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THE PREDICTION OF ISOTHERMAL PHASE EQUILIBRIA FOR NON-IDEAL MULTICOMPONENT MIXTURES FROM HEATS OF MIXING*

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ABSTRACT

A method is presented for predicting both vapor-liquid and liquid-liquid equilibria for multicomponent mixtures using heat of mixing data for the constituent binary pairs together with pure component vapor pressures. Its application to two highly non-ideal hydrocarbon ternary systems is discussed. The parameters of the hybrid local composition model of Renon and Prausnitz, known as the NRTL equation, were evaluated from heat of mixing data for the three binary pairs in each of the two ternary systems. The parameters thus obtained were used in the multicomponent form of the NRTL equation to predict the ternary vapor–liquid equilibrium data for the completely miscible system cyclohexane(1)–n-heptane(2)–toluene(3) and for the partially miscible system acetonitrile(1)–benzene(2)–n-heptane(3) without the need for any ternary or higher order parameters.

This method predicted compositions of the single phase region of the partially miscible ternary system with a standard deviation of 10%. It also predicted compositions for the fully miscible system with a standard deviation of 4.6%. Total pressure curves for the partially miscible and miscible ternaries were predicted with standard deviations of 6.6% and 4.5% respectively. Poor predictions of the binodal curve for the partially miscible region were obtained. The method offers a means of predicting the whole range of ternary phase equilibria for miscible systems.

INTRODUCTION

Accurate vapor-liquid equilibrium (VLE) data are vital to the successful operation of a wide variety of separation processes. Good experimental multicomponent phase equilibrium data are rather difficult and time consuming to obtain and require skillful techniques and experience. The difficulty of direct VLE measurements increases with the number of constituents present in a given liquid mixture. This provides an incentive to calculate VLE data by theoretical means using only pure

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component data. No generally valid theoretical liquid model exists which will permit this to be done, and one has to rely on a combination of experimental data and a semi-theoretical model to predict the properties of mixtures.

Conventional methods used for predicting binary as well as multicomponent vapor–liquid equilibria and heat of mixing for liquid mixtures involve fitting the binary VLE data to an arbitrarily chosen thermodynamic model to determine empirical constants. These in turn give expressions for the excess Gibbs free energy, g^E, from which liquid phase activity coefficients may be derived[1, 2]. The heat of mixing, h^E, is obtained from the free energy expression by differentiation as indicated by eqn (1).

$$h^E = -T^2[(\partial g^E/T)/\partial T]_{p,x} \tag{1}$$

A disadvantage inherent in the above procedure is that it requires very accurate x–y data to produce good g^E data, and the expression for g^E must be differentiated to produce h^E values. Poor h^E values usually result because of a substantial loss of accuracy in the differentiation process. Hanks et al.[3] have described a method in which this process is reversed. The procedure consists of the following: (1) Choosing an algebraic expression for g^E and differentiating it as indicated by eqn (1) to get an algebraic expression for h^E; (2) fitting the resulting h^E equation to experimental h^E data, and evaluating the constants in the equation; and (3) using these constants in the original g^E expression to calculate the activity coefficients and the corresponding x–y data. The merits of this method are: (1) Only heat of mixing data together with pure component vapor pressures are necessary to predict vapor–liquid equilibrium data accurately; (2) the effect of random experimental errors in the heat of mixing data on the prediction of vapor–liquid equilibria are reduced due to the error smoothing characteristic of the integration process; and (3) the method, when coupled with techniques for the rapid and accurate measurement of heat of mixing data, has considerable practical potential for the prediction of VLE data. Gupta[4] has used four different types of composition dependent excess Gibbs energy equations to predict binary VLE data using only binary h^E data. His results indicate that, for solutions which show small deviation from ideality, a regular solution model can sufficiently represent the g^E data. For solutions which have appreciable polarity and/or hydrogen bonding effects present, a chemical type model should be used. For solutions which have large deviations from ideality, a hydrid local composition type model works best.

In this study, the method described by Hanks et al.[3], is extended to allow the prediction of the behavior of ternary mixtures. This paper contains a description of the prediction scheme, and the results obtained for two ternary mixtures and the three binary systems comprising each ternary.

CALCULATION PROCEDURE

The local composition model of Renon-Prausnitz[1] is used with heat of mixing data to predict binary and ternary vapor–liquid equilibria, as well as the binodal distribution curve for the two liquid phase region of a partially miscible ternary mixture.

Binary mixtures

Renon and Prausnitz[5] applied the Wilson local composition concept to Scott's two liquid theory and obtained the following equation, known as the NRTL equation, for excess free energy:

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \tag{2}$$

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 equations for the liquid phase activity coefficients, γ_i, derived from eqn (2), are

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{3}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{4}$$

The following expression for h^E can be derived from eqns (1) and (2) if the parameters in eqn (2) are assumed to be independent of temperature:

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

Equation (5) together with heat of mixing data can be used to evaluate the numerical values of the three parameters.

Renon and Prausnitz suggest that the α parameter, which is a non-randomness parameter, may be fixed according to solution type. In this study, two approaches were used to evaluate the parameters from heat of mixing data. In the first, α was assumed to be equal to 0.3 as recommended by Renon and Prausnitz. In the second, α together with the other two parameters, was evaluated from the data. Subsequently, in this paper the NRTL equation is defined as a 3-parameter equation when the value of α is not fixed, and as a 2-parameter equation when α is fixed according to solution type. A computer program based on Powells's[6, 7] non-gradient technique of minimizing a function using the concept of conjugate directions has been developed to determine the numerical values of the parameters. The function minimized is S_e^2 as defined in Table 1. Once the parameters have been evaluated g^E data and activity coefficients of the liquid phase can be calculated from eqns (2)–(4). The activity coefficients coupled with pure component vapor pressure data, P_i, can be used to calculate the x–y distribution from eqn (6) (assuming ideal vapor phase behavior)

$$y_1 = \frac{x_1 P_1 \gamma_1}{x_1 P_1 \gamma_1 + (1 - x_1) P_2 \gamma_2} \tag{6}$$

Ternary mixtures

The NRTL equation can be extended[1, 5] to multicomponent mixtures without incorporating any additional or higher order interaction parameters. g^E and $\ln \gamma_i$ can be computed from the following expressions:

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

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

Equations (7) and (8) involve nine parameters which can be determined from the three binary systems comprising the ternary. Assuming ideal vapor phase behavior, the x–y distribution can be calculated from the expression:

$$y_i = \frac{x_i P_i \gamma_i}{\sum_{i=1}^{3} x_i P_i \gamma_i} \tag{9}$$

The validity of ideal vapor phase behavior assumption is sufficient for most multicomponent VLE calculations.

Some researchers[8] have suggested that correction for vapor phase non-ideality improves the vapor–liquid equilibrium prediction. Such a correction may be incorporated into the theory as follows. The basic relationship between y_i and x_i for the general case of non-ideal vapor and liquid phases is given by eqn (10) which reduces to eqn (6) for the case of ideal vapor behavior.

$$y_i = \gamma_i x_i f_i^{(\mathrm{OL})} \exp(\bar{v}_i^{\mathrm{L}} P/RT)/\phi_i P \tag{10}$$

In this expression ϕ_i is the vapor phase fugacity coefficient which accounts for non-ideal gas behavior. $f_i^{(\mathrm{OL})}$ is the fugacity of liquid i in the standard state, $\bar{v}_i^{\mathrm{L}}$ is the partial molar liquid volume and P is the total pressure. The partial molar liquid volume $\bar{v}_i^{\mathrm{L}}$ is usually taken to be equal to the pure liquid molar volume v_i^{L}. The vapor fugacity coefficient is expressed by the virial equation truncated after the second term as

$$\ln \phi_i = (2/v) \sum_{j=1}^{m} y_j B_{ij} - \ln(Pv/RT) \tag{11}$$

where the B_{ij} are the virial coefficients (see Table 2), and v is the molar volume of the gas mixture which is related to the virial coefficient by

$$Pv/RT = 1 + \left(\sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j B_{ij} \right) \Big/ v \tag{12}$$

The fugacity of the pure liquid corrected to zero pressure is given by

$$f_i^{OL} = \phi_i^s P_i^s \exp\left(- v_i^L P_i^s / RT\right) \tag{13}$$

where ϕ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s. If P_i^s is well below the critical pressure P_{ci}, ϕ_i^s can be calculated from the virial equation

$$\ln \phi_i^s = (2/v_i^s)B_{ii} - \ln Z_i^s \tag{14}$$

where Z_i^s is calculated from eqn (15)

$$Z_i^s = P_i^s v_i^s / RT = 1 + B_{ii}/v_i^s \tag{15}$$

where v_i^s is the saturated molar volume of pure vapor i.

Virial coefficients are available from the literature, or they may be estimated from a correlation based on the three-parameter theory of corresponding states treatment of Pitzer and Curl[9]. Liquid molar volumes are available from the literature. Virial coefficients and liquid molar volumes used in this study are given in Table 2.

Liquid–liquid equilibria

The concept of equal chemical potential when two phases are in equilibrium at a given temperature and pressure is utilized to calculate the solubility envelope exhibited by the two liquid phases in a partially miscible ternary mixture. Mutual solubility can be calculated if activity coefficients are available. In this study, the activity coefficients were determined from the NRTL equation, and the following equations were solved simultaneously to determine the solubility curve:

$$\gamma_1' x_1' = \gamma_1'' x_1'' \tag{16}$$

$$\gamma_2' x_2' = \gamma_2'' x_2'' \tag{17}$$

$$\gamma_3' x_3' = \gamma_3'' x_3'' \tag{18}$$

$$x_1' + x_2' + x_3' = 1 \tag{19}$$

$$x_1'' + x_2'' + x_3'' = 1 \tag{20}$$

where $\gamma_i' = f(x_1', x_2', x_3')$ and $\gamma_i'' = f(x_1'', x_2'', x_3'')$

A computer program using the method of steepest descent has been developed to handle the iteration process involved in solving eqns (16)–(20).

RESULTS

Table 1 contains a summary for the sources of x–y and h^E data of the six binary and two ternary systems investigated in this study. For systems 2 and 5, two different

TABLE 1

BINARY SYSTEMS

(A) Parameters for NRTL equation determined from heat of mixing data and (B) statistical measures of fits of h^E and x–y data

Binary system No.	*System components*	*Temp. (°C)*	*NRTL parameters*[f]			*Statistical measure of fit*		*Source of experimental data, reference*	
			α_{ij}	$g_{ij} - g_{jj}$ (cal mol⁻¹)	$g_{ji} - g_{ii}$ (cal mol⁻¹)	S_e^2 [g]	σ_y [h]	*VLE data*	h^E
1	Cyclohexane(1)-n-heptane(2)	25	0.300	442.1	−110.2	1.2	9.8	10	11
1	Cyclohexane(1)-n-heptane(2)	25	−2.415	41.8	120.5	0.9	6.1	10	11
2[a]	n-Heptane(2)-toluene(3)	25	0.300	448.5	162.3	2.3	11.8	10	11
2[a]	n-Heptane(2)-toluene(3)	25	0.571	474.4	325.2	3.7	15.5	10	11
2[b]	n-Heptane(2)-toluene(3)	25	0.300	174.6	489.9	5.6	15.1	10	12
2[b]	n-Heptane(2)-toluene(3)	25	−2.366	189.0	119.8	27.4	7.8	10	12
3	Cyclohexane(1)-toluene(3)	25	0.300	357.4	292.5	17.8	12.4	10	11
3	Cyclohexane(1)-toluene(3)	25	−2.618	128.7	183.9	80.4	5.9	10	11
5[c]	Acetonitrile(1)-benzene(2)	45	0.300	579.9	44.1	2.1	10.6	13	13
5[c]	Acetonitrile(1)-benzene(2)	45	0.619	545.9	256.4	1.5	7.4	13	13
5[d]	Acetonitrile(1)-benzene(2)	45	0.300	511.9	92.9	13.3	6.6	14	14
5[d]	Acetonitrile(1)-benzene(2)	45	0.692	580.2	377.0	41.1	3.3	14	14
6	Benzene(2)-n-heptane(3)	45	0.300	917.5	−365.3	13.8	1.2	13	13
6	Benzene(2)-n-heptane(3)	45	0.369	1111.0	−558.0	54.8	9.3	13	13
7[e]	Acetonitrile(1)-n-heptane(3)	45	−0.316	903.9	864.9	146.7	12.3	13	13

[a] Using Schnaible[11] heat of mixing data. [b] Using Lundberg[12] heat of mixing data. [c] Using Palmer and Smith[13] heat of mixing data. [d] Using Brown and Smith[14] heat of mixing data. [e] System 7 exhibits a 2-phase heterogeneous azeotrope, and the value of α was not set according to solution type but was determined from heat of mixing data. [f] The subscripts i and j refer to the numbers given after the names of the components, respectively.

[g] $$S_e^2 = \frac{1}{N-2} \sum_j [h^E_{\text{cal}} - h^E_{\text{exptl}}]_j^2$$

[h] $$\sigma_y = \left\{ \frac{1}{N-1} [\sum_j [(y_{\text{cal}} - y_{\text{exptl}})/y_{\text{exptl}}]^2] \right\}^{1/2} \times 100$$

sets of h^E are available in the literature. For the n-heptane–toluene binary (system 2) there is a significant difference between the data of Schnaible[11] and those of Lundberg[12]. There is much less deviation between the data of Palmer and Smith[13] and those of Brown and Smith[14] for the acetonitrile–benzene binary (system 5). Each of these sets of data were examined separately to test the sensitivity of the method to variability in the h^E data used. The data giving the best predicted h^E values were used in the final correlation. Table 1 also summarizes the values of the various parameters determined from the heat of mixing data and eqn (5) for each binary system studied. Also included is a listing of statistical measures of the agreement between experimental heat of mixing and VLE data and those calculated from the NRTL equation. A typical set of results for the binary system cyclohexane–n-heptane is shown in Fig. 1.

Table 2 lists all the parameters used in the ternary VLE calculations. This includes the parameters determined from the six binary systems and the parameters used to calculate the correction for vapor phase non-ideality for the two ternary systems. Table 3 shows a comparison of the standard per cent deviation between the

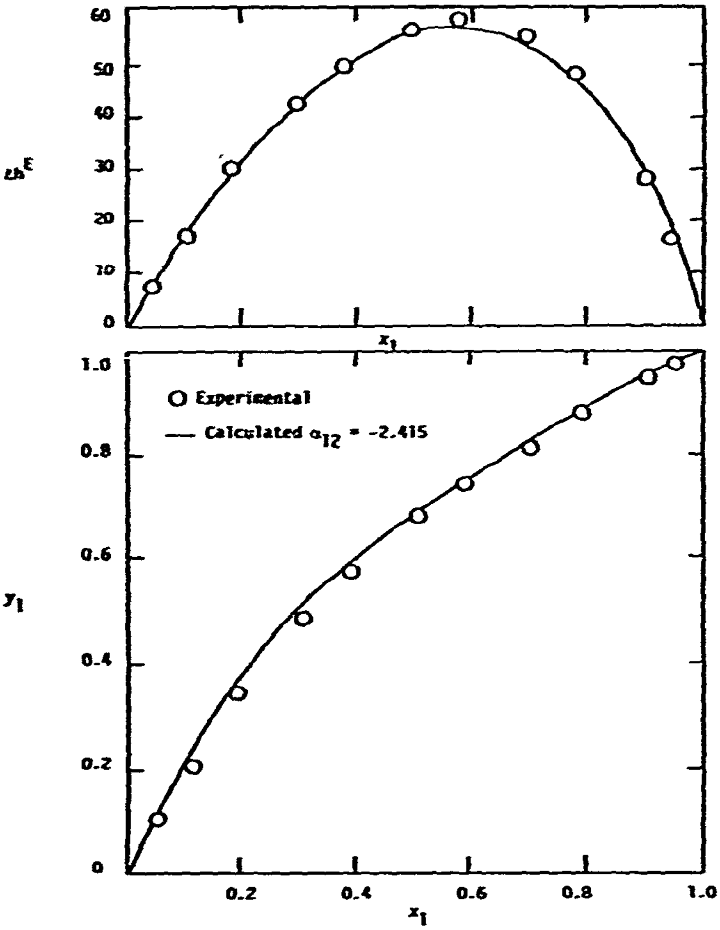

Fig. 1. Comparison of calculated and experimental data for the cyclohexane (1)–heptane(2) system at 25°C.

TABLE 2

PARAMETERS USED TO CALCULATE VAPOR–LIQUID EQUILIBRIUM DATA FOR THE TWO TERNARY SYSTEMS STUDIED

System	*Calculation*	α_{12}	α_{13}	α_{23}	$g_{12}-g_{22}$	$g_{21}-g_{11}$	$g_{13}-g_{33}$	$g_{31}-g_{11}$	$g_{23}-g_{33}$	$g_{32}-g_{22}$
					(cal mol⁻¹)					
Parameters used in eqn (8)										
4[a]	a	0.300	0.300	0.300	442.1	−110.2	357.4	292.5	448.5	162.3
4	b	0.300	0.300	0.300	442.1	−110.2	357.4	292.5	174.6	489.9
4	c	−2.415	−2.618	0.571	41.8	120.5	128.7	183.9	474.4	325.2
4	d	−2.415	−2.366	−2.618	41.8	120.5	128.7	183.9	189.0	119.8
8[b]	a	0.300	−0.316	0.300	579.9	44.1	903.9	864.9	917.5	−365.3
8	b	0.300	−0.316	0.300	511.9	92.9	903.9	864.9	917.5	−365.3
8	c	0.620	−0.316	0.369	545.9	256.4	903.9	864.9	1111.0	−558.0
8	d	0.692	−0.316	0.369	580.2	377.0	903.9	864.9	1111.0	−558.0

Parameters used in eqns (11) through (15)

	v_1^L	v_2^L	v_3^L	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
	(cc mol⁻¹)								
4	108.82	147.37	106.94	−1741.7	−2861.8	−2691.9	−2254.2	−2061.8	−2770.4
8	54.30	91.62	151.20	−4797.0	−1298.0	−2345.0	−1167.0	−1639.0	−1765.0

[a] System 4 consists of cyclohexane(1)-n-heptane(2)-toluene(3); *x*–*y* data from ref. 10. [b] System 8 consists of acetonitrile(1)-benzene(2)-n-heptane(3); *x*–*y* data from ref. 13.

TABLE 3

COMPARISON OF VAPOR PHASE MOLE FRACTIONS CALCULATED FROM EQN (8) BASED ON IDEAL AND NON-IDEAL VAPOR PHASE BEHAVIOR FOR THE TWO TERNARY SYSTEMS STUDIED

System[a]	*Calculation*[b]	*Vapor phase behavior assumption*	*Standard deviation*[c] *of fit of vapor phase mole fraction (%)*			
			σ_{y_1}	σ_{y_2}	σ_{y_3}	*Avg.* σ
4	a	ideal	10.0	9.1	19.9	13.0
4	a	non-ideal	9.8	9.4	21.4	13.6
4	b	ideal	9.0	11.8	21.3	14.0
4	b	non-ideal	8.8	12.4	22.8	14.7
4	c	ideal	6.0	12.2	17.2	11.8
4	c	non-ideal	6.2	12.4	18.7	12.4
4	d	ideal	3.6	3.8	5.2	4.2
4	d	non-ideal	2.8	4.8	6.3	4.6
8	a	ideal	7.5	13.0	17.6	12.7
8	a	non-ideal	7.6	9.3	24.6	13.8
8	b	ideal	7.5	12.9	18.5	13.0
8	b	non-ideal	7.9	9.4	24.9	14.1
8	c	ideal	9.7	16.4	9.3	11.8
8	c	non-ideal	6.9	13.7	10.2	10.2
8	d	ideal	10.6	15.8	10.7	12.3
8	d	non-ideal	7.2	13.4	9.4	10.0

[a] System 4 consists of cyclohexane–n-heptane–toluene; System 8 consists of acetonitrile–benzene–n-heptane. [b] See Table 2 for values of parameters used in eqn (8). [c] See Table 1 for definition of σ_y.

experimental and calculated vapor phase mole fractions for each of the ternary systems studied for both the cases of ideal and non-ideal vapor phase behavior. Typical calculations* comparing calculated and experimental vapor–liquid equilibrium data for the two ternary systems are given in Tables 4 and 5. The results shown represent the calculations giving the best agreement between calculated and experimental x–y data for the various combinations of parameters (see Table 2) used in eqn (8). Table 6 gives a comparison of the calculated and experimental total pressure of the two ternary systems. Figure 2 shows the agreement obtained in the partially miscible region between the calculated and experimental binodal distribution curve for the acetonitrile–benzene–n-heptane system. Only one calculated curve is reported in Fig. 2 (parameters used are found in Table 2—System 8, Calculation a). However, calculations* based on other combinations of parameters listed in Table 2 resulted in essentially the same values as those shown in Figure 2.

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* Detailed tabulations of all data used and results obtained are available upon request.

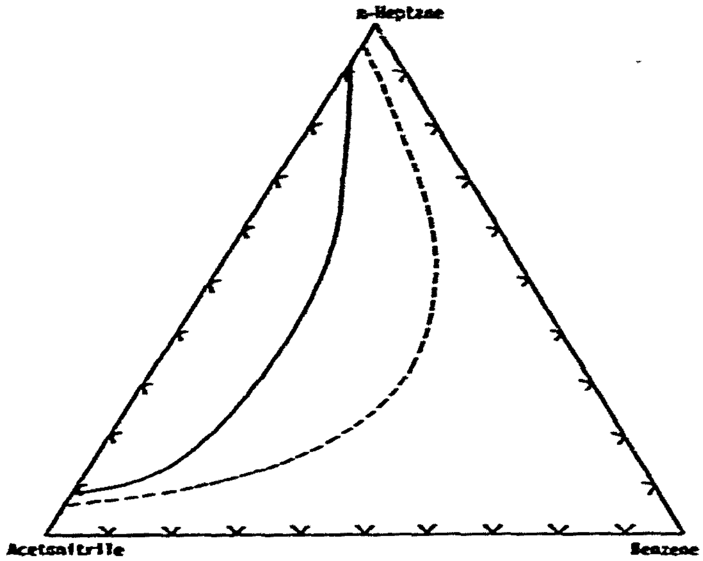

Fig. 2. Comparison of calculated and experimental data for the partially miscible region of the acetonitrile(1)–benzene(2)–n-heptane(3) system at 45 °C. ——, Experimental; – – –, calculated (based on eqns (8), (16)–(20) using parameters in Table 2, System 8, Calculation a and Palmer and Smith[13] heat of mixing data).

DISCUSSION

The quantity S_c^2 listed and defined in Table 1 is a statistical measure of the variance of the fit of the theoretical model to the data. Calculated h^E values were generated from eqn (5) using constants determined from experimental h^E data. The goodness of fit between calculated and experimental h^E values is not a good criterion as to whether the constants when used in eqns (3) and (4) will predict VLE data which agree well with experimental values. This is more clearly revealed by the σ_y values reported in Table 1. The quantity σ_y is the percent standard deviation of the calculated fit of the VLE data and is defined in Table 1. It is evident that there is no relationship between the values of S_c^2 and σ_y. An examination of the values of σ_y for system 2 ($\sigma_y = 15.5$ and $\sigma_y = 7.8$) and for system 5 ($\sigma_y = 7.4$ and $\sigma_y = 3.3$), shows the marked effect of using different sets of h^E data on the accuracy of the VLE prediction.

Two observations may be made from the results reported in Tables 2 and 3. First, it is observed for ternary calculations that the 3-parameter version of the NRTL equation consistently gives a better fit of the data than does the 2-parameter version. Secondly, because the ternary system cyclohexane–n-heptane–toluene shows small deviations from ideal vapor phase behavior, corrections for vapor-phase non-ideality do not significantly improve the calculations. However, for the ternary system acetonitrile–benzene–n-heptane, which is a highly non-ideal hydrocarbon system, definite improvement in the data fit is attained when the vapor phase non-ideality correction is applied. Improvements of as much as 20% were obtained.

TABLE 4

COMPARISON OF CALCULATED AND EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR THE TERNARY SYSTEM CYCLOHEXANE(1)-n-HEPTANE(2)-TOLUENE(3) AT 25°C

N	*Experimental*						*Calculated from eqn (8) ideal vapor phase calculation*[a]			*Calculated from eqn (8) non-ideal vapor phase calculation*[a]		
	x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3
1	0.1010	0.1001	0.7989	0.3072	0.1483	0.5445	0.3253	0.1623	0.5124	0.3196	0.1659	0.5189
2	0.1009	0.2505	0.6486	0.2628	0.3051	0.4320	0.2704	0.3132	0.4164	0.2664	0.3146	0.4233
3	0.1001	0.4494	0.4505	0.2292	0.4652	0.3056	0.2359	0.4574	0.3067	0.2335	0.4572	0.3130
4	0.1003	0.6492	0.2505	0.2129	0.6074	0.1797	0.2242	0.5854	0.1904	0.2227	0.5851	0.1949
5	0.1007	0.7990	0.1003	0.2091	0.7137	0.0772	0.2263	0.6872	0.0865	0.2253	0.6872	0.0891
6	0.2499	0.1005	0.6496	0.5343	0.1048	0.3609	0.5531	0.1089	0.3379	0.5474	0.1116	0.3441
7	0.2510	0.2493	0.4997	0.4971	0.2273	0.2756	0.4981	0.2286	0.2734	0.4930	0.2310	0.2792
8	0.2509	0.4986	0.2505	0.4492	0.3985	0.1523	0.4561	0.3875	0.1564	0.4529	0.3894	0.1603
9	0.2510	0.6489	0.1001	0.4376	0.4951	0.0673	0.4520	0.4778	0.0703	0.4498	0.4796	0.0723
10	0.3335	0.3325	0.3340	0.5616	0.2575	0.1809	0.5636	0.2542	0.1822	0.5590	0.2568	0.1865
11	0.4495	0.0999	0.4506	0.7052	0.0768	0.2179	0.7131	0.0776	0.2092	0.7076	0.0796	0.2139
12	0.4502	0.4484	0.1014	0.6394	0.3018	0.0588	0.6486	0.2917	0.0597	0.6452	0.2944	0.0611
13	0.5001	0.2500	0.2499	0.7058	0.1680	0.1262	0.7049	0.1681	0.1270	0.6999	0.1708	0.1300
14	0.6502	0.0996	0.2502	0.8172	0.0636	0.1192	0.8160	0.0645	0.1194	0.8110	0.0661	0.1220
15	0.6493	0.2501	0.1006	0.7471	0.1507	0.0521	0.7906	0.1547	0.0547	0.7863	0.1571	0.0557
16	0.7992	0.0997	0.1011	0.8905	0.0589	0.0506	0.8824	0.0623	0.0553	0.8780	0.0636	0.0559
	Standard deviation, σ[b]						3.6%	3.8%	5.2%	2.8%	4.8%	6.3%

[a] See Table 2, System 4, Calculation d for parameters used in calculations. [b] See Table 1 for definition of σ.

COMPARISON OF CALCULATED AND EXPERIMENTAL VAPOR–LIQUID EQUILIBRIUM DATA FOR THE TERNARY SYSTEM ACETONITRILE(1)–BENZENE(2)–n-HEPTANE(3) AT 45°C

N	*Experimental*						*Calculated from eqn (8) ideal vapor phase calculation* [a]			*Calculated from eqn (8) non-ideal vapor phase calculation* [a]		
	x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3
1	0.0827	0.1417	0.7756	0.5299	0.1384	0.3317	0.6622	0.0810	0.2568	0.6115	0.0873	0.2762
2	0.0686	0.2483	0.6831	0.4422	0.2444	0.3134	0.5569	0.1760	0.2671	0.5240	0.1866	0.2839
3	0.0297	0.8648	0.1055	0.0874	0.8367	0.0759	0.0864	0.8424	0.0712	0.0850	0.8677	0.0751
4	0.1460	0.7601	0.0939	0.2816	0.6427	0.0757	0.2864	0.6446	0.0690	0.2764	0.6690	0.0731
5	0.8869	0.0991	0.0140	0.7170	0.1810	0.1020	0.6967	0.2004	0.1029	0.6566	0.2149	0.1109
6	0.8018	0.1669	0.3130	0.6234	0.2387	0.1379	0.6130	0.2467	0.1403	0.5769	0.2628	0.1505
7	0.7427	0.2339	0.2340	0.5906	0.3092	0.1002	0.5979	0.3170	0.0850	0.5638	0.3371	0.0914
8	0.6497	0.3312	0.0191	0.5445	0.3995	0.0560	0.5611	0.3887	0.0502	0.5302	0.4118	0.0539
9	0.5719	0.4120	0.0161	0.5150	0.4453	0.0397	0.5285	0.4382	0.0333	0.5003	0.4629	0.0357
10	0.4733	0.5137	0.0130	0.4688	0.5050	0.0262	0.4841	0.4953	0.0206	0.4595	0.5212	0.0220
11	0.4615	0.5030	0.0355	0.4600	0.4774	0.0626	0.4828	0.4656	0.0521	0.4576	0.4899	0.0557
12	0.4393	0.4827	0.0780	0.4649	0.4239	0.1112	0.4832	0.4168	0.1000	0.4578	0.4388	0.1068
13	0.3974	0.4407	0.1619	0.4669	0.3589	0.1742	0.4966	0.3394	0.1640	0.4693	0.3578	0.1747
14	0.3527	0.3942	0.2531	0.4810	0.3146	0.2044	0.5225	0.2738	0.2037	0.4922	0.2894	0.2169
15	0.0746	0.7427	0.1827	0.2053	0.6738	0.1209	0.2144	0.6739	0.1117	0.2085	0.6971	0.1179
16	0.1345	0.6930	0.1725	0.2855	0.5862	0.1283	0.3090	0.5797	0.1113	0.2977	0.6024	0.1178
17	0.2684	0.5872	0.1444	0.3914	0.4766	0.1320	0.4221	0.4610	0.1168	0.4020	0.4828	0.1242
18	0.3470	0.5231	0.1299	0.4395	0.4287	0.1318	0.4610	0.4144	0.1246	0.4374	0.4353	0.1327
19	0.4020	0.4791	0.1189	0.4582	0.4024	0.1394	0.4815	0.3881	0.1304	0.4559	0.4085	0.1390
20	0.5212	0.3845	0.0943	0.5056	0.3484	0.1460	0.5156	0.3407	0.1437	0.4868	0.3597	0.1534
21	0.6021	0.3219	0.0760	0.5247	0.3228	0.1525	0.5357	0.3142	0.1501	0.5051	0.3324	0.1603
22	0.1177	0.3317	0.5506	0.4487	0.2878	0.2635	0.5513	0.2199	0.2288	0.5177	0.2332	0.2438
23	0.2602	0.2766	0.4632	0.5307	0.2152	0.2541	0.6073	0.1567	0.2359	0.5653	0.1674	0.2526
24	0.3790	0.2314	0.3896	0.5608	0.1794	0.2598	0.5992	0.1330	0.2678	0.5583	0.1420	0.2859
25	0.4282	0.2132	0.3593	0.5680	0.1678	0.2642	0.5908	0.1251	0.2841	0.5505	0.1342	0.3025
26	0.4779	0.2977	0.2244	0.5262	0.2493	0.2245	0.5420	0.2131	0.2449	0.5089	0.2258	0.2606
27	0.6093	0.2229	0.1678	0.5482	0.2082	0.2436	0.5396	0.1820	0.2784	0.5061	0.1929	0.2957
28	0.0622	0.5379	0.3999	0.2555	0.5211	0.2234	0.3095	0.4878	0.2027	0.2988	0.5071	0.2134
29	0.1003	0.5151	0.3846	0.3288	0.4549	0.2163	0.3908	0.4165	0.1927	0.3739	0.4352	0.2037
30	0.2648	0.4206	0.3146	0.4603	0.3318	0.2079	0.5168	0.2841	0.1991	0.4871	0.3001	0.2120
31	0.3704	0.3597	0.2699	0.4973	0.2884	0.2143	0.5371	0.2438	0.2192	0.5049	0.2581	0.2334
32	0.2958	0.1880	0.5162	0.5795	0.1452	0.2753	0.6504	0.0951	0.2545	0.6008	0.1023	0.2736
33	0.4891	0.1970	0.3139	0.5691	0.1622	0.2687	0.5751	0.1228	0.3021	0.5369	0.1307	0.3213
	Standard deviation, σ[b]						10.6%	15.8%	10.7%	7.2%	13.4%	9.4%

TABLE 6

COMPARISON OF THE CALCULATED AND EXPERIMENTAL TOTAL PRESSURE FOR THE TWO TERNARY SYSTEMS STUDIED

Cyclohexane(1)–n-heptane(2)–toluene(3)
T = 25°C

N	x_1	P_{exp}	P_{cal}[a]
1	0.1010	0.0561	0.0598
2	0.1009	0.0610	0.0637
3	0.1001	0.0646	0.0671
4	0.1003	0.0671	0.0693
5	0.1007	0.0669	0.0700
6	0.2499	0.0737	0.0771
7	0.2510	0.0738	0.0793
8	0.2509	0.0775	0.0821
9	0.2510	0.0781	0.0831
10	0.3335	0.0817	0.0877
11	0.4495	0.0915	0.0952
12	0.4502	0.0949	0.0978
13	0.5001	0.0960	0.1001
14	0.6502	0.1093	0.1093
15	0.6493	0.1077	0.1100
16	0.7992	0.1171	0.1178
Standard deviation, σ[c]			4.5%

Acetonitrile(1)–benzene(2)–n-heptane(3)
T = 45°C

N	x_1	P_{exp}	P_{cal}[b]
1	0.0827	0.3705	0.4524
2	0.0686	0.3567	0.3839
3	0.0297	0.3115	0.2877
4	0.1460	0.3557	0.3305
5	0.8869	0.3486	0.3392
6	0.8018	0.3772	0.3658
7	0.7427	0.3757	0.3597
8	0.6497	0.3732	0.3592
9	0.5710	0.3754	0.3590
10	0.4733	0.3734	0.3576
11	0.4615	0.3791	0.3621
12	0.4393	0.3887	0.3690
13	0.3974	0.3962	0.3794
14	0.3527	0.4011	0.3898
15	0.0746	0.3530	0.3090
16	0.1345	0.3663	0.3322
17	0.2684	0.3882	0.3601
18	0.3470	0.3961	0.3687
19	0.4020	0.3997	0.3728
20	0.5212	0.4018	0.3783
21	0.6021	0.4000	0.3796
22	0.1177	0.3887	0.3968
23	0.2602	0.4166	0.4277
24	0.3790	0.4167	0.4246
25	0.4282	0.4180	0.4232
26	0.4779	0.4078	0.4007
27	0.6093	0.4100	0.4081
28	0.0622	0.3400	0.3136
29	0.1003	0.3591	0.3413
30	0.2648	0.3970	0.3876
31	0.3704	0.4045	0.3955
32	0.2958	0.4163	0.4536
33	0.4891	0.4159	0.4215
Standard deviation, σ[c]			6.6%

[a] Denominator of eqn (9) using parameters for calculation 4d, Table 2. [b] Denominator of eqn (9) using parameters for calculation 8d, Table 2. [c] See Table 1 for definition of σ.

The present prediction scheme can also be used to calculate the total pressure of the system without resorting to actual experimental measurement. The results of this type of calculation are tabulated in Table 6 and indicate quite acceptable agreement with the experimental data.

Figure 2 illustrates the limitation of the method in predicting the solubility envelope of the partially miscible ternary mixture. Apparently the NRTL equation does not possess sufficient generality to describe both the miscible and immiscible regions using parameters obtained from the miscible region. These results are consistent with the observation made by Renon and Prausnitz[5] in their study that the parameters obtained from x–y analysis of miscible regions cannot be used to predict liquid–liquid phase equilibrium data accurately for the immiscible region. Solubility data are very sensitive to the parameters used and a more accurate excess function model is required if they are to be predicted successfully.

CONCLUSION

This study shows that the multicomponent NRTL equation using parameters obtained from binary heat of mixing data can be used to calculate ternary VLE data without the need for any higher order or additional parameters. Better predictions of VLE data are obtained using the three-parameter version of the NRTL equation than the two-parameter version for both binary and ternary calculations.

In most cases agreement between calculated and experimental equilibrium data is within 10–15% and in some cases 1–5%.

This technique offers a new method for calculating multicomponent VLE data without resorting to actual measurement of these data.

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