THREE-PHASE EQUILIBRIUM CALCULATIONS USING MODIFIED CHAO-SEADER PROCEDURES

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PREFACE

A critical review of three-phase flash algorithms was made. A computer program originally written by Professor J. H. Erbar was used in the study and modified to perform three-phase flash calculations. The original computer program contained the Chao-Seader data system. Modifications were made to the system to provide equilibrium data needed for three-phase flash calculations. Calculated results were compared against published equilibrium data to demonstrate the ability of the algorithm to perform three-phase flash calculations.

I wish to express my sincere appreciation for the advice and guidance provided by Professors J. H. Erbar and R. N. Maddox, both of whom gave generously of their time and whose suggestions and guidance were of great value. I would also thank Continental Oil Company for the generous use of their computing facilities.

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CHAPTER I

INTRODUCTION

Vapor-liquid equilibrium calculations are basic to the design and operation of most processing units in the chemical and hydrocarbon processing industries. Frequently equilibrium separations involve systems of a vapor phase and two partially miscible liquid phases. Water and hydrocarbon mixtures are the most common of these.

Three-phase equilibrium calculations are generally based on rather inaccurate simplifying assumptions. Usually, Raoult's Law is used to determine the vapor phase concentration of water. Liquid phases are either assumed to be insoluble or are calculated using solubility data. Prausnitz and Shair (33), Li and McKetta (26), Anthony and McKetta (2), and others have developed correlations for predicting hydrocarbon in water and water in hydrocarbon solubilities. However, due to their complexities, these correlations are not commonly used in engineering practice. There are no correlations currently available that calculate water and hydrocarbon K-values in three-phase systems.

High speed digital computers are now used routinely for phase equilibrium calculations. It seems logical to extend this practice to three-phase systems.

The scope of this study involves modification of the Chao-Seader data system for prediction of equilibrium data for water and hydrocarbon systems. Test problems were solved using the computer and the results compared to published data to evaluate the new procedures.

CHAPTER II

BACKGROUND

Vapor-Liquid Equilibria

Process calculations for coexisting vapor-liquid mixtures at equilibrium are made using the convenient vapor-liquid K-value, sometimes called the "equilibrium phase distribution ratio" which is defined for component i as

$$K_i = \frac{Y_i}{X_i} = \frac{\text{mole fraction vapor phase}}{\text{mole fraction liquid phase}}$$

The K-values can be measured experimentally. However, experimental measurements are costly and time consuming. Theoretical and empirical methods have been developed for predicting these K-values, thus making the experimental data go further.

High-speed digital computers have made possible the use of relatively complex thermodynamic functions for the prediction of K-values. Perhaps the best known and most widely used of these is the Chao-Seader correlation (8). This method is based upon regular solution theory, thermodynamic rigor, and empiricism. The general correlation takes the form:

$$K_i = \frac{Y_i}{X_i} = \left(\frac{\nu\gamma}{\phi}\right)_i$$

The pure component liquid phase fugacity coefficient, ν, is correlated empirically within the framework of Pitzer's modified form of the principle of corresponding states. The correlation is as follows:

$$\log \nu = \log \nu^{(0)} + \omega \log \nu^{(1)}$$

The first term on the right gives the fugacity coefficient of a simple fluid. The second term is a correction factor giving the deviation of properties of real fluids from simple fluids. The correlating factor, ω, is Pitzer's modified accentric factor. The terms $\log \nu^{(0)}$ and $\log \nu^{(1)}$ are defined as polynomial functions of reduced temperature and pressure of the component. These functions together with the appropriate constants are given in Appendix A.

The activity coefficient of components in liquid solution, γ, is assumed to follow regular solution theory using the following equation proposed by Hildebrand (19):

$$\ln \gamma_i = \frac{V_i (\delta_i - \bar{\delta})^2}{RT}$$

The parameters for this equation are: V_i, liquid molar volume; R, gas law constant; T, temperature; and δ_i, solubility parameter. Minor adjustments of the values of ω, V_i, and δ_i were made by the authors to fit experimental data. The volumetric average of solubility parameters for the liquid phase, $\bar{\delta}$, is defined as:

$$\bar{\delta} = \frac{\Sigma X_i V_i \delta_i}{\Sigma X_i V_i}$$

The third parameter in the Chao-Seader correlation is the component's fugacity coefficient in the vapor phase mixture, ϕ_i. The Redlich and Kwong equation of state (36) is used to derive the expression for the fugacity coefficient by standard procedures:

$$\ln \phi_i = (Z-1) \frac{B_i}{B} - \ln (Z-BP) - \frac{A^2}{B} \left[2 \frac{A_i}{A} - \frac{B_i}{B}\right] \ln \left(1 + \frac{BP}{Z}\right)$$

The terms in this expression are defined in Appendix A.

In its original form, the Chao-Seader correlation is limited to use in systems that form regular solutions. This restriction excludes water since it is a highly polar component.

Water-Hydrocarbon Equilibria

Regular solution theory excludes systems containing water. Yet, water and hydrocarbon systems exist and must be dealt with. These systems frequently have three phases consisting of two liquid phases and one vapor phase.

Usually, the solubilities of water in hydrocarbon or hydrocarbon in water are very small. In many cases, the solubilities are negligible and the two liquid phases may be assumed to be completely immiscible. If Raoult's and Dalton's Laws are assumed to apply, the problem may be solved by standard procedures. Example problems are solved using this approach in Appendix B.

If interphase solubilities are significant, they must be estimated. One way to do this is by comparison to published data. Liquid-liquid solubility data are available for many common hydrocarbons. Table I gives a partial listing of sources that are useful in such cases. Unfortunately, the list is incomplete and most of the data are measured at standard temperature and pressure conditions of 25°C. and 1 atmosphere which limits their usefulness.

TABLE I

LITERATURE REFERENCES FOR WATER-HYDROCARBON EQUILIBRIA DATA

System	Liquid-Liquid Data		Gas-Liquid-Liquid Data	Other
	HC in Water	Water in HC		
Methane, Water	12,30			
Ethane, Water	10,11,35			
Ethylene, Water	1,6			
Propane, Water			20	
Propylene, Water	25			
n-Butane, Water	34		7	
Hexane, Water	22			
Methane, Butane, Water			28	
Butane, Butylene, Water			39	
Benzene, Heptane, Water			29	
Pyridine, Hexane, Water			38	
Misc. Aromatics, Water	5			
Misc. Hydorcarbons, Water	9,27	4,37		
Petroleum Products, Water		17,18		
Hydrogen Sulfide, Methane				21
Carbon Dioxide, Propane				3
Carbon Dioxide, Hydrogen Sulfide, Methane, Water				16

NOTE: Numbers Refer to Bibliography Items

Several correlations have been published for prediction of water-hydrocarbon solubility behavior. Prausnitz and Shair (33) proposed a method for determining liquid phase solubilities which is similar to the present work in that Hildebrand's equation for liquid activity coefficient is used. These authors suggested that their method could be empirically extended to polar solvents. However, they did no more than suggest the possibility. No working correlation was proposed.

Li and McKetta (26) proposed a method based upon graphical determinations of fugacities and fugacity coefficients of components in water solution. Use of this correlation for components other than those studied by the original authors is cumbersome since a great deal of data plotting is required. It is not suitable for computer solution.

Anthony and McKetta (2) published a procedure based upon Hildebrand's solution theories and Scatchard's principle of "cohesive energy density." Extensive volumetric and thermal data are required and the procedure is unworkable for more than three components in solution.

Leinonen, Mackay and Phillips (23) developed a correlation for the solubility of C_4 through C_{10} hydrocarbons in water based upon molecular structure. This procedure is applicable only for binary mixtures of hydrocarbons and water, and it applies only at standard conditions of $25^{o}C.$ and 1 atm. pressure.

All of the above-mentioned correlations are limited in application and degree of reliability. The sample problems in Appendix B, though rather simple in practice, could not be solved using these procedures.

Algorithms for Three-Phase Equilibria

Algorithms for three-phase equilibria have been very slow to develop compared to the procedures used for two-phase vapor-liquid equilibrium.

Osborne (31) proposed a procedure for such calculations based on the principle of simultaneous equilibria. For every component in a three-phase system, there exists two sets of vapor-liquid equilibrium data, one associated with each liquid phase. Calculations may be made since each liquid phase must simultaneously be in equilibrium with the same vapor phase. This means that for two separate liquid phases (A and B) there exists two sets of K-values defined as follows:

$$K_{i_A} = \frac{Y_i}{X_{i_A}} \quad \text{and} \quad K_{i_B} = \frac{Y_i}{X_{i_B}}$$

These two K-values together with basic material balance relationships allowed Osborne to develop two equations which could be solved by a double trial and error procedure to determine the composition of each phase.

Deam and Maddox (13) rederived these equations to make them more suitable for computer solution. They also developed convergence algorithms based upon the Newton-Raphson method in two unknowns.

Erbar (15) has further refined these procedures making them compatible with an earlier developed computer program for two-phase vapor-liquid equilibrium calculations. This algorithm includes procedures for bubble-point and dew-point calculations as well as fixed temperature and pressure flash calculations. The Erbar algorithm consists of the following relationships for each component, i:

$$x_{i_A} = \frac{Z_i}{\frac{L_A}{F}(1-K_{i_A}) + \frac{L_B}{F}\left(\frac{K_{i_A}}{K_{i_B}} - K_{i_A}\right) + K_{i_A}}$$

$$y_i = K_{i_A} X_{i_A} = \frac{K_{i_A} Z_i}{\frac{L_A}{F}(1-K_{i_A}) + \frac{L_B}{F}\left(\frac{K_{i_A}}{K_{i_B}} - K_{i_A}\right) + K_{i_A}}$$

$$X_{i_B} = \frac{y_i}{K_{i_B}} = \frac{K_{i_A} Z_i}{K_{i_B}\left[\frac{L_A}{F}(1-K_{i_A}) + \frac{L_B}{F}\left(\frac{K_{i_A}}{K_{i_B}} - K_{i_A}\right) + K_{i_A}\right]}$$

These, together with the basic material balance equations

$$\sum_i x_{i_A} = 1.0 \quad , \quad \sum_i y_i = 1.0 \quad , \quad \text{and} \quad \sum_i x_{i_A} - \sum_i y_i = 0$$

provide the basis for the double trial and error solution.

Erbar also used the Newton-Raphson procedure in two unknowns to develop the convergence algorithms. The bubblepoint calculations are special cases where the L/F functions are set equal to either 0 or 1 and the temperature or pressure is adjusted by trial and error to obtain convergence.

CHAPTER III

PRESENT WORK

Extension of the Chao-Seader Correlation

The Chao-Seader correlation is defined in Chapter II and reference 8 as follows:

$$K_i = \frac{y_i}{x_i} = \frac{\nu\gamma}{\phi}_i = \frac{\nu_i\gamma_i}{\phi_i}$$

The basic concept of this work was to use the same values of ν_i and ϕ_i for both sets of equilibrium data but to develop a different set of liquid phase activity coefficients, γ_i, for each liquid phase. This would allow the two sets of K data to be calculated as follows:

$$K_{i_A} = \frac{\nu_i\gamma_{i_A}}{\phi_i}$$

$$K_{i_B} = \frac{\nu_i\gamma_{i_B}}{\phi_i}$$

Vapor Fugacity Coefficient, ϕ_i

The original Chao-Seader correlation for vapor fugacity coefficients, based upon the Redlich-Kwong equation of state, was used unaltered in this correlation. The Redlich-Kwong is a relatively simple equation of state involving only two constants. It is reasonably accurate for most hydrocarbons and some non-hydrocarbons.

The Redlich-Kwong equations are also very convenient. Lacking any better way to predict vapor fugacity coefficients, the Redlich-Kwong equation was retained and used for all components, including water.

Pure Component Liquid Fugacity, ν_i

In the Chao-Seader correlation, liquid phase fugacities of pure components were predicted using polynomial functions of reduced temperature, pressure, and Pitzer's acentric factor. Water was excluded from the original Chao-Seader correlation. Therefore, a new polynomial correlation had to be developed for the liquid fugacity of water. To do this data for the pure component liquid fugacity of water were needed.

These data were derived from the experimental equilibrium K-data, back calculating for the values of the pure component liquid fugacity of water.

By definition, the liquid activity coefficient of any component approaches unity as the concentration of that component approaches 100% of the solution. Mathematically, this can be expressed as a limit function:

$$\lim_{X_i \to 1.0} \gamma_i = 1.0$$

Using this concept, the liquid activity coefficient of water in water solution can be ignored. The pure component liquid fugacity can then be derived as follows:

$$\nu_{(H_2O)} = K_{(H_2O)} \phi_{(H_2O)}$$

or

$$\ln \nu_{(H_2O)} = \ln K_{(H_2O)} + \ln \phi_{(H_2O)}$$

Using the Chao-Seader equations for $\phi_{(H_2O)}$, a number of experimental data were plotted as a function of reduced temperature and pressure, as shown in Figure 1. The lines of Figure 1 were extrapolated, smoothed graphically, and fit by standard curve fit procedures into the following polynomial function:

$$\text{Log } \nu_{(H_2O)} = A_0 + A_1/T_R + A_2T_R + A_3T_R^{\ 2}$$

$$+ A_4T_R^{\ 3} + (A_5 + A_6T_R + A_7T_R^{\ 2})P_R$$

$$+ (A_8 + A_9T_R)P_R^{\ 2} - \text{Log } P_R$$

This is the same form of polynomial function used in the original correlation. The values of the constants are as follows:

$A_0 = 444.3928$

$A_1 = -\ 62.55608$

$A_2 = -1226.785$

$A_3 = 1511.249$

$A_4 = -\ 696.3381$

$A_5 = -\ 10.75673$

$A_6 = 37.73094$

$A_7 = -\ 31.52760$

$A_8 = 0$

$A_9 = -\ 3.252798$

The curve fit relationship fits the plotted data within the accuracy of the original experimental data.

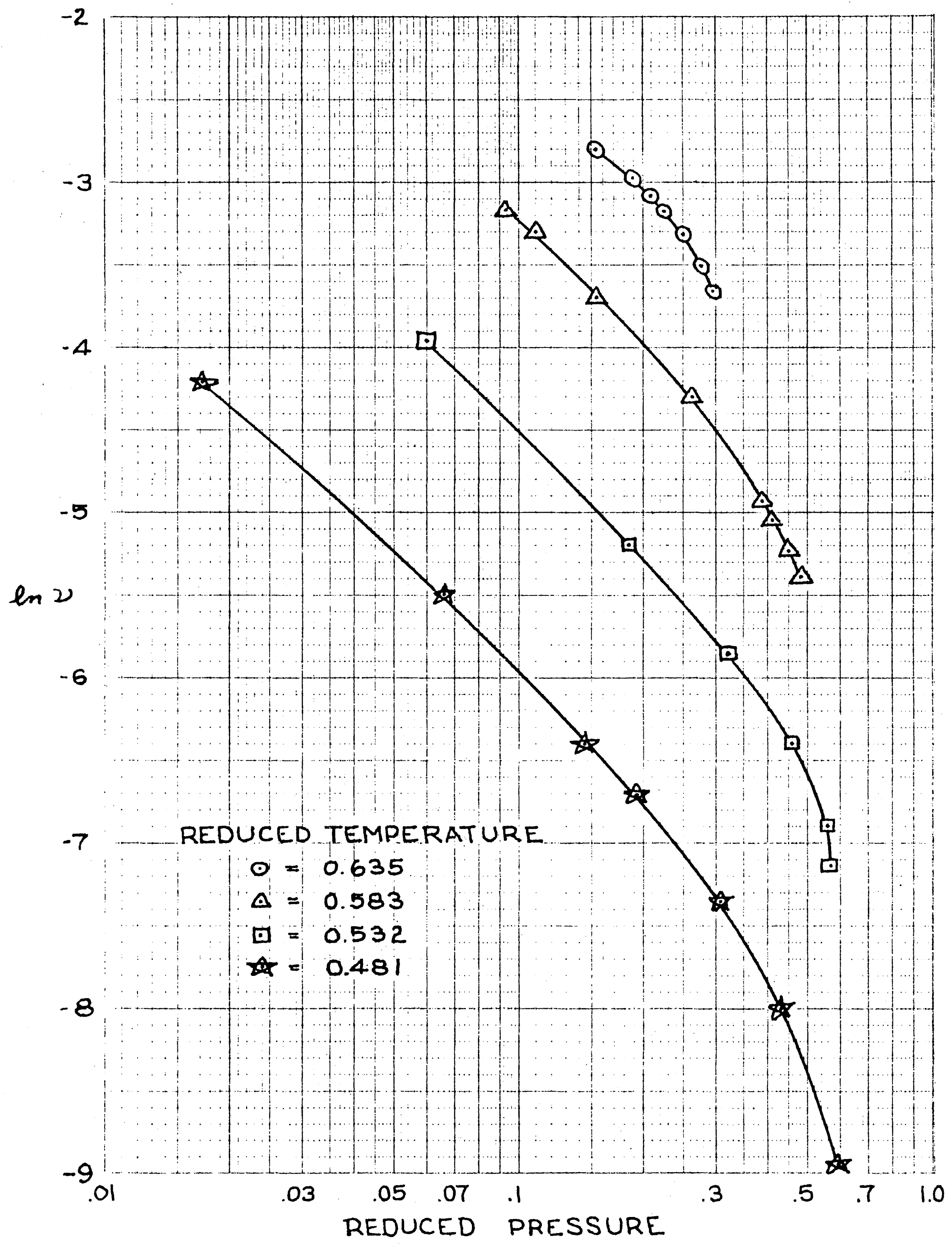

Figure 1. Correlation of Liquid Fugacity of Water (20,28,39)

Hydrocarbon Phase Liquid Activity Coefficients, $\gamma_{i(HC)}$

Chao-Seader used the Hildebrand equation for liquid activity coefficients,

$$\ln \gamma_i = \frac{V_i}{RT} (\delta_i - \bar{\delta})^2$$

and they tabulated the values of the solubility parameter, δ_i, and the liquid molar volume, V_i, for each component included in the original correlation. In some cases, the values of these component properties were adjusted slightly to give the best fit to equilibrium data.

The revised correlation also uses the Hildebrand equation. However, since water is highly non-ideal component in hydrocarbon solution, special values for the solubility parameter had to be back calculated from experimental data. Assuming that the same values of ϕ_i and ν_i can be used for calculation of K-values for either hydrocarbon or water phases, and assuming that $(\gamma_{H_2O})_{H_2O} = 1.0$, the liquid of water was calculated by ratio as follows:

$$(\gamma_{H_2O})_{HC} = (K_{H_2O})_{HC} / (K_{H_2O})_{H_2O}$$

Once values for the $(\gamma_{H_2O})_{HC}$ were determined, the solubility parameter of water was calculated using the following form of the Hildebrand relations:

$$\delta_i = \bar{\delta} + \sqrt{\frac{RT}{V_i} \ln \gamma_i}$$

Since the concentrations of water in hydrocarbon phase are very small, the value of $\bar{\delta}$ can be taken to the same as the volumetric average of the hydrocarbon components, ignoring the contribution of water. The value for V_i used for water was 18.0 ml./g.mole.

Data calculated in this manner are plotted in Figures 2 as a function of temperature. The variation in temperature is significant and must be dealt with. Luckily, a simple linear relationship was all that was needed. The function that was derived is as follows:

$$(\delta_{H_2O})_{HC} = 22.1 - 0.0161\ (T - 560.0)$$

where

T = Temperature, ^{o}R.

Water Phase Liquid Activity Coefficients, $\gamma_{i_{(H_2O)}}$

The Hildebrand equation was also used to determine water phase activity coefficients using a modified set of solubility parameters. All the original Chao-Seader derived solubility parameters for hydrocarbons were left unchanged. However, a new value of the solubility parameter of water in water solution was derived to best fit literature data.

The procedure used was to first determine liquid activity coefficients for various hydrocarbons in water solution. Data from the literature were used to determine γ_i values using the relationship:

$$(\gamma_i)_{H_2O} = \frac{\phi_i}{\nu_i}\ (K_i)_{H_2O}$$

ν_i and ϕ_i are determined using the standard Chao-Seader procedures. The Hildebrand equation is then used to solve for the apparent differences in solubility parameters between the hydrocarbon component and water. The solubility parameter of water is then determined by difference using the known values for the hydrocarbon components.

The calculated values ranged between 13.6 and 14.9 and were scattered. Therefore, the simple arithmetic average of 14.5 was used for the new correlation.

Other Non-Ideal Components

H_2S and CO_2 are also of interest in water-hydrocarbon systems. One source of data (16) had considerable information about the CH_4, H_2S, CO_2, and H_2O system. Using the value of 14.5 for the solubility parameter of water, solubility parameters for CO_2 and H_2S were determined using the same procedure outlines above. The best average values determined for hydrogen sulfide and carbon dioxide were 7.51 and 7.45, respectively.

Summary

The present work extends the Chao-Seader correlation to allow calculation of K-data for both hydrocarbon and water rich liquid phases. A new polynomial function for the pure component liquid fugacity of water was determined. A function for predicting the solubility parameter of water in hydrocarbon solution was derived. Special solubility parameters were developed for water, hydrogen sulfide, and carbon dioxide in aqueous solutions.

CHAPTER IV

DISCUSSION OF RESULTS

For the purposes of this work, the Redlich-Kwong equation for the vapor phase fugacity coefficient was assumed to apply for water as well as all other components considered. The vapor phase activity coefficients were used in turn to derive data for the pure component liquid fugacity of water. No attempt was made to evaluate the sensitivity of the correlation to the equation of state used to determine the vapor fugacity coefficients. A better correlation for the vapor phase could perhaps improve the data derived for the liquid phases.

As can be seen in Figure 1, the data derived for the liquid fugacity of water ranged in reduced temperature from 0.481 to 0.635 and in reduced pressure from 0.017 to 0.600. Any applications of the new correlation outside these limits would be highly suspect. The data were fit to the polynomial function using standard curve fit procedures. The curve fit procedures are mathematically correct and the fit is considered to be at least as accurate as the experimental data themselves. The form of the polynomial was chosen to be consistent with the original Chao-Seader correlation, thus simplifying the computer application of the new correlation.

The original authors chose to ignore the temperature dependence of the solubility parameter for the various components considered.

This was acceptable since the Hildebrand equation is only concerned with the differences in solubility parameters. Chao-Seader found that the differences were relatively insensitive to temperature. Judging from the data plotted in Figure 2, water in hydrocarbon solution is significantly different in temperature-solubility behavior. However, a simple linear relationship gives an adequate fit to the experimental data. The correlation was developed graphically.

The use of a constant for the solubility parameter of water in water solution was necessary since the calculated values were scattered. Since the range of the scatter was relatively small (between 13.6 and 14.9) and the anticipated differences between the solubility parameter of water and any other components are relatively large, the use of the average factor of 14.5 is not considered to be a major drawback.

To test the new correlation, three sets of three phase experimental data were simulated with the new correlation. In each calculation, the experimental vapor phase composition and pressure were fixed and the dew point temperature was determined. Tables II, III, and IV are tabulations of the results of those calculations compared to the experimental data.

The calculated dew point temperatures agree quite well with the experimental data. These comparisons of experimental and calculated data are indications that under the right conditions the new correlation will do a reasonably good job of predicting actual phase conditions in three phase systems. However, the data are insufficient for any meaningful statistical analysis.

Appendix B contains several sample calculations that show that the new procedure is applicable to multicomponent systems. These

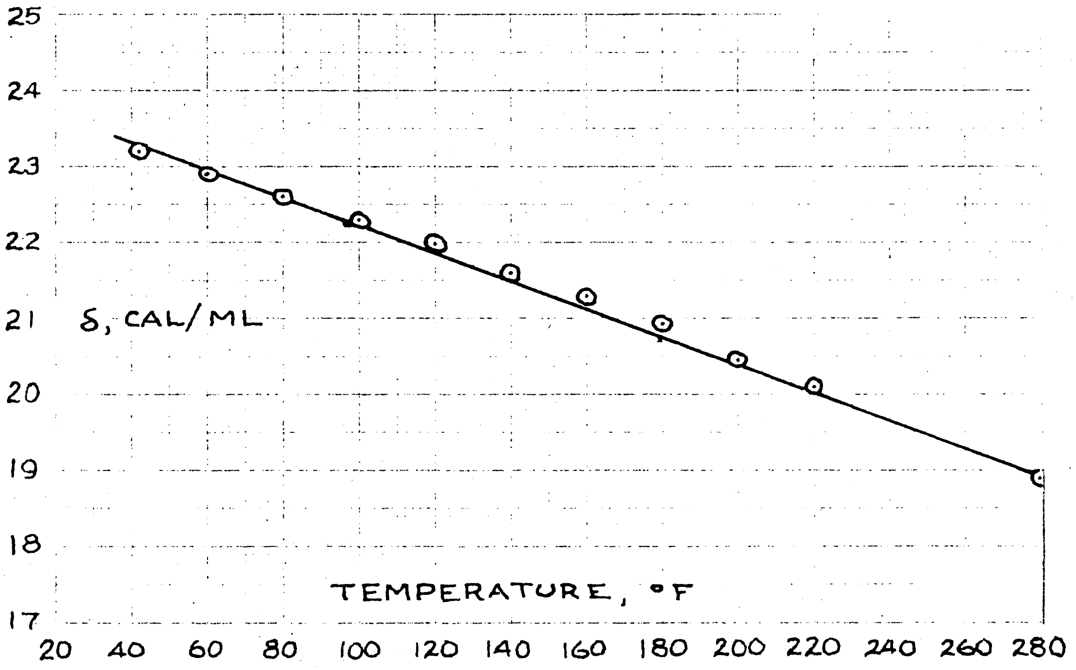

Figure 2. Solubility Parameter of Water (20,28,39)

TABLE II

DATA COMPARISON: PROPANE, WATER SYSTEM (DEW POINT CALCULATIONS USING EXPERIMENTAL VAPOR PHASE COMPOSITIONS)

Pressure	Temperature °F		$(K_{H_2O})_{H_2O}$		$(K_{H_2O})_{HC}$	
Psia	Exp	Calc	Exp	Calc	Exp	Calc
82.2	42.3	45.8	.00140	.00149	13.33	10.5
108.5	60.0	63.8	.00218	.00247	11.66	9.59
146.0	80.0	84.3	.00335	.00387	9.74	7.99
191.5	100.0	104.	.00465	.00550	7.56	6.46
246	120	123	.00625	.00738	5.73	5.23
311	140	143	.00813	.00963	4.42	4.31
389	160	161	.01002	.0124	3.44	3.63
432	170	171	.01097	.0140	3.06	3.38
483	180	180	.01191	.0160	2.67	3.15
538	190	190	.01280	.0183	2.29	2.97
468	195	194	.01278	.0216	2.02	3.25
602	200	198	.01237	.0231	1.71	3.23
637	206	203	.00998	.00998	1.0	3.19

Source: Reference (20)

TABLE III

DATA COMPARISON: METHANE, N-BUTANE, WATER SYSTEM (DEW POINT CALCULATIONS USING EXPERIMENTAL VAPOR PHASE COMPOSITIONS)

Pressure	Temperature °F		$(K_{H_2O})_{H_2O}$		$(K_{H_2O})_{HC}$	
Psia	Exp	Calc	Exp	Calc	Exp	Calc
631	100	101	.00184	.00215	2.196	1.98
202	100	104	.00568	.00589	8.68	4.71
1406	100	103	.00103	.00118	1.19	1.15
979	100	106	.00132	.00152	1.51	1.48
474	100	101	.00232	.00270	2.86	2.41
212	100	103	.00485	.00562	7.01	4.51
1838	100	105	.000860	.000971	1.04	.965
1900	100	100	.000842	.00840	1.01	1.07
1910	100	95	.000833	.000935	.999	1.22
1912	100	94	.000837	.000834	1.00	1.28
1880	100	104	.000843	.000950	1.02	.968
1220	100	100	.00106	.00122	1.29	1.27
1683	160	165	.00381	.00379	1.09	.973
1479	160	166	.00430	.00480	1.23	1.05
1022	160	159	.00540	.00537	1.74	1.46
192	160	162	.0221	.0247	9.13	4.95
1635	160	168	.00399	.00443	1.13	.933
1729	160	161	.00367	.00403	1.03	.978
1051	160	160	.00539	.00607	1.64	1.42
1796	160	155	.00354	.00387	.957	1.09
604	160	156	.00783	.00886	2.79	2.10
1810	160	154	.00360	.00392	.997	1.13

Source: Reference (28)

TABLE IV

DATA COMPARISON: N-BUTANE, 1-BUTENE, WATER SYSTEM (DEW POINT CALCULATIONS USING EXPERIMENTAL VAPOR PHASE COMPOSITIONS)

Pressure Psia	Temperature °F		$(K_{H_2O})_{H_2O}$		$(K_{H_2O})_{HC}$	
	Exp	Calc	Exp	Calc	Exp	Calc
52.2	100	102.2	.0151	.0169	24.4	15.6
53.3	100	102.5	.0147	.0167	20.4	15.2
54.5	100	103.0	.0143	.0166	17.4	14.9
55.6	100	103.3	.0138	.0164	14.8	14.6
56.8	100	103.7	.0134	.0163	13.0	14.2
57.9	100	104.0	.0130	.0161	11.4	13.9
58.9	100	104.3	.0126	.0160	10.1	13.7
60.0	100	104.6	.0122	.0158	9.17	13.4
61.0	100	104.9	.0118	.0157	8.25	13.2
62.0	100	105.1	.0114	.0155	7.50	13.0

Source: Reference (39)

sample problems were constructed to be representative of systems of interest in the design of hydrocarbon processing units.

The new procedure is easily as simple to use as the standard Chao-Seader correlation and the predicted solubilities agree well with those calculated using solubility data from the API Technical Data Book. An added advantage of the new correlation is that the multicomponent compositions of hydrocarbons in water solution are predicted. This cannot be done with the standard procedure using binomial solubility data.

CHAPTER V

RECOMMENDATIONS

There is a need for a three-phase flash correlation such as developed in this work. This type of correlation would have many applications. Water-hydrocarbon separations are particularly important, and no procedures are available that are both accurate and convenient to use. While the extended Chao-Seader correlation developed in this work is both reasonably accurate and convenient, it could be improved.

The first thing that is needed is more experimental data involving three equilibrium phases over a wide range of temperature and pressure. The correlation developed here is based on data for systems of methane, propane, n-butane, and butylene. This is a rather limited list to say the least. More data are needed to make this or any similar correlation reliable for wide ranges of temperature, pressure, and composition.

A second thing that would improve the accuracy of this procedure is a better correlation for the vapor phase fugacity coefficient of water, perhaps based on a different equation of state than the Redlich-Kwong. This could in turn be used to rederive the correlation for the pure component fugacity of water.

The correlation could be extended further by considering chemical interactions of components in water solution. Chemical equilibria relationships have been developed for a number of these systems which could be included in the basic phase equilibria calculations. A combined correlation of this type would be very useful in designing systems for hydrogen sulfide removal. It also could be used to adjust operating conditions to obtain more optimum results.

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APPENDIX A

CHAO-SEADER EQUATIONS AND CONSTANTS

Introduction

The Chao-Seader correlation for vapor-liquid equilibrium takes the general form:

$$K_i = \frac{Y_i}{x_i} = \frac{\nu_i \gamma_i}{\phi_i}$$

where ν_i is the liquid-phase fugacity of the component. γ_i is the liquid-phase activity coefficient of the component and ϕ_i is the component vapor-phase fugacity coefficient.

Liquid Fugacity of Pure Components

The liquid-phase fugacity is a pure liquid component property which is correlated within the framework of Pitzer's modified form of the principle of corresponding states. Accordingly, ν is given by

$$\log \nu = \log \nu^{(0)} + \omega \log \nu^{(1)}$$

The first term on the right-hand side of the equation gives the fugacity of a simple fluid characterized by a zero value of the acentric factor. The second term accounts for deviation from the properties of the simple fluid. The two quantities $\nu^{(0)}$ and $\nu^{(1)}$ are functions of reduced temperature and pressure only. The term

$\nu^{(0)}$ is given by

$$\log \nu^{(0)} = A_0 + A_1/T_R + A_2T_R^{\ 2} + A_3T_R^{\ 3} + (A_5 + A_6T_R + A_7T_R)^2P_R + (A_8 + A_9T_R)P_R^{\ 2} - \log P_R$$

$\nu^{(1)}$ is given by:

$$\log \nu^{(1)} = -4.23893 + 8.56808\ T_R - 1.22060/T_R - 3.15224\ T_R^{\ 2} - 0.025\ (P_R - 0.6)$$

The constants in the first equation are given in the following table:

TABLE V

CHAO-SEADER POLYNOMIAL COEFFICIENTS

	Simple Fluid	Methane	Hydrogen
A_0	5.75748	2.43840	1.96718
A_1	-3.01761	-2.24550	1.02972
A_2	-4.98500	-0.34084	-0.054009
A_3	2.02299	0.00212	0.0005288
A_4	0.00000	-0.00223	0.000000
A_5	0.08427	0.10486	0.008585
A_6	0.26667	-0.03691	0.000000
A_7	-0.31138	0.00000	0.00000
A_8	-0.02655	0.00000	0.00000
A_9	0.02883	0.00000	0.00000

The constants are different for methane and hydrogen because these two components required special derivations of the general function. The acentric factors for methane and hydrogen are taken as zero, which makes the second function non-applicable. Table VI shows the remainder of the component acentric factors published in the original correlation.

Activity Coefficient in Liquid Solution

Liquid solutions of hydrocarbons are considered to be regular solutions. The liquid activity coefficients are represented by the following equation originally proposed by Hildebrand (19).

$$\ln \gamma_i = \frac{V_i(\delta_i - \bar{\delta})^2}{RT}$$

The constants V_i and δ_i are the liquid molar volume and the solubility parameter of the component, respectively. The term $\bar{\delta}$ designates the volumetric average of the solubility parameters of the components in liquid solution.

$$\bar{\delta} = \frac{\Sigma_i X_i V_i \delta_i}{\Sigma_i X_i V_i}$$

The values of the constants δ_i and V_i given in the original correlation as shown in Table VI. These constants were derived at standard conditions of 25°C. and 1 atm. except for a few which were specially derived to fit experimental data.

Fugacity Coefficient in Vapor Phase

The third parameter in the Chao-Seader correlation is the component's fugacity coefficient in the vapor phase mixture, ϕ_i. The

TABLE VI

CHAO-SEADER CONSTANTS OF PURE COMPONENTS

Component	Modified ω	δ_i (cal/ml)	V_i ml/g.-mole
Hydrogen	0	3.25	31
Paraffins			
Methane	0	5.68	52
Ethane	0.1064	6.05	68
Propane	0.1538	6.40	84
i-Butane	0.1825	6.73	105.5
n-Butane	0.1953	6.73	101.4
i-Pentane	0.2104	7.02	117.4
n-Pentane	0.2387	7.02	116.1
neo-Pentane	(0.195)	7.02	123.3
n-Hexane	0.2927	7.27	131.6
n-Heptane	0.3403	7.430	147.5
n-Octane	0.3992	7.551	163.5
n-Nonane	0.4439	7.65	179.6
n-Decane	0.4869	7.72	196.0
n-Undecane	0.5210	7.70	212.2
n-Dodecane	0.5610	7.84	228.6
n-Tridecane	0.6002	7.89	244.9
n-Tetradecane	0.6399	7.92	261.3
n-Pentadecane	0.6743	7.96	277.8
n-Hexadecane	0.7078	7.99	294.1
n-Heptadecane	0.7327	8.03	310.4
Olefins			
Ethylene	0.0949	6.08	61
Propylene	0.1451	6.43	79
1-Butene	0.2085	6.76	95.3
cis-2-Butene	0.2575	6.76	91.2
trans-2-Butene	0.2230	6.76	93.8
i-Butene	0.1975	6.76	95.4
1, 3-Butadiene	0.2028	6.94	88.0
1-Pentene	0.2198	7.05	110.4
cis-2-Pentene	(0.206)	7.05	107.8
trans-2-Pentene	(0.209)	7.05	109.8
2-Methyl-1-Butene	(0.200)	7.05	108.7
3-Methyl-1-Butene	(0.149)	7.05	112.8
2-Methyl-2-Butene	(0.212)	7.05	106.7
1-Hexene	0.2463	(7.40)	125.8

TABLE VI (Continued)

Component	Modified ω	δ_i (cal/ml)	V_i ml/g.-mole
Napthenes			
Cyclopentane	0.2051	8.11	94.7
Methylcyclopentane	0.2346	7.85	113.1
Cyclohexane	0.2032	8.20	108.7
Methylcyclohexane	0.2421	7.83	128.3
Aromatics			
Benzene	0.2130	9.16	89.4
Toluene	0.2591	8.92	106.8
o-Xylene	0.2904	8.99	121.2
m-Xylene	0.3045	8.82	123.5
p-Xylene	0.2969	8.77	124.0
Ethylbenzene	0.2936	8.79	123.1

The following expression is used which is derived from the Redlich-Kwong equation of state (36).

$$\ln \phi_i = (Z - 1) \frac{B_i}{B} - \ln (Z - BP) - \frac{A^2}{B} \left[2 \frac{A_i}{A} - \frac{B_i}{B}\right] \ln \left(1 + \frac{BP}{Z}\right)$$

where

$$Z = \frac{1}{1 - h} - \frac{A^2}{B} \frac{h}{1 + h}$$

$$h = \frac{BP}{Z}$$

$$A = \Sigma_i Y_i A_i$$

$$A_i = \left(\frac{0.4278}{P_{c_i} T_{R_i}} 2.5\right)^{0.5}$$

$$B = \Sigma_i Y_i B_i$$

$$B_i = \frac{0.0867}{P_{C_i} T_{R_i}}$$

APPENDIX B

SAMPLE PROBLEMS

Three sample problems are included to demonstrate the conventional procedure using Raoult's Law (procedure A) and the use of the extended Chao-Seader procedure developed as part of this work (procedure B).

The sample problems are all multicomponent mixtures of hydrocarbons and water. Problems 1 and 2 also contain hydrogen sulfide in the system.

Solution by Raoult's Law (procedure A) involves the following assumptions and steps:

1. The two liquid phases are assumed to be immiscible, each exerting its own vapor pressure.
2. The partial pressure of water in the vapor phase is the same as the vapor pressure of water at the system temperature. The partial pressure of the hydrocarbon liquid phase is equal to the system pressure less the water partial pressure.
3. The vapor phase concentration of water is assumed equal to its vapor pressure divided by the system pressure. (Raoult's Law)

For each of the sample problems, the hydrocarbon partial pressure was determined and conventional flash calculations were made for the hydrocarbons at the hydrocarbon partial pressure. The liquid-vapor distribution of water is thus calculated using assumption 3 above. Since the two liquid phases were entirely assumed to be immiscible, there is no distribution of components calculated between the two liquid phases.

Procedure B is the technique developed as part of this work and is completely described in Chapter III.

TABLE VII

SAMPLE PROBLEM 1

TEMPERATURE = 116°F, PRESSURE = 24.2 PSIA

Component	Feed Moles/Hr	Liquid A Moles/Hr	Liquid B Moles/Hr	Vapor Moles/Hr
	PROCEDURE A			
Hydrogen	10.90	0.01	0	10.89
Methane	43.00	0.16	0	42.84
Ethylene	14.70	0.17	0	14.53
Ethane	28.80	0.45	0	28.35
Propylene	82.40	3.66	0	78.74
Propane	28.30	1.40	0	26.90
1-Butene	75.70	10.08	0	65.62
Isobutane	37.80	4.22	0	33.58
N-Butane	12.50	1.81	0	10.69
1-Pentene	50.30	16.12	0	34.18
Isopentane	27.30	8.01	0	19.29
N-Pentane	8.40	2.90	0	5.50
Hexane plus	220.40	216.62	0	3.78
Nitrogen	26.50	0.03	0	26.47
Carbon Dioxide	4.60	0.05	0	4.55
Hydrogen Sulfide	1.10	0.05	0	1.06
Water	247.00	0	217.96	29.04
	919.70	265.74	217.96	436.00

H_2O Vapor Pressure at 116°F. = 1.512 psia

HC Partial Pressure = 24.2 - 1.5 = 22.7 psia
(Flash made at 22.7 psia)

Vapor Concentration of H_2O = 1.512/22.7 = 0.0666

Moles of HC Vapor = 406.96

$$\text{Moles of } H_2O \text{ Vapor} = \frac{0.0666\ (406.96)}{1.0 - 0.0666}$$

Moles of H_2O Liquid = 247 - 29.04 = 217.96

TABLE VII (Continued)

Component	Feed Moles/Hr	Liquid A Moles/Hr	Liquid B Moles/Hr	Vapor Moles/Hr
	PROCEDURE B			
Hydrogen	10.90	0.01	0	10.89
Methane	43.00	0.16	0	42.84
Ethylene	14.70	0.17	0	14.53
Ethane	28.80	0.45	0	28.35
Propylene	82.40	3.69	0	78.71
Propane	28.30	1.41	0	26.89
1-Butene	75.70	10.15	0	65.55
Isobutane	37.80	4.25	0	33.55
N-Butane	12.50	1.82	0	10.68
1-Pentene	50.30	16.20	0	34.10
Isopentane	27.30	8.04	0	19.26
N-Pentane	8.40	2.91	0	5.49
Hexane plus	220.40	216.60	0.06	3.74
Nitrogen	26.50	0.03	0	26.47
Carbon Dioxide	4.60	0.05	0	4.55
Hydrogen Sulfide	1.10	0.04	0	1.06
Water	247.00	1.52	223.30	22.16
	919.70	267.51	223.36	428.83

TABLE VIII

SAMPLE PROBLEM 2

TEMPERATURE = 120°F, PRESSURE = 97.2 PSIA

Component	Feed Moles/Hr	Liquid A Moles/Hr	Liquid B Moles/Hr	Vapor Moles/Hr
	PROCEDURE A			
Hydrogen	11.4	0.07	0	11.33
Methane	45.8	1.75	0	44.05
Ethylene	16.8	1.77	0	15.03
Ethane	44.3	6.19	0	38.11
Propylene	83.5	26.10	0	57.40
Propane	35.7	12.09	0	23.61
Butylene	75.5	44.45	0	31.27
Isobutane	37.8	20.55	0	17.25
N-Butane	12.5	7.65	0	4.85
Pentene	50.3	40.52	0	9.78
Isopentane	27.3	21.44	0	5.86
N-Pentane	8.4	6.90	0	1.50
Hexane plus	221.0	220.34	0	0.66
Nitrogen	27.8	0.38	0	27.42
Carbon Dioxide	4.6	0.43	0	4.17
Hydrogen Sulfide	1.0	0.23	0	0.77
Water	550.0	0.0	544.81	5.19
	1253.9	410.84	544.81	298.25

H_2O Vapor Pressure at 120°F. = 1.692 psia

HC Partial Pressure = 97.2 - 1.7 = 95.5 psia
(Flash Made at 95.5 psia)

Vapor Concentration of H_2O = 1.692/97.2 = 0.0174

Moles HC Vapor = 293.06

$$\text{Moles } H_2O \text{ Vapor} = \frac{0.0174\ (293.06)}{1.0 - 0.0174} = 5.19$$

Moles H_2O Liquid Phase = 550 - 5.19 = 544.81

TABLE VIII (Continued)

Component	Feed Moles/Hr	Liquid A Moles/Hr	Liquid B Moles/Hr	Vapor Moles/Hr
	PROCEDURE B			
Hydrogen	11.4	0.07	0	11.33
Methane	45.8	1.64	0.01	44.14
Ethylene	16.8	1.67	0	15.13
Ethane	44.3	5.85	0.01	38.45
Propylene	83.5	24.94	0.01	58.54
Propane	35.7	11.57	0	24.12
Butylene	75.7	43.24	0.01	32.45
Isobutane	37.8	19.94	0	17.86
N-Butane	12.5	7.46	0	5.04
Pentene	50.3	40101	0	10.28
Isopentane	27.3	21.15	0	6.15
N-Pentane	8.4	6.83	0	1.57
Hexane plus	221.0	220.20	0.11	0.70
Nitrogen	27.8	0.35	0	27.45
Carbon Dioxide	4.6	0.41	0.02	4.17
Hydrogen Sulfide	1.0	0.22	0.01	0.77
Water	550.0	1.84	543.50	4.66
	1253.9	407.38	543.70	302.82

TABLE IX

SAMPLE PROBLEM 3

TEMPERATURE = 104°F, PRESSURE = 547.2

Component	Feed Moles/Hr	Liquid A Moles/Hr	Liquid B Moles/Hr	Vapor Moles/Hr
		PROCEDURE A		
Hydrogen	1630.0	35.39	0	1594.61
Methane	245.0	30.30	0	214.70
Ethane	240.5	94.24	0	146.26
Propane	176.2	116.28	0	59.92
Isobutane	7.3	5.96	0	1.34
N-Butane	4.8	4.11	0	0.69
Isopentane	1.9	1.77	0	0.13
N-Pentane	3.8	3.59	0	0.21
Hexane plus	1442.0	1438.87	0	3.14
Water	500.0	0.00	496.05	3.95
	4251.5	1730.50	496.05	2024.95

H_2O Vapor Pressure at 104°F. = 1.0689 psia

HC Partial Pressure = 547.2 - 1.1 = 546.1 psia
(Flash made at 546.1 psia)

Vapor Concentration of H_2O = 1.0689/547.2 = 0.00195

Moles HC Vapor = 2021.0

$$\text{Moles } H_2O \text{ Vapor} = \frac{0.00195\ (2021.0)}{1.0 - 0.00195} = 3.95$$

Moles H_2O Liquid = 500 - 3.95 = 496.05

Component	Feed Moles/Hr	Liquid A Moles/Hr	Liquid B Moles/Hr	Vapor Moles/Hr
		PROCEDURE B		
Hydrogen	1630.0	35.42	0.05	1594.52
Methane	245.0	30.31	0.04	214.65
Ethane	240.5	94.24	0.01	146.25
Propane	176.2	116.26	0.01	59.94
Isobutane	7.3	5.96	0.00	1.34
N-Butane	4.8	4.11	0.00	0.69
Isopentane	1.9	1.77	0.00	0.13
N-Pentane	3.8	3.59	0.00	0.21
Hexane plus	1442.0	1438.86	0.01	3.14
Water	500.0	4.25	492.13	3.61
	4251.5	1734.77	492.25	2024.48

a

VITA

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