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Correlation of heats of mixing data by the NRTL and UNIQUAC models.
Part 2. Predictions of the calorimetric properties

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Abstract

Using heats of mixing data only, the temperature dependent parameters of the local composition models NRTL and UNIQUAC have been estimated and presented in the first part of this series. Here, these parameters are employed to predict the calorimetric properties: these are the heats of mixing h^E, partial molar heats of mixing at infinite dilution ΔH_i and excess heat capacities C_p^E. Limiting activity coefficients are also estimated at different isotherms. All the predictions have been compared with experimental values.

The NRTL and UNIQUAC models satisfactorily represent heats of mixing data at different isotherms for highly non-ideal and partially miscible systems. However, predictions in the region of high dilution are not always satisfactory, especially for associating mixtures. The values of C_p^E obtained from the differentiation of equations for h^E are poor. Also, the predicted values of γ_i^∞ show large deviations from the experimental values.

INTRODUCTION

Heats of mixing data determine the dependence for the activity coefficients, hence the relative volatilities, on the temperature profile inside a distillation column. In vacuum systems, especially, the combination of low pressure and a large number of trays widens the temperature range within the fractionating columns. Consequently, h^E and its variations with temperature are significant. As Murthy and Zudkevitch [1] state, more data on heats of mixing are needed for reliable and economic designs of important industrial separations.

Heats of mixing data are also needed for testing models for liquid mixtures and understanding the effect of molecular structure on the thermodynamic properties of mixtures. Predictions of h^E data [2,3] for a large number of liquid mixtures of various types have recently been obtained from the local composition models of NRTL [4] and UNIQUAC [5], the parameters of which are estimated by using h^E and g^E data simultaneously. Later, these parameters are also used to predict partial molar heats of mixing at infinite dilution [6].

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In order to facilitate more satisfactory calorimetric predictions over a wide range of temperatures, the parameters of the NRTL and UNIQUAC models have been estimated using only h^E data for 57 systems of liquid mixtures, and are presented in Part 1 of this series. In this study, the parameters are employed to predict the calorimetric properties, namely heats of mixing h^E, partial molar heats of mixing at infinite dilution, ΔH_i, and excess heat capacities C_p^E for various temperatures. Limiting activity coefficients γ_i^∞ are also estimated. The systems considered represent a wide variety, including associating and partially miscible mixtures.

CALORIMETRIC PREDICTIONS

Thermal effects that accompany the mixing of polar and non-polar compounds and production of non-ideal mixtures may be collected in calorimetric properties. These are due mainly to any one, or a combination, of the following factors [7]: (1) the difference in the molecular interaction energy between like and unlike molecules; (2) the formation of strong interactions between unlike molecules, such as hydrogen bonding; (3) differences in size and shape of the component molecule. The first factor makes a positive contribution to h^E whereas the second makes a negative contribution.

The values of h^E/x_1x_2 at liquid compositions $x_1 = 0$ and $x_2 = 0$ are identical with partial molar heats of mixing of component 1 and 2, ΔH_1 and ΔH_2 respectively, at infinite dilution. For better understanding of solution behaviour, it is advantageous to examine derivative excess properties in the limit of infinite dilution, where a single solute molecule is completely surrounded by the solvent. Since solute–solute interactions are no longer present, infinite dilution excess properties reflect almost completely unlike pair interactions, and yield information about such intermolecular forces [8].

Values of C_p^E indicate the temperature dependence of h^E, and should not be attributed to the difference in numbers of hydrogen bonds on mixing, but depend rather on the difference in numbers of hydrogen bonds broken with increase in temperature between the pure state and the solution state. The order of the absolute magnitude of C_p^E appears to be in agreement with that of the formation of strong hydrogen bonds and to be inversely proportional to that of the steric effect, by which unstable associate species are formed in mixture. The more the steric effect exists in the pure alcohol, the more the hydrogen bonds are broken down with increase of temperature [9]. C_p^E is also related closely to the behaviour of component molecules in the solution state, thus it will be connected with the local concentration fluctuation in solution [10].

Equations for h^E obtained from the models were given in the first part of this series. Using the NRTL model, ΔH_i and C_p^E are estimated from the following equations

$$\Delta H_1 = \frac{T}{T'}\left\{c_2 + R\tau_{21}T' + G_{12}\left[(c_4 + R\tau_{12}T')(1 - \tau_{22}\alpha_{12}) - RT\tau_{12}^2 c_6\right]\right\} \quad (1)$$

$$\Delta H_2 = \frac{T}{T'}\left\{c_4 + R\tau_{12}T' + G_{21}\left[(c_2 + R\tau_{21}T')(1 - \tau_{21}\alpha_{12}) - RT\tau_{21}^2 c_6\right]\right\} \quad (2)$$

$$\begin{aligned} C_p^{\mathrm{E}} = \frac{Rx_1x_2G_{21}}{T'S_1^2} & \left\{T\beta_1\left[2(T-273.15)\tau_{21} - \frac{\delta_1}{T}\right] + x_1Tc_6\tau_{21}\left(\frac{2c_2}{RT'} + \tau_{21}\right)\right. \\ & + \frac{w_1S_1\delta_1}{T'} \\ & \left. + \left[\frac{c_2\beta_1}{R} + \tau_{21}(T'\beta_1 - x_1c_6T\tau_{21})\right]\left[\frac{w_1}{T'}\left(1 - \frac{2x_2G_{21}}{S_1}\right) - \frac{T+273.15}{T-273.15}\right]\right\} \\ + \frac{Rx_1x_2G_{12}}{T'S_2^2} & \left\{T\beta_2\left[2(T-273.15)\tau_{12} - \frac{\delta_2}{T}\right] + x_2Tc_6\tau_{12}\left(\frac{2c_4}{RT'} + \tau_{12}\right)\right. \\ & + \frac{w_2S_2\delta_2}{T'} \\ & \left. + \left[\frac{c_4\beta_2}{R} + \tau_{12}(T'\beta_2 - x_2c_6T\tau_{12})\right]\left[\frac{w_2}{T'}\left(1 - \frac{2x_1G_{12}}{S_2}\right) - \frac{T+273.15}{T-273.15}\right]\right\} \end{aligned} \quad (3)$$

where

$\tau_{12} = (g_{12} - g_{22})/RT$; $\tau_{21} = (g_{21} - g_{11})/RT$

$G_{12} = \exp(-\alpha_{12}\tau_{12})$: $G_{21} = \exp(-\alpha_{21}\tau_{21})$

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

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

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

$S_1 = x_1 + x_2G_{21}$; $S_2 = x_2 + x_1G_{12}$

$\delta_1 = c_2/R + T'\tau_{21}$; $\delta_2 = c_4/R + T'\tau_{12}$

$w_1 = \alpha_{12}\delta_1 + T\tau_{21}c_6$; $w_2 = \alpha_{12}\delta_2 + T\tau_{12}c_6$

$\beta_1 = S_1 - x_1\tau_{21}\alpha_{12}$; $\beta_2 = S_2 - x_2\tau_{12}\alpha_{12}$

$T' = (T - 273.15)^2$

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 and c_5

are the values of the parameters at 0 °C, while c_2, c_4 in J K mol^{-1} and c_6 are the coefficients of temperature.

Using the UNIQUAC model ΔH_i and C_p^E are estimated from the following equations

$$\Delta H_1 = Rq_1'[(d_1 + 2d_2/T) + \tau_{12}^*(d_3 + 2d_4/T)] \tag{4}$$

$$\Delta H_2 = Rq_2'[(d_3 + 2d_4/T) + \tau_{21}^*(d_1 + 2d_2/T)] \tag{5}$$

$$C_p^E = \frac{Rq_1'x_1\Theta_2\tau_{21}^*}{T^2(\Theta_1 + \Theta_2\tau_{21}^*)^2}\left[\Theta_1(d_1 + 2d_2/T)^2 - 2d_2(\Theta_1 + \Theta_2\tau_{21}^*)\right]$$
$$+ \frac{Rq_2'x_2\Theta_1\tau_{12}^*}{T^2(\Theta_2 + \Theta_1\tau_{12}^*)^2}\left[\Theta_2(d_3 + 2d_4/T)^2 - 2d_4(\Theta_2 + \Theta_1\tau_{12}^*)\right] \tag{6}$$

where $\tau_{12}^* = \exp(-a_{12}/T)$; $\tau_{21}^* = \exp(-a_{21}/T)$

$a_{12} = d_3 + d_4/T$; $a_{21} = d_1 + d_2/T$

$\Theta_1 = x_1q_1'/(x_1q_1' + x_2q_2')$; $\Theta_2 = x_2q_2'/(x_1q_1' + x_2q_2')$.
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 are the coefficients related to the parameters a_{ij}; R and q_i' are the gas constant in J mol^{-1} K^{-1} and the molecular interaction area parameter respectively for pure component i.

LIMITING ACTIVITY COEFFICIENTS

The activity coefficient at infinite dilution γ_i^∞ characterizes the behaviour of a single solute molecule i which is completely surrounded by the solvent molecules. It mainly indicates the maximum non-ideality. Due to the Gibbs–Helmholtz equation, the values of γ_i^∞ are interrelated with the partial molal heat of mixing at infinite dilution

$$\frac{\ln \gamma_i^\infty}{(1/T)} = \frac{\Delta H_i}{R} \tag{7}$$

Except for highly solvated and associated mixtures, ΔH_i should be constant over narrow temperature ranges, in which the plot of ln γ_i^∞ versus $1/T$ should be approximately linear. Expressions for limiting activity coefficients obtained from the NRTL and UNIQUAC models were given elsewhere [11].

RESULTS AND DISCUSSION

Using the parameters estimated in the first part of this series, calorimetric properties, namely h^E, ΔH_i and C_p^E, have been predicted and compared with experimental values. The comparisons are given as average absolute errors, S, for h^E and C_p^E, while deviations, D_i, are calculated for ΔH_i values.

$$S(h^E) = \frac{1}{n}\left[\sum^{n}\left|\frac{h^E_{i,\mathrm{exptl}} - h^E_{i,\mathrm{calcd}}}{h^E_{i,\mathrm{exptl}}}\right|\right] \times 100 \tag{8}$$

$$S\left(C_p^E\right) = \frac{1}{n}\left[\sum^{n}\left|\frac{C^E_{p_{\iota,\mathrm{exptl}}} - C^E_{p_{\iota,\mathrm{calcd}}}}{C^E_{p_{\iota,\mathrm{exptl}}}}\right|\right] \times 100 \tag{9}$$

$$D_i = \left|\frac{\Delta H_{i,\mathrm{exptl1}} - \Delta H_{i,\mathrm{calcd}}}{\Delta H_{i,\mathrm{exptl}}}\right| \times 100 \tag{10}$$

Here n shows the number of data points at each isotherm. The value of $S(h^E)$ was calculated at each temperature for h^E data. The values of D_i indicate the percentage error for each component. The values of $S(h^E)$ and D_i are given in Table 1.

The values of ΔH_i are finite but indeterminate. Hence the experimental values of ΔH_i were determined by graphical extrapolation of finite concentration data. Although all necessary care has been exercised in the extrapolation stage, the obtained values of ΔH_i are subject to some uncertainty, especially for those systems where the values of h^E/x_1x_2 exhibit a steep change in the highly dilute region. The percentage uncertainties, U_i, based on the average absolute deviation in the extrapolation, have been expressed as

$$U_i = \left|\frac{\Delta H_{i,\mathrm{max}} - \Delta H_{i,\mathrm{min}}}{2\Delta H_i}\right| \times 100 \tag{11}$$

Here the deviation is taken as one-half of the difference between the maximum $\Delta H_{i,\mathrm{max}}$ and minimum $\Delta H_{i,\mathrm{min}}$ values of the extrapolations. Comparisons of experimental $\Delta H_{i,\mathrm{exptl}}$ and calculated $\Delta H_{i,\mathrm{calcd}}$ partial molar enthalpies at infinite dilution by the models are given in Table 1. For the systems with very high uncertainties no extrapolation was carried out, hence no experimental values of ΔH_i are tabulated.

In the nearly ideal systems 40–42 and 56 and 57 an unusual experimental accuracy is required in VLE measurements, if the Gibbs–Helmholtz equation is to give even the right order of magnitude of h^E [37]. For the system 2-propanol–water, the plot of h^E versus x shows an S shape for which the predictions are poor, although the average absolute errors are slightly better than those obtained by Battler et al. [22].

In pure alcohol, all the molecules form hydrogen bonds with each other, while each alcohol in the infinite dilution of alcohol in a non-polar compound is surrounded by these molecules and the hydrogen bonds are broken. Hence the values of ΔH_1 for the alcohol–polar liquid systems correspond to the energy change from the pure alcohol state to that in

TABLE 1

Comparison of experimental and predicted values of h^E and ΔH_t

T (°C)	n	Uncertainties (%)		Percentage average absolute errors $S(h^E)$ and percentage deviations D_i					
		U_1	U_2	NRTL			UNIQUAC		
				S	D_1	D_2	S	D_1	D_2
1. Methanol(1)–methyl acetate(2) [12]									
25	14	2.1	3.2	1.1	4.5	0.6	2.2	2.0	2.2
35	16	3.0	5.0	1.1	1.7	3.2	1.0	1.2	2.4
45	10	5.1	3.1	0.6	1.1	0.2	2.4	3.4	9.6
2. Methanol(1)–ethyl acetate(2) [13]									
25	12	5.1	5.0	2.2	7.2	14.5	3.7	4.0	5.5
35	12	6.2	5.4	1.7	14.9	8.1	3.9	4.3	17.3
3. Methanol(1)–ethyl formate(2) [14]									
25	8	2.5	2.1	0.9	26.4	7.9	4.1	14.3	6.2
35	11	2.0	2.0	2.0	18.3	5.8	3.6	4.2	7.5
45	9	2.1	2.1	1.2	17.6	6.3	2.6	6.7	14.4
4. Methanol(1)–*n*-hexane(2) [a] [15]									
25	11	–	4.3	5.9	–	1.8	5.8	–	10.8
40	17	–	3.7	7.2	–	4.6	2.6	–	6.5
45	17	–	3.6	6.5	–	1.9	3.2	–	2.6
50	17	–	4.2	6.2	–	0.9	4.0	–	1.2
5. Methanol(1)–*n*-heptane(2) [a] [15]									
30	8	–	4.3	6.0	–	14.1	4.9	–	20.3
45	11	–	3.9	8.3	–	7.2	3.2	–	9.0
60	17	–	3.5	6.2	–	0.6	4.2	–	0.2
6. Methanol(1)–water(2) [16]									
5	6	0.5	2.1	2.0	2.2	2.1	7.0	20.6	10.4
15	6	1.6	0.7	8.3	36.3	5.1	5.9	23.3	5.1
25	6	0.4	1.7	7.4	33.3	16.6	5.1	25.5	4.5
40	6	1.2	0.6	5.7	22.9	14.2	3.9	21.1	0.8
50	6	0.7	0.6	7.9	17.5	5.4	5.4	19.8	6.2
7. Ethanol(1)–methyl acetate(2) [12]									
25	11	6.1	6.2	0.7	1.7	1.9	1.7	11.4	5.1
35	12	5.2	4.0	1.4	0.9	3.7	1.5	10.2	3.3
5	7	5.0	5.0	1.3	0.6	3.5	2.5	13.6	8.5
8. Ethanol(1)–ethyl acetate(2) [13]									
25	12	6.2	4.5	1.2	12.9	8.7	2.6	2.6	4.3
35	16	7.1	5.3	1.3	24.3	14.5	2.8	9.3	4.5
9. Ethanol(1)–ethyl formate(2) [14]									
25	6	6.3	4.1	0.7	5.4	4.1	4.2	6.2	10.1
35	13	3.7	4.4	2.2	9.8	6.4	3.1	7.3	5.4
45	9	3.0	2.6	1.5	15.2	9.9	2.5	9.7	10.5
10. Ethanol(1)–acetone(2) [17]									
25	12	2.0	1.0	0.4	7.2	4.9	2.4	4.2	1.6
50	12	1.0	2.0	0.3	5.7	4.4	2.3	4.8	6.3
11. Ethanol(1)–toluene(2) [18]									
25	26	3.5	5.7	7.8	39.3	31.1	5.2	8.2	12.2
45	23	4.6	4.6	5.1	61.2	35.6	2.8	6.9	14.7
60	26	5.7	3.5	4.8	62.7	17.8	3.9	3.2	9.2

TABLE 1 (continued)

T (°C)	n	Uncertainties (%)		Percentage average absolute errors $S(h^E)$ and percentage deviations D_i					
		U_1	U_2	NRTL			UNIQUAC		
				S	D_1	D_2	S	D_1	D_2
12. Ethanol(1)–hexane(2) [19]									
10	24	0.5	0.5	1.3	0.8	0.6	7.2	19.5	5.6
25	24	1.0	1.2	8.9	9.4	7.0	3.3	18.1	13.3
45	25	1.4	0.7	10.1	13.5	4.7	12.8	36.8	17.6
13. Ethanol(1)–cyclohexane(2) [20]									
5	10	10.5	1.7	5.8	37.6	3.4	2.8	43.4	21.3
20	10	0.1	17.5	2.4	36.1	18.6	2.2	24.9	13.7
35	10	5.0	1.5	1.9	22.8	5.8	2.5	19.2	10.6
50	10	4.1	2.8	2.0	18.4	3.0	0.8	13.8	9.7
65	10	5.9	2.9	1.7	13.0	7.4	2.4	8.7	7.9
14. Ethanol(1)–water(2) [b] [21]									
150	18	3.0	0.2	0.8	3.9	0.4	9.6	34.2	10.6
175	19	0.9	0.6	0.6	4.4	4.8	5.4	3.2	15.4
200	19	0.2	0.3	1.0	1.5	0.1	11.8	16.9	10.4
15. 1-Propanol(1)–ethyl acetate(2) [13]									
25	11	6.1	5.2	1.7	9.5	2.7	1.9	0.8	6.9
35	20	4.1	3.0	1.3	13.0	2.5	1.6	0.1	2.1
45	9	5.0	2.2	0.9	9.8	2.8	1.3	6.1	1.2
16. 1-Propanol(1)–ethyl formate(2) [13]									
25	8	4.2	3.1	0.3	12.1	6.8	4.3	8.6	12.2
35	13	6.3	3.2	1.4	9.0	7.4	2.7	6.1	9.9
45	9	3.0	3.2	0.9	11.6	9.8	2.4	2.5	0.2
17. 2-Propanol(1)–ethyl acetate(2) [13]									
25	13	4.3	2.2	0.9	6.9	2.1	1.2	0.6	1.4
35	18	4.2	7.2	0.9	11.3	1.9	1.9	6.2	0.3
18. 2-Propanol(1)–ethyl formate(2) [14]									
25	13	5.3	5.1	0.8	16.1	14.1	3.0	8.2	15.9
35	12	5.0	5.4	1.0	12.1	16.1	1.2	0.8	18.3
45	11	4.1	3.1	0.7	5.6	10.8	3.1	10.0	14.8
19. 2-Propanol(1)–*n*-heptane(2) [18]									
30	24	2.4	5.6	10.3	13.6	11.9	10.3	2.4	32.4
45	22	1.4	5.4	6.1	11.3	1.2	8.5	5.6	40.7
60	21	2.1	2.7	9.8	6.0	17.1	8.0	9.3	3.1
20. 2-Propanol(1)–cyclohexane(2) [22]									
20	18	2.7	2.9	5.0	26.6	0.5	6.7	4.3	23.8
25	18	3.3	1.0	5.8	3.3	15.0	5.9	4.8	30.6
50	18	1.7	0.7	8.7	18.7	18.3	13.9	35.7	47.4
21. 2-Propanol(1)–water(2) [c] [22]									
20	15	3.7	4.2	42.7	92.2	42.5	32.5	68.1	60.0
25	15	2.6	1.5	42.6	93.9	19.8	28.6	69.6	53.4
30	15	4.9	1.7	48.3	94.0	32.9	41.2	65.0	34.7
50	15	3.1	2.9	60.1	96.3	81.5	29.9	68.2	50.9
22. 1-Butanol(1)–*n*-heptane(2) [23,24]									
15	9	–	6.8	4.8	–	5.4	18.3	–	57.7
30	17	–	6.7	15.9	–	51.3	12.2	–	43.6
45	17	–	4.5	11.1	–	26.9	8.1	–	35.5
55	9	–	3.5	13.2	–	8.6	9.6	–	24.8

TABLE 1 (continued)

T (°C)	n	Uncertainties (%)		Percentage average absolute errors $S(h^E)$ and percentage deviations D_i					
		U_1	U_2	NRTL			UNIQUAC		
				S	D_1	D_2	S	D_1	D_2
23. 1-Butanol(1)–nitromethane(2) [a] [25]									
18	18	1.6	2.7	3.5	0.9	0.3	4.8	17.5	2.6
22	18	1.9	3.8	2.9	3.1	5.7	2.9	15.6	5.6
25	18	1.1	4.0	2.8	3.7	13.0	3.5	13.7	14.0
30	18	1.3	4.6	3.4	5.5	25.0	3.7	0.5	27.5
24. *n*-Butanol(1)–ethyl acetate(2) [26]									
25	13	2.5	3.3	0.5	4.6	2.3	0.9	2.0	4.7
35	18	1.9	2.4	2.7	2.6	2.5	2.3	4.0	0.4
25. *n*-Butanol(1)–ethyl formate(2) [26]									
25	14	1.2	2.5	0.6	14.3	4.5	3.5	9.9	10.5
35	11	1.8	2.0	1.3	14.0	10.9	2.2	0.4	16.2
45	11	1.2	1.2	1.2	14.8	2.9	1.5	5.2	9.8
26. *n*-Butanol(1)–methanol(2) [27]									
5	25	0.8	0.8	1.3	2.4	1.3	2.2	4.1	4.1
25	26	0.4	0.4	15.6	8.0	34.2	4.9	3.0	7.1
40	21	0.5	1.7	10.6	3.1	28.3	5.2	7.2	20.3
27. *n*-Pentanol(1)–*n*-hexane(2) [23,28]									
25	9	14.1	5.6	1.3	63.9	2.3	9.9	14.8	21.0
30	17	14.2	4.5	11.5	60.4	26.3	10.9	30.5	28.1
45	17	13.2	5.6	12.5	50.3	26.1	8.7	27.0	30.0
28. Hexanol(1)–*n*-amylamine(2) [29]									
15	19	2.5	2.2	0.6	2.4	6.4	4.7	15.2	12.6
35	19	2.8	2.2	3.3	3.1	5.6	5.4	7.1	18.2
29. *n*-Hexanol(1)–*n*-octane(2) [24]									
15	9	–	3.8	3.5	–	4.7	4.7	–	8.8
25	8	–	1.4	2.3	–	8.8	11.8	–	18.5
30. Heptanol(1)–*n*-amylamine(2) [29]									
15	19	1.8	1.6	1.9	15.9	6.8	3.6	6.8	3.8
35	19	1.7	1.4	2.7	4.1	4.3	4.3	1.6	10.2
31. *n*-Octanol(1)–*n*-heptane(2) [24]									
15	9	–	12.2	7.3	–	6.2	5.4	–	3.7
55	9	–	6.6	5.6	–	7.2	4.9	–	7.3
32. *n*-Octanol(1)–*n*-octane(2) [24]									
15	9	12.8	10.8	4.1	1.7	0.5	4.6	69.8	14.2
25	9	15.9	6.9	6.4	16.7	11.9	1.9	46.0	4.0
33. *n*-Octanol(1)–*n*-amylamine(2) [29]									
15	19	3.5	2.7	1.2	4.2	9.5	4.9	10.8	10.9
35	19	2.1	2.6	2.2	8.3	3.6	3.4	5.0	11.5
34. Decanol(1)–*n*-amylamine(2) [29]									
15	19	3.2	1.6	1.1	7.6	12.2	3.6	2.6	6.9
35	19	2.2	1.7	3.8	14.9	7.0	3.8	8.2	11.7
35. Methyl acetate(1)–benzene(2) [30]									
25	13	7.5	3.5	2.4	14.9	31.7	3.1	13.5	7.3
35	12	4.1	11.2	4.5	0.7	13.0	8.1	5.3	16.1

TABLE 1 (continued)

T (°C)	n	Uncertainties (%)		Percentage average absolute errors $S(h^E)$ and percentage deviations D_i					
		U_1	U_2	NRTL			UNIQUAC		
				S	D_1	D_2	S	D_1	D_2
36. Methyl acetate(1)–cyclohexane(2) [30]									
25	11	5.5	4.6	0.4	10.7	8.1	0.5	2.7	2.2
35	11	4.1	4.5	0.7	15.2	11.0	0.6	1.5	0.5
45	9	5.2	5.0	0.8	13.0	8.2	1.1	0.1	3.1
37. Methyl acetate(1)–*n*-hexane(2) [26]									
25	14	2.0	6.4	1.2	33.6	40.5	2.6	1.7	9.9
45	13	3.7	1.5	1.0	8.3	6.0	2.7	0.1	6.0
38. Benzene(1)–*n*-heptane(2) [32,33,34]									
25	14	2.0	3.4	1.0	1.8	3.4	0.8	1.8	1.3
45	8	3.5	3.4	0.5	1.3	19.7	1.3	4.9	2.3
50	4	–	4.7	1.0	–	2.3	0.8	–	2.3
39. Benzene(1)–cyclohexane(2) [34]									
25	12	0.2	0.2	1.1	10.4	6.0	0.5	1.1	1.2
50	12	0.2	0.2	1.6	3.0	1.1	0.5	4.2	1.4
40. 1-Chlorohexane(1)–ethylbenzene(2) [d] [35]									
15	17	3.7	3.6	1.1	2.9	6.9	0.8	3.2	6.2
25	19	2.6	4.3	0.6	1.6	2.9	0.4	3.3	1.7
41. 1-Chlorohexane(1)–*n*-propylbenzene(2) [d] [35]									
15	19	3.4	4.5	0.5	0.9	1.7	0.7	2.3	5.4
25	19	3.6	3.6	1.9	10.3	12.0	2.0	12.4	12.7
42. 1-Chlorohexane(1)–toluene(2) [d] [35]									
15	19	2.3	3.5	1.6	5.8	9.5	4.8	16.2	5.4
25	17	3.4	3.5	1.3	6.5	10.6	5.0	0.2	0.5
43. 1,2-Dichloroethane(1)–di-*n*-butyl ether(2) [31]									
5	19	8.1	3.5	1.3	17.0	52.7	1.4	3.4	3.7
25	19	8.2	6.9	2.1	4.5	4.8	0.9	5.5	3.2
44. 1,1,1-Trichloroethane(1)–di-*n*-butyl ether(2) [31]									
10	11	11.1	6.9	2.4	8.1	5.1	13.2	27.1	20.0
25	12	12.5	7.5	9.1	14.2	14.0	9.3	30.9	5.1
35	11	12.5	4.5	6.9	3.5	4.0	6.3	33.8	0.9
45. *n*-Heptane(1)–acetic acid(2) [26]									
25	17	2.6	3.5	1.1	25.3	12.9	4.5	3.1	6.9
35	14	1.7	2.3	0.9	21.7	7.6	4.6	2.4	4.9
46. *n*-Heptane(1)–propionic acid(2) [26]									
25	14	2.0	4.3	2.0	17.4	6.5	6.1	8.9	13.4
35	15	4.5	5.3	3.0	8.3	11.6	7.0	2.5	3.0
47. *n*-Heptane(1)–*n*-amylamine(2) [29]									
15	19	1.4	0.9	0.4	3.1	14.5	1.3	0.1	6.0
35	19	1.4	1.0	0.5	0.9	2.8	1.3	3.5	0.4
48. *n*-Heptane(1)–toluene(2) [34]									
25	8	1.3	0.9	0.9	1.1	9.9	0.4	2.6	4.1
50	8	0.6	1.6	1.0	0.5	4.5	0.4	1.7	6.5
49. *n*-Heptane(1)–*m*-xylene(2) [34]									
25	8	2.8	1.5	0.2	3.0	8.9	0.4	1.6	11.4
50	8	1.0	1.1	0.2	0.9	0.7	0.4	2.2	4.1

TABLE 1 (continued)

T (°C)	n	Uncertainties (%)		Percentage average absolute errors $S(h^E)$ and percentage deviations D_i					
		U_1	U_2	NRTL			UNIQUAC		
				S	D_1	D_2	S	D_1	D_2
50. Cyclohexane(1)–i-octane(2) [34]									
25	12	2.8	1.1	0.8	0.1	4.0	1.0	1.7	6.1
50	8	1.9	1.5	0.7	8.9	2.5	1.2	4.7	1.7
51. *n*-Amylamine(1)–nonane(2) [29]									
15	19	0.6	2.1	0.2	9.1	10.4	1.3	4.4	15.3
35	19	0.6	0.7	0.4	3.4	1.0	0.9	1.4	4.0
52. 2-Methylpropanoic acid(1)–water(2) [a] [25]									
20	14	6.9	0.9	3.7	1.7	4.9	7.8	8.2	20.7
25	14	5.0	0.9	4.1	1.3	3.4	3.7	6.2	10.5
30	11	5.0	0.9	3.2	6.4	13.7	6.3	23.3	10.2
35	11	2.0	0.3	4.5	10.4	3.9	8.4	9.0	1.3
53. Nitroethane(1)–2,2,4-trimethylpentane(2) [a] [25]									
20	13	6.8	6.3	11.9	27.8	9.8	4.1	31.3	23.2
30	13	3.7	3.4	4.9	15.6	7.8	4.8	23.5	24.9
35	13	3.5	1.3	8.8	2.7	3.9	2.1	10.9	22.3
40	13	3.8	1.5	9.4	10.9	3.4	2.5	2.9	23.7
54. *n*-Butylamine(1)–toluene(2) [36]									
15	19	0.6	0.8	0.4	10.7	2.4	0.9	2.1	2.7
25	19	0.7	0.8	1.7	1.0	1.8	0.7	1.0	2.8
35	19	0.7	0.8	1.2	3.7	2.9	0.5	0.4	0.7
55. *n*-Butylamine(1)–methylcyclohexane(2) [36]									
15	19	0.7	1.2	0.4	16.0	0.9	0.9	5.3	3.8
25	19	2.2	1.3	1.1	0.3	0.8	0.9	7.9	0.1
35	15	0.9	1.4	0.8	4.9	0.6	0.7	0.4	0.7
56. *n*-Octane(1)–2-methylpentane(2) [d] [37]									
10	7	3.4	2.8	4.7	27.6	7.1	6.3	20.1	23.8
20	8	2.4	1.7	2.7	8.0	0.4	5.4	8.0	0.4
30	7	3.3	1.8	4.8	14.3	5.9	2.7	13.4	3.9
40	7	2.9	1.6	3.0	14.0	10.9	3.5	1.3	7.5
57. *n*-Octane(1)–3-methylpentane(2) [d] [37]									
10	7	0.7	2.1	1.6	8.3	11.3	6.0	20.5	14.0
20	8	3.3	1.4	1.5	5.5	4.3	4.2	1.7	11.4
30	7	2.2	1.1	2.3	15.4	3.3	4.6	16.0	10.1
40	7	1.4	1.9	3.3	8.3	4.9	5.1	7.3	1.7

[a] Partially miscible systems. [b] $P = 5$ MPa, where P is the system pressure. [c] System showing S shape for the plot of h^E versus x. [d] Nearly ideal systems.

which each alcohol molecule makes a hydrogen bond with a polar molecule and in which such complexes are surrounded by a large amount of the polar liquid medium. Therefore, the difference between the values of ΔH_1 for the alcohol–polar liquid systems and that for the alcohol–non-polar system may correspond roughly to a measure of the alcohol–polar liquid

TABLE 2

Comparison of predicted and experimental values of ΔH_i obtained by direct calorimetric measurement of h^E in the highly diluted region of x_i [8]

System	$T(i)$ (°C)	ΔH_i [this work] (J-mol^{-1})					ΔH_i [8] (J-mol^{-1})		
		exptl [a]	x_i min.	NRTL	UNIQUAC	T range (°C)	exptl	x_i min.	Ref.
Ethanol(1)–cyclohexane(2)	25(1)	–	0.05	9703	15045	5–65	23300	0.0008	
	40(1)	–	0.05	9965	14598	5–65	23200	–	[20]
Benzene(1)–cyclohexane(2)	25(1)	3074	0.201	3395	3038	25–50	3190	0.005	[34]
Methanol(1)–*n*-hexane(2)	25(2)	4743	0.025	4829	5255	25–50	4820	0.0012	[15]
Methanol(1)–*n*-heptane(2)	25(2)	–	0.025	5138	6284	30–60	5730	0.0006	[15]
Water(1)–methanol(2)	25(1)	−7512	0.1	−6269	−7176	5–50	−2890	0.0027	[16]
1-Butanol(1)–nitromethane(2)	25(1)	14896	0.082	15448	16943	18–30	16000	0.0002	[25]
Ethanol(1)–acetone(2)	40(1)	–	0.049	5279	5135	25–50	4750	–	[17]
2-Propanol(1)–cyclohexane(2)	40(1)	–	0.073	10184	8602	20–50	21300	–	[22]
	60(2)	–	0.073	3844	5184	20–50	4280	–	
2-Propanol(1)–heptane(2)	60(2)	5060	0.006	5125	5217	30–60	5250	–	[18]

[a] Experimental values obtained by extrapolation of finite concentration data of h^E.

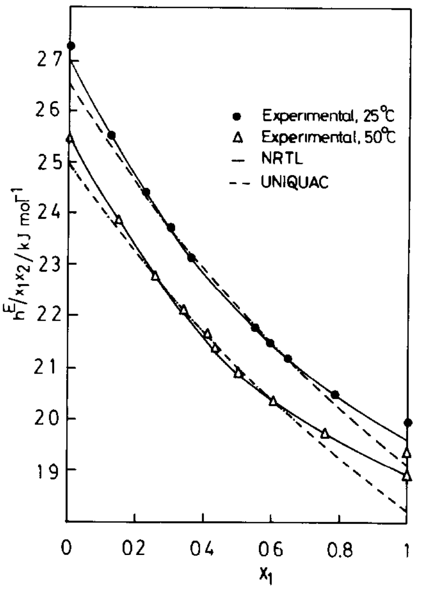

Fig. 1. Comparison of h^E/x_1x_2 predictions with the experimental values [34] at finite concentration and infinite dilution for the system *n*-heptane(1)–toluene(2).

intermolecular hydrogen bonding [38]. In a strict treatment, the dipolar stabilization energy must be also included, because alcohol–polar liquid complex molecules are embedded in the polar medium. Using the thermodynamic cycle [39], intermolecular hydrogen bonding energies may be estimated. These agree with the results obtained from a spectroscopic study [38,40,41].

The alcohol solutions have a higher enthalpy of mixing at 25 °C with benzene than with *n*-hexane, which is consistent with the view that more hydrogen bonds are broken in benzene solution than in hexane solution. For a given alcohol, the value of h^E at 25 °C decreases as more alkyl groups are substituted on the benzene ring [42].

Table 1 indicates that, for 2128 data points of h^E, excluding the points of the system 2-propanol–water, the average absolute errors are obtained as 3.3% and 4% for the NRTL and UNIQUAC models respectively. Deviations, D_i, between the predicted and experimental values of ΔH_i obtained by the extrapolation of finite concentration h^E data may be assumed as satisfactory. In Table 2, the predicted and experimental values of ΔH_i obtained by direct calorimetric measurements of h^E in the highly diluted region of x_i [8] are compared. Figures 1–4 show the values of h^E/x_1x_2 at finite and at infinite dilution for various types of systems. Tables 1 and 2 and Figs. 1–4 indicate that predictions obtained from the NRTL and UNIQUAC models are mainly satisfactory, except for the region of high dilution.

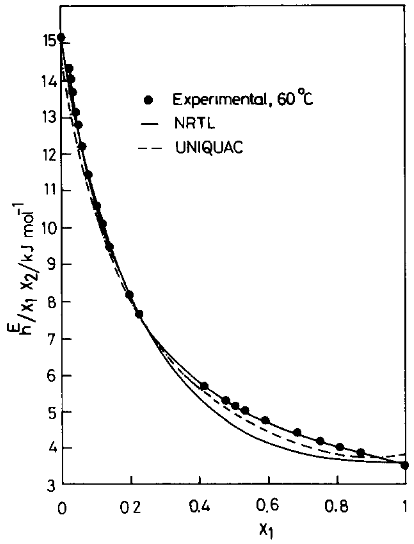

Fig. 2. Comparison of h^{E}/x_1x_2 predictions with the experimental values [18] at finite concentration and infinite dilution for the system ethanol(1)–toluene(2).

As Table 3 and Fig. 5 indicate, the agreement between the predicted and experimental values of C_p^E is mainly poor for both of the models. As Trampe and Eckert [8] state, by measuring derivative excess properties directly, one avoids the inherent loss of precision incurred when differenti-

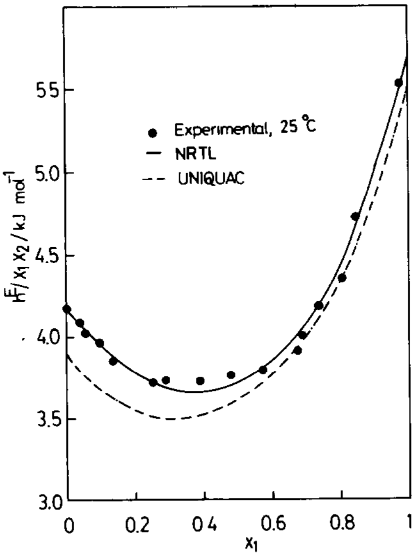

Fig. 3. Comparison of h^{E}/x_1x_2 predictions with the experimental values [26] at finite concentration and infinite dilution for the system n-heptane(1)–acetic acid(2).

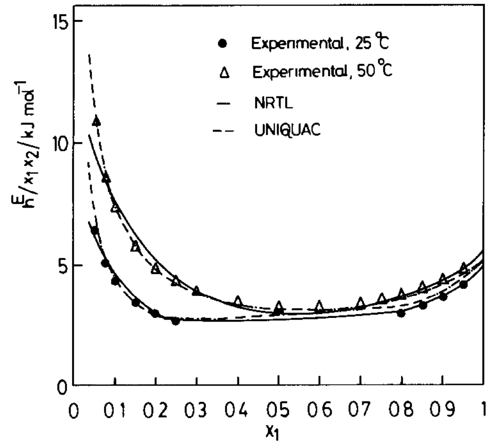

Fig. 4. Comparison of h^E/x_1x_2 predictions with the experimental values [15] at finite concentration and infinite dilution for the system methanol(1)–*n*-hexane(2).

ating data. When estimating the values of C_p^E from $(\partial h^E/\partial T)_x$, the accuracy of h^E determination should be high [10]. The temperature dependence of C_p^E for aqueous alcohol mixtures is relatively large and complicated [43].

In Table 4 the predicted values of limiting activity coefficients for some of the systems are compared with the experimental values [47]. Because of the empirical character of the models [2,3], the predicted and experimental values show large deviations.

TABLE 3

Comparison of the experimental and predicted values of excess heat capacities C_p^E

System and refs.	T (°C)	Average absolute error $S(C_p^E)$	
		NRTL	UNIQUAC
Methanol(1)–water(2) [15,10,43]	15	300.8	215.8
	25	115.0	79.5
	35	78.1	67.5
Ethanol(1)–water(2) [20]	150	93.7	671.7
	175	45.3	607.0
Ethanol(1)–toluene(2) [17]	30	26.8	5.5
2-Propanol(1)–*n*-heptane(2) [17,44]	30	47.6	15.9
	35	11.6	73.7
	40	17.9	73.6
	45	31.9	73.6
1-Butanol(1)–methanol(2) [26,45]	25	107.4	0.05
Benzene(1)–cyclohexane(2) [33,39]	25	164.3	7.5
Benzene(1)–*n*-heptane(2) [32,34,46]	20	459.5	23.2
	25	173.8	23.1
	30	58.3	22.5

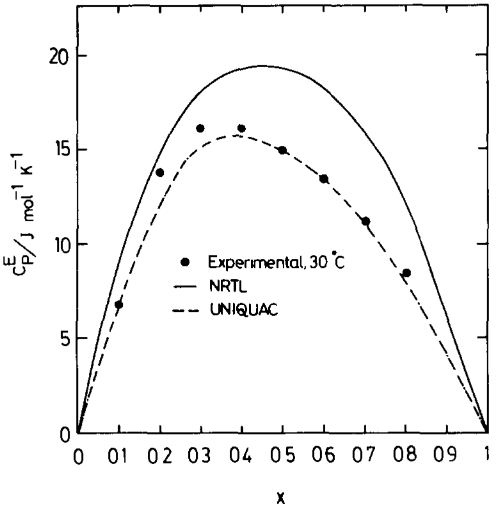

Fig. 5. Comparison of C_p^E predictions with the experimental values [18] for the system ethanol(1)–toluene(2).

TABLE 4

Comparison of the experimental [47] and predicted values of limiting activity coefficients γ_1^∞

System	T (°C)	γ_i^∞		
		Experimental	Predicted	
			NRTL	UNIQUAC
Methanol(1)–*n*-hexane(2)				
	68.05	34.40	305.89	49.97
Ethanol(1)–acetone(2)				
	25	2.44	11.67	2.07
	35	2.24	10.92	2.01
	45	2.07	10.23	1.96
	55	1.92	9.61	1.92
Ethanol(1)–cyclohexane(2)				
	39.65	29.90	81.96	2.09
	49.75	24.30	72.74	2.04
	59.85	19.10	64.97	1.99
	69.85	15.10	58.43	1.95
	79.75	11.70	52.88	1.91
Ethanol(1)–ethyl acetate(2)				
	55.25	2.55	60.38	5.96
	65.25	2.44	54.69	5.51
	75.95	2.34	49.42	5.10
2-Propanol(1)–cyclohexane(2)				
	39.65	23.40	121.89	27.07
	49.75	18.34	107.43	24.42
	59.85	15.72	94.95	22.19
	69.85	12.74	84.39	20.32
	79.75	10.45	75.46	18.73

The measurements at high dilutions and the examination of partial molar functions and activity coefficients rather than simple excess functions, which disguise the extreme non-ideality of the dilute solutions, are very important. Models must also account well for the partial properties [6,8,11,47].

CONCLUSIONS

Using the local composition models of NRTL and UNIQUAC, calorimetric properties have been predicted at different isotherms for a large number of binary liquid mixtures. The adjustable parameters of the models are estimated using h^E data alone. The performance of the models is mainly satisfactory for the predictions of heats of mixing and partial molar heats of mixing at infinite dilution, but not so for the predictions of excess heat capacity and limiting activity coefficients.

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