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Correlation of heats of mixing of liquid mixtures by the NRTL model

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Abstract

Using data for heats of mixing h^E, the temperature-dependent parameters of the NRTL model have been estimated for 55 systems of binary liquid mixtures. In order to test the model thoroughly, systems of various types, including associating and partially miscible systems that have data for h^E at more than one different isotherm, are considered. The temperature dependence for the parameters of the model is assumed to be linear. The physical meanings and non-uniqueness of the parameters are discussed. Later these parameters are employed to predict the heats of mixing, partial molar heats of mixing and activity coefficients at infinite dilution. In previous studies, the same properties were predicted by assuming a non-linear temperature dependence for the parameters of the NRTL model. Hence the performance of the model is tested by comparing the predictions with experimental values when the linear and non-linear temperature dependences of the parameters are introduced into the model.

INTRODUCTION

Introducing empirical temperature dependences into the original version of the NRTL model [1] improves the performance considerably, especially for high non-ideal mixtures [2]. However, the nature of the temperature dependence of the parameters needs to be investigated further in order to achieve the best use of the model.

In a previous study the NRTL model was used in correlating of h^E data at different isotherms by assuming a non-linear temperature dependence for the parameters [3]. This form was especially suitable for predicting the excess heat capacity from the differentiation of the equation for h^E [4]. In this study, the temperature-dependent parameters of the model are estimated from h^E data by assuming only a conventional linear temperature dependence for the parameters. Therefore, the performances of the model are compared in predicting the values of h^E, the partial molar heats of mixing at infinite dilution, and the limiting activity coefficients, when the linear and non-linear empirical temperature dependences are introduced into the model parameters.

HEATS OF MIXING

Heats of mixing data are needed for to test models for liquid mixtures and to understand the effect of molecular structure on the thermodynamic properties of mixtures.

In the a previous study [3], the temperature dependence of the parameters of the NRTL model were assumed as

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

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

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

and the obtained parameters were used to calculate the values of excess heat capacities by differentiation of the equation for h^E.

In this study, it is assumed that the NRTL parameters change with temperature in a linear form [1]

$$g_{21}-g_{11}=c_1+c_2(T-273.15) \tag{4}$$

$$g_{12}-g_{22}=c_3+c_4(T-273.15) \tag{5}$$

$$\alpha_{12}=\alpha_{21}=c_2+c_6(T-273.15) \tag{6}$$

where $g_{21}-g_{11}$, $g_{12}-g_{22}$ and α_{12} are the interaction energies in J mol^{-1} and the non-randomness parameters, respectively. The terms c_1, c_3 and c_5 show the values of the parameter at 273.15 K, while c_2 and c_4 (J mol^{-1} K^{-1}) and c_6 (K^{-1}) are the coefficients of temperature.

From the Gibbs-Helmholtz equation

$$\frac{h^E}{T^2}=-\left[\frac{\partial(g^E/T)}{\partial T}\right]_{P,x} \tag{7}$$

and using eqns. (4)–(6), the enthalpy of mixing becomes

$$h^E=\frac{(x_1x_2G_{21})}{(x_1+x_2G_{21})}\left[\left(1-\frac{(\alpha_{12}\tau_{21}x_1)}{(x_1+x_2G_{21})}\right)(c_1-273.15c_2)+\frac{\tau_{21}^2x_1c_6RT^2}{x_1+x_2G_{21}}\right]$$
$$+\frac{(x_1x_2G_{12})}{(x_2+x_1G_{12})}\left[\left(1-\frac{(\alpha_{12}\tau_{12}x_2}{(x_2+x_1G_{12})}\right)(c_3-273.15c_4)+\frac{\tau_{12}^2x_2c_6RT^2}{x_2+x_1G_{12}}\right] \tag{8}$$

where $G_{21}=\exp(-\alpha_{12}\tau_{21})$, $G_{12}=\exp(-\alpha_{12}\tau_{12})$, $\tau_{21}=(g_{21}-g_{11})/RT$ and $\tau_{12}=(g_{12}-g_{22})/RT$.

The values of h^E/x_1x_2 at liquid compositions $x_1=0$ and $x_1=1$ are identical with the partial molar heats of mixing of components 1 and 2, ΔH_1 and ΔH_2, at infinite dilution respectively. To understand the behaviour of the mixture, it is advantageous to examine derivative excess properties at the limit of infinite dilution, where a single solute molecule is completely surrounded by the solvent. Because solute–solute interactions are no longer present, excess properties at infinite dilution reflect almost completely the unlike-pair intermolecular forces [5, 6]. Expressions for partial molar heats of mixing at infinite dilution ΔH_i are

$$\Delta H_1 = c_1 - 273.15c_2 + G_{12}[(1 - \alpha_{12}\tau_{12})(c_3 - 273.15c_4) + \tau_{12}^2 c_6 RT^2] \tag{9}$$

$$\Delta H_2 = c_3 - 273.15c_4 + G_{21}[(1 - \alpha_{12}\tau_{21})(c_1 - 273.15c_2) + \tau_{21}^2 c_6 RT^2] \tag{10}$$

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. From the Gibbs–Helmholtz equation

$$\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)} = \frac{\Delta H_i}{R} \tag{11}$$

the limiting activity coefficient is related to the partial molar heats of mixing at infinite dilution. Expressions for limiting activity coefficients are

$$\ln \gamma_1^\infty = \tau_{21} + \tau_{12}G_{12} \tag{12}$$

$$\ln \gamma_2^\infty = \tau_{12} + \tau_{21}G_{21} \tag{13}$$

ESTIMATION OF PARAMETERS

In estimating the temperature-dependent parameters, the following objective function has been minimized

$$F = \frac{1}{N}\left\{\sum_j^N \frac{\sum_i^n [w(h_{i,\mathrm{exp}}^{\mathrm{E}} - h_{i,\mathrm{calc}}^{\mathrm{E}})/h_{i,\mathrm{exp}}^{\mathrm{E}}]_j^2}{n}\right\} \tag{14}$$

where n is the number of experimental data points of h^{E} at a specified temperature, N is the number of isothermal systems and w denotes a weight factor. To minimize the function F, a package program called MINUIT [7] was used. The MINUIT program performs minimization and analysis of the shape of a multi-parameter function. It incorporates the Fletcher and Simplex techniques. Some global logic is built into the program: if one of the techniques fails or is not satisfactory, then it automatically causes another technique to be called to make further attempts.

All the parameters of the NRTL model were regressed. In order to maintain the physical meanings of the parameters [1], the values of α_{ij} were forced to change in the range of 0.1–0.7. An analytical method due to Tassios [8] was used to determine whether or not the estimated parameters could predict the physical behaviour of the liquid mixtures. Because of the multi-root property of the model, some of the parameter sets may not predict the phase splitting for a partially miscible mixture and vice versa.

RESULTS AND DISCUSSIONS

Using data for h^E at more than one different isotherm, the temperature-dependent parameters of the NRTL model were estimated for 55 systems of binary liquid mixtures. These include highly non-ideal, associating, and partially miscible systems. The estimated parameters and variance of the fit σ are given in Table 1. The variance of the fit is obtained from

$$\sigma = \frac{1}{\left(\sum_j^N n_j - \mathrm{NP}\right)} \sum_j^N \sum_i^n [(h_{i,\mathrm{exp}}^E - h_{i,\mathrm{calc}}^E)/h_{i,\mathrm{exp}}^E]_j^2 \tag{15}$$

where $\sum n_j$ is the total number of data points and NP is the number of parameters. Other terms are as previously defined. The values of σ provide a measure of how well the h^E data are represented by the model.

Multiple roots were estimated from the model. However the multiplicity of the roots does not seem to represent a problem when all the parameters are regressed [8]. The set of parameters which yields the best variance of the fit has been tabulated.

For some of the systems which do not show partial miscibility, the estimated parameters predict phase splitting and vice versa, as can be seen from Table 1. The physical meaning of the parameters may be lost when all of them are treated as adjustable parameters. However, as Tassios [8] points out, the selection of a meaningful value of α_{ij} is ambiguous and difficult to apply and the NRTL model performs best when all the parameters are obtained by regression of the available experimental data.

Using the estimated parameters, the values of h^E and ΔH_i have been predicted and compared with experimental values. The accuracy of the predictions are given as average absolute errors S for h^E, and relative absolute deviations D_i for ΔH_i values

$$S = \frac{1}{n}\left[\sum_i^n \left|\frac{h_{i,\mathrm{exp}}^E - h_{i,\mathrm{calc}}^E}{h_{i,\mathrm{exp}}^E}\right|\right]100 \tag{16}$$

$$D_i = \left|\frac{\Delta H_{i,\mathrm{exp}} - \Delta H_{i,\mathrm{calc}}}{\Delta H_{i,\mathrm{exp}}}\right| 100 \tag{17}$$

The values of S and D_i were calculated at each temperature and are given in Table 2.

TABLE 1

Temperature-dependent parameters of the NRTL model and variances of the fit σ

c_1 (J mol^{-1})	c_2 (J mol^{-1} K^{-1})	c_3 (J mol^{-1})	c_4 (J mol^{-1} K^{-1})	c_5	c_6 (K^{-1})	σ $\times 10^3$	(σ) $\times 10^3$ [a]
1. Methanol(1)–ethyl acetate(2), 25–35 [9]							
2519.31	−28.91	4616.62	28.03	0.2823	-0.1708×10^{-2}	1.65	(0.79)
2. Methanol(1)–ethyl formate(2), 25–45 [10]							
1999.74	−3.13	1130.81	−7.40	0.6940	-0.4620×10^{-2}	0.98	(0.42)
3. Methanol(1)–*n*-heptane(2) [b], 30–60 [11]							
9060.03	−6.62	865.83	−22.15	0.5998	-0.6354×10^{-3}	7.92	(10.62)
4. Ethanol(1)–methyl acetate(2), 25–45 [12]							
2491.99	−10.48	1460.10	−10.32	0.6231	0.1970×10^{-3}	0.25	(0.24)
5. Ethanol(1)–ethyl formate(2), 25–45 [10]							
−1357.54	−9.96	1928.53	−8.25	0.1143	0.5531×10^{-2}	1.23	(0.47)
6. Ethanol(1)–acetone(2), 25–50 [13]							
2431.95	−7.72	2492.49	−0.35	0.2794	-0.1650×10^{-2}	0.05	(0.04)
7. Ethanol(1)–cyclohexane(2) [c], 5–65 [14]							
6113.66	−15.16	1409.96	−9.85	0.7499	0.1900×10^{-2}	2.08	(3.41)
8. 1-Propanol(1)–ethyl acetate(2), 25–45 [9]							
3878.10	−8.26	3398.99	−0.94	0.2802	0.3460×10^{-3}	0.42	(0.35)
9. 1-Propanol(1)–ethyl formate(2), 25–45 [10]							
4062.24	−6.23	3702.88	−4.79	0.2226	-0.1457×10^{-2}	0.50	(0.19)
10. 2-Propanol(1)–ethyl acetate(2), 25–35 [9]							
895.75	−18.59	667.05	−15.59	0.1763	0.1579	0.21	(0.16)
11. 2-Propanol(1)–ethyl formate(2), 25–45 [10]							
3530.25	−8.63	3640.33	−8.23	0.3226	-0.7036×10^{-3}	0.13	(0.15)
12. *n*-Butanol(1)–ethyl acetate(2) [d], 25–35 [15]							
9274.25	11.47	2519.52	−9.56	0.4172	0.1465×10^{-2}	0.16	(1.28)
13. *n*-Butanol(1)–ethyl formate(2), 25–45 [15]							
3175.16	−8.67	2381.36	−11.68	0.4562	-0.4808×10^{-3}	0.41	(0.19)
14. *n*-butanol(1)–octane(2), 15–55 [16]							
12271.20	98.03	−15738.53	−35.89	0.1234	0.1260×10^{-3}	1.03	(3.61)
15. *n*-Hexanol(1)–*n*-amylamine(2) [d], 15–35°C, [17]							
14871.61	23.67	−6009.06	−14.64	0.1002	-0.1021×10^{-3}	0.36	(0.90)
16. *n*-Hexanol(1)–*n*-octane(2), 15–55°C, [16]							
2974.69	−47.15	−1675.06	30.25	0.2632	0.1174×10^{-1}	2.94	(1.77)
17. Heptanol(1)–*n*-amylamine(2), 15–35°C, [17]							
−1219.85	−24.32	82.84	59.35	0.1818	-0.1857×10^{-2}	2.79	(0.89)
18. *n*-Octanol(1)–*n*-heptane(2), 15–55°C, [16]							
2352.28	−37.40	−1217.54	22.63	0.4027	0.2043×10^{-1}	9.33	(11.6)
19. *n*-Octanol(1)–*n*-octane(2), 15–55°C, [16]							
2641.19	−41.84	−1425.48	26.56	0.3178	0.1547×10^{-1}	9.98	(6.48)
20. *n*-Octanol(1)–*n*-amylamine(2), 15–35°C, [17]							
1196.45	6.36	−362.54	27.53	0.6739	-0.1121×10^{-1}	1.48	(0.53)
21. Decanol(1)–*n*-amylamine(2), 15–35°C, [17]							
1251.43	2.00	−526.76	28.87	0.4918	-0.8271×10^{-2}	2.32	(1.28)
22. Methyl acetate(1)–benzene(2) [e], 25–35°C, [18]							
−998.51	−17.40	9606.88	45.52	0.2319	-0.3928×10^{-3}	1.29	(3.22)

TABLE 1 (continued)

c_1 (J mol^{-1})	c_2 (J mol^{-1} K^{-1})	c_3 (J mol^{-1})	c_4 (J mol^{-1} K^{-1})	c_5	c_6 (K^{-1})	σ $\times 10^3$	(σ) $\times 10^{3}$ [a]
23. Diethylamine(1)–benzene(2), 25–45°C, [19]							
−42.84	−7.18	5957.18	25.48	0.5993	-0.5128×10^{-3}	1.36	(1.66)
24. Triethylamine(1)–benzene(2), 25–45°C, [19]							
2917.08	7.53	4794.44	15.98	0.5886	0.6616×10^{-3}	1.77	(1.30)
25. Benzene(1)–i-octane(2), 25–50°C, [20]							
−2792.40	4.87	2648.05	−23.38	0.1572	0.2503×10^{-2}	0.14	(0.02)
26. Benzene(1)–*n*-hexadecane(2), 25–50°C, [20]							
−524.08	4.58	1851.52	−31.04	0.1741	0.7539×10^{-1}	0.41	(0.07)
27. Benzene(1)–octene-1(2), 25–50°C, [20]							
−254.01	26.19	2562.86	−4.98	0.5998	0.4926×10^{-2}	0.36	(0.06)
28. Benzene(1)–decalin(2), 25–50°C, [20]							
−587.35	1.87	859.39	−12.42	0.1505	0.2670×10^{-1}	0.07	(0.07)
29. Benzene(1)–tetralin(2), 25–50°C, [20]							
1053.28	−1.26	−629.90	1.69	0.1500	0.7333×10^{-2}	0.37	(0.09)
30. Methyl acetate(1)–*n*-hexane(2) [c], 25–45°C, [15]							
5799.86	0.94	2987.12	−13.76	0.3441	0.4360×10^{-3}	1.54	(2.72)
31. Cyclohexane(1)–tetralin(2), 25–50°C, [20]							
−954.03	2.06	753.54	−9.58	0.1545	0.9322×10^{-2}	0.06	(0.01)
32. Cyclohexane(1)–hexadecane(2), 25–50, [20]							
−2654.07	−20.46	6195.66	31.17	0.4214	-0.8067×10^{-3}	0.10	(0.14)
33. Cyclohexane(1)–*n*-heptane(2), 25–50°C, [20]							
−2518.76	−0.86	2511.40	0.17	0.1592	0.2438×10^{-2}	0.33	(0.56)
34. Cyclohexane(1)–*m*-xylene(2), 25–50°C, [20]							
−204.13	36.40	2045.38	−1.60	0.5024	0.4294×10^{-2}	0.08	(0.01)
35. Cyclohexane(1)–octene-1(2), 25–50°C, [20]							
−821.73	6.61	1142.44	−12.59	0.4887	0.1186×10^{-1}	0.26	(0.02)
36. Methyl cyclohexane(1)–*n*-heptane(2), 25–50°C, [20]							
−2200.78	−9.12	2610.81	0.69	0.2252	0.1532×10^{-2}	0.62	(0.43)
37. Cyclohexane(1)–i-octane-1(2), 25–50°C, [20]							
−478.02	3.91	2035.51	−1.53	0.2103	0.1436×10^{-2}	0.11	(0.12)
38. 1-Chlorohexane(1)–ethylbenzene(2) [c], 15–25°C, [21]							
675.21	3.69	576.80	4.26	0.1000	0.3950×10^{-2}	0.25	(0.11)
39. 1-Chlorohexane(1)–*n*-propylbenzene(2), 15–25°C, [21]							
−188.40	6.73	216.73	−4.22	0.4478	-0.2689×10^{-1}	0.35	(0.31)
40. 1-Chlorohexane(1)–toluene(2) [d], 15–25°C, [21]							
37.65	1.42	22.25	2.19	0.2403	0.8323×10^{-1}	0.41	(0.37)
41. *n*-Heptane(1)–acetic acid(2), 25–35°C, [15]							
4568.93	0.08	2698.68	−0.50	0.7000	0.2791×10^{-2}	0.38	(0.19)
42. *n*-Heptane(1)–propionic acid(2), 25–35°C, [15]							
2273.16	−1.07	3215.82	4.56	0.5999	0.1009×10^{-2}	2.58	(1.28)
43. *n*-Heptane(1)–*n*-amylamine(2), 15–35°C, [17]							
1638.91	6.61	1753.59	−9.75	0.6999	0.4458×10^{-2}	0.26	(0.04)
44. *n*-Heptane(1)–toluene(2) [c], 25–50°C, [20]							
11564.57	45.81	−1893.26	−17.90	0.1078	-0.6823×10^{-4}	0.23	(0.01)
45. *n*-Heptane(1)–*m*-xylene(2), 25–50°C, [20]							
1039.89	−2.08	92.90	0.11	0.5519	0.5568×10^{-2}	0.13	(0.01)

TABLE 1 (continued)

c_1 (J mol^{-1})	c_2 (J mol^{-1} K^{-1})	c_3 (J mol^{-1})	c_4 (J mol^{-1} K^{-1})	c_5	c_6 (K^{-1})	σ $\times 10^3$	(σ) $\times 10^{3\,a}$
46. *n*-Heptane(1)-*n*-hexadecane(2), 25-50°C, [20]							
28.75	13.05	28.58	−13.10	0.5993	-0.6819×10^{-2}	0.23	(0.82)
47. *n*-Heptane(1)-decaline(2), 25-50°C, [20]							
1843.05	9.70	−140.20	−8.11	0.5856	-0.8728×10^{-3}	0.03	(0.07)
48. *n*-Heptane(1)-tetraline(2), 25-50°C, [20]							
−801.23	1.12	2339.10	−1.90	0.1500	0.2482×10^{-2}	0.49	(0.02)
49. *n*-Butylamine(1)-toluene(2), 15-35°C, [22]							
240.28	−3.62	427.60	−1.49	0.1000	0.4435×10^{-1}	0.30	(0.19)
50. *n*-butylamine(1)-methylcyclohexane(2), 15-35°C, [22]							
2667.72	−6.72	2002.04	1.28	0.6437	0.4174×10^{-2}	0.18	(0.14)
51. *n*-Octane(1)-2-methylpentane(2) [d], 10-40°C, [23]							
132.04	−0.97	76.14	0.93	0.1000	0.5320×10^{-1}	1.65	(2.45)
52. *n*-Octane(1)-3-methylpentane(2) [d], 10-40°C, [23]							
575.72	−1.28	−451.87	1.42	0.3358	0.5208×10^{-2}	1.56	(0.92)
53. Toluene(1)-*n*-hexadecane(2), 25-50°C, [20]							
−487.43	0.87	3450.10	−8.24	0.5999	0.5422×10^{-2}	0.61	(0.09)
54. i-Octane(1)-*n*-octane(2), 25-50°C, [20]							
736.80	0.11	−697.47	0.15	0.2174	0.4364×10^{-2}	0.06	(0.07)
55. Decalin(1)-*n*-hexadecane(2), 25-50°C, [20]							
−1963.55	1.67	1852.76	2.31	0.1500	0.6789×10^{-2}	0.41	(0.34)

[a] Values obtained using the non-linear temperature dependence for the parameters of the NRTL model, eqns. (1)-(3) [3].

[b] Partially miscible system.

[c] Prediction of complete miscibility with linear dependence of temperature, and partial miscibility with non-linear dependence of temperature for the parameters of the NRTL model.

[d] Prediction of partial miscibility for completely miscible systems.

[e] Prediction of partial miscibility with linear dependence of temperature, and complete miscibility with non-linear dependence of temperature for the parameters of the NRTL model.

TABLE 2

Comparison of the percentages of absolute average errors for h^E and the percentages of deviation for ΔH_i when using the NRTL model with linear and non-linear temperature dependences

T (°C)	Percentage uncertainties			Percentage of absolute average errors S and deviations D					
	n	U_1	U_2	S	$(S)^a$	D_1	$(D_1)^a$	D_2	$(D_2)^a$
1. Methanol(1)-ethyl acetate(2)									
25	12	5.1	5.0	3.6	(2.2)	3.4	(7.2)	1.0	(14.5)
35	12	6.2	5.4	2.2	(1.7)	11.8	(14.9)	0.4	(8.1)
2. Methanol(1)-ethyl formate(2)									
25	8	2.5	2.1	1.7	(0.9)	6.4	(26.4)	10.2	(7.9)

TABLE 2 (continued)

T (°C)	Percentage uncertainties			Percentage of absolute average errors S and deviations D					
	n	U_1	U_2	S	$(S)^a$	D_1	$(D_1)^a$	D_2	$(D_2)^a$
35	11	2.0	2.0	3.1	(2.0)	0.2	(18.3)	3.6	(5.8)
45	9	2.1	2.1	1.5	(1.2)	0.2	(17.6)	2.5	(6.3)
3. Methanol(1)–*n*-heptane(2)[b]									
30	8	–	4.3	6.2	(6.0)	–		10.2	(14.1)
45	11	–	3.9	4.1	(8.3)	–		20.7	(7.2)
60	17	–	3.5	7.8	(6.2)	–		30.0	(0.6)
4. Ethanol(1)–methyl acetate(2)									
25	11	6.1	6.2	1.2	(0.7)	1.7	(1.7)	5.1	(1.9)
35	12	5.2	4.0	1.2	(1.4)	5.1	(0.9)	0.1	(3.7)
5	7	5.0	5.0	1.5	(1.3)	2.3	(0.6)	0.1	(3.5)
5. Ethanol(1)–methyl formate(2)									
25	6	6.3	4.1	1.8	(0.7)	4.5	(5.4)	0.1	(4.1)
35	13	3.7	4.4	3.7	(2.2)	7.1	(9.8)	2.6	(6.4)
45	9	3.0	2.6	1.8	(1.5)	0.6	(15.2)	1.4	(9.9)
6. Ethanol(1)–acetone(2)									
25	12	2.0	1.0	0.4	(0.4)	1.2	(7.2)	0.4	(4.9)
50	12	1.0	2.0	0.4	(0.3)	0.1	(5.7)	1.4	(4.4)
7. Ethanol(1)–cyclohexane(2)									
5	10	10.5	1.7	2.8	(4.4)	9.4	(37.6)	16.2	(3.4)
20	10	0.1	17.5	2.1	(2.9)	18.9	(36.1)	27.4	(18.6)
35	10	5.0	1.5	2.5	(3.5)	4.4	(22.8)	8.0	(5.8)
50	10	4.1	2.8	0.8	(2.7)	3.1	(18.4)	10.6	(3.0)
65	10	5.9	2.9	2.7	(2.4)	10.7	(13.0)	8.0	(7.4)
8. 1-Propanol(1)–ethyl acetate(2)									
25	11	6.1	5.2	1.7	(1.7)	1.5	(9.5)	9.1	(2.7)
35	20	4.1	3.0	1.4	(1.3)	1.6	(13.0)	0.3	(2.5)
45	9	5.0	2.2	0.8	(0.9)	1.1	(9.8)	3.7	(2.8)
9. 1-Propanol(1)–ethyl formate(2)									
25	8	4.2	3.1	1.1	(0.3)	5.2	(12.1)	2.9	(6.8)
35	13	6.3	3.2	2.3	(1.4)	3.9	(9.0)	1.9	(7.4)
45	9	3.0	3.2	1.2	(0.9)	2.5	(11.6)	0.2	(9.8)
10. 2-Propanol(1)–ethyl acetate(2)									
25	13	4.3	2.2	0.9	(0.9)	1.0	(6.9)	1.8	(2.1)
35	18	4.2	7.2	1.0	(0.9)	0.2	(11.3)	4.8	(1.9)
11. 2-Propanol(1)–ethyl formate(2)									
25	13	5.3	5.1	0.8	(0.8)	3.1	(16.1)	0.7	(14.1)
35	12	5.0	5.4	0.9	(1.0)	0.2	(12.1)	2.2	(16.1)
45	11	4.1	3.1	0.8	(0.7)	4.7	(5.6)	1.1	(10.8)
12. *n*-butanol(1)–ethyl acetate(2)									
25	13	2.5	3.3	0.6	(0.5)	4.4	(4.6)	2.3	(2.3)
35	18	1.9	2.4	1.1	(2.7)	2.5	(2.6)	2.4	(2.5)
13. *n*-Butanol(1)–ethyl formate(2)									
25	14	1.2	2.5	1.1	(0.6)	5.2	(14.3)	3.1	(4.5)
35	11	1.8	2.0	2.2	(1.3)	0.7	(14.0)	0.4	(10.9)
45	11	1.2	1.2	1.4	(1.2)	1.4	(14.8)	6.5	(2.9)

TABLE 2 (continued)

T (°C)	Percentage uncertainties			Percentage of absolute average errors S and deviations D					
	n	U_1	U_2	S	(S) [a]	D_1	(D_1) [a]	D_2	(D_2) [a]
14. *n*-Butanol(1)–octane(2)									
15	25	0.8	0.8	1.5	(1.8)	2.4	(53.2)	1.3	(46.0)
55	26	0.4	0.4	2.6	(5.1)	8.0	(18.4)	34.2	(3.8)
15. Hexanol(1)–*n*-amylamine(2)									
15	19	2.5	2.2	1.6	(0.6)	2.5	(2.4)	6.0	(6.4)
35	19	2.8	2.2	1.4	(3.3)	3.3	(3.1)	5.4	(5.6)
16. *n*-Hexanol(1)–*n*-octane(2) [b]									
15	9	–	3.8	3.2	(3.5)	–		1.9	(4.7)
25	8	–	1.4	3.6	(2.3)	–		7.9	(8.8)
17. Heptanol(1)–*n*-amylamine(2)									
15	19	1.5	1.7	4.9	(1.9)	14.3	(41.0)	13.1	(24.2)
35	19	1.4	1.7	3.4	(2.7)	7.7	(13.5)	8.6	(7.2)
18. *n*-Octanol(1)–*n*-heptane(2) [b]									
15	9	–	12.2	4.4	(7.3)	–		1.9	(6.2)
55	9	–	6.6	7.8	(5.6)	–		12.2	(7.2)
19. *n*-Octanol(1)–*n*-octane(2)									
15	9	12.8	10.8	3.9	(4.1)	6.6	(1.7)	0.5	(0.5)
25	9	15.9	6.9	8.2	(6.4)	16.7	(16.7)	11.9	(11.9)
20. *n*-Octanol(1)–*n*-amylamine(2)									
15	19	3.5	2.7	3.7	(1.2)	0.8	(9.5)	3.9	(4.2)
35	19	2.1	2.6	2.3	(2.2)	5.5	(3.6)	7.4	(11.4)
21. Decanol(1)–*n*-amylamine(2)									
15	19	3.2	1.6	3.6	(1.1)	12.2	(0.1)	7.6	(3.6)
35	19	2.2	1.7	3.9	(3.8)	14.9	(13.8)	0.6	(8.2)
22. Methyl acetate(1)–benzene(2)									
25	13	7.5	3.5	2.0	(2.4)	5.2	(14.9)	6.2	(31.7)
35	12	4.1	11.2	2.6	(4.5)	2.6	(0.7)	8.7	(13.0)
23. Diethylamine(1)–benzene(2) [b]									
25	6	–	–	3.2	(3.3)	–		–	
45	7	3.1	4.6	0.6	(1.4)	6.7	(1.7)	16.1	(0.1)
24. Triethylamine(1)–benzene(2)									
25	8	–	–	2.7	(1.9)	–		–	
45	7	–	–	2.6	(2.9)	–		–	
25. Benzene(1)–i-octane(2) [b]									
25	16	2.8	1.6	0.9	(0.4)	3.5	(2.9)	1.8	(2.9)
50	4	–	–	0.1	(0.1)	–		–	
26. Benzene(1)–*n*-hexadecane(2) [b]									
25	12	–	4.0	1.4	(0.6)	–		6.1	(1.1)
50	4	–	2.2	0.7	(0.1)	–		0.9	(11.7)
27. Benzene(1)–ocetene-1(2) [b]									
25	8	3.1	1.8	0.9	(0.6)	4.6	(3.0)	2.7	(19.9)
50	4	–	–	1.5	(0.1)	–		–	
28. Benzene(1)–decalin(2) [b]									
25	8	–	–	0.6	(0.6)	–		–	
50	4	–	–	0.2	(0.2)	–		–	

TABLE 2 (continued)

T (°C)	Percentage uncertainties			Percentage of absolute average errors S and deviations D					
	n	U_1	U_2	S	(S) [a]	D_1	(D_1) [a]	D_2	(D_2) [a]
29. Benzene(1)–tetralin(2) [b]									
25	8	–	–	1.3	(0.7)	–		–	
50	4	–	–	0.4	(0.0)	–		–	
30. Methyl acetate(1)–n-hexane(2)									
25	14	2.0	6.4	2.6	(1.2)	0.3	(1.7)	1.0	(7.8)
45	13	3.7	1.5	2.6	(1.0)	4.0	(0.1)	7.4	(6.0)
31. Cyclohexane(1)–tetralin(2) [b]									
25	8	–	–	0.5	(0.1)	–		–	
50	4	–	–	0.1	(0.0)	–		–	
32. Cyclohexane(1)–hexadecane(2) [b]									
25	8	–	–	0.6	(0.9)	–		–	
50	4	–	–	0.6	(0.1)	–		–	
33. Cyclohexane(1)–n-heptane(2) [b]									
25	8	–	–	1.2	(1.6)	–		–	
50	4	–	–	0.3	(0.4)	–		–	
34. Cyclohexane(1)–m-xylene(2) [b]									
25	6	–	–	0.3	(0.1)	–		–	
50	4	–	–	0.5	(0.1)	–		–	
35. Cyclohexane(1)–octene-1(2) [b]									
25	8	–	–	1.2	(0.3)	–		–	
50	4	–	–	0.2	(0.1)	–		–	
36. Methyl cyclohexane(1)–n-heptane(2) [b]									
25	8	–	–	1.7	(1.7)	–		–	
50	4	–	–	0.6	(0.5)	–		–	
37. Cyclohexane(1)–i-octane-1(2) [b]									
25	12	–	–	0.7	(0.8)	–		–	
50	8	–	–	0.7	(0.7)	–		–	
38. 1-Chlorohexane(1)–ethylbenzene(2)									
15	17	3.7	3.6	1.4	(1.1)	5.6	(2.9)	12.1	(6.9)
25	19	2.6	4.3	0.9	(0.6)	11.4	(1.6)	10.4	(2.9)
39. 1-Chlorohexane(1)–n-propylbenzene(2)									
15	19	3.4	4.5	0.6	(0.5)	6.7	(0.9)	1.8	(1.7)
25	19	3.6	3.6	2.0	(1.9)	23.0	(10.3)	20.6	(12.0)
40. 1-Chlorohexane(1)–toluene(2)									
15	19	2.3	3.5	1.7	(1.6)	5.8	(5.8)	9.5	(9.5)
25	17	3.4	3.5	1.4	(1.3)	7.2	(6.5)	11.5	(10.6)
41. n-heptane(1)–acetic acid(2)									
25	17	2.6	3.5	1.5	(1.1)	2.3	(25.3)	2.1	(12.9)
35	14	1.7	2.3	1.5	(0.9)	1.5	(21.7)	0.9	(7.6)
42. n-Heptane(1)–propionic acid(2)									
25	14	2.0	4.3	3.7	(2.0)	0.5	(17.4)	3.7	(6.5)
35	15	4.5	5.3	3.9	(3.0)	2.5	(8.3)	3.0	(11.6)
43. n-heptane(1)–n-amylamine(2)									
15	19	1.4	0.9	1.1	(0.4)	1.1	(3.1)	4.3	(14.5)
35	19	1.4	1.0	1.1	(0.5)	1.3	(0.9)	3.2	(2.8)

TABLE 2 (continued)

T (°C)	Percentage uncertainties			Percentage of absolute average errors S and deviations D					
	n	U_1	U_2	S	(S)[a]	D_1	(D_1)[a]	D_2	(D_2)[a]
44. *n*-Heptane(1)–toluene(2)									
25	8	1.3	0.9	0.9	(0.9)	2.8	(1.1)	0.7	(9.9)
50	8	0.6	1.6	1.0	(1.0)	5.6	(0.5)	5.8	(4.5)
45. *n*-Heptane(1)–*m*-xylene(2)									
25	8	2.8	1.5	0.7	(0.2)	3.7	(3.0)	10.6	(8.9)
50	8	1.0	1.1	0.8	(0.2)	0.5	(0.9)	4.1	(0.7)
46. *n*-Heptane(1)–*n*-hexadecane(2)[b]									
25	4	0.9	0.9	0.2	(0.4)	1.0	(2.2)	0.7	(15.0)
50	8	–	–	1.1	(2.0)	–		–	
47. *n*-Heptane(1)–decaline(2)[b]									
25	8	2.2	1.6	0.3	(0.5)	2.9	(2.4)	1.4	(2.9)
50	4	–	–	0.1	(0.2)	–		–	
48. *n*-Heptane(1)–tetraline(2)[b]									
25	8	–	–	1.5	(0.3)	–		–	
50	8	–	–	1.3	(0.3)	–		–	
49. *n*-Butylamine(1)–toluene(2)									
15	19	0.6	0.8	1.6	(0.4)	4.2	(10.7)	4.7	(2.4)
25	19	0.7	0.8	1.2	(1.7)	4.5	(1.0)	5.1	(1.8)
35	19	0.7	0.8	1.0	(1.2)	2.8	(3.7)	1.1	(2.9)
50. *n*-Butylamine(1)–methylcyclohexane(2)									
15	19	0.7	1.2	1.1	(0.4)	4.3	(16.0)	2.6	(0.9)
25	19	2.2	1.3	0.3	(1.1)	4.7	(0.3)	5.2	(0.8)
35	15	0.9	1.4	1.1	(0.8)	6.0	(4.9)	2.9	(0.6)
51. *n*-Octane(1)–2-methyl pentane(2)									
10	7	3.4	2.8	4.1	(4.7)	20.1	(27.6)	17.5	(7.1)
20	8	2.4	1.7	3.6	(2.7)	0.1	(8.0)	6.3	(0.4)
30	7	3.3	1.8	1.0	(4.8)	10.1	(14.3)	0.1	(5.9)
40	7	2.9	1.6	2.5	(3.0)	12.2	(14.0)	3.9	(10.9)
52. *n*-Octane(1)–3-methyl pentane(2)									
10	7	0.7	2.1	3.5	(1.6)	8.6	(8.3)	19.8	(11.3)
20	8	3.3	1.4	2.5	(1.5)	4.5	(5.5)	4.9	(4.3)
30	7	2.2	1.1	2.9	(2.3)	10.0	(15.4)	8.0	(3.3)
40	7	1.4	1.9	2.5	(3.3)	2.2	(8.3)	6.1	(4.9)
53. Toluene(1)–*n*-hexadecane(2)[b]									
25	12	6.2	2.4	1.3	(0.6)	3.9	(8.8)	7.1	(27.2)
50	4	–	–	1.8	(0.1)	–		–	
54. i-Octane(1)–*n*-octane(2)[b]									
25	12	0.6	0.6	0.4	(0.4)	0.9	(0.5)	1.8	(0.6)
50	4	–	–	0.5	(0.6)	–		–	
55. Decalin(1)-hexadecane(2)[b]									
25	8	2.3	1.8	1.4	(1.3)	7.1	(5.5)	5.1	(4.7)
50	4	–	–	0.5	(0.5)	–		–	

[a] Values obtained using the non-linear temperature dependence for the parameters of the NRTL model [4].

[b] No extrapolated values determined due to insufficient data, especially in the dilute region of each component.

TABLE 3

Comparison of the experimental and predicted values of the limiting activity coefficients

System	T (°C)	Limiting activity coefficients			
		Experimental		Predicted	
		γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
Methanol(1)–methyl acetate(2) [6]	50	3.80	2.80	6.30	13.59
Ethanol(1)–acetone(2) [24]	25	2.44	–	5.43	–
	35	2.24	–	5.07	–
	45	2.07	–	4.76	–
	55	1.92	–	4.48	–
Ethanol(1)–cyclohexane(2) [24]	39.65	29.90	–	11.06	–
	49.65	24.30	–	9.51	–
	59.85	19.10	–	8.24	–
	69.85	15.10	–	7.20	–
	79.75	11.70	–	6.34	–

The values of ΔH_i are finite but indeterminant. Hence the experimental values of ΔH_i were determined by graphical extrapolation of finite concentration data. Although necessary care has been exercised in the extrapolation, 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 and for systems with insufficient data. The percentage uncertainties U_i based on the average absolute deviation in the extrapolation have been expressed as

$$U_i = \left| \frac{\Delta H_{i,\max} - \Delta H_{i,\min}}{2\Delta H_i} \right| 100 \tag{18}$$

Here the deviation is taken as one-half of the difference between the maximum $\Delta H_{i,\max}$ and minimum $\Delta H_{i,\min}$ values of the extrapolations. For the systems with very high uncertainties, no extrapolation was carried out, and, hence, no experimental values of ΔH_i are given for these systems.

Table 2 indicates that for 680 data points of h^E for the systems containing alcohols, the percentages of average absolute errors are 2.65 for a linear temperature dependence and 2.51 for a non-linear temperature dependence. The values for the 672 data points for the systems containing no alcohols or acids are 1.27 and 1.07 respectively. For 60 data points for the systems containing weak acids, the values are 2.65 and 1.75 respectively. These results indicate that the NRTL model performs better when a non-linear temperature dependence is introduced into the model. The values of D_i obtained from both types of temperature dependences change from one system to another. In general, the predictions at infinite dilution are not satisfactory for highly non-ideal and associating mixtures.

Table 3 compares the predicted values of the limiting activity coefficients for some of the systems with the experimental values. Because of the empirical character of the model, the predicted and experimental values of γ_i^∞ show large deviations.

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. The model must also take good account of the partial properties [6].

CONCLUSIONS

With the linear temperature dependence, the interaction energy parameters of the NRTL model are estimated using h^E data alone for 55 binary liquid mixtures of various types. All the parameters are estimated by regression of the data at more than one different temperature. The model produces multiple roots. For some of the systems, the parameters estimated predict the liquid-phase splitting erroneously. The effect of the type of temperature dependence on the performance of the model is marginal, although the model with the non-linear temperature dependence performs better than that with the linear temperature dependence for all types of systems considered.

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