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THE PREDICTION OF ISOBARIC PHASE EQUILIBRIA FOR NON-IDEAL MULTICOMPONENT MIXTURES FROM HEAT OF MIXING DATA*

ROMEO L. TAN, RICHARD W. HANKS AND JAMES J. CHRISTENSEN
Department of Chemical Engineering, Brigham Young University, Provo, UT 84602 (U.S.A.)
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ABSTRACT

A method for predicting isobaric binary and ternary vapor-liquid equilibrium data using only isothermal binary heat of mixing data and pure component vapor pressure data is presented. Three binary and two ternary hydrocarbon liquid mixtures were studied. The method consists of evaluating the parameters of the NRTL equation from isothermal heat of mixing data for the constituent binary pairs. These parameters are then used in the multicomponent NRTL equation to compute isobaric vapor–liquid equilibrium data for the ternary mixture. No ternary or higher order interaction terms are needed in the ternary calculations because of the nature of the NRTL equation. NRTL parameters derived from heat of mixing data at one temperature can be used to predict vapor–liquid equilibrium data at other temperatures up to the boiling temperature of the liquid mixture.

For the systems studied this method predicted the composition of the vapor phase with a standard deviation ranging from 1–8% for the binary systems and from 4–12% for the ternary systems.

INTRODUCTION

A method for predicting isothermal binary vapor liquid equilibrium (VLE) data using only binary heat of mixing (h^E) data proposed by Hanks et al.[1] was extended recently by the present authors[2] to include the prediction of ternary isothermal VLE data. The use of h^E data to generate correlation constants in an excess free energy model is attractive because h^E data can usually be measured more accurately and easily than can VLE data.

Since, most separation processes in the chemical industry are carried out under isobaric rather than isothermal conditions, isobaric VLE data are needed for the successful design of a wide variety of separation processes. Thus, there exists a need to extend the present prediction method to include the isobaric case.

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This paper shows how the method of Hanks et al. can be extended to the prediction of isobaric VLE data and demonstrates the feasibility of calculating isobaric binary and ternary VLE data for hydrocarbon mixtures from isothermal binary h^E data.

CALCULATION PROCEDURE

An expression for h^E derived from the local composition model of Renon-Prausnitz[3] (NRTL equation) is fitted to experimental binary h^E data to determine the adjustable parameters[1, 2]. Using these parameters both binary and ternary VLE data under either isothermal or isobaric conditions are predicted.

For binary mixtures, the following equations derived by Renon and Prausnitz are used to represent the excess free energy (g^E) and the liquid phase activity coefficients (γ_i):

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21}G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1 G_{12}}\right] \tag{1}$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right] \tag{2}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right] \tag{3}$$

where $\tau_{ij} = (g_{ij} - g_{jj})/RT$, $G_{ij} = \exp(-\alpha_{12}\tau_{ij})$ and α_{12}, $(g_{12} - g_{11})$, $(g_{12} - g_{22})$ are three adjustable parameters. The h^E function is related to the excess free energy function by the following expression:

$$h^E = -T^2[(\partial g^E/T)/\partial T]_{p,x} \tag{4}$$

If the three NRTL parameters are assumed to be independent of temperature, the following expression for h^E can be derived using eqns (1) and (4):

$$h^E = x_1 x_2 \left\{\frac{\tau_{21}G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1 G_{12}} - \frac{\alpha_{12}}{RT}\left[\frac{x_1 \tau_{21}^2 G_{21}}{(x_1 + x_2 G_{21})^2} + \frac{x_2 \tau_{12}^2 G_{12}}{(x_2 + x_1 G_{12})^2}\right]\right\} \tag{5}$$

Equation (5) is fitted to the experimental h^E data to evaluate the numerical values of the parameters α_{12}, $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$. A computer program was developed based on Powell's[4, 5] non-gradient technique to evaluate the parameters by minimizing the function given in eqn (6).

$$S_e^2 = \frac{1}{N-2}\sum_j [h^E_{\mathrm{cal}} - h^E_{\mathrm{expt}}]_j^2 \tag{6}$$

Once the parameters have been evaluated, the g^E data and activity coefficients can be evaluated from eqns (1), (2) and (3). Using these activity coefficients together with vapor pressure data (calculated using a correlation given by Renon and Prausnitz[illegible]) binary VLE data can be calculated[2].

For ternary mixtures, g^E and γ data can be computed using the following expressions for multicomponent mixtures obtained from the NRTL equation.

$$\frac{g^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{7}$$

$$\ln \gamma_j = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right) \tag{8}$$

The nine parameters in eqns (7) and (8) can be determined from binary h^E data for the three binary systems comprising the ternary. These activity coefficients coupled with pure component vapor pressure data can then be used to calculate ternary VLE data.

RESULTS AND DISCUSSION

This section is divided into the following three main areas:

1. Temperature dependence of NRTL parameters
2. Prediction of isobaric binary VLE data
3. Prediction of isobaric ternary VLE data

The first area deals with the use of the NRTL equation to calculate VLE data at one temperature using NRTL parameters evaluated at a different temperature. The second area reports the results of predicting isobaric binary VLE data from isothermal binary h^E data; the temperature of the h^E data being different from the temperature at which the VLE data are calculated. The third area contains the results of predicting isobaric ternary VLE data from isothermal binary h^E data for the constituent binary pairs.

Temperature dependence of NRTL parameters

Isobaric VLE data are measured over the solution boiling temperature range at a particular pressure. This temperature range frequently differs significantly from the common temperatures (15–45°C) used in measuring isothermal h^E data. Also it is usually impractical to measure h^E data over the solution boiling temperature range. The temperature dependence of the NRTL parameters and the possibility of using parameters obtained from h^E data at one temperature to predict VLE data at another temperature were examined for the following three binary systems:

TABLE I

BINARY SYSTEMS: A. PARAMETERS FOR NRTL EQUATION DETERMINED FROM h^E DATA. B. STATISTICAL MEASURES OF FITS OF h^E AND VLE DATA

System	*Calculation*	*VLE data* (°C)	*NRTL*		*Parameters*		*Statistical measure of fit*		*Source of exptl data ref.*	
			°C[a]	α_{12}	$g_{12}-g_{11}$	$g_{12}-g_{22}$	S_e^2	σ_y[b]	*VLE data*	h^E
Ia	1	70	15	0.3	401.0	−91.85	2.0	10.00	8	9
Ib	1	70	25	0.3	400.4	−105.60	2.1	9.26	8	10
Ic	1	70	45	0.3	392.8	−130.5	1.6	7.69	8	9
Id	2[c]	70	—	0.3	387.0	−164.0	—	5.82	8	—
Ia	3	70	15	−1.617	−252.4	199.9	2.0	2.17	8	9
Ib	3	70	25	−3.825	−265.5	106.1	51.4	2.38	8	10
Ic	3	70	45	−1.102	−232.8	230.9	0.4	2.37	8	9
IIa	1	50	25	0.3	208.3	206.2	40.4	8.45	11	11
IIb	1	50	35	0.3	202.7	153.2	29.0	6.14	11	11
IIc	2[d]	50	—	0.3	192.0	78.0	—	2.84	11	—
IIa	3	50	25	0.001416	371.8	−0.002612	44.9	7.48	11	11
IIb	3	50	35	0.04404	332.4	0.03441	30.7	5.64	11	11
IIIa	1	75	25	0.3	917.5	−365.3	13.8	5.13	12	13
IIIa	3	75	25	0.369	1111.0	−558.0	54.8	4.50	12	13

[a] Temperatures at which h^E was measured. [b] $\sigma_y = \{1/N-1\ [\Sigma_j\ [(y_{cal} - y_{exptl})/y_{exptl}]^2]\}^{1/2} \times 100$. [c] Extrapolated NRTL values at 70°C obtained from values of parameters at 15°C, 25°C and 45°C (Fig. 1). [d] Extrapolated NRTL values at 50°C obtained from values of parameters at 25°C and 35°C (Fig. 2).

System I — cyclohexane(1)–n-hexane(2)
System II — methylacetate(1)-benzene(2)
System III — benzene(1)–n-heptane(2)

For these systems NRTL parameters at one or more temperatures were used to calculate NRTL parameters and the corresponding VLE data at a higher temperature and the results compared with experimental VLE data (Table 1).

In Table 1 S_e^2 and σ_y are statistical measures of the fit of the h^E and VLE data, respectively. S_e^2 is defined by eqn (6) and σ_y is the percent standard deviation of the predicted fit of the VLE data. Two versions of the NRTL equation were used in the calculation routine: (1) α was set equal to 0.3 as recommended by Renon[7] (two-parameter equation); (2) α was allowed to be free and was determined directly from the experimental h^E data (three-parameter equation). Systems Ia, Ib, Ic in Table I represent three sets of h^E data measured at 15, 25, and 45°C, respectively. Systems IIa and IIb represent two sets of h^E data measured at 25 and 35°C, respectively. Each individual set of h^E data was used to determine NRTL parameters.

Three kinds of calculations were employed in Table I. In calculation 1 the α parameter was set equal to 0.3 and the other two energy parameters were determined

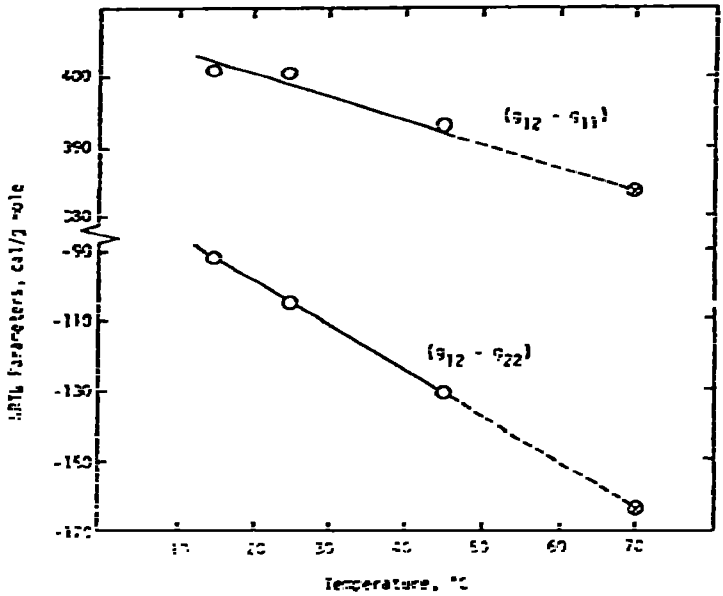

Fig. 1. NRTL parameters for System I—cyclohexane(1)–n-hexane(2) as a function of temperature for the case where α = 0.3.

from the h^E data. In calculation 2 the energy parameters derived at other temperatures for the case where $\alpha = 0.3$ were extrapolated to the particular temperature of interest. In calculation 3 all three NRTL parameters were determined directly from the h^E data.

System I — cyclohexane(1)-n-hexane(2). The binary h^E data were available at 15, 25 and 45°C, while the VLE data were available at 70°C. The three sets of h^E data were individually fitted with eqn (5) for the two cases where α was set equal to 0.3 (calculation 1) and α was allowed to be free (calculation 3) giving two values for each NRTL parameter for each data set.

Calculation 1 for systems Ia, Ib and Ic (Table 1) gives the values of the two parameters $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ at 15, 25 and 45°C when α is set equal to 0.3. These values were found to vary linearly with temperature (Fig. 1) and values were obtained at 70°C by extrapolation. For these systems an examination of the σ_y values in Table 1 indicates that the accuracy of the x-y fit increases as the temperature of the binary h^E data used increases. No such trend is observed when α is not fixed (calculation 3). When α is not fixed, the three parameters show no systematic dependence on temperature; hence, no extrapolation to another temperature is possible. Generally, the 3-parameter NRTL equation offers a much better VLE correlation than the 2-parameter equation. Details of the vapor phase calculations are tabulated in Table 2.

System II — methylacetate(1)-benzene(2). The binary h^E data were reported at 25 and 35°C, and the VLE data were available at 50°C. Calculation 1 of systems IIa and IIb (Table 1) for the case where $\alpha = 0.3$ produced parameters $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ which differed and were treated as a linear function of temperature. These values were extrapolated as shown in Fig. 2 to obtain NRTL parameters at 50°C. Calculation 3 for systems IIa and IIb reveals that the NRTL parameters are

TABLE 2

COMPARISON OF CALCULATED AND EXPERIMENTAL VLE DATA FOR SYSTEM I—CYCLOHEXANE(1)–N-HEXANE (2) AT 70°C

Experimental		*Calculated* y_1^a						
		System–calculation						
x_1	y_1	*Ia–1*	*Ib–1*	*Ic–1*	*Id–2*	*Ia–3*	*Ib–3*	*Ic–3*
0.1250	0.0990	0.1156	0.1139	0.1105	0.1063	0.0955	0.0937	0.0967
0.2500	0.1940	0.2259	0.2241	0.2200	0.2150	0.2009	0.1976	0.2029
0.3750	0.2910	0.3170	0.3157	0.3129	0.3093	0.2981	0.2939	0.3004
0.5000	0.4100	0.4130	0.4129	0.4124	0.4119	0.4086	0.4037	0.4103
0.6250	0.5350	0.5141	0.5153	0.5179	0.5211	0.5287	0.5243	0.5290
0.7500	0.6640	0.6300	0.6325	0.6378	0.6445	0.6627	0.6614	0.6609
0.8750	0.8210	0.7785	0.7814	0.7877	0.7953	0.8169	0.8225	0.8813
% Standard deviation, σ_y		10.00	9.26	7.69	5.82	2.17	2.38	2.37

[a] See Table 1 for parameters used in calculations.

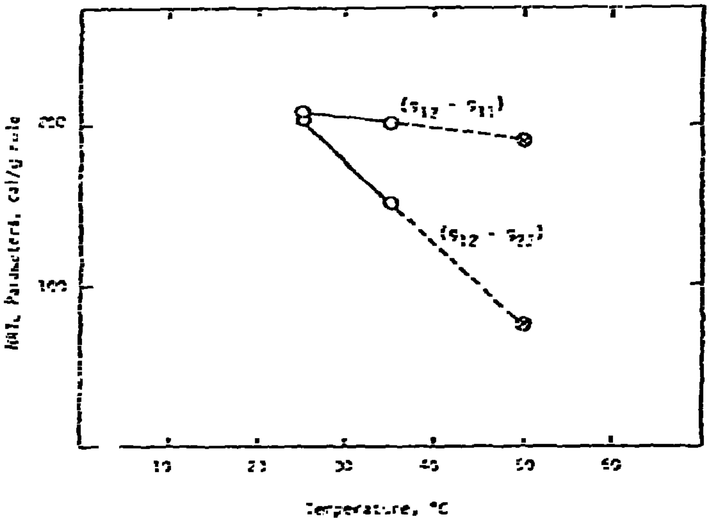

Fig. 2. NRTL parameters for System II—methylacetate(1)–benzene(2) as a function of temperature for the case where $\alpha = 0.3$.

not a function of temperature when α is allowed to float. These observations are consistent with those found for system I. Calculation 2 was found to give the best VLE prediction. Comparing the values of σ_y in Table 1, it is observed that the 3-parameter NRTL equation gives a slightly better VLE prediction than the 2-parameter equation.

System III — benzene(1)–n-heptane(2). This system was studied previously under isothermal conditions at 25°C and the NRTL parameters used here were obtained from that study[2]. Because of the lack of h^E data at other temperatures, no extrapolation of the NRTL parameters was possible. The values of σ_y for calculations 1 and 3 show that the 3-parameter equation offers a 14% improvement in VLE accuracy over the 2-parameter equation.

It appears from the above results that one can use NRTL parameters obtained from binary H^E data at one temperature to correlate VLE data at another significantly different temperature. This eliminates the need of introducing the cumbersome additional parameters of Asselineau and Renon[19]. Typical percentage standard deviations of the fit of the x–y data vary from 2–6% which is within the range of experimental accuracy. Also, the above results show that when α is fixed according to solution type as defined by Renon and Prausnitz[3], the two parameters $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ vary linearly with temperature. If α is permitted to float as a free third parameter, however, no systematic temperature variation of the parameters can be observed.

Prediction of isobaric binary VLE data

It was shown above that NRTL parameters obtained at one temperature can be used to predict isothermal VLE data at another temperature. This suggests that it might be possible to extend the scheme to predict isobaric VLE data for multicomponent mixtures. This possibility was examined using two of the systems studied in the previous section (Systems I and II). Ideal vapor phase behavior was assumed. The two binary systems considered were:

System I — cyclohexane(1)–n-hexane(2) at 1 atm.

System II — methylacetate(1)–benzene(2) at 1 atm.

The results are given in Table 3 together with the temperature range over which

TABLE 3

BINARY SYSTEMS: A. PARAMETERS FOR NRTL EQUATION DETERMINED FROM h^E DATA. B. STATISTICAL MEASURES OF FITS OF h^E AND VLE DATA

System	*Calculation*	*VLE data (°C)*	*NRTL*		*Parameters*		*Statistical measure of fit*		*Source of exptl data ref.*	
			°C	α_{12}	$g_{12}-g_{11}$	$g_{12}-g_{22}$	S_t^2	σ_y	*VLE*	h^E
Ib	1	70.05–79.50	25	0.3	300.2	−79.12	33.3	7.90	14	14
Ib	2	70.05–79.50	25	−1.321	−252.8	202.10	32.1	1.34	14	14
Id	3^a	70.05–79.50	70	0.3	387.0	−164.0	—	6.90	8	—
IIb	1	57.90–76.90	35	0.3	202.7	153.2	29.0	13.87	15	11
IIb	2	57.90–76.90	35	0.04404	332.4	0.03441	37.0	12.66	15	11
IIc	3^b	57.90–76.90	50	0.3	192.0	78.0	—	6.75	15	—

[a] Extrapolated NRTL values at 70°C obtained from values of parameters for system I at 15°C, 25°C and 45°C (Fig. 1). [b] Extrapolated NRTL values at 50°C obtained from values of parameters for system II at 25 and 35°C (Fig. 2).

the two systems were studied, the NRTL parameters used in the calculations, and the statistical measure of the h^E and VLE fit. The α parameter was fixed at 0.3 in calculation 1 and allowed to be free in calculation 2.

System I — cyclohexane(1)-n-hexane(2). The NRTL parameters used for calculations 1 and 2 (Table 3) were obtained from binary h^E data at 25°C. The boiling temperature range of the mixtures is 70 to 79.5°C. The parameters used for calculation 3 were obtained by extrapolating the values of the parameters obtained at 15, 25 and 45 to 70°C (see Fig. 1). Comparison of the values of σ_y for calculations 1 and 3 shows that for the two-parameter equation the extrapolated parameters at 70°C offer a 14% improvement in the VLE prediction over that obtained using the parameters derived at 25°C. The three-parameter NRTL equation gives a prediction which is 6 times more accurate than the two-parameter equation for this system. Calculated and experimental vapor phase mole fractions values are summarized in Table 4 for this system.

System II — methylacetate(1)-benzene(2). NRTL parameters for this system for calculations 1 and 2 were determined from binary h^E data at 35°C. The boiling temperature range of the system is from 57.9 to 76.9°C. Parameters used in calculation 3 were obtained by extrapolating the values of the parameters at 25 and 35 to 50°C assuming a linear relation (see Fig. 2). These extrapolated parameters at 50°C compared to the parameters at 35°C gave the best VLE prediction with improvements as high as 100% being attained. The 3-parameter equation gives a 9% improvement in VLE prediction over the 2-parameter equation.

The results of the above computations indicate that parameters obtained from

TABLE 4

COMPARISON OF CALCULATED AND EXPERIMENTAL VLE DATA FOR SYSTEM I—CYCLOHEXANE(1)-N-HEXANE (2) AT 1 ATM

Experimental			*Calculated y_1^a*		
			System–calculation		
B.P. (°C)	x_1	y_1	*Ib–1*	*Ib–2*	*Id–3*
70.05	0.1230	0.0960	0.1094	0.0931	0.1071
70.85	0.2030	0.1600	0.1792	0.1562	0.1764
72.05	0.3290	0.2600	0.2877	0.2597	0.2851
72.90	0.4090	0.3290	0.3574	0.3292	0.3553
74.70	0.5620	0.4770	0.4966	0.4732	0.4957
75.40	0.6160	0.5320	0.5489	0.5283	0.5484
76.40	0.7000	0.6160	0.6320	0.6168	0.6318
78.20	0.8330	0.7740	0.7788	0.7725	0.7789
79.50	0.9180	0.8790	0.8864	0.8846	0.8865
% Standard deviation, σ_y			7.90	1.34	6.90

[a] See Table 3 for NRTL parameters used in calculations.

TABLE 5

PARAMETERS USED TO CALCULATE VLE DATA FOR TERNARY SYSTEMS BENZENE(1)-N-HEPTANE(2)-ACETONITRILE(3) (IV) AND CYCLOHEXANE(1)-N-HEPTANE(2)-TOLUENE(3) (V)

System	*Temp. (°C)*	α_{12}	α_{13}	α_{23}	$g_{12}-g_{22}$	$g_{21}-g_{11}$	$g_{13}-g_{33}$	$g_{31}-g_{11}$	$g_{23}-g_{33}$	$g_{32}-g_{22}$	*Source of exptl h^E data ref.*
IV	45	0.369	0.692	−0.316	1111.0	−558.0	377.0	580.2	864.9	903.9	16
V	25	−2.415	−2.618	−2.366	41.8	120.5	128.7	183.9	189.0	119.8	16

binary isothermal h^E data at one temperature can be used successfully to correlate binary isobaric VLE data at a higher temperature. The σ_y, values obtained fall within the range of 1–7%. Generally, the 3-parameter form of the NRTL equation offers a slight improvement in prediction accuracy over the 2-parameter form of the equation. The accuracy of the 2-parameter form is improved if low temperature parameters can be extrapolated to the boiling temperature range.

Prediction of isobaric ternary VLE data

It was demonstrated above that the isothermal prediction scheme could be applied successfully to the prediction of isobaric binary VLE data using parameters obtained from isothermal h^E data. In this section the method of Hanks et al. is extended to include the prediction of isobaric ternary VLE data. The two ternary hydrocarbon systems at 1 atm which were studied are:

System IV -- benzene(1)-n-heptane(2)-acetonitrile(3)

System V — cyclohexane(1)-n-heptane(2)-toluene(3)

The NRTL parameters used were taken from a previous analysis by Tan[16] of isothermal h^E data for the binary pairs and are given in Table 5. Only those parameters giving the best binary isothermal VLE correlations were used in the present study.

The three vapor phase mole fractions can either be calculated separately from the NRTL equation, or two can be calculated from the NRTL equation and the third

TABLE 6

COMPARISON OF CALCULATED AND EXPERIMENTAL VLE DATA FOR SYSTEM IV—BENZENE(1)-N-HEPTANE(2)-ACETONITRILE(3) AT 1 ATM

Experimental[a]						*Calculated*[b]			
x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	*Sum y*[c]
0.9070	0.0530	0.0400	0.8590	0.0460	0.0950	0.8628	0.0434	0.0957	1.0019
0.8810	0.0510	0.0680	0.8070	0.0440	0.1490	0.8106	0.0419	0.1490	1.0015
0.7830	0.1000	0.1170	0.6860	0.0820	0.2320	0.6830	0.0763	0.2371	0.9964
0.6790	0.1890	0.1320	0.5870	0.1400	0.2730	0.5736	0.1288	0.2916	0.9940
0.6540	0.2590	0.0870	0.5890	0.1770	0.2340	0.5886	0.1632	0.2525	1.0043
0.6090	0.2080	0.1830	0.4980	0.1500	0.3520	0.4923	0.1459	0.3652	1.0034
0.5310	0.3940	0.0750	0.4880	0.2240	0.2880	0.4846	0.2257	0.2986	1.0089
0.5080	0.3190	0.1730	0.4100	0.1960	0.3940	0.3994	0.1990	0.4233	1.0217
0.4990	0.3800	0.1210	0.4280	0.2180	0.3540	0.4151	0.2195	0.3912	1.0258
0.4780	0.3630	0.1590	0.3950	0.2140	0.3910	0.3773	0.2166	0.4385	1.0324
0.4750	0.3590	0.1660	0.3880	0.2110	0.4010	0.3728	0.2165	0.4456	1.0349
0.4470	0.3030	0.2500	0.3390	0.2080	0.4530	0.3314	0.2089	0.4862	1.0265
% Standard deviation, σ_y						2.31	4.54	7.26	

[a] VLE data from Ref. 17. [b] See Table 5 for values of NRTL parameters used. [c] Sum y = $y_1 + y_2 + y_3$, Avg = 1.013.

TABLE 7

STATISTICAL MEASURE OF FIT OF ISOBARIC VLE DATA FOR SYSTEM V—CYCLOHEXANE(1)-N-HEPTANE(2)-TOLUENE(3)

System	*Number of data points*	*VLE data*[a] *(°C)*	*Ratio cyclohexane/hexane*	*Sum y*	σ_{y1}	σ_{y2}	σ_{y3}	σ_{ave}[b]
V	25	95.0–107.6	0.25	1.0648	23.28	13.21	8.19	14.89
V	26	91.2–107.7	0.67	1.0730	15.11	11.24	6.62	10.59
V	22	88.0–102.7	1.5	1.0727	13.53	10.35	3.85	9.24
V	28	84.55–104.7	4.0	1.0708	11.69	15.57	5.96	11.07

[a] VLE data from ref. 18. [b] $\sigma_{ave} = \sigma_{y1} + \sigma_{y2} + \sigma_{y3}$.

obtained from an overall material balance. When calculated separately the summation of the vapor phase mole fractions averaged between 1.01 and 1.07, corresponding to a 1–7% error in the overall material balance.

System IV — benzene(1)-n-heptane(2)-acetonitrile(3). The 9 NRTL parameters used were obtained from h^E data at 45°C (Table 5). The ternary isobaric VLE data[17] consist of 12 actual experimental data points and 36 calculated points. Only the 12 experimental data points were used in this study. Table 6 reports the agreement between calculated and measured VLE data for the case where all three vapor phase mole fractions were calculated separately. A slightly better correlation between calculated and experimental VLE data was achieved for this method than for the one where one of the vapor phase mole fractions was determined from an overall material balance.

System V — cyclohexane(1)-n-heptane(2)-toluene(3). The 9 NRTL parameters used were obtained from h^E data at 25°C (Table 5). The isobaric ternary VLE data[18] were divided into 4 cases corresponding to cyclohexane/heptane ratios of 0.25, 0.67, 1.5 and 4.0, respectively. The results of the VLE calculations are given in Table 7. Standard deviations were calculated for each case separately and were found to range from 9.2 to 14.9%. A composite standard deviation was calculated for all the data points together and was found to be 11.9%.

The results obtained from these two systems indicate that the method can be extended to the prediction of ternary isobaric VLE data to within a standard deviation of about 12%, a result comparable to those obtained for isothermal conditions.

CONCLUSIONS

Several conclusions can be drawn from this study: (1) Using the method of predicting VLE data from heat of mixing data, isobaric binary and ternary VLE data can be predicted to within 12%; (2) isobaric VLE data can be predicted almost as accurately as can isothermal VLE data using isothermal heat of mixing data; (3) the 3-parameter NRTL equation usually correlates isobaric VLE data better than does the 2-parameter equation; (4) NRTL parameters obtained at a particular temperature can be used to correlate VLE data at another temperature to within 2–5%; (5) if α is fixed at the value of 0.3 recommended by Renon and Prausnitz, the other two energy parameters are linearly dependent on temperature; (6) if α is allowed to float freely, no systematic temperature variation was observed in any of the three parameters.

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