Thermochimica Acta, 198 (1992) 329–344
Elsevier Science Publishers B.V., Amsterdam

Calculation of excess heat capacities for liquid mixtures

Y. Demirel and H.Ö. Paksoy

Faculty of Art and Science, University of Çukurova, 01330 Adana (Turkey)

(Received 16 August 1991)

Abstract

Experimental data of excess heat capacities for 29 binary liquid mixtures of various types have been correlated by the NRTL and UNIQUAC models. For nine of these mixtures data at several isotherms is included. The parameters of the models, six for the NRTL and four for the UNIQUAC, have been estimated by a minimization technique using Simplex and Fletcher techniques simultaneously. The partial molar excess heat capacities at infinite dilution are also calculated. Agreement between experimental and calculated values is satisfactory except for associating and highly non-ideal mixtures. The UNIQUAC model performs better than the NRTL model.

INTRODUCTION

The excess heat capacity C_p^E of binary liquid mixtures is an important thermodynamic property because it provides information about molecular interactions in mixtures. The heat capacity of a liquid mixture can only be calculated with a knowledge of the excess heat capacity at various temperatures and compositions. Previously, excess heat capacities were calculated by differentiation of the values of excess enthalpy h^E (obtained from the NRTL and UNIQUAC models) with respect to temperature, but the results were unsatisfactory [1,2]. In order to predict C_p^E data accurately from this indirect method, the accuracy of the measurement of h^E must be very high over a narrow temperature range [3]. We have therefore decided to correlate the experimental C_p^E data directly with the UNIQUAC and NRTL models.

The parameters have been estimated by the models for nearly ideal, associating, highly non-ideal and partially miscible mixtures. The estimated parameters are also used to calculate the partial molar excess heat capacities at infinite dilution for each component and specific heat capacities for some aqueous alcohol mixtures which have heat capacities higher than that of water [4].

Correspondence to: Y. Demirel, Faculty of Art and Science, University of Çukurova, 01330 Adana, Turkey.

0040-6031/92/$05.00

The parameters are estimated from the experimental C_p^E data by the NRTL [5] and UNIQUAC [6] excess Gibbs free energy (g^E) models. The effect of temperature on the NRTL parameters are assumed [1] to be

$$g_{21} - g_{11} = c_1 + c_2/(T - 273.15) \tag{1}$$

$$g_{12} - g_{22} = c_3 + c_4/(T - 273.15) \tag{2}$$

$$\alpha_{21} = \alpha_{12} = c_5 + c_6/(T - 273.15) \tag{3}$$

Here, $g_{21} - g_{11}$, $g_{12} - g_{22}$ and α_{12} are the energies of interaction (in J mol^{-1}) and the non-randomness parameters respectively. The terms c_1, c_3, c_5 (in J mol^{-1}) c_2, c_4 (in J K mol^{-1}) and c_6 (in K) are the coefficients of temperature.

Based on the Gibbs–Helmholtz equation

$$h^E = -RT^2 \left[\frac{\partial (g^E/RT)}{\partial T} \right] \tag{4}$$

the equations for h^E have been derived for the NRTL and UNIQUAC models and explained in detail elsewhere [1,2]. Differentiating the expression for h^E with respect to temperature gives eqn. (5) for C_p^E.

$$\begin{aligned}
C_p^E = {} & \frac{R x_1 x_2 G_{21}}{T' S_1^2} \left\{ T\beta_1 \left[2(T - 273.15)\tau_{21} - \frac{\delta_1}{T} \right] + x_1 T c_6 \tau_{21} \left(\frac{2c_2}{RT'} + \tau_{21} \right) \right. \\
& + \frac{w_1 S_1 \delta_1}{T'} + \left[\frac{c_2 \beta_1}{R} + \tau_{21}(T'\beta_1 - x_1 c_6 T \tau_{21}) \right] \\
& \left. \times \left[\frac{w_1}{T'} \left(1 - \frac{2 x_2 G_{21}}{S_1} \right) - \frac{T + 273.15}{T - 273.15} \right] \right\} \\
& + \frac{R x_1 x_2 G_{12}}{T' S_2^2} \left\{ T\beta_2 \left[2(T - 273.15)\tau_{12} - \frac{\delta_2}{T} \right] + x_2 T c_6 \tau_{12} \left(\frac{2c_4}{RT'} + \tau_{12} \right) \right. \\
& + \frac{w_2 S_2 \delta_2}{T'} + \left[\frac{c_4 \beta_2}{R} + \tau_{12}(T'\beta_2 - x_2 c_6 T \tau_{12}) \right] \\
& \left. \times \left[\frac{w_2}{T'} \left(1 - \frac{2 x_1 G_{12}}{S_2} \right) - \frac{T + 273.15}{T - 273.15} \right] \right\}
\end{aligned} \tag{5}$$

where $\tau_{21} = (g_{21} - g_{11})/RT$; $\tau_{12} = (g_{12} - g_{22})/RT$; $G_{21} = \exp(-\tau_{21}\alpha_{12})$; $G_{12} = \exp(-\tau_{12}\alpha_{12})$; $S_1 = x_1 + x_2 G_{21}$; $S_2 = x_2 + x_1 G_{12}$; $\delta_1 = c_2/R + T'\tau_{21}$; $\delta_2 = c_4/R + T'\tau_{12}$; $w_1 = \alpha_{12}\delta_1 + T\tau_{21}c_6$; $w_2 = \alpha_{12}\delta_2 + T\tau_{12}c_6$; $\beta_1 = S_1 - x_1\tau_{21}\alpha_{12}$; $\beta_2 = S_2 - x_2\tau_{12}\alpha_{12}$; $T' = (T - 273.15)^2$; R is the gas constant in J K^{-1} mol^{-1}.

The effect of temperature on the parameters for the UNIQUAC model are given by the eqns. (6) and (7) [1].

$$a_{21} = d_1 + d_2/T \tag{6}$$

$$a_{12} = d_3 + d_4/T \tag{7}$$

Here a_{21} and a_{12} are the interaction parameters (in K). Terms d_1 and d_3 (in K) and d_2 and d_4 (in K^2) are the coefficients related to the parameters a_{ij}. The UNIQUAC model contains a pure-component structural parameter q. Anderson and Prausnitz [7] slightly modified the UNIQUAC model and introduced new values of surface parameters q' for the alcohols and water, to be used in the residual part of the equation. The equation for C_p^E is obtained as [2]

$$C_p^E = \frac{Rq_1' x_1 \Theta_2 \tau_{21}^*}{T^2(\Theta_1 + \Theta_2 \tau_{21}^*)}\left[\Theta_1 (d_1 + 2d_2/T)^2 - 2d_2(\Theta_1 + \Theta_2 \tau_{21}^*)\right] + \frac{Rq_2' x_2 \Theta_1 \tau_{12}^*}{T^2(\Theta_2 + \Theta_1 \tau_{12}^*)}\left[\Theta_2 (d_3 + 2d_4/T)^2 - 2d_4(\Theta_2 + \Theta_1 \tau_{12}^*)\right] \tag{8}$$

where $\tau_{12}^* = \exp(-a_{12}/T)$; $\tau_{21}^* = \exp(-a_{21}/T)$; $\Theta_1 = x_1 q_1'/(x_1 q_1' + x_2 q_2')$; $\Theta_2 = x_2 q_2'/(x_1 q_1' + x_2 q_2')$

ESTIMATION OF PARAMETERS

In estimating the parameters, the objective function of eqn. (9) was minimized.

$$F = \frac{1}{N}\left\{\sum^{N} \frac{\sum^{n}\left[w\left(C_{p,i,\text{exptl}}^E - C_{p,i,\text{calcd}}^E\right)/C_{p,i,\text{exptl}}^E\right]^2}{n}\right\} \tag{9}$$

where n is the number of experimental data points of C_p^E at a specified temperature. N is the number of isothermal systems. The term w denotes a weight factor with the changing value of 10 or 100, according to the maximum value of C_p^E for the system considered. For minimizing the function F, a package program called MINUIT [8] was used. The MINUIT program performs minimization and analysis of the shape of a multiparameter function. It incorporates Fletcher and Simplex techniques. According to the global logic built into the program, if one of the techniques fails or is not satisfactory, then another technique is called automatically to make further attempts.

RESULTS AND DISCUSSION

Using C_p^E data for various types of binary liquid mixtures, the parameters of the NRTL and UNIQUAC models have been estimated. The mixtures

TABLE 1

Comparison of excess heat capacity predictions by the NRTL and UNIQUAC models

n	T (°C)	Parameter													
		NRTL								UNIQUAC					
		c_1 [a]	c_2 [b]	c_3	c_4	c_5	c_6 [c]	σ [d] $\times 100$	S [e]	d_1 [c]	d_2 [c]	d_3 [f]	d_4 [f]	σ [d] $\times 100$	S [e]
(1) Methanol(1)–ethanol(2) [9]															
11	25	0.3185	0.0678	0.3039	0.0271	0.6818	1.0511	0.53	4.24	−222.4	28152	463.7	−32461	0.05	1.36
(2) Methanol(1)–1-propanol(2) [9]															
12	25	0.1297	0.1023	0.0010	0.0308	0.1023	7.2340	0.24	1.93	−44.4	43342	224.1	6624	0.13	1.85
(3) Methanol(1)–1-butanol(2) [9]															
12	25	0.5866	0.1700	−0.0482	0.0214	0.1509	0.4649	0.05	1.31	−136.9	4038	−325.2	26129	0.01	0.28
(4) Methanol(1)–iso-butanol(2) [10]															
11	25	−0.0477	0.9126	1.0634	−0.7217	0.4674	0.0803	0.10	1.55	−440.2	113000	162.9	−32937	0.07	1.56
*(5) Methanol(1)–*sec*-butanol(2) [10]*															
11	25	0.1901	1.1080	0.0037	−0.0042	0.1014	14.6070	0.10	1.78	−570.6	43585	−822.9	72854	0.07	2.03
*(6) Methanol(1)–*tert*-butanol(2) [10]*															
11	25	−1.8959	17.5900	2.4143	−20.3970	0.2271	0.7860	0.05	1.29	−728.7	199090	−910.5	203850	0.04	1.34
(7) Ethanol(1)–heptane(2) [g] [11]															
19	−20	32.8050	−0.9116	19.4740	−0.3738	0.1482	−0.0038	2.68	–	−463.0	643290	−157.2	38	2.57	9.77
19	−5								–						9.25
19	5								–						11.71
19	15								–						14.36
19	25								13.15						14.33
19	35								11.28						13.95
19	45								11.20						15.57

*(8) 2-propanol(1)–*n*-heptane(2)* ^{g} *[11]*															
15	−35	−3.3515	23.1860	23.1860	0.0099	0.1000	−0.0009	8.69	–	200.3	371810	179.9	672	12.5	24.31
15	−15								–						33.42
15	−5								–						33.33
15	5								8.34						31.13
15	15								26.46						27.64
*(9) 1-propanol(1)-*n*-hexene(2)* ^{g} *[12]*															
7	−8	38.0210	−0.2828	22.7440	0.0086	0.1465	0.0002	2.27	–	−452.2	576180	237.2	60826	1.47	13.45
7	−3								–						9.57
7	2								–						8.94
7	7								–						7.22
7	12								11.41						7.30
7	17								9.46						8.41
7	22								9.10						11.22
*(10) 1-hexanol(1)–*n*-hexane(2)* ^{g} *[13]*															
8	−8	0.1055	1.0682	1.1773	−0.8664	0.1000	1.2387	47.89	–	131.1	443730	−157.4	69463	4.12	16.09
8	−3								–						13.77
8	2								–						11.52
8	7								54.31						13.67
8	12								36.71						18.04
8	17								66.65						20.34
(11) Water(1)–methanol(2) [3,14]															
21	15	−6.7845	0.0919	6.7837	−0.0461	0.2522	0.0038	2.20	12.25	−1167.3	99361	−916.6	547300	2.27	18.39
19	25								13.16						6.94
22	35								8.82						5.13
(12) Water(1)–ethanol(2) [3,14]															
15	15	16.3330	−0.0628	29.4530	−0.3407	0.1794	0.0001	1.93	10.54	1114.7	285610	−970.2	605870	1.33	7.92
17	25								7.87						5.98
22	35								7.45						8.71

TABLE 1 (continued)

n	T (°C)	Parameter													
		NRTL								UNIQUAC					
		c_1 [a]	c_2 [b]	c_3	c_4	c_5	c_6 [c]	σ [d] ×100	S [e]	d_1 [c]	d_2 [c]	d_3 [f]	d_4 [f]	σ [d] ×100	S [e]
(13) Water(1)–1-propanol(2) [3,14]															
22	15	17.6540	−0.2404	30.5120	−1.2378	0.1685	0.0015	3.41	13.56	876.2	−170580	−1142.4	712600	0.87	9.01
22	25								14.06						4.77
21	30								11.09						5.78
(14) Water(1)–butanol(2) [h] *[3]*															
8	25	−4.0637	63.2530	3.8090	−66.3190	0.6306	−1.9827	0.02	0.72	−294.2	299740	−848.8	705830	0.34	3.73
*(15) Benzene(1)–*n*-heptane(2) [15]*															
9	20	0.5866	−10.2360	−0.5039	11.0100	0.5096	−5.1706	0.35	2.81	159.7	−1682	−113.2	34165	0.02	1.51
9	25								5.05						1.11
9	35								4.55						1.21
(16) Benzene(1)–toluene(2) [16]															
9	25	0.0804	0.0332	0.0209	−0.0006	0.1235	0.4560	0.82	4.35	−158.2	6071	108.6	2838	0.07	1.70
(17) Benzene(1)–ethylbenzene(2) [16]															
9	25	0.0061	0.1013	0.1039	0.0076	0.6954	8.9866	0.01	0.47	−103.3	5046	42.6	2732	0.01	0.25
*(18) Benzene(1)-*o*-xylene(2) [16]*															
9	25	0.0308	0.0801	0.0684	0.0817	0.6043	5.2380	0.05	1.13	−42.0	19312	−9.6	−5421	0.03	1.17
*(19) Benzene(1)–*m*-xylene(2) [16]*															
9	25	0.2609	0.1504	0.3476	0.0873	0.6526	2.1606	0.01	1.57	−16.0	1514	−57.3	6465	0.05	1.39

(20) Benzene(1)–p-*xylene(2) [16]*															
9	25	0.0247	0.0871	0.3006	0.0012	0.1015	1.0650	0.07	1.31	9.3	−6878	−30.9	13273	0.14	2.30
(21) Benzene(1)–cyclohexane(2) [17]															
19	25	0.4376	0.4702	0.9088	0.1290	0.6973	0.7134	0.05	1.40	−21.9	25378	63.9	16658	0.04	1.11
(22) Benzonitrile(1)–cyclohexane(2) [18]															
13	20	1.9767	−0.4209	−0.0624	0.4264	0.5997	0.3238	35.7	33.81	386.8	2504	−0.9	22104	19.8	43.38
15	25								44.72						26.23
9	45								57.82						34.40
(23) Toluene(1)–ethylbenzene(2) [16]															
9	25	0.0986	−0.0023	0.0644	−0.0014	0.6999	0.4448	0.86	4.62	19.2	−147	16.9	−48	0.51	4.63
(24) Toluene(1)–o-*xylene(2) [16]*															
9	25	−0.0058	0.0707	0.1950	−0.0207	0.1000	0.3155	0.26	2.36	0.4	2508	−6.2	586	0.16	2.38
(25) Toluene(1)–m-*xylene(2) [16]*															
9	25	−0.0008	0.0232	0.0831	0.0004	0.1239	0.9990	0.04	0.95	−50.3	1477	32.4	578	0.02	0.94
(26) 2-methylpentanol(1)–n-*hexane(2) [19]*															
11	25	4.7851	6.6107	−3.1265	−13.6020	0.5555	−2.6397	2.21	7.91	534.4	298850	422.9	28044	0.15	2.36
(27) 3-methyl-3-pentanol(1)-n-*hexane(2) [19]*															
13	25	12.1360	5.1199	−3.1977	−1.4426	0.4919	−0.1580	0.80	4.45	137.1	283240	348.6	−13537	0.12	1.83
(28) 3-methyl-2-pentanol(1)–n-*hexane(2) [19]*															
10	25	1.5924	−11.6400	−3.6026	5.5930	0.6998	2.0095	1.32	5.40	444.1	273360	57.8	−5752	0.80	5.00
(29) 4-methyl-2-pentanol(1)–n-*hexane(2) [19]*															
11	25	7.5110	9.2127	0.0118	−12.7520	0.2268	−0.7364	2.20	8.84	327.1	325650	−71.4	7071	0.55	4.75

---

[a] In kJ mol^{-1}. [b] In kJ K mol^{-1}. [c] In K. [d] Variance. [e] Absolute average error. [f] In K^2. [g] No convergence obtained for the whole range of temperatures. [h] Partially miscible system.

TABLE 2

Structural parameters for the UNIQUAC model

System	q	q'	System	q	q'
Methanol	1.43	0.96	Hexanol	4.13	1.78
Ethanol	1.97	0.92	Ethylbenzene	3.51	3.51
1-Propanol	3.13	0.89	Benzene	2.40	2.40
2-Propanol	3.13	0.89	*n*-Hexane	3.86	3.86
1-Butanol	3.05	0.88	*n*-Hexene	3.64	3.64
iso-Butanol	3.05	0.88	*n*-Heptane	4.40	4.40
sec-Butanol	3.05	0.88	Toluene	2.97	2.97
tert-Butanol	3.05	0.88	Cyclohexane	3.01	3.01
2-Methylpentanol	4.13	1.78	*o*-Xylene	3.54	3.54
3-Methyl-2-pentanol	4.12	1.78	*p*-Xylene	3.54	3.54
3-Methyl-3-pentanol	4.82	1.78	*m*-Xylene	3.54	3.54
4-Methyl-2-pentanol	4.12	1.78	Water	1.40	1.00

include nearly ideal, associating and partially miscible systems. Nine of them have data at more than one isotherm. When using the NRTL model, some convergence difficulties occurred with the low temperature data for C_p^{E} for systems 7–10. The estimated parameters and the variances of the fits are given in Table 1. The variance of the fit is calculated from

$$\sigma = \frac{1}{\left(\sum n - N_{\mathrm{P}}\right)} \sum^{N} \sum^{n} \left[\left(C_{p,i,\mathrm{exptl}}^{\mathrm{E}} - C_{p,i,\mathrm{calcd}}^{\mathrm{E}}\right) / C_{p,i,\mathrm{exptl}}^{\mathrm{E}}\right]^2 \tag{10}$$

where $\sum n$ is the total number of data points, and N_{P} is the number of parameters. Other terms are as previously defined. The values of σ provide a measure of how well C_p^{E} data is correlated by the models. All the parameters (six for NRTL and four for UNIQUAC) are obtained by regression of the available experimental data. In order to maintain the physical meanings of the parameters [5], the values of α_{ij} are forced to change in the range 0.1–0.7 for the NRTL model. The models may produce multi-roots, so the parameters that yield the best value of variance of the fit have been tabulated. The structural parameters of the UNIQUAC model are given in Table 2. These parameters are obtained from van der Waals areas of the molecules [20] and the group contribution method [21].

C_p^{E} values provide valuable information about molecular interactions in the mixture state: hydrogen bonding [10]; steric relations [13]; orientation [15]; extent of association [18]. A negative C_p^{E} indicates that less energy is required by the molecules in the mixture than in the pure liquid state [9].

The comparisons between the experimental and calculated values of C_p^{E} are given as average absolute errors S which are expressed as

$$S = \frac{1}{n}\left[\sum^{n} \left| \frac{C_{p,i,\mathrm{exptl}}^{\mathrm{E}} - C_{p,i,\mathrm{calcd}}^{\mathrm{E}}}{C_{p,i,\mathrm{exptl}}^{\mathrm{E}}} \right| \right] \times 100 \tag{11}$$

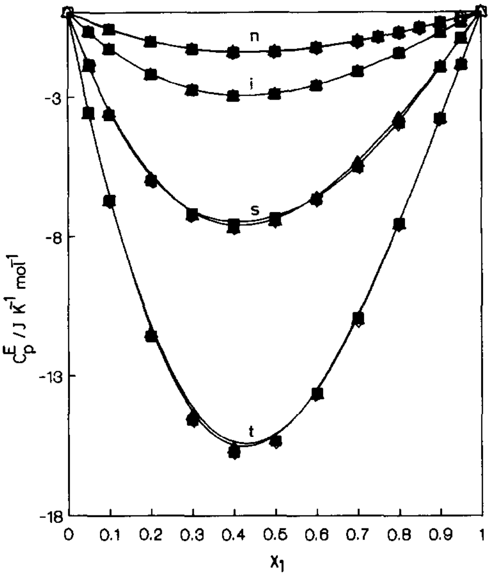

Fig. 1. Excess heat capacity C_p^E for the system methanol(1)–butanol(2) at 298.15 K: ◇, experimental [9,10]; ■, calculated from the UNIQUAC model; ▲, calculated from the NRTL model. The labels n, i, s and t indicate the four isomeric butanols.

and are given in Table 1. The values of S are rather too high for associating mixtures such as alcohol–hydrocarbon mixtures and mixtures containing very polar components like benzonitrile. For the other systems, the performance of the models is satisfactory, although in general the UNIQUAC model performs better. The behaviour of isomers for the mixtures methanol–butanol and benzene–xylene have been represented satisfactorily by both of the models, as can be seen in Figs. 1 and 2. In Figs. 3 and 4 the performances of the UNIQUAC and NRTL models respectively are shown, for the system of isomers of hexanol and *n*-hexane. These curves are highly asymmetrical and show peculiar shapes, depending upon whether the alkanol is primary, secondary or tertiary [19]. These properties are usually predicted by the models. As can be seen in Fig. 5, the performance of the models is poor for the system water–1-propanol. The system 1-hexanol–*n*-hexane produces the S shape for a plot of C_p^E versus the composition of 1-hexanol. Steric relations [13] are responsible for this kind of behaviour, which is predicted satisfactorily only by the UNIQUAC model, as can be seen in Fig. 6.

For the systems water–methanol, water–ethanol and water–propanol, the values of specific heat capacities $C_{\mathrm{p,m}}$ have been calculated as

$$C_{p,\mathrm{m}} = C_p^{\mathrm{E}} + x_1 C_{p,1} + (1 - x_1) C_{p,2} \qquad (12)$$

where $C_{p,1}$ and $C_{p,2}$ are the specific heat capacities of components 1 and 2 respectively. These systems have heat capacities higher than that of water

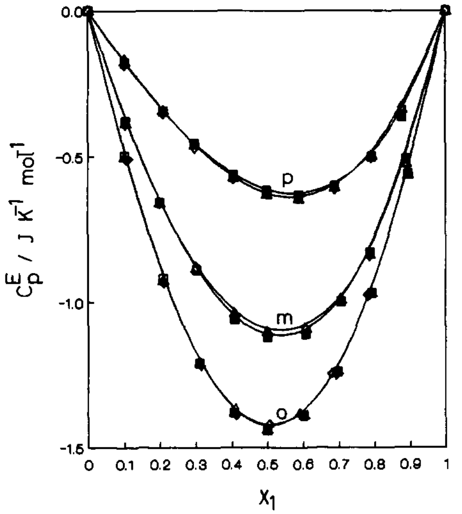

Fig. 2. Excess heat capacity C_p^E for the system benzene(1)–xylene(2) at 298.15 K: ◇, experimental [16]; ■, calculated from the UNIQUAC model; ▲, calculated from the NRTL model. The labels p, m and o indicate *para*, *meta* and *ortho* xylenes.

in the dilute region of alcohols [4]. Figures 7–9 show the predictions of the models for such systems when the alcohol composition changes between 0 and 0.2. Although the trend is predicted, the predictions are usually poor.

In order to determine the contribution of the component molecules to the excess quantities, the difference in the partial molar excess heat

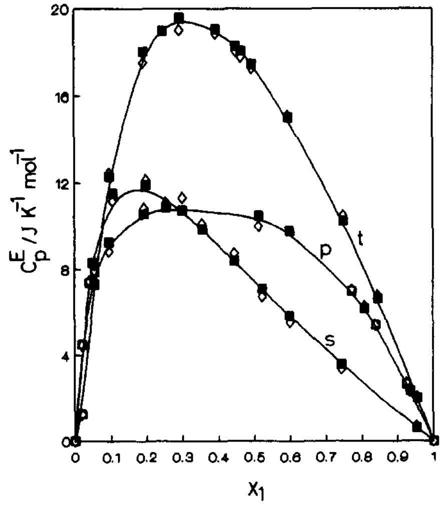

Fig. 3. Excess heat capacity C_p^E calculated from the UNIQUAC model for the system methylpentanol(1)–*n*-hexane(2) at 298.15 K; ◇, experimental [19]; ■, UNIQUAC. The labels p, s and t indicate primary, secondary and tertiary alcohols.

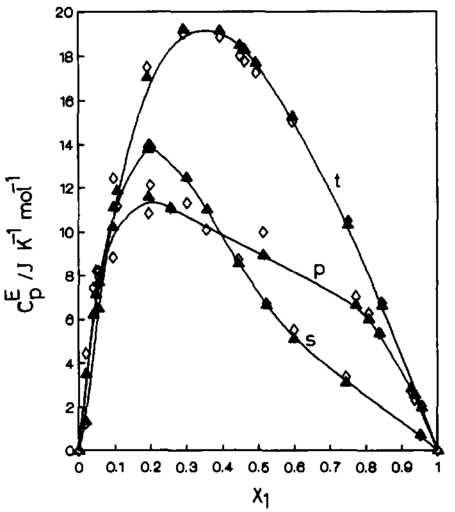

Fig. 4. Excess heat capacity C_p^E obtained from the NRTL model for the system methylpentanol(1)–*n*-hexane(2) at 298.15 K: ◇, experimental [19]; ▲, NRTL. The labels p, s and t indicate primary, secondary and tertiary alcohols.

capacity at infinite dilution from that of the pure state was obtained from

$$X_i = C_{p,i}^{\infty} - C_{p,i} \tag{13}$$

and are given in Table 3. The same molecule in a binary mixture yields different values of X_i as the second component changes.

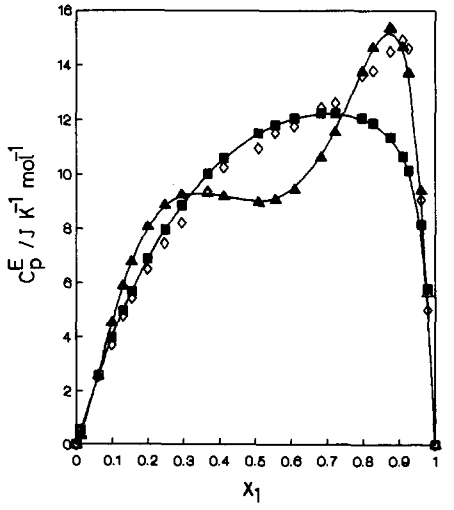

Fig. 5. Excess heat capacity C_p^E for the system water(1)–1-propanol(2) at 288.15 K; ◇, experimental [3,14]; ■, calculated from the UNIQUAC model; ▲, calculated from the NRTL model.

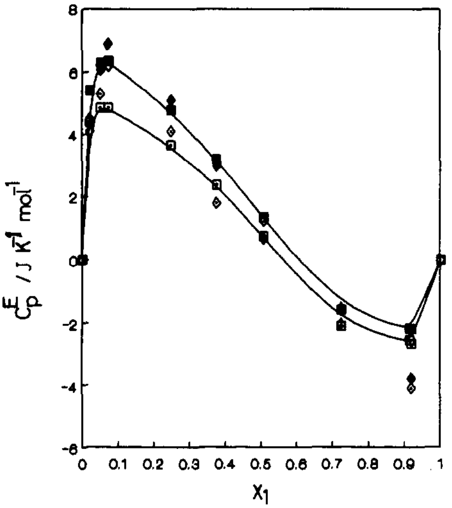

Fig. 6. Excess heat capacity C_p^E for the system hexanol(1)–*n*-hexane(2): ◇ and ◆, experimental [13] at 265.15 and 280.15 K respectively; □ and ■, calculated from UNIQUAC at 265.15 and 180.15 K, respectively.

Partial molar excess heat capacities at infinite dilution are calculated from

$$C_{p,i}^{\infty} = \left(\frac{C_p^E}{x_1 x_2}\right)_{x_i \to 0} \tag{14}$$

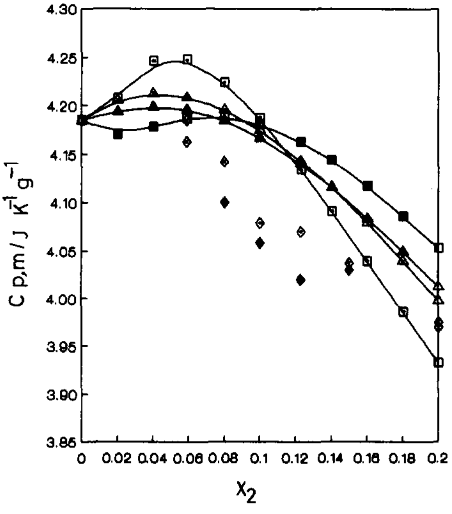

Fig. 7. Specific heat capacity $C_{p,m}$ for the system water(1)–methanol(2): ◇ and ◆, experimental [3,14] at 293.15 and 313.15 K respectively; □ and ■, calculated from the UNIQUAC model at 293.15 K and 313.15 K respectively; △ and ▲, calculated from the NRTL model at 293.15 K and 313.15 K respectively.

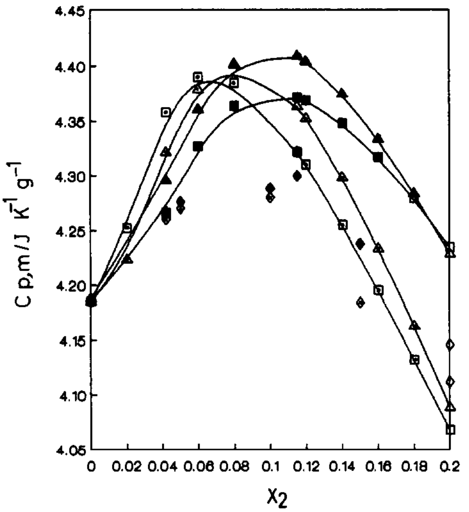

Fig. 8. Specific heat capacity $C_{p,\mathrm{m}}$ for the system water(1)–ethanol(2): ◇ and ◆, experimental [3,14] at 296.15 and 314.15 K respectively; □ and ■, calculated from the UNIQUAC model at 296.15 and 314.15 K respectively; △ and ▲, calculated from the NRTL model at 296.15 and 314.15 K respectively.

Experimental values of $C_{p,i}^{\infty}$ were determined by graphical extrapolation of finite concentration data of C_p^{E}/x_1x_2. Although necessary care has been exercised at the extrapolation stage, the values of $C_{p,i}^{\infty}$ are subject to some uncertainty, especially for those systems where the values of C_p^{E}/x_1x_2

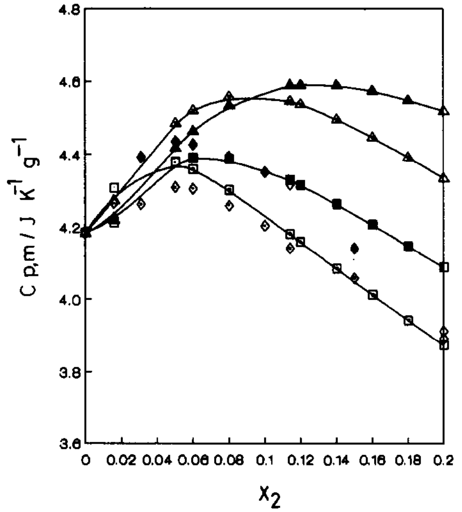

Fig. 9. Specific heat capacity $C_{p,\mathrm{m}}$ for the system water(1)–1-propanol(2): ◇ and ◆, experimental [3,14] at 293.15 and 313.15 K respectively; □ and ■, calculated from the UNIQUAC model at 293.15 and 313.15 K respectively; △ and ▲, calculated from the NRTL model at 293.15 and 313.15 K respectively.

TABLE 3

The values of X_i, uncertainties U_i and discrepancies D_i

T (°C)	X_i (J K^{-1} mol^{-1})		% Uncertainty		Discrepancies			
					UNIQUAC		NRTL	
	X_1	X_2	U_1	U_2	D_1	D_2	D_1	D_2
(1) Methanol(1)–ethanol(2) [9]								
25	−82.7	−114.3	8.1	8.1	7.2	30.6	17.6	0.1
(2) Methanol(1)–1-propanol(2) [9]								
25	−86.0	−146.8	2.0	2.4	8.4	0.4	5.7	0.3
(3) Methanol(1)–1-butanol(2) [9]								
25	−87.9	−181.0	0.8	1.3	1.2	3.3	8.3	0.3
(4) Methanol(1)–iso-butanol(2) [10]								
25	−96.6	−188.2	0.5	1.9	0.6	2.8	2.2	0.1
*(5) Methanol(1)–*sec*-butanol(2) [10]*								
25	−121.0	−216.4	0.2	0.9	1.8	0.9	5.7	6.1
*(6) Methanol(1)–*tert*-butanol(2) [10]*								
25	−154.7	−257.7	2.6	0.5	15.3	64.7	5.3	0.6
(16) Benzene(1)–toluene(2) [16]								
25	−136.9	−158.0	6.6	12.3	1.2	16.1	4.5	23.5
(17) Benzene(1)–ethylbenzene(2) [16]								
25	−138.4	−189.5	0.7	0.1	3.7	6.9	6.6	3.5
*(18) Benzene(1)–*o*-xylene(2) [16]*								
25	−141.3	−193.5	0.5	0.6	1.5	1.7	0.9	2.4
*(19) Benzene(1)–*m*-xylene(2) [16]*								
25	−139.9	−186.8	0.7	0.4	6.9	0.6	1.0	5.6
*(20) Benzene(1)–*p*-xylene(2) [16]*								
25	−137.4	−185.0	1.5	0.4	8.9	13.8	2.2	7.1
(21) Benzene(1)–cyclohexane(2) [17]								
25	−146.8	−171.5	8.1	0.2	6.0	2.5	8.4	0.3
(23) Toluene(1)–ethylbenzene(2) [16]								
25	−156.8	−185.4	24.3	26.7	33.5	9.7	32.2	6.6
*(24) Toluene(1)–*o*-xylene(2) [16]*								
25	−158.6	−189.6	1.2	0.6	8.3	5.4	7.8	5.6
*(25) Toluene(1)–*m*-xylene(2) [16]*								
25	−157.8	−182.5	19.7	4.7	3.5	3.6	3.9	4.0

exhibit a steep change in the dilute region [18]. The percentage uncertainties U_i, based on the average absolute deviation in the extrapolation, have been expressed as

$$U_i = \left| \frac{C^{\infty}_{p,i,\max} - C^{\infty}_{p,i,\min}}{2C^{\infty}_{p,i}} \right| \times 100 \qquad (15)$$

Here the deviation is taken as one-half of the difference between the maximum ($C^{\infty}_{p,i,\max}$) and minimum ($C^{\infty}_{p,i,\min}$) values of the extrapolations. Comparison of experimental ($C^{\infty}_{p,i,\mathrm{exptl}}$) and calculated ($C^{\infty}_{p,i,\mathrm{calcd}}$) heat capacities at infinite dilution by the NRTL and UNIQUAC models, are given in Table 3 for some systems. Discrepancies between the experimental and the calculated values of $C^{\infty}_{p,i}$ for each isotherm were assessed as

$$D_i = \left| \frac{C^{\infty}_{p,i,\mathrm{exptl}} - C^{\infty}_{p,i,\mathrm{calcd}}}{C^{\infty}_{p,i,\mathrm{exptl}}} \right| \times 100 \qquad (16)$$

The values of D_i indicate the percentage error for each component. The discrepancies are due to the uncertainties of extrapolation in addition to the limitations of the models.

CONCLUSIONS

For nonlinear temperature dependencies, the parameters of the NRTL and UNIQUAC models are estimated using C_p^{E} data for 29 binary liquid mixtures of various types, including associating and partially miscible. All the parameters are estimated by regression of the available experimental data. The models may produce multi-roots and some convergence problems, (especially in the NRTL model), so necessary care should be exercised in the parameter estimation.

The models are usually capable of correlating C_p^{E} data satisfactorily at different isotherms for various types of mixtures. However, the predictions for mixtures including highly polar components and hydrogen bonding are poor. The performance of the UNIQUAC model, although it has fewer parameters, is comparatively better than that of the NRTL model.

ACKNOWLEDGEMENTS

The authors thank the State Planning Organization for providing financial support under the project 90K120430, and the Computer Centre of the University of Çukurova for providing the computation facilities.

REFERENCES

1 Y. Demirel, H. Gecegörmez and H.Ö. Paksoy, Thermochim. Acta, 194 (1992) 329.
2 Y. Demirel, H.Ö. Paksoy and H. Gecegörmez, Thermochim. Acta, 194 (1992) 343.
3 H. Ogawa and S. Murakami, Thermochim. Acta, 109 (1986) 145.
4 R.H. Perry, C.H. Chilton and S.D. Kirkpatrick, Chemical Engineer's Handbook, 4th edn., McGraw-Hill, New York, 1963.
5 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.
6 D.S. Abrams and J.M. Prausnitz, AIChE J., 21 (1975) 116.
7 T.F. Anderson and J.M. Prausnitz, Ind. Eng. Chem. Process Des. Dev., 17 (1978) 552.

8 F. James, Data Handling Division, CERN, Geneva, 1979.
9 H. Ogawa and S. Murakami, J. Solution Chem., 16 (1987) 315.
10 T. Okana, H. Ogawa and S. Murakami, Can. J. Chem., 66 (1988) 713.
11 G.N. Brown and W.T. Ziegler, J. Chem. Eng. Data, 24 (1979) 319.
12 B. Kalinowska and W. Woycicki, J. Chem. Thermodyn., 17 (1985) 829.
13 B. Kalinowska and W. Woycicki, J. Chem. Thermodyn., 16 (1984) 609.
14 G.C. Benson and P.J.D'Arcy, J. Chem. Eng. Data, 27 (1982) 439.
15 R. Tanaka, J. Chem. Eng. Data, 32 (1987) 176.
16 J.-L. Fortier and G.C. Benson, J. Chem. Eng. Data, 24 (1979) 34.
17 H. Ogawa and S. Murakami, Thermochim. Acta, 88 (1985) 255.
18 R. Tanaka, T. Nakamichi and S. Murakami, J. Solution Chem., 14 (1985) 795.
19 R. Bravo, M. Pintos, M.C. Baluja, M.I. Paz Andrade, G. Roux-Desgranges and J-P.E. Grolier, J. Chem. Thermodyn., 16 (1984) 73.
20 A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.
21 Aa. Fredenslund, J. Gmehling and P. Rasmussen, Vapor–Liquid Equilibria Using UNIFAC, Elsevier, Amsterdam, 1977.