COMPUTATION OF BINARY VAPOR-LIQUID EQUILIBRIUM DATA FROM TOTAL PRESSURE DATA*

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A precise procedure is presented to estimate vapor compositions from the total pressure and liquid composition data for isothermal binary systems. The method is based upon the Gibbs-Duhem equation. Forsythe orthogonal polynomials were used to correlate the total pressure data in terms of liquid mole fraction. The numerical integration of the Gibbs-Duhem equation was carried out by using the Runge-Kutta-Gill method. Calculated results for the binary chloroform-ethanol system are in better agreement with experimental data than are those by the previous methods.

Introduction

Several methods have been proposed for the calculation of equilibrium vapor compositions from total pressure and liquid composition data^{1,3-5,7-9,13,16}. These methods are classified into two types: the first method consists in calculating vapor compositions by direct integration of a first-order differential equation derived from the Gibbs-Duhem equation. The Redlich-Kister type equation was used to correlate the total pressure data in terms of liquid mole fraction. The second method involves the calculation of the liquid activity coefficient to obtain subsequent best fit to the experimental vapor pressure data. This method avoids numerical integration. The accuracy of the method seems to depend on the analytical form used to express the liquid activity coefficients.

Recently Vera and Prausnitz¹⁷ determined the constants of the Redlich-Kister and Wilson equations from total pressure data for binary hydrocarbon mixtures. Subsequent calculations showed that excess free energies from these two equations differ slightly from each other. This suggests that the well-known equations such as the Redlich-Kister and Wilson are not always perfect in the determination of vapor composition. Further, the Wilson equation is found to be quite useful in correlation of vapor-liquid equilibria, but to be unsuccessful in some cases, as pointed out by Nagata¹⁰. Therefore, this investigation presents a method to obtain vapor compositions from total pressure data. The method uses a set of Forsythe polynomials^{2,15} to cover the total pressure data.

Calculation Procedure for Equilibrium Vapor Compositions

At constant temperature, a coexistence equation for binary vapor-liquid equilibria is derived by Ljungrin and Van Ness⁵ as follows.

$$\frac{dy_1}{dP} = \frac{\phi - (1-2y_1)(y_1-x_1)(\delta_{12}/RT)}{\frac{y_1-x_1}{y_1(1-y_1)} - (y_1-x_1)(2P\delta_{12}/RT)} \quad (1)$$

Multiplication of Eq.(1) by dP/dx_1 gives

$$\frac{dy_1}{dx_1} = \frac{\phi - (1-2y_1)(y_1-x_1)(\delta_{12}/RT)}{\frac{y_1-x_1}{y_1(1-y_1)} - (y_1-x_1)(2P\delta_{12}/RT)} \left(\frac{dP}{dx_1} \right) \quad (2)$$

where ϕ is given for low pressures to a very close approximation by

$$\phi = \frac{y_1 y_2 \delta_{12} - v^L + x_1 B_{11} + x_2 B_{22}}{RT} + \frac{1}{P} \quad (3)$$

In Eq.(2), P and dP/dx_1 are calculated from $P-x$ relation correlated by a set of orthogonal polynomials described by Forsythe. That is, the total pressure P is represented as

$$P = C_1 F_1(x_1) + C_2 F_2(x_1) + C_3 F_3(x_1) + \dots + C_j F_j(x_1) \quad (4)$$

where $F(x_1)$'s are the orthogonal polynomials and are given by

$$\begin{aligned} F_1(x_1) &= 0 \\ F_2(x_1) &= 1 \\ F_3(x_1) &= (x_1 - A_3)F_2(x_1) - B_2 F_1(x_1) \\ F_4(x_1) &= (x_1 - A_4)F_3(x_1) - B_3 F_2(x_1) \\ &\dots \dots \dots \\ F_j(x_1) &= (x_1 - A_j)F_{j-1}(x_1) - B_{j-1} F_{j-2}(x_1) \end{aligned} \quad (5)$$

First to 10th polynomials were necessary for the chloroform-ethanol system described below. A_j , B_{j-1} , C_j are constants to be obtained from experimental points.

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$$A_j = \frac{\sum_{k=1}^N x_{1k} [F_{j-1}(x_{1k})]^2}{\sum_{k=1}^N [F_{j-1}(x_{1k})]^2} \quad (6)$$

$$B_{j-1} = \frac{\sum_{k=1}^N x_{1k} F_{j-2}(x_{1k}) F_{j-1}(x_{1k})}{\sum_{k=1}^N [F_{j-2}(x_{1k})]^2} \quad (7)$$

$$C_j = \frac{\sum_{k=1}^N P_k F_j(x_{1k})}{\sum_{k=1}^N [F_j(x_{1k})]^2} \quad (8)$$

Table 1 Second virial coefficients and molar volumes					
System	Temp. [°C]	B_{11} [cc/mol]	B_{22} [cc/mol]	B_{12} [cc/mol]	v_1^L v_2^L [cc/mol]
Chloroform(1)-35		-1173	-1920	-1520	81.7
Ethanol(2)					59.3
	55	-963	-1523	-1217	83.8
					60.7

Table 2 Calculated results for chloroform(1)-ethanol(2) system at 35°C

x_1	P [mmHg]		exptl. ^a	y_1		
	exptl. ^a	calc. This work		calc.		
				(I) ^b	This work (II) ^c	Tao ⁽⁶⁾
0.050	121.58	121.57	0.2000	0.1972	0.2000	0.2006
0.100	143.23	143.26	0.3588	0.3538	0.3557	0.3589
0.150	166.80	166.90		0.4774	0.4787	0.4833
0.200	190.19	189.77	0.5754	0.5671	0.5681	0.5750
0.250	210.00	210.52		0.6320	0.6328	0.6359
0.300	228.88	228.65	0.6844	0.6798	0.6805	0.6862
0.350	244.10	244.12		0.7160	0.7165	0.7221
0.400	257.17	257.14	0.7446	0.7442	0.7447	0.7496
0.450	268.00	267.99		0.7668	0.7672	0.7720
0.500	276.98	276.94	0.7858	0.7853	0.7857	0.7906
0.550	284.10	284.26		0.8009	0.8013	0.8050
0.600	290.20	290.17	0.8136	0.8144	0.8147	0.8182
0.650	295.10	294.93		0.8264	0.8267	0.8307
0.700	298.53	298.75	0.8378	0.8377	0.8379	0.8401
0.750	302.10	301.87		0.8491	0.8493	0.8527
0.800	304.22	304.40	0.8618	0.8617	0.8619	0.8637
0.850	306.30	306.24		0.8769	0.8770	0.8804
0.900	306.84	306.84	0.8976	0.8942	0.8945	0.8976
0.950	304.89	304.89	0.9304	0.9274	0.9304	0.9232

^a Interpolated values in ref. (14)

^b from only $P-x$ data

^c Used y data at $x_1 = 0.05, 0.95$

Table 3 Calculated results for chloroform(1)-ethanol(2) system at 55°C

x_1	P [mmHg]		exptl. ^a	y_1		
	exptl. ^a	calc. This work		calc.		
				This work (I) ^b	(II) ^c	Mixon <i>et al.</i> ⁹⁾
0.050	320.64	320.65	0.1694	0.1709	0.1694	0.1750
0.100	364.32	364.30	0.3054	0.3054	0.3044	0.3139
0.150	409.80	409.80		0.4155	0.4148	0.4211
0.200	452.00	452.07	0.4988	0.4985	0.4980	0.5033
0.250	489.25	489.22		0.5607	0.5603	0.5666
0.300	521.14	521.02	0.6108	0.6083	0.6080	0.6158
0.350	547.85	547.94		0.6459	0.6456	0.6546
0.400	570.62	570.60	0.6774	0.6764	0.6762	0.6854
0.450	589.50	589.58		0.7020	0.7018	0.7105
0.500	605.23	605.35	0.7252	0.7238	0.7236	0.7314
0.550	618.60	618.27		0.7429	0.7427	0.7494
0.600	628.77	628.73	0.7598	0.7600	0.7599	0.7657
0.650	636.75	637.08		0.7759	0.7758	0.7813
0.700	643.65	643.68	0.7914	0.7914	0.7913	0.7972
0.750	648.95	648.73		0.8077	0.8076	0.8139
0.800	652.23	652.13	0.8264	0.8258	0.8258	0.8311
0.850	652.95	653.24		0.8460	0.8461	0.8396
0.900	650.84	650.68	0.8774	0.8776	0.8782	0.8723
0.950	642.22	642.25	0.9226	0.9203	0.9226	0.9234

^a Interpolated values in ref.(14)

^b From only $P-x$ data

^c Used y data at $x_1 = 0.05, 0.95$

A. Pressure vs. composition diagram
B. $x-y$ diagram
C. Activity coefficient vs. composition diagram

Fig. 1 Chloroform(1)-ethanol(2) at 35°C

where N is the number of data points.

The second virial coefficients B_{11} , B_{22} and the second virial cross coefficient B_{12} in Eq.(3) were calculated from a correlation based on the corresponding states theory of O'Connell and Prausnitz¹¹). An additional factor δ_{12} was evaluated by $\delta_{12}=2B_{12}-B_{11}-B_{22}$. The molar volume v^L of the mixture was mole fraction average of pure component volumes. The equilibrium vapor compositions were successively obtained by the Runge-Kutta-Gill numerical integration of Eq.(2).

The chloroform(1)-ethanol(2) system presented here was chosen because it is a highly nonideal system and the data are of the highest quality. The integration procedure started from the pure component compositions toward an azeotrope. We carried out numerical integration of Eq.(2) using the starting values of y_1 at $x_1=0.05$ and $x_1=0.95$ in two cases:

- (I) The starting values were calculated from the total pressure data in accordance with

A. Pressure vs. composition diagram
B. $x-y$ diagram
C. Activity coefficient vs. composition diagram

Fig. 2 Chloroform(1)-ethanol(2) at 55°C

the method described in detail in Hala's monograph³).

- (II) The starting values were taken from experimental vapor mole fraction data.

An increment of x_1 was taken to be 0.001 mole fraction.

Calculation of Activity Coefficients

The activity coefficients are calculated from the following equation, using computed values of y_i .

$$\gamma_i = \frac{\varphi_i y_i P}{\varphi_i^s x_i P_i^s \exp[v_i^L(P - P_i^s)/RT]} \quad (9)$$

where vapor-phase nonideality is taken into consideration and the partial molar volume of component

i is assumed to be equal to the saturated molar volume of pure liquid i . The fugacity coefficient is calculated by using the virial equation truncated after the second term^{6,12}.

Calculated Results

Calculations were done for the chloroform(1)-ethanol(2) system at 35° and 55°C.

Table 1 presents the second virial coefficients and molar volumes for the pure components.

Calculated vapor-liquid equilibrium data are compared with experimental results in **Tables 2** and **3**. Calculated vapor compositions are nearly the same in two cases and the calculated data are in excellent agreement with experimental data. This may come mainly from the fact that the orthogonal polynomials are successful in a nearly complete fit of the experimental total pressure data for the present system. **Figs. 1** and **2**, respectively, show calculated and experimental total pressures, vapor compositions and activity coefficients against liquid compositions. In these figures we represented the calculated vapor compositions and calculated activity coefficients in both cases using a single solid line, because the one is so close to the other that we could not separate them.

Root-mean-square deviations in P and y_1 are summarized as

ΔP [mmHg]	Δy_1		
	(I)	(II)	
0.19	0.0037	0.0031	at 35°C
0.15	0.0013	0.0013	at 55°C

Tables 2 and 3 involve, respectively, the calculated values of y_1 of Tao¹⁶) and Mixon *et al.*⁹) for comparison. Apparently, the present method gives results of a high degree of accuracy.

Conclusions

The Forsythe polynomials fit accurately the total pressure-liquid composition data of a strongly nonideal system such as chloroform-ethanol. Once the total pressure data are represented by the polynomials, numerical integration of the coexistence equation gives precise equilibrium vapor composition. However, it is to be noted that the polynomials are very sensitive to any experimental errors, which reduces the accuracy of the present method to obtain vapor composition. The method is entirely rigorous. Calculated results for the chloroform-ethanol system are in excellent agreement with the experimental data.

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Nomenclature

A_j	= constant as defined in Eq.(6)	
B_j	= constant as defined in Eq.(7)	
B_{11}, B_{22}, B_{12}	= second virial coefficients	[cc/mol]
C_j	= constant as defined in Eq.(8)	
F_j	= orthogonal function as defined in Eq.(5)	
P	= total pressure	[mmHg]
P_i^s	= saturation pressure of pure component i	[mmHg]
R	= gas constant	
T	= absolute temperature	[°K]
v_i^L	= molar liquid volume of pure component i	[cc/mol]
x_i	= liquid-phase mole fraction of component i	
y_i	= vapor-phase mole fraction of component i	
<Greek letters>		
γ_i	= activity coefficient of component i	
δ_{12}	= additional factor as defined by $\delta_{12} = 2B_{12} - B_{11} - B_{22}$	[cc/mol]
ϕ_i	= fugacity coefficient of component i	
ϕ_i^s	= fugacity coefficient of pure component i	
ψ	= coefficient as defined in Eq.(3)	

Literature Cited

- 1) Barker, J. A.: *Austral. J. Chem.*, **6**, 207 (1953)
- 2) Forsythe, G.E.: *J. Soc. Ind. Appl. Math.*, **5**, 74 (1957)
- 3) Hala, E., J. Pick, V. Fried and O. Vilim: "Vapour-Liquid Equilibrium", 2nd ed., pp. 125-133, Pergamon, Oxford, 1967
- 4) Ho, J. C. K., O. Boshko and B. C. Y. Lu: *Can. J. Chem. Eng.*, **39**, 205 (1961)
- 5) Lunglin, J. J. and J. H. Van Ness: *Chem. Eng. Sci.*, **17**, 531 (1962)
- 6) Lyckman, E., C. A. Eckert and J. M. Prausnitz: *Chem. Eng. Sci.*, **20**, 685 (1965)
- 7) Mackay, D. and K. K. Wong: *Can. J. Chem. Eng.*, **48**, 127 (1970)
- 8) Minh, D. C. and M. Ruel: *Can. J. Chem. Eng.*, **48**, 501 (1970)
- 9) Mixon, F. O., B. Gumowski and B. H. Carpenter: *Ind. Eng. Chem., Fundamentals*, **4**, 455 (1965)
- 10) Nagata, I.: 10th Symposium, Soc. Chem. Engrs., Japan, (1971)
- 11) O'Connell, J. P., and J. M. Prausnitz: *Ind. Eng. Chem., Process Design Develop.*, **6**, 245 (1967)
- 12) Prausnitz, J. M., C. A. Eckert, R. V. Orye and J. P. O'Connell: "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Prentice Hall, Englewood Cliffs, N.J., 1967
- 13) Ramalho, R. S., and J. Delmas: *Can. J. Chem. Eng.*, **46**, 32 (1968)
- 14) Scatchard, G. and C. L. Raymond: *J. Am. Chem. Soc.*, **60**, 1278 (1938)
- 15) Southworth, R. W. and S. L. Deleeuw: "Digital Computation and Numerical Methods", pp. 483-485, McGraw-Hill, 1965
- 16) Tao, L. C.: *Ind. Eng. Chem.*, **53**, 307 (1961)
- 17) Vera, J. H. and J. M. Prausnitz: *J. Chem. Eng. Data*, **16**, 149 (1971)