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Isothermal Vapor–Liquid Equilibria for *n*-Hexane–Methyl Methacrylate, Methyl *n*-Propyl Ketone–Acetic Acid, *n*-Pentane–Methyl Acetate, and Ethyl Acetate–Acetic Anhydride

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Isothermal vapor-liquid equilibria were measured for mixtures of *n*-hexane with methyl methacrylate and methyl *n*-propyl ketone with acetic acid at 333.15 K, *n*-pentane with methyl acetate at 298.15 K, and ethyl acetate with acetic anhydride at 348.15 K. The experimental results for each system were correlated by using the method of Barker to fit the total pressure and liquid composition values. A binary azeotrope was found for *n*-pentane–methyl acetate.

Introduction

A previous paper (*1*) from our laboratory presented vapor–liquid equilibria for mixtures of cyclohexane with methyl methacrylate. Such data are of interest in ester interchange reactions between methyl methacrylate and alcohols.

The present paper reports similar isothermal studies of four diverse systems: (A) *n*-hexane (1)–methyl methacrylate (2) at 333.15 K, (B) methyl *n*-propyl ketone (1)–acetic acid (2) at 333.15 K, (C) *n*-pentane (1)–methyl acetate (2) at 298.15 K, and (D) ethyl acetate (1)–acetic anhydride (2) at 348.15 K, which are also of relevance in esterification and related processes. Equilibria for system C have been reported previously (*2*, *3*); we are not aware of other comparable investigations.

Experimental Section

Isothermal vapor–liquid equilibria for the four binary systems were established in a modified Dvorâk and Boublík recirculating still (*4*) operated as described previously (*4*, *5*). The auxiliary equipment for measuring temperature and pressure was the same as used by Hull and Lu (*1*). Analyses of the condensed vapor and liquid samples were based either on determinations of density made with an Anton-Paar K.G. (Model DMA 02A) digital densimeter or on measurements of refractive index made with a Bausch & Lombe Model Abbe-3L precision refractometer. In either case, a calibration curve was established from measurements on a series of mixtures of known composition.

The component liquids are described in Table I, where their physical properties (density and/or refractive index and vapor pressure) are given, along with values from the literature (*6*–*9*) for comparison. In all cases, these materials were used for the vapor–liquid studies without further purification.

Results and Discussion

The experimentally determined pressures, P, and liquid and vapor compositions, x_1 and y_1, for the isothermal equilibrium of the mixtures at temperature, T, are listed in Tables II–V and plotted in Figures 1–4. In each case, the method of obtaining the compositions (either from density or refractive index) is indicated in the footnote of the table, along with estimates of the uncertainties ($\epsilon(T)$, $\epsilon(P)$, $\epsilon(x_1)$, and $\epsilon(y_1)$) in the primary measurements.

The results for each system were correlated by the Barker method (*10*), assuming a Redlich–Kister form

$$G^{E} = x_1 x_2 \sum_{j=1}^{n} c_j (x_2 - x_1)^{j-1} \qquad (1)$$

for the excess molar Gibbs energy, G^E, of the mixture. The corresponding activity coefficients, γ_i, in the liquid phase are

$$\gamma_i = \exp\{[G^E + (1 - x_i)(\mathrm{d}G^E/\mathrm{d}x_i)]/RT\} \qquad (2)$$

and the pressure and vapor compositions are given by

$$P = \gamma_1 p_1' + \gamma_2 p_2' \qquad (3)$$

and

$$y_i = \gamma_i p_i'/P \qquad (4)$$

where

$$p_i' = x_i P_i^\circ \exp\{[(V_i^\circ - B_{ii})(P - P_i^\circ) + (B_{11} + B_{22} - 2B_{12})(1 - y_i)^2 P]/RT\} \qquad (5)$$

Values of the coefficients, c_j, were determined by an iterative least-squares analysis in which eq 3 was fitted to the observed (x_1,P) data. At each step in the calculation, y_i was computed from eq 4. The quantities P_i°, B_{ii}, and V_i°, in eq 5, are the vapor pressure, second virial coefficient, and liquid molar volume of pure component i at temperature T, and B_{12} is the cross second virial coefficient in the mixture. The experimental P_i° listed in Table I were used in the calculation. The footnotes of Tables II–V summarize the values of V_i° and B_{ii}. In most cases, these were taken from the literature (*6*, *9*, *11*–*15*); however, experimental values of B_{ii} for methyl methacrylate and acetic anhydride were not available. Values of B_{ii} for those components and of B_{12} for all of the mixtures were estimated by the method of Hayden and O'Connell (*16*).

The coefficients c_j, obtained from the least-squares analysis of the (x_1,P) data for each system, are listed in Table VI. Values of $G^E(x_1)$, calculated from eq 1, are given in Tables II–V, along with the deviations of the calculated P and y_1 values from the corresponding experimental results. The standard deviations σ_p and σ_y for system A are smaller than the estimated uncertainties of the measurements. However, σ_p and

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Table I. Densities ρ, Refractive Indices n_D, and Vapor Pressures $P_i°$ of Pure Components at Various Temperatures T

	$\rho(T)/(\mathrm{g\ cm^{-3}})$			$n_D(T)$			$P_i°(T)/\mathrm{Torr}$		
	T, K	this work	lit.	T, K	this work	lit.	T, K	this work	lit.
n-hexane[a]				298.15	1.37225	1.37226 (*6*)	333.15	573.7	572.91 (*6*)
methyl methacrylate[b]				298.15	1.41203	1.4120 (*7*)	333.15	180.7	181.3 (*8*)
methyl *n*-propyl ketone[c]	298.15	0.8024	0.8015 (*9*)	303.15	1.38627	1.38614 (*7*)	333.15	176.59	176.68 (*9*)
acetic acid[d]	298.15	1.04437	1.04391 (*9*)				333.15	90.45	90.46 (*9*)
n-pentane[a]	298.15	0.62134	0.6213 (*6*)	298.15	1.35469	1.35472 (*6*)	298.15	512.4	512.63 (*6*)
methyl acetate[e]	298.15	0.92784	0.9273 (*9*)	298.15	1.35878	1.3589 (*9*)	298.15	216.1	216.38 (*9*)
ethyl acetate[f]	298.15	0.89395	0.8940 (*9*)	298.15	1.36981	1.3704 (*9*)	348.15	710.8	710.07 (*9*)
acetic anhydride[g]	298.15	1.07474	1.0751 (*7*)	298.15	1.38788	1.3884 (*7*)	348.15	78.4	78.1 (*8*)

[a] Phillips Petroleum Co., Pure Grade material with minimum purity 99 mol %. [b] Aldrich Chemical Co., Analyzed Reagent with purity 99 mol %, inhibited by 65 ppm hydroquinone monomethyl ether. [c] Supplied by Halcon SD Group Inc., estimated purity 99.6 mol %. [d] J. T. Baker Chemical Co., Ultrex Grade material with purity 99.8 mol %. [e] Matheson, Coleman and Bell, material with minimum purity 99 mol %. [f] J. T. Baker Chemical Co., Analyzed Reagent. [g] Fisher Scientific Co., Certified A.C.S. reagent with purity 99.6 mol %.

Table II. Isothermal Vapor–Liquid Equilibria for System A, *n*-Hexane (1)–Methyl Methacrylate (2) at 333.15 K[a]

x_1	y_1	P, Torr	G^E, J/mol	P(calcd) − P(exptl), Torr	y_1(calcd) − y_1(exptl)
0.0295	0.1725	214.1	69.1	−0.8	0.0022
0.0620	0.3005	245.5	140.0	−0.4	0.0017
0.1035	0.4095	279.7	222.6	0.9	0.0028
0.1480	0.4895	313.2	301.6	0.3	0.0042
0.2154	0.5783	354.5	402.9	0.6	0.0001
0.2510	0.6110	374.8	447.7	−0.8	0.0010
0.3412	0.6745	415.8	534.9	−1.2	0.0029
0.4775	0.7433	461.6	596.2	0.7	0.0045
0.5593	0.7815	485.2	592.2	0.5	0.0010
0.5795	0.7945	491.1	586.5	−0.1	−0.0039
0.6580	0.8205	509.3	546.0	1.0	0.0012
0.7370	0.8503	527.8	475.0	0.2	0.0034
0.8060	0.8795	542.2	387.2	−0.1	0.0043
0.8553	0.9072	552.1	309.0	−0.6	0.0005
0.9110	0.9380	562.4	204.5	−1.2	0.0003
0.9435	0.9595	567.4	135.3	−1.1	−0.0008

[a] Compositions determined from measurements of refractive index. Estimated uncertainties $\epsilon(T) = \pm 0.05$ K, $\epsilon(P) = \pm 1.2$ Torr, $\epsilon(x_1) = \epsilon(y_1) = \pm 0.005$. Liquid molar volumes and second virial coefficients in cm^3/mol: $V_1° = 138.55$ (*6*), $V_2° = 111.67$ (*12*), $B_{11} = -1385$ (*11*), $B_{22} = -1796$, and $B_{12} = -1350$ estimated by the method of Hayden and O'Connell (*16*).

Table III. Isothermal Vapor–Liquid Equilibria for System B, Methyl *n*-Propyl Ketone (1)–Acetic Acid (2) at 333.15 K[a]

x_1	y_1	P, Torr	G^E, J/mol	P(calcd) − P(exptl), Torr	y_1(calcd) − y_1(exptl)
0.0430	0.0615	92.93	0.5	−0.07	0.0000
0.0935	0.1268	95.84	2.2	0.07	0.0082
0.1895	0.2558	102.09	7.4	0.18	0.0188
0.2680	0.3660	107.58	12.0	0.34	0.0187
0.3867	0.5200	116.65	17.3	0.42	0.0177
0.4985	0.6488	125.87	18.7	0.44	0.0137
0.6118	0.7625	135.82	16.1	0.51	0.0064
0.7015	0.8375	144.11	11.7	0.68	0.0019
0.7925	0.9010	152.88	6.3	1.02	−0.0013
0.8715	0.9430	161.33	2.0	0.93	0.0007
0.9398	0.9730	169.33	−0.2	0.45	0.0028

[a] Compositions determined from measurements of density. Estimated uncertainties $\epsilon(T) = \pm 0.02$ K, $\epsilon(P) = \pm 0.3$ Torr, $\epsilon(x_1) = \epsilon(y_1) = \pm 0.005$. Liquid molar volumes and second virial coefficients in cm^3/mol: $V_1° = 112.19$ (*13*), $V_2° = 59.80$ (*9*), $B_{11} = -2725$ (*11*), $B_{22} = -7.0 \times 10^4$ (*14*), and $B_{12} = -608$ estimated by the method of Hayden and O'Connell (*16*).

Table IV. Isothermal Vapor–Liquid Equilibria for System C, *n*-Pentane (1)–Methyl Acetate (2) at 298.15 K[a]

x_1	y_1	P, Torr	G^E, J/mol	P(calcd) − P(exptl), Torr	y_1(calcd) − y_1(exptl)
0.0251	0.1992	269.8	98.1	−0.4	0.0144
0.0717	0.4043	344.0	263.3	−0.7	0.0000
0.1455	0.5290	416.0	482.6	0.8	0.0041
0.2258	0.5962	461.8	666.8	1.2	0.0025
0.2900	0.6327	487.8	776.3	−1.3	−0.0021
0.3740	0.6626	508.2	872.3	−0.6	−0.0020
0.5053	0.6970	528.7	921.4	0.4	0.0004
0.5920	0.7206	539.0	888.7	0.0	0.0001
0.6592	0.7407	544.7	827.9	0.2	−0.0001
0.6963	0.7530	547.2	780.8	0.2	−0.0001
0.7708	0.7841	550.2	656.4	0.2	−0.0017
0.8062	0.8020	550.3	582.9	0.3	−0.0022
0.8449	0.8244	550.1	491.4	−0.8	−0.0018
0.8839	0.8540	545.8	387.2	0.1	−0.0030
0.9309	0.8993	537.7	244.7	0.1	−0.0033
0.9472	0.9176	533.3	190.9	0.3	−0.0020
0.9755	0.9568	524.4	91.8	−0.6	−0.0008

[a] Compositions determined from measurements of density. Estimated uncertainties $\epsilon(T) = \pm 0.02$ K, $\epsilon(P) = \pm 0.2$ Torr, $\epsilon(x_1) = \epsilon(y_1) = \pm 0.002$. Liquid molar volumes and second virial coefficients in cm^3/mol: $V_1° = 116.15$ (*6*), $V_2° = 79.89$ (*9*), $B_{11} = -1274$ (*11*), $B_{22} = -1653$ (*11*), and $B_{12} = -982$ estimated by the method of Hayden and O'Connell (*16*).

Table V. Isothermal Vapor–Liquid Equilibria for System D, Ethyl Acetate (1)–Acetic Anhydride (2) at 348.15 K[a]

x_1	y_1	P, Torr	G^E, J/mol	P(calcd) − P(exptl), Torr	y_1(calcd) − y_1(exptl)
0.0276	0.2481	99.0	17.2	0.7	−0.0139
0.0590	0.4156	123.8	36.3	−0.1	−0.0142
0.1083	0.5777	160.7	64.6	−0.1	−0.0164
0.1739	0.6931	208.4	98.7	−0.5	−0.0093
0.1969	0.7221	223.8	109.5	0.2	−0.0083
0.2491	0.7731	259.6	131.5	0.0	−0.0058
0.3166	0.8208	303.4	154.7	0.5	−0.0040
0.3896	0.8600	350.2	172.8	−0.3	−0.0044
0.4823	0.8942	406.0	184.8	0.4	−0.0023
0.5542	0.9150	449.6	185.6	−0.4	−0.0010
0.6467	0.9373	503.8	175.6	−0.4	−0.0002
0.7092	0.9502	538.9	161.6	0.7	0.0003
0.8221	0.9708	605.2	119.7	−0.3	0.0006
0.8777	0.9802	636.9	90.3	0.3	0.0004
0.9240	0.9871	665.0	60.6	−0.5	0.0009

[a] Compositions determined from measurements of density. Estimated uncertainties $\epsilon(T) = \pm 0.03$ K, $\epsilon(P) = \pm 0.2$ Torr, $\epsilon(x_1) = \epsilon(y_1) = \pm 0.002$. Liquid molar volumes and second virial coefficients in cm^3/mol: $V_1° = 106.29$ (*9*), $V_2° = 100.77$ (*15*), $B_{11} = -1279$ (*11*), $B_{22} = -1465$, and $B_{12} = -1431$ estimated by the method of Hayden and O'Connell (*16*).

σ_y for the other three systems are somewhat larger. For some of the systems, it appears that the deviations of P and/or y_1 are nonrandom. This may be attributable in part to uncertainties in the correction for the nonideality of the vapor phase.

For comparison with the experimental (P,x_1) and (P,y_1) data, curves of calculated P values are plotted against x_1 and against calculated y_1 values in Figures 1–4. The correlation of the results, assuming the Redlich–Kister form for G^E, seems reasonable, bearing in mind that the experimental vapor compositions were not used in the analyses.

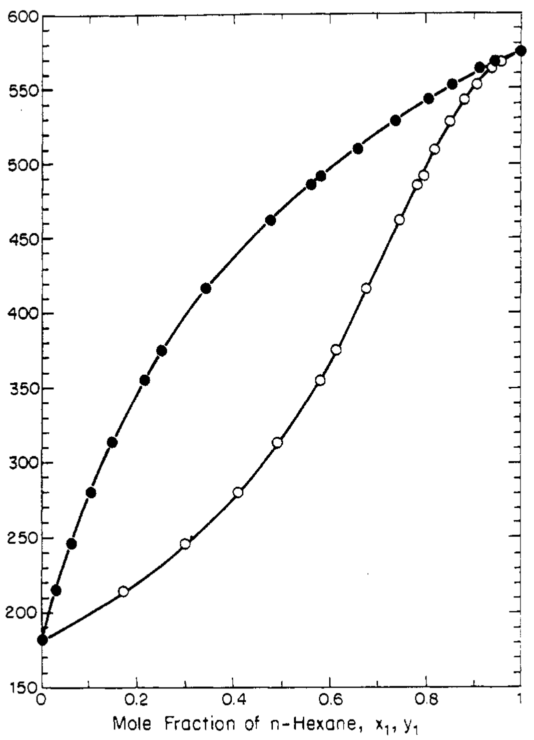

Figure 1. Comparison of calculated total pressures, P, and vapor mole fractions, y_1, with experimental results at liquid mole fraction, x_1, for n-hexane (1)-methyl methacrylate (2) at 333.15 K.

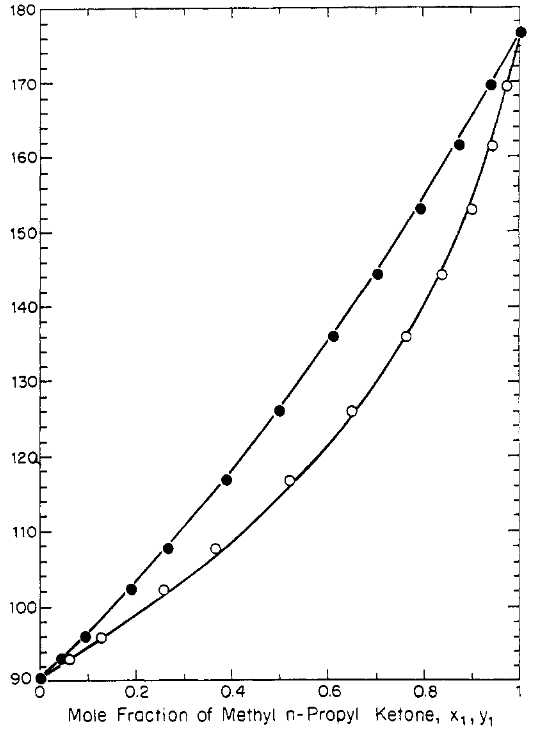

Figure 2. Comparison of calculated total pressures, P, and vapor mole fractions, y_1, with experimental results at liquid mole fraction, x_1, for methyl n-propyl ketone (1)-acetic acid (2) at 333.15 K.

Table VI. Coefficients c_j (J/mol) for Equation 1 and Standard Deviations[a] of the Calculated P and y_1 Values

system	c_1	c_2	c_3	c_4	σ_P, Torr	σ_y
A	2392.60	-73.35	103.16		0.8	0.003
B	74.68	11.49	-87.48		0.6	0.011
C	3686.81	89.08	262.00		0.6	0.004
D	742.70	-75.93	25.15	-61.65	0.4	0.008

[a] $\sigma_P = \{\sum[P(\text{calcd}) - P(\text{exptl})]^2/m\}^{1/2}$ and $\sigma_y = \{\sum[y_1(\text{calcd}) - y_1(\text{exptl})]^2/m\}^{1/2}$ where the sums are taken over the set of m experimental measurements on the system.

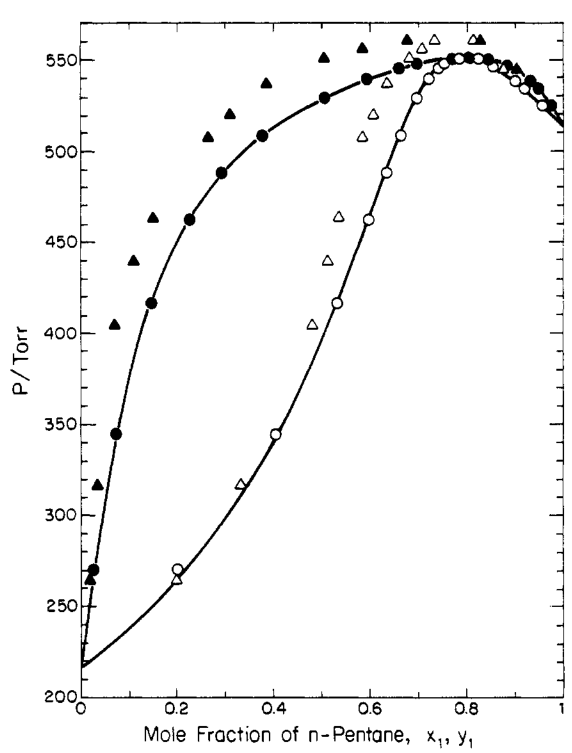

Figure 3. Comparison of calculated total pressures, P, and vapor mole fractions, y_1, with experimental results at liquid mole fraction, x_1, for n-pentane (1)-methyl acetate (2) at 298.15 K: this work (●, ○), (—); Zurita et al. (2) (▲, △).

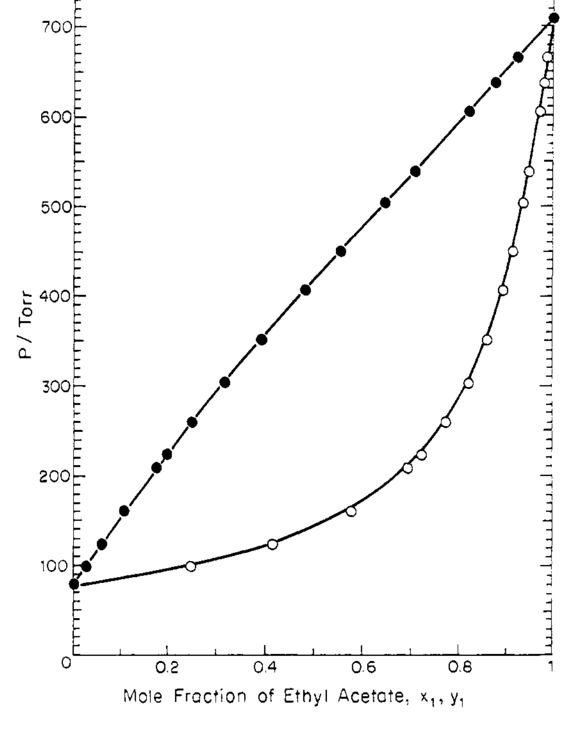

Figure 4. Comparison of calculated total pressures, P, and vapor mole fractions, y_1, with experimental results at liquid mole fraction, x_1, for ethyl acetate (1)-acetic anhydride (2) at 348.15 K.

The values of vapor pressure and G^E reported in the previous investigations of n-pentane-methyl acetate at 298.15 K (2, 3) are consistently higher than our results. For $x_1 = 0.5$, the differences are ~20 Torr and ~120 J mol^{-1}, respectively. A comparison of the (P,x_1,y_1) data is shown in Figure 3. It is evident that an azeotrope exists for this system. The corresponding calculated composition and pressure are $x_1 = 0.793$ and $P = 550.6$ Torr. These results can be compared with x_1

= 0.76 and P = 560 Torr reported by Zurita et al. (*2*).

Glossary

B_{ii}	second virial coefficient of pure component i, cm^3/mol
B_{12}	cross virial coefficient, cm^3/mol
c_j	coefficient in eq 1, J/mol
G^E	excess molar Gibbs energy, J/mol
m	number of measurements on a system
n	number of coefficients in eq 1
n_D	refractive index for sodium D line
P_i^o	vapor pressure of pure component i, Torr
p_i'	defined by eq 5, Torr
R	gas constant
T	thermodynamic temperature, K
V_i^o	molar volume of pure liquid i, cm^3/mol
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapor
γ_i	activity coefficient of component i in liquid
ϵ	estimated experimental uncertainty
ρ	density, g/cm^3
σ	standard deviation, defined in the footnote of Table VI

Registry No. $CH_3(CH_2)_4CH_3$, 110-54-3; $CH_3(CH_2)_3CH_3$, 109-66-0; $H_2C{=}C(CH_3)CO_2Me$, 80-62-6; MeCOPr, 107-87-9; H_3CCO_2H, 64-19-7; H_3CCO_2Et, 141-78-6; H_3CCO_2Me, 79-20-9; $(CH_3CO)_2O$, 108-24-7.

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Excess Enthalpy of Four Partially Miscible Binary Liquid Mixtures near Their Critical Solution Temperatures

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Heats of mixing for the *n*-hexane + methanol, 2-methylpropanoic acid + water, nitroethane + 2,2,4-trimethylpentane, and nitromethane + 1-butanol systems were measured as a function of composition at from six to eight temperatures bracketing each system's critical solution temperature. The estimated uncertainty in the results is less than 1.0%. Heats of mixing were endothermic in all four systems. Above the critical solution temperature, heat of mixing curves plotted vs mole fraction of the first component were everywhere convex. Below the critical solution temperature, intersections of the straight (two-phase) and curved (one-phase) heat of mixing lines were used to provide a calorimetric estimate of the binodal compositions.

Introduction

The need for accurate prediction of liquid mixture properties for use in process design simulators has led to considerable interest in Gibbs free energy models. The local composition (LC) concept of Wilson (*1*) has been shown to be particularly effective in correlating vapor–liquid equilibrium (VLE). On the basis of the LC concept, several models have been developed to correlate VLE and liquid–liquid equilibrium (LLE) data (*2–6*), and simultaneously VLE and molar excess enthalpy h^E (*5*, *7–10*) data.

In order to facilitate multiproperty correlation based on the Gibbs–Helmholtz relation, several investigators have incorporated additional empirical temperature dependencies into the original versions of LC models for the molar Gibbs free energy g^E (*11–15*). While some success has been reported (*7–10*), other investigators have found simultaneous correlation of VLE and h^E with these models to be applicable to only a few mixtures (*5*, *12–14*). Studies have shown these empirically

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