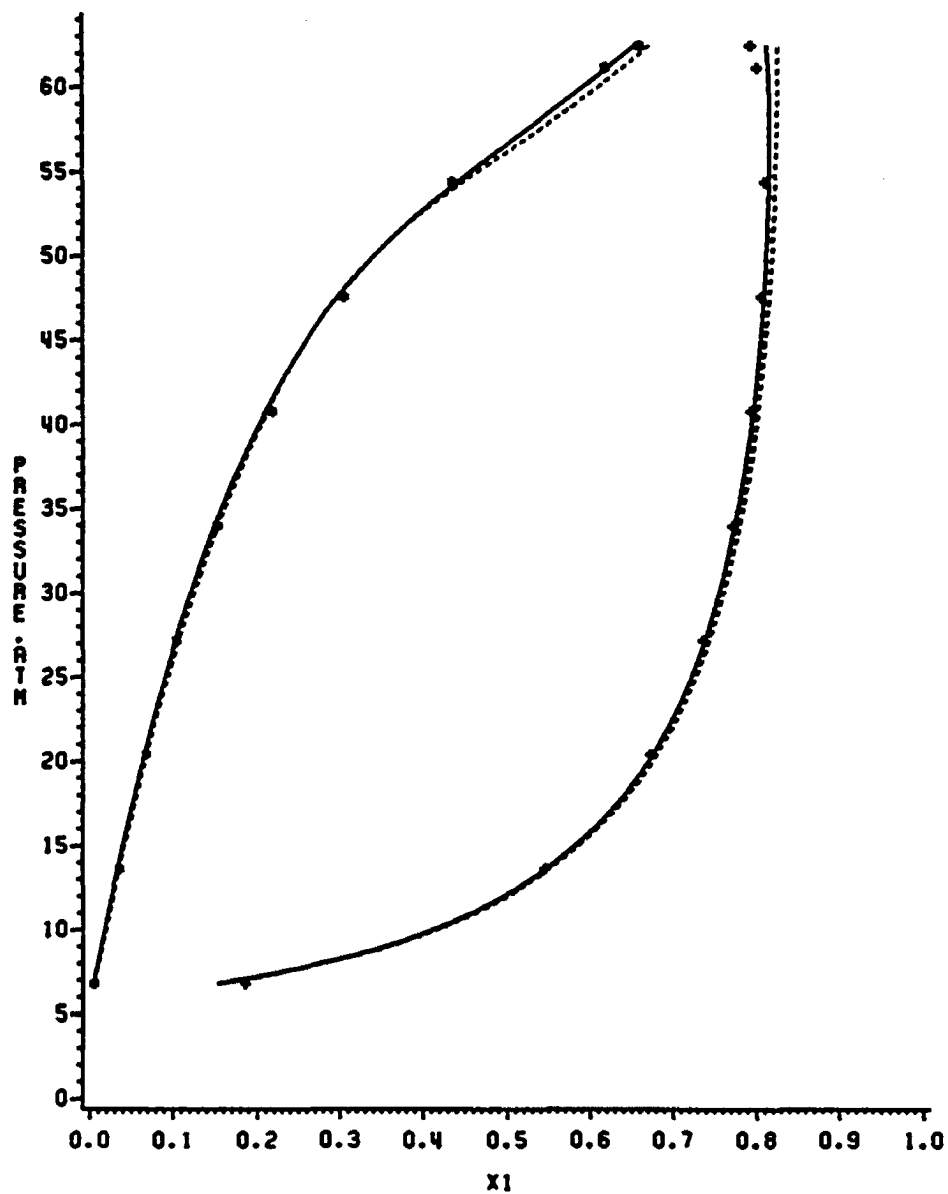


FIGURE C1. PRESSURE-COMPOSITION DIAGRAM

CO₂(1)-N-HEXANE(2)

TEMPERATURE : 25 C
 * + : DATA OF OHGAKI, 1976
 - - - - : CSM
 ——— : LCM

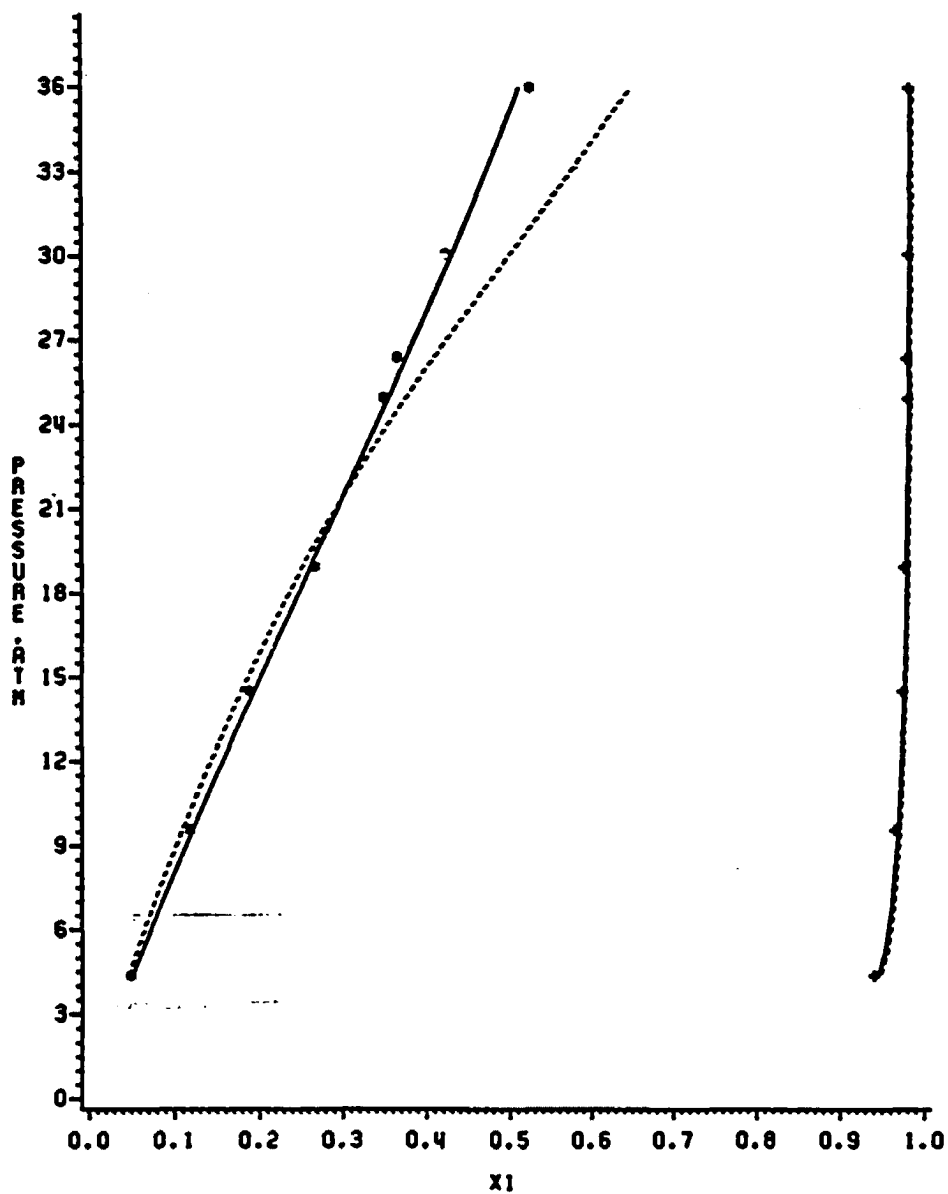


FIGURE C2 . PRESSURE-COMPOSITION DIAGRAM

ACETONE(1)-CO2(2)

TEMPERATURE : 25 C
 * + : DATA OF KATAYAMA, 1975
 - - - : CSM
 — : LCM

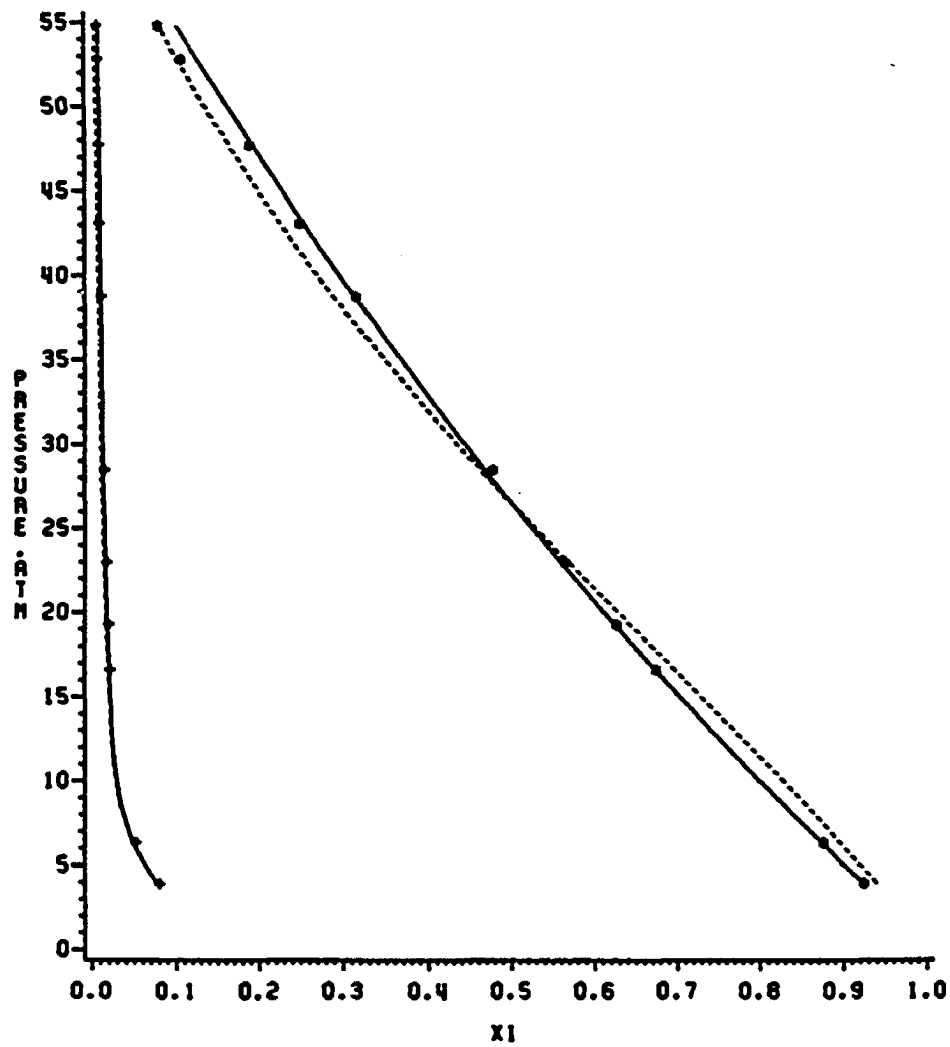


FIGURE C3 . PRESSURE-COMPOSITION DIAGRAM

ETHANE(1)-ACETONE(2)

TEMPERATURE : 25 C

* + : DATA OF KATAYAMA, 1976

- - - : CSM

— : LCM

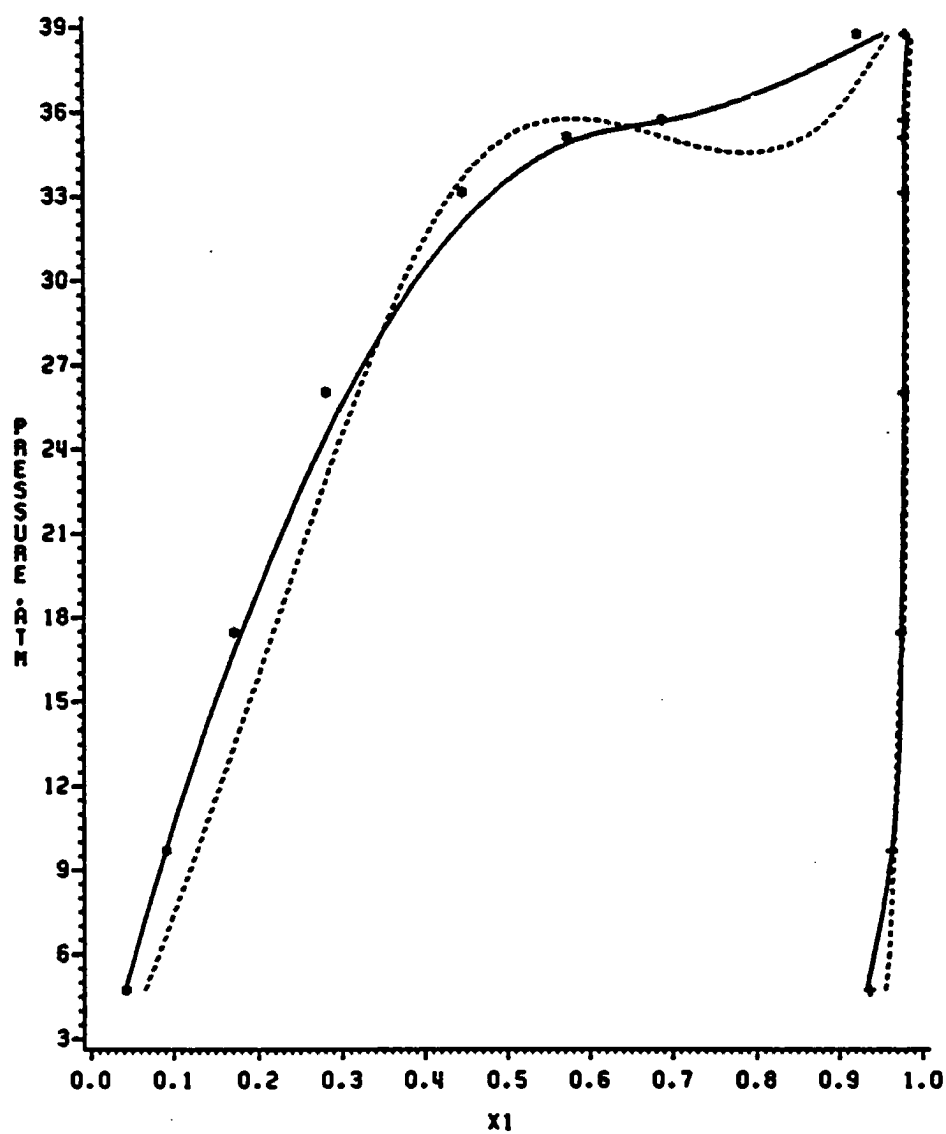


FIGURE C4. PRESSURE-COMPOSITION DIAGRAM

METHANOL(1)-CO₂(2)

TEMPERATURE : 25 C

* + : DATA OF KATAYAMA, 1975

--- : CSM

— : LCM

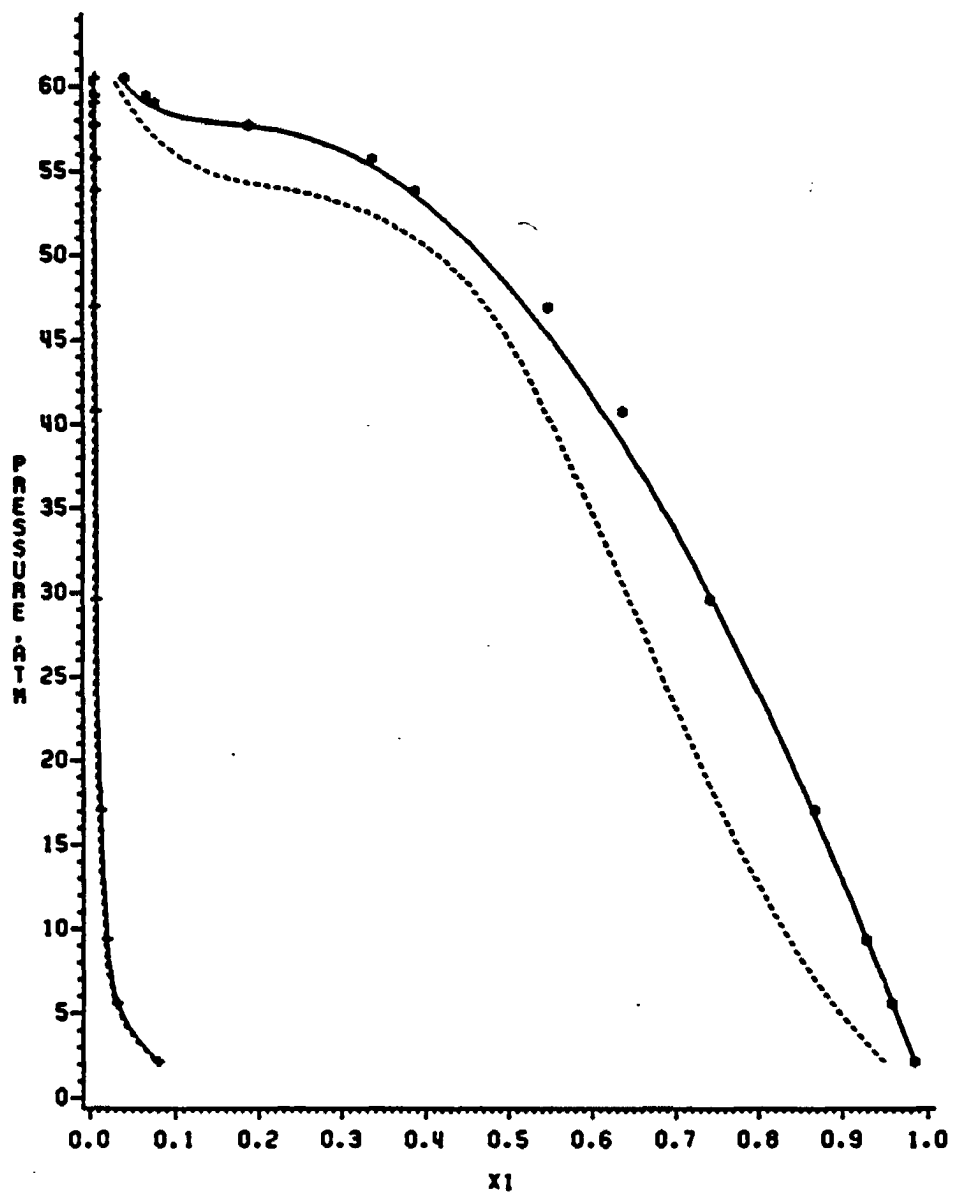


FIGURE c5 . PRESSURE-COMPOSITION DIAGRAM

Appendix D

ELUCIDATION OF MIXTURE PRESSURE PROBLEMS USING A MULTIFLUID MODEL FOR REDUCED DENSITY

The LCM, using a multifluid model for ρ_{ij}^* ($=\rho v_{ij}^*$), has been shown to work well for nonideal mixtures of similarly sized molecules such as methanol-carbon dioxide, and ethane-acetone. However, for mixtures with large molecular size differences, problems are encountered using the multifluid model for ρ_{ij}^* ($=\rho v_{ij}^*$). Using the multifluid model for ρ_{ij}^* ($=\rho v_{ij}^*$), the local composition model expression used for the mixture pressure (eqn. (3.7)) can become infinite when component molecular size differences are sufficiently large (even at conditions where the real fluid mixture is known to exist at finite pressure). For example, the ratio of V^* (volume parameter) is 4 : 1 for the acetone-water system (V^* for acetone is 0.45, and for water is 0.11 cu.ft./lbmole). The experimental pressure for the acetone-water system at 200 C ranges from 15.8 to 30.1 atm (Griswold, 1952). Fig. D1 shows plots of pressure versus reduced density, based on multifluid model, for pure acetone and pure water on the same diagram. The saturated liquid densities at 200 C are 0.55 and 2.99 lbmole/cu.ft. for pure

ACETONE(1)-WATER(2)

TEMPERATURE : 200 C

----- : ACETONE

----- : WATER

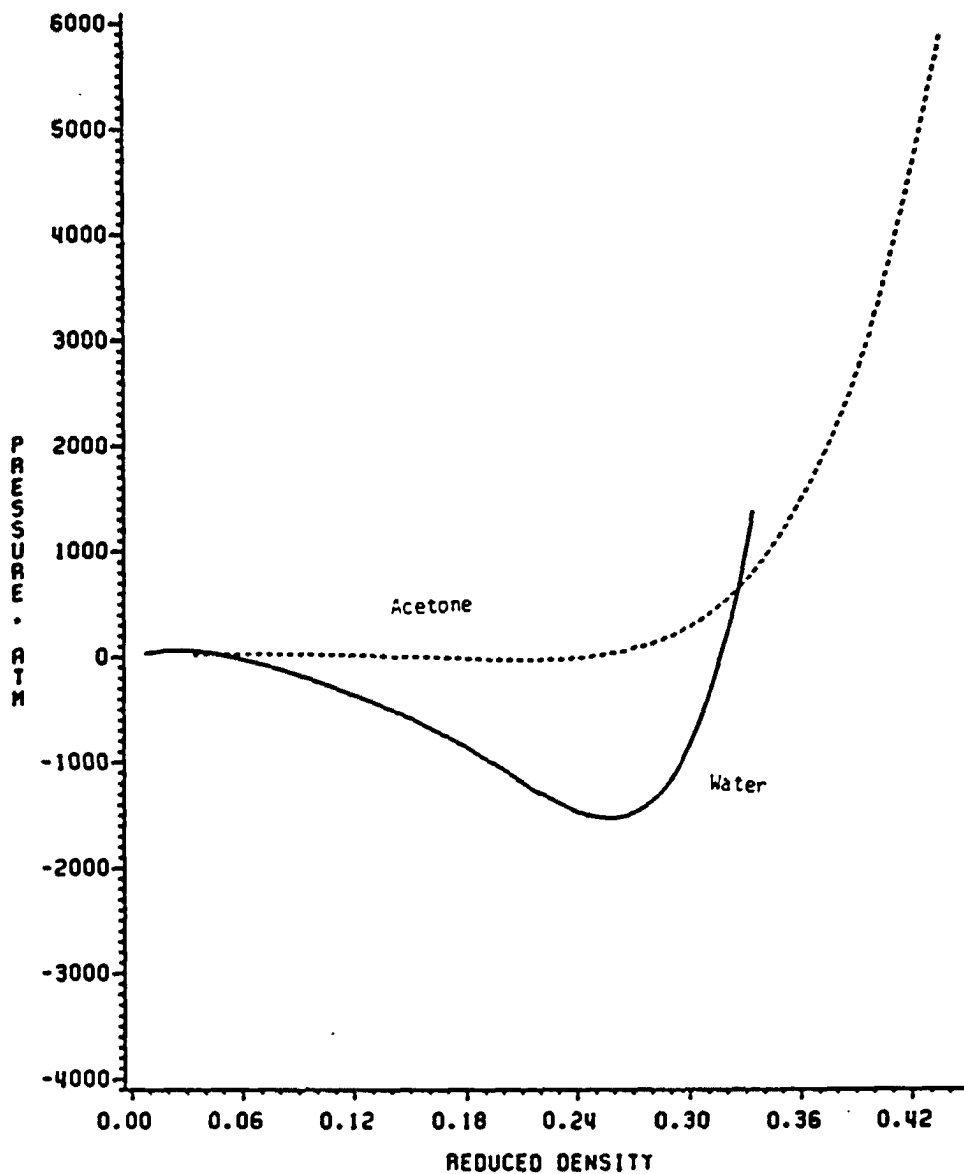


FIGURE 31. PLOT OF PRESSURE VS. REDUCED DENSITY

acetone and pure water, respectively. In this and most cases, the excess volume is small, of the order of 5 % of the total volume at most, so the mixture density for acetone-water generally will fall between the pure fluid densities (in this instance 0.55, and 2.99 lbmole/cu.ft.) For a mixture density (ρ) of 1.5 lbmole/cu.ft., the corresponding pressure P_{11} for acetone is 6.8×10^5 atm, using $\rho_{11}^* = 1.5 \times 0.45 = 0.675$. When a density of the mixture (ρ) is 2.5 lbmole/cu.ft., the corresponding pressure P_{11} for acetone is 2×10^7 atm, using $\rho_{11}^* = 2.5 \times 0.45 = 1.125$. In Table D1. the estimated pressures at these two mixture densities for the acetone-water system at 200 C is given. For a mixture density approaches to 2.99 lbmole/cu.ft. (pure fluid density for water), the corresponding pressure for acetone approaches to infinite. This phenomena cause the local composition model expression for the mixture pressure to be infinite; consequently, there is no calculated mixture liquid density exists to match the experimental mixture pressure.

Table D1. Estimated P11 and P22 in eqn. (3.7) using
a multifluid model for reduced density
for Acetone(1)-Water(2) system
at 200 C.

ρ lbmol/cu.ft.	ρ_{11}^*	P11 atm	ρ_{22}^*	P22 atm
1.5	0.675	6.8×10^5	0.165	-690
2.5	1.125	2.0×10^7	0.275	-1402

a.	T_c, C	den. (saturated, 200 C) lbmole/cu.ft.	V^* cu.ft./lbmole
Acetone (1)	235	0.5525	0.45
Water (2)	318.7	2.9989	0.11

Appendix E

ELIMINATION OF THE MIXTURE PRESSURE PROBLEMS USING ONE FLUID MODEL FOR REDUCED DENSITY

In this study, the one fluid model for ρ_{ij}^* was used. it is now of interest to check whether the same mixture pressure problems, which impedes the LCM, using a multifluid model for $\rho_{ij}^* (= \rho v_{ij}^*)$, to calculate the properties of mixtures of dissimilarly sized molecules (acetone-water system), still occurs(see Appendix D). To calculate P11 and P22 for acetone-water system, we need to calculate ρ_{ij}^* from v_x^* , which involves the binary interaction parameter, ξ , and the composition. The binary interaction parameter, ξ , set equal to 1.0862, which is an arbitrary choice. Three compositions, 0.25, 0.5, and 0.75 are chosen for illustration. The values of v_x^* are 0.195, 0.281, and 0.365 for composition of 0.25, 0.5, and 0.75, respectively. In Fig. E1 plots of pressure verse reduced density, based on one fluid model eqn. (3.9), for pure acetone and water on the same diagram are given. The P11 and P22 have the same ρ^* , but they have different T^* , and λ .

The mixture density, based on the ideal solution mixing, can be estimated from the composition and the

ACETONE(1)-WATER(2)

TEMPERATURE : 200 C

X1 : 0.25, 0.50, 0.75

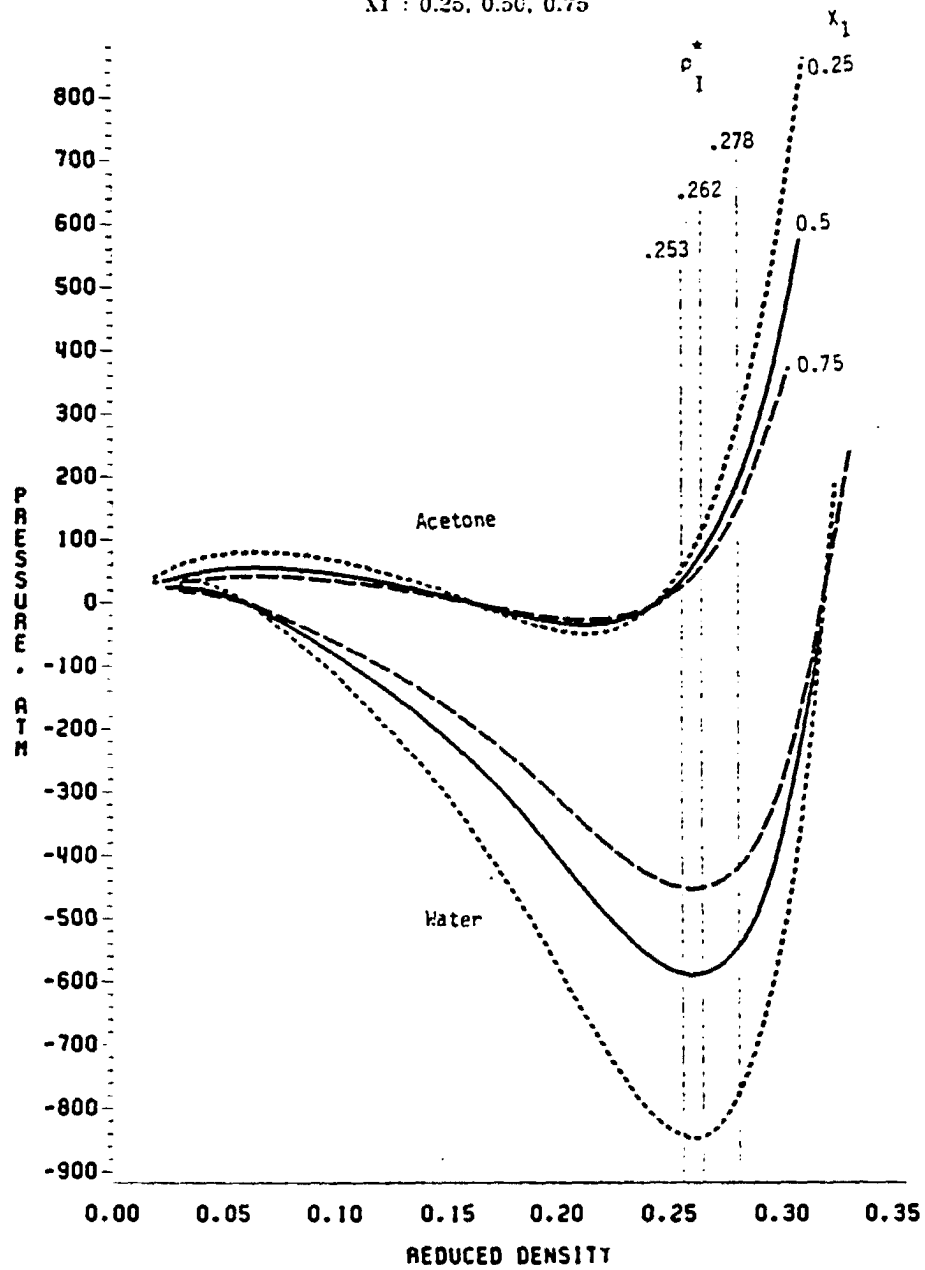


FIGURE E1 PLOT OF PRESSURE VS. REDUCED DENSITY

saturated liquid densities for pure components (assumed both exist) as follows,

$$\rho_I = \frac{1}{V_I} = \frac{1}{x_1 / \rho_1 + x_2 / \rho_2} \quad (E1)$$

where ρ_1 , and ρ_2 are the saturated liquid densities at system temperature for pure component 1 and 2, respectively. The mixture densities, based on the ideal solution mixing, are 1.423, 0.933, and 0.694 lbmole/cu.ft. for compositions of 0.25, 0.5, and 0.75, respectively. The corresponding calculated P11 and P22 at mixture densities, based on the ideal solution mixing, are given in Table E1. Since the excess volume usually is small, it is expected that the mixture density should fall in the neighborhood of the density, based on the ideal solution mixing. Therefore, the pressure, calculated from the mixture density, should be close to the pressure, estimated from the mixture density based on the ideal solution mixing. Since neither P11 nor P22 is an extremely large value, the calculated mixture pressure, eqn. (3.7), can match the experimental pressure.

Table E1. Estimated P11 and P22 in eqn. (3.7) using a one fluid model for reduced density at ideal solution mixture densities for Acetone(1)-Water(2) system at 200 C.

Composition x_1	V_x^*	^a V Ideal Solution	ρ lbmol/ft ³	ρ_{ij}^*	P11 atm	P22 atm
0.25	0.195	0.703	1.423	0.278	284	-777
0.50	0.281	1.072	0.933	0.262	81	-576
0.75	0.365	1.441	0.694	0.253	30	-452

a.	Tc, C	den. (saturated, 200 C) lbmole/cu.ft.
Acetone(1)	235	0.5525 (den1)
Water (2)	318.7	2.9989 (den2)

Ideal solution mixing,
Volume;

$$V_m = x_1 v_1 + x_2 v_2 = x_1/\text{den1} + x_2/\text{den2}$$

Appendix F

Samples of the detailed calculations of
vapor-liquid equilibria
and mixture density

Table F1. Detailed calculations of vapor-liquid
equilibria from LCM(see Table 2)

MIXTURE IS : METHANOL(1) - CO2(2)

DATA SOURCE: KATAYAMA, 1976

	T (R)	P (PSIA)	X1 (EXP)	X1 (CAL)	DEV.	Y1 (EXP)	Y1 (CAL)	DEV.
1	536.670	31.699	0.98500	0.98479	-0.0	0.0798	0.0789	-1.1
2	536.670	81.974	0.95900	0.95797	-0.1	0.0315	0.0315	0.0
3	536.670	137.951	0.93000	0.92708	-0.3	0.0203	0.0194	-4.3
4	536.670	251.008	0.86900	0.86089	-0.9	0.0122	0.0115	-5.5
5	536.670	435.295	0.74400	0.73949	-0.6	0.0083	0.0076	-8.1
6	536.670	599.597	0.63900	0.61059	-4.4	0.0072	0.0064	-11.5
7	536.670	690.271	0.55000	0.52493	-4.6	0.0070	0.0060	-13.7
8	536.670	791.821	0.39000	0.39876	2.2	0.0071	0.0059	-17.1
9	536.670	819.596	0.33800	0.34770	2.9	0.0078	0.0059	-24.8
10	536.670	848.988	0.19000	0.12856	-32.3	0.0074	0.0058	-21.0
11	536.670	867.799	0.07750	0.05759	-25.7	0.0070	0.0053	-24.9
12	536.670	873.824	0.06750	0.04897	-27.5	0.0074	0.0050	-32.7
13	536.670	888.814	0.04270	0.03266	-23.5	0.0063	0.0042	-33.9

	T (R)	P (PSIA)	X2 (EXP)	X2 (CAL)	DEV.	Y2 (EXP)	Y2 (CAL)	DEV.
1	536.670	31.699	0.01500	0.01521	1.4	0.9202	0.9211	0.1
2	536.670	81.974	0.04100	0.04203	2.5	0.9695	0.9685	-0.0
3	536.670	137.951	0.07000	0.07292	4.2	0.9797	0.9806	0.1
4	536.670	251.008	0.13100	0.13911	6.2	0.9878	0.9885	0.1
5	536.670	435.295	0.25600	0.26051	1.8	0.9917	0.9924	0.1
6	536.670	599.597	0.36100	0.38941	7.9	0.9928	0.9936	0.1
7	536.670	690.271	0.45000	0.47507	5.6	0.9930	0.9940	0.1
8	536.670	791.821	0.61000	0.60124	-1.4	0.9929	0.9941	0.1
9	536.670	819.596	0.66200	0.65230	-1.5	0.9922	0.9941	0.2
10	536.670	848.988	0.81000	0.87144	7.6	0.9926	0.9942	0.2
11	536.670	867.799	0.92250	0.94241	2.2	0.9930	0.9947	0.2
12	536.670	873.824	0.93250	0.95103	2.0	0.9926	0.9950	0.2
13	536.670	888.814	0.95730	0.96734	1.0	0.9937	0.9958	0.2

Table F1. (Continued)

	T (R)	P (PSIA)	K1 (EXP)	K1 (CAL)	DEV.	K2 (EXP)	K2 (CAL)	DEV.
1	536.670	31.699	0.08102	0.08011	-1.1	61.3467	60.5424	-1.3
2	536.670	81.974	0.03285	0.03289	0.1	23.6219	23.0455	-2.4
3	536.670	137.951	0.02183	0.02095	-4.0	13.9957	13.4465	-3.9
4	536.670	251.008	0.01404	0.01340	-4.6	7.5405	7.1055	-5.8
5	536.670	435.295	0.01116	0.01032	-7.5	3.8738	3.8094	-1.7
6	536.670	599.597	0.01127	0.01043	-7.4	2.7501	2.5516	-7.2
7	536.670	690.271	0.01273	0.01151	-9.6	2.2067	2.0922	-5.2
8	536.670	791.821	0.01821	0.01475	-19.0	1.6277	1.6534	1.6
9	536.670	819.596	0.02308	0.01688	-26.9	1.4988	1.5240	1.7
10	536.670	848.988	0.03895	0.04547	16.7	1.2254	1.1408	-6.9
11	536.670	867.799	0.09032	0.09123	1.0	1.0764	1.0555	-1.9
12	536.670	873.824	0.10963	0.10177	-7.2	1.0645	1.0462	-1.7
13	536.670	888.814	0.14754	0.12743	-13.6	1.0380	1.0295	-0.8

A.A.D. % OF K1 NPTS
9.13 13

A.A.D. % OF K2 NPTS
3.24 13

Table F2. Detailed calculations of vapor-liquid equilibria from CSM(see Table 2)

MIXTURE IS : METHANOL(1) - CO2(2)

DATA SOURCE: KATAYAMA, 1976

	T (R)	P (PSIA)	X1 (EXP)	X1 (CAL)	DEV.	Y1 (EXP)	Y1 (CAL)	DEV.
1	536.670	31.699	0.98500	0.98571	0.1	0.0798	0.0793	-0.6
2	536.670	81.974	0.95900	0.96118	0.2	0.0315	0.0319	1.4
3	536.670	137.951	0.93000	0.93375	0.4	0.0203	0.0199	-2.0
4	536.670	251.008	0.86900	0.87683	0.9	0.0122	0.0121	-0.9
5	536.670	435.295	0.74400	0.77231	3.8	0.0083	0.0084	1.0
6	536.670	599.597	0.63900	0.63968	0.1	0.0072	0.0074	2.2
7	536.670	690.271	0.55000	0.47815	-13.1	0.0070	0.0071	1.9
8	536.670	791.821	0.39000	0.12579	-67.7	0.0071	0.0060	-15.8
9	536.670	819.596	0.33800	0.08889	-73.7	0.0078	0.0053	-32.3
10	536.670	848.988	0.19000	0.05870	-69.1	0.0074	0.0044	-41.1
11	536.670	867.799	0.07750	0.04278	-44.8	0.0070	0.0037	-47.8
12	536.670	873.824	0.06750	0.03815	-43.5	0.0074	0.0034	-54.0
13	536.670	888.814	0.04270	0.02749	-35.6	0.0063	0.0027	-56.5
	T (R)	P (PSIA)	X2 (EXP)	X2 (CAL)	DEV.	Y2 (EXP)	Y2 (CAL)	DEV.
1	536.670	31.699	0.01500	0.01429	-4.7	0.9202	0.9207	0.1
2	536.670	81.974	0.04100	0.03882	-5.3	0.9685	0.9681	-0.0
3	536.670	137.951	0.07000	0.06625	-5.4	0.9797	0.9801	0.0
4	536.670	251.008	0.13100	0.12317	-6.0	0.9878	0.9879	0.0
5	536.670	435.295	0.25600	0.22769	-11.1	0.9917	0.9916	-0.0
6	536.670	599.597	0.36100	0.36032	-0.2	0.9928	0.9926	-0.0
7	536.670	690.271	0.45000	0.52185	16.0	0.9930	0.9929	-0.0
8	536.670	791.821	0.61000	0.87421	43.3	0.9929	0.9940	0.1
9	536.670	819.596	0.66200	0.91111	37.6	0.9922	0.9947	0.3
10	536.670	848.988	0.81000	0.94130	16.2	0.9926	0.9956	0.3
11	536.670	867.799	0.92250	0.95722	3.8	0.9930	0.9963	0.3
12	536.670	873.824	0.93250	0.96185	3.1	0.9926	0.9966	0.4
13	536.670	888.814	0.95730	0.97251	1.6	0.9937	0.9973	0.4

Table F2. (Continued)

	T(R)	P(PSIA)	K1(EXP)	K1(CAL)	DEV.	K2(EXP)	K2(CAL)	DEV.
1	536.670	31.699	0.08102	0.08044	-0.7	61.3467	64.4140	5.0
2	536.670	81.974	0.03285	0.03323	1.2	23.6219	24.9387	5.6
3	536.670	137.951	0.02183	0.02130	-2.4	13.9957	14.7941	5.7
4	536.670	251.008	0.01404	0.01379	-1.7	7.5405	8.0209	6.4
5	536.670	435.295	0.01116	0.01086	-2.7	3.8738	4.3552	12.4
6	536.670	599.597	0.01127	0.01150	2.0	2.7501	2.7549	0.2
7	536.670	690.271	0.01273	0.01492	17.2	2.2067	1.9026	-13.8
8	536.670	791.821	0.01821	0.04753	161.1	1.6277	1.1370	-30.1
9	536.670	819.596	0.02308	0.05944	157.6	1.4988	1.0918	-27.2
10	536.670	848.988	0.03895	0.07425	90.6	1.2254	1.0577	-13.7
11	536.670	867.799	0.09032	0.08533	-5.5	1.0764	1.0409	-3.3
12	536.670	873.824	0.10963	0.08921	-18.6	1.0645	1.0361	-2.7
13	536.670	888.814	0.14754	0.09966	-32.5	1.0380	1.0255	-1.2

A.A.D. % OF K1 NPTS
37.9 13

A.A.D. % OF K2 NPTS
9.78 13

Table F3. Detailed calculations of mixture density
from LCM(see Table 3)

MIXTURE IS : ACETONE(1) - WATER(2)

DATA SOURCES: NODA, 1982 (NPTS=9)
THOMAS, 1957 (NPTS=34)

T(R)	P(PSIA)	X1	DEN(EXP) LBMOLE/CU.FT.	DEN(CAL)	% DEV
536.670	14.700	0.05830	2.9905	3.0536	2.1089
536.670	14.700	0.14600	2.4705	2.4531	-0.7055
536.670	14.700	0.20560	2.2006	2.1614	-1.7833
536.670	14.700	0.30200	1.8618	1.8097	-2.7968
536.670	14.700	0.45970	1.4763	1.4246	-3.5070
536.670	14.700	0.52660	1.3539	1.3054	-3.5798
536.670	14.700	0.61810	1.2145	1.1710	-3.5801
536.670	14.700	0.76990	1.0351	1.0008	-3.3117
536.670	14.700	0.81950	0.9871	0.9562	-3.1398
527.670	14.700	0.99920	0.8496	0.8347	-1.7503
527.670	14.700	0.99820	0.8503	0.8353	-1.7597
527.670	14.700	0.99340	0.8536	0.8382	-1.8037
527.670	14.700	0.99240	0.8543	0.8388	-1.8153
527.670	14.700	0.98880	0.8568	0.8409	-1.8470
527.670	14.700	0.98740	0.8577	0.8418	-1.8598
527.670	14.700	0.78840	1.0238	0.9916	-3.1506
527.670	14.700	0.49060	1.4247	1.3774	-3.3163
527.670	14.700	0.25010	2.0408	1.9979	-2.1044
527.670	14.700	0.14500	2.4863	2.4750	-0.4519
536.670	14.700	0.99580	0.8460	0.8300	-1.8957
536.670	14.700	0.80310	1.0029	0.9704	-3.2377
536.670	14.700	0.48210	1.4321	1.3824	-3.4699
536.670	14.700	0.38020	1.6497	1.5966	-3.2186
536.670	14.700	0.25300	2.0211	1.9734	-2.3570
536.670	14.700	0.14550	2.4741	2.4558	-0.7357
536.670	14.700	0.06935	2.9152	2.9627	1.6296
559.673	14.700	0.99580	0.8302	0.8129	-2.0899
559.673	14.700	0.76460	1.0221	0.9853	-3.6025
559.673	14.700	0.50120	1.3755	1.3221	-3.8796
559.673	14.700	0.37220	1.6450	1.5862	-3.5770
559.673	14.700	0.25020	2.0049	1.9487	-2.8072
559.673	14.700	0.14520	2.4501	2.4161	-1.3873
559.673	14.700	0.07166	2.8787	2.8962	0.6087
581.760	14.700	0.99580	0.8145	0.7965	-2.2041
581.760	14.700	0.78130	0.9875	0.9506	-3.7361
581.760	14.700	0.48550	1.3814	1.3244	-4.1255
581.760	14.700	0.24860	1.9849	1.9213	-3.2057
581.760	14.700	0.14400	2.4303	2.3835	-1.9277
581.760	14.700	0.07152	2.8567	2.8520	-0.1646
599.867	14.700	0.11000	2.5938	2.5494	-1.7100
618.030	14.700	0.04716	2.9885	2.9753	-0.4439
618.030	14.700	0.02063	3.1992	3.2215	0.6954
636.300	14.700	0.02109	3.1792	3.1765	-0.0846

AVE. ABS. PERCENT.
2.25967

NO. OF PTS.
43

Table F4. Detailed calculations of mixture density
from CSM(see Table 3)

MIXTURE IS : ACETONE(1) - WATER(2)

DATA SOURCES: NODA, 1982 (NPTS=9)
THOMAS, 1957 (NPTS=34)

T(R)	P(PSIA)	X1	DEN(EXP) LB/MOLE/CU.FT.	DEN(CAL)	% DEV
536.670	14.700	0.05830	2.9905	3.2574	8.9244
536.670	14.700	0.14600	2.4705	2.7722	12.2113
536.670	14.700	0.20560	2.2006	2.4952	13.3842
536.670	14.700	0.30200	1.8618	2.1204	13.8911
536.670	14.700	0.45970	1.4763	1.6566	12.2093
536.670	14.700	0.52660	1.3539	1.5021	10.9476
536.670	14.700	0.61810	1.2145	1.3219	8.8447
536.670	14.700	0.76990	1.0351	1.0846	4.7783
536.670	14.700	0.81950	0.9871	1.0203	3.3539
527.670	14.700	0.99920	0.8496	0.8350	-1.7190
527.670	14.700	0.99820	0.8503	0.8359	-1.6893
527.670	14.700	0.99340	0.8536	0.8404	-1.5464
527.670	14.700	0.99240	0.8543	0.8413	-1.5191
527.670	14.700	0.98880	0.8568	0.8447	-1.4113
527.670	14.700	0.98740	0.8577	0.8460	-1.3700
527.670	14.700	0.78840	1.0238	1.0682	4.3366
527.670	14.700	0.49060	1.4247	1.5942	11.9007
527.670	14.700	0.25010	2.0408	2.3278	14.0635
527.670	14.700	0.14500	2.4863	2.7956	12.4419
536.670	14.700	0.99580	0.8460	0.8314	-1.7316
536.670	14.700	0.80310	1.0029	1.0409	3.7901
536.670	14.700	0.48210	1.4321	1.6025	11.8985
536.670	14.700	0.38020	1.6497	1.8707	13.3919
536.670	14.700	0.25300	2.0211	2.3006	13.8313
536.670	14.700	0.14550	2.4741	2.7747	12.1513
536.670	14.700	0.06935	2.9152	3.1906	9.4480
559.673	14.700	0.99580	0.8302	0.8142	-1.9249
559.673	14.700	0.76460	1.0221	1.0702	4.7009
559.673	14.700	0.50120	1.3755	1.5292	11.1747
559.673	14.700	0.37220	1.6450	1.8602	13.0773
559.673	14.700	0.25020	2.0049	2.2714	13.2925
559.673	14.700	0.14520	2.4501	2.7297	11.4145
559.673	14.700	0.07166	2.8787	3.1251	8.5588
581.760	14.700	0.99580	0.8145	0.7979	-2.0382
581.760	14.700	0.78130	0.9875	1.0279	4.0925
581.760	14.700	0.48550	1.3814	1.5368	11.2532
581.760	14.700	0.24860	1.9949	2.2398	12.8404
581.760	14.700	0.14400	2.4303	2.6918	10.7615
581.760	14.700	0.07152	2.8567	3.0773	7.7199
599.867	14.700	0.11000	2.5938	2.8273	9.0050
618.030	14.700	0.04716	2.9885	3.1417	5.1243
618.030	14.700	0.02063	3.1992	3.3065	3.3517
636.300	14.700	0.02109	3.1792	3.2621	2.6094

AVE. ABS. PERCENT. NO. OF PTS.
7.90054 43