Thermochimica Acta, 194 (1992) 329–341
Elsevier Science Publishers B.V., Amsterdam

Correlation of heats of mixing data by the NRTL and UNIQUAC models.
Part 1. Estimation of the model parameters

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(Received 26 April 1991)

Abstract

Using data for heats of mixing h^E, temperature dependent parameters of the NRTL and UNIQUAC models have been estimated for 57 systems of binary mixtures. In order to test the models 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. Temperature dependences of the models are assumed as non-linear. This form of dependence is found to be more suitable for associating systems and for prediction of excess heat capacity C_p^E from differentiation of a correlation for h^E. No fixed values are assumed for the parameters of the models. The physical meanings and non-uniqueness of the parameters are discussed.

INTRODUCTION

The need for accurate prediction of liquid mixture properties for modelling chemical processes has caused considerable attention to be given to excess Gibbs free energy (g^E) models. The local composition concept has been shown to be particularly effective in correlating vapour–liquid equilibria (VLE) and heats of mixing (h^E) simultaneously for multi-component, multi-phase systems. In order to facilitate multi-property correlation based on the Gibbs–Helmholtz equation, additional empirical temperature dependences have been introduced into the original version of the local composition models. This improves the performance of the models considerably, especially for highly non-ideal mixtures, which have limiting activity coefficients on the order of 10 or more. High non-ideality may lead to phase splitting in some systems. Studies on such systems provide information about the temperature dependence of liquid–liquid equilibria, which is significant for the development of the correct temperature dependence in the models for g^E [1].

In previous studies, the local composition models of NRTL [2] and UNIQUAC [3] were used in representing h^E and VLE data simultaneously at different isotherms [4,5]. The models are also employed in predicting partial molar heats of mixing at infinite dilution, ΔH_i, presented elsewhere [6]. Although the models are capable of correlating h^E and VLE data satisfactorily for various kinds of mixtures, the type of the data regressed in parameter estimation plays an important role in such capability owing to the empirical character of the models [4]. In this first part, therefore, the temperature dependent parameters of the NRTL and UNIQUAC models are estimated from h^E data only, at more than one different isotherm, for 57 systems of binary mixtures. These include associating and partially miscible systems.

In the second part of this series the models are tested in predicting the calorimetric properties h^E, C_p^E and ΔH_i, and the limiting activity coefficients, for which experimental measurements are rare at the desired temperatures.

ESTIMATION OF PARAMETERS

It is commonly assumed that the NRTL parameters change with temperature in a linear form. For systems with strong hydrogen bonding, such as those containing alcohols, it has been observed that the heat of mixing and energy interaction parameters can not be represented by linear relationships [7]. The linear form is not suitable for C_p^E calculations that involve the differentiation of h^E with respect to temperature. Therefore the following expressions, similar to those of the UNIQUAC model, are assumed for the NRTL model

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

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

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

In order to maintain the physical meanings of the parameters [2], the values of α_{ij} are forced to change in the range 0.1–0.7.

From the Gibbs–Helmholtz equation

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

the enthalpy of mixing becomes

$$h^E = \frac{Tx_1x_2G_{21}}{T'(x_1 + x_2G_{21})}\left[\left(1 - \frac{x_1\alpha_{12}\tau_{21}}{x_1 + x_2G_{21}}\right)(c_2 + RT'\tau_{21}) - \frac{x_1T\tau_{21}^2c_6R}{x_1 + x_2G_{21}}\right]$$
$$+ \frac{Tx_1x_2G_{12}}{T'(x_2 + x_1G_{12})}\left[\left(1 - \frac{x_2\alpha_{12}\tau_{12}}{x_2 + x_1G_{12}}\right)(c_4 + RT'\tau_{12}) - \frac{x_2T\tau_{12}^2c_6R}{x_2 + x_1G_{12}}\right] \tag{5}$$

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

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

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

Here $g_{21} - g_{11}$, $g_{12} - g_{22}$ and α_{12} are the interaction energies in J mol^{-1} and non-randomness parameters respectively. The terms c_1, c_3 and c_5 denote the values of the parameter at 0 °C, whereas c_2 and c_4 in J K mol^{-1} and c_6 in K are the coefficients of temperature.

The effect of temperature on the UNIQUAC parameters are expressed as

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

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

With these parameters the enthalpy of mixing becomes

$$h^{\mathrm{E}} = R\left[\frac{q_1' x_1 \theta_2 \tau_{21}^*(d_1 + 2d_2/T)}{\theta_1 + \theta_2 \tau_{21}^*} + \frac{q_2' x_2 \theta_1 \tau_{12}^*(d_3 + 2d_4/T)}{\theta_2 + \theta_1 \tau_{12}^*}\right] \tag{8}$$

where $\tau_{21}^* = \exp(-a_{21}/T)$; $\tau_{12}^* = \exp(-a_{12}/T)$
$\theta_1 = x_1 q_1'/(x_1 q_1' + x_2 q_2')$; $\theta_2 = x_2 q_2'/(x_1 q_1' + x_2 q_2')$.
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 the pure component structural parameters r and q. Anderson and Prausnitz [8] modified the UNIQUAC model slightly and introduced new values of surface parameters, q', for alcohols and water to be used in the residual part of the equation.

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

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

where n is the number of experimental data points of h^{E} at a specified temperature and N is the number of isothermal systems. Term w denotes a weight factor with the changing values of 100 or 1000 according to the maximum value of h^{E} for the system considered. For minimizing the function F, a program package called MINUIT [9] was used. The MINUIT program performs minimization and analysis of the shape of a multiparameter function. It incorporates the Fletcher and the 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.

TABLE 1

Temperature dependent parameters of the NRTL and UNIQUAC models and variances of the fit, σ

NRTL				UNIQUAC		
c_1 (kJ mol^{-1})	c_2 (kJ K mol^{-1})	c_5	$\sigma\times100$	d_1 (K)	d_2 (K^2)	$\sigma\times100$
c_3 (kJ mol^{-1})	c_4 (kJ K mol^{-1})	c_6 (K)		d_3 (K)	d_4 (K^2)	
1. Methanol (1)–methyl acetate (2) 25–45 °C [e] [15]						
5.0438	−1.3189	0.2564	0.0174	276.86	63411	0.0594
2.3546	−0.6294	−0.0779		144.39	−17614	
2. Methanol (1)–ethyl acetate (2) 25–35 °C [16]						
5.1023	−0.4702	0.3369	0.0793	487.18	33151	0.3620
5.1413	−6.8529	−0.3612		22.38	4267	
3. Methanol (1)–ethyl formate (2) 25–45 °C [17]						
4.2070	1.8537	0.3354	0.0424	518.66	5527	0.2025
2.1889	−0.4266	0.0245		404.46	−54160	
4. Methanol (1)–*n*-hexane (2) [a] 25–50 °C [18]						
12.8563	−10.4930	0.2553	0.9842	−162.96	561000	0.2077
6.1714	−1.3734	0.0235		−314.95	27417	
5. Methanol (1)–*n*-heptane (2) [a] 30–60 °C [18]						
15.8983	−16.7840	0.2121	1.0627	−291.63	615450	0.2455
7.4741	−1.5736	0.0759		−2.27	24447	
6. Methanol (1)–water (2) 5–50 °C [19]						
−2.5380	2.1599	0.4505	0.8337	−221.52	−36272	0.4987
0.8077	−2.6369	1.1850		713.03	79796	
7. Ethanol (1)–methyl acetate (2) 25–45 °C [15]						
6.5979	−2.0201	0.2164	0.0239	47.35	138020	0.0702
4.8866	−3.0871	−0.1642		329.02	−33451	
8. Ethanol (1)–ethyl acetate (2) 25–35 °C [16]						
7.7346	−3.2899	0.2392	0.0322	327.93	90019	0.1494
5.9137	−4.0748	−0.1447		57.99	7150	
9. Ethanol (1)–ethyl formate (2) 25–45 °C [17]						
5.6260	−2.6906	0.2579	0.0476	238.58	81898	0.2031
4.0608	−2.8210	−0.1638		463.40	−57688	
10. Ethanol (1)–acetone (2) 25–50 °C [20]						
3.4976	0.4873	0.2172	0.0033	96.95	84517	0.0828
3.5743	−1.5329	0.0313		397.90	−50796	
11. Ethanol (1)–toluene (2) 25–60 °C [21]						
13.5078	−3.3456	0.2019	0.6358	−6.75	315690	0.2652
3.9071	−3.8564	−0.0208		354.83	−52034	
12. Ethanol (1)–*n*-hexane (2) 10–45 °C [22]						
7.3421	−1.1829	0.3648	0.7637	1060.70	−49391	1.1099
3.0904	−0.2838	−0.0059		322.99	−39804	
13. Ethanol (1)–cyclohexane (2) 5–65 °C [23]						
8.8022	−0.2421	0.3164	0.3410	700.04	169720	0.0697
4.7408	0.0277	−0.0007		−25.27	27837	
14. Ethanol (1)–water (2) [b] 150–200 °C [24]						
11.3850	−389.17	0.1011	0.0123	81.08	111980	1.4146
−2.0125	171.79	−0.0747		712.47	−116870	
15. 1-Propanol (1)–ethyl acetate (2) 25–45 °C [16]						
5.9915	−1.1949	0.1655	0.0357	121.46	130370	0.0519
3.6842	2.0349	0.0988		−143.98	35801	

TABLE 1 (continued)

NRTL				UNIQUAC		
c_1 (kJ mol^{-1}) c_3 (kJ mol^{-1})	c_2 (kJ K mol^{-1}) c_4 (kJ K mol^{-1})	c_5 c_6 (K)	$\sigma \times 100$	d_1 (K) d_3 (K)	d_2 (K^2) d_4 K^2)	$\sigma \times 100$
16. 1-Propanol (1)–ethyl formate (2) 25–45 ° C [17]						
5.8117	−1.9449	0.2071	0.0195	49.08	127860	0.0395
5.0104	−1.9629	−0.0680		444.2	−47519	
17. 2-Propanol (1)–ethyl acetate (2) 25–35 ° C [16]						
7.3181	−2.9875	0.1766	0.0166	106.02	134920	0.0552
4.8080	0.5591	−0.0931		−263.06	59217	
18. 2-Propanol (1)–ethyl formate (2) 25–45 ° C [17]						
5.8318	−0.3663	0.1871	0.0157	45.1	136050	0.1032
6.0279	−0.6531	0.0459		259.13	−4406	
19. 2-Propanol (1)–*n*-heptane (2) 30–60 ° C [21]						
20.1342	−16.6255	0.1647	1.8677	−300.59	500890	1.2336
7.4105	−10.1873	−0.0567		−0.20	11599	
20. 2-Propanol (1)–cyclohexane (2) 20–50 ° C [14]						
10.0729	−6.0722	0.2487	0.6248	518.98	95968	1.0409
3.6983	−2.7144	−0.0694		538.03	−71297	
21. 2-Propanol (1)–water (2) [c] 20–50 ° C [14]						
−0.9999	−2.0859	0.3504	40.2340	−1064.10	348860	19.5026
5.2925	3.4787	−0.1044		71.08	−113690	
22. *n*-Butanol (1)–*n*-heptane (2) 15–55 ° C [25,26]						
12.4770	−5.7572	0.2504	2.5241	107.34	398400	2.2260
3.8770	−2.4136	−0.0413		398400	−24202	
23. *n*-Butanol (1)–nitromethane (2) [a] 18–30 ° C [1]						
12.6550	−2.1185	0.1159	0.1889	−600.62	382480	0.2352
5.6788	5.2524	0.1208		−335.07	105650	
24. *n*-Butanol (1)–ethyl acetate (2) 25–35 ° C [27]						
5.5186	3.4422	0.1638	0.1287	143.85	137600	0.1176
4.4965	2.0956	0.3239		−188.39	49149	
25. *n*-Butanol (1)–ethyl formate (2) 25–45 ° C [27]						
6.4587	−1.9508	0.1911	0.0199	34.69	147550	0.1314
5.3399	−0.7722	−0.0094		280.68	−13845	
26. *n*-Butanol (1)–methanol (2) 5–45 ° C [28]						
1.1517	0.0480	0.7984	1.7205	625.14	−77726	0.2752
−0.2434	−0.0334	−0.0921		−362.54	56550	
27. *n*-Pentanol (1)–*n*-hexane (2) 25–45 ° C [25,29]						
11.9959	−10.6713	0.2704	2.2550	810.16	133260	1.4729
3.3365	−5.2852	−0.1298		294.69	−41495	
28. *n*-Hexanol (1)–*n*-amylamine (2) 15–35 ° C [30]						
−1.7314	−15.8280	0.4744	0.0901	327.76	74713	0.3931
−2.3467	−6.2073	−6.2257		226.04	2404	
29. *n*-Hexanol (1)–*n*-octane (2) 15–55 ° C [26]						
6.9951	−3.5426	0.1656	0.1777	952.45	−96479	1.3759
0.0259	1.0625	0.0755		314.24	−47025	
30. *n*-Heptanol (1)–*n*-amylamine (2) 15–35 ° C [30]						
−3.3516	−15.5863	0.1592	0.0899	−668.31	105320	0.2751
−4.0429	5.8686	−1.4800		433.75	−128250	

TABLE 1 (continued)

NRTL				UNIQUAC		
c_1 (kJ mol^{-1}) c_3 (kJ mol^{-1})	c_2 (kJ K mol^{-1}) c_4 (kJ mol^{-1})	c_5 c_6 (K)	$\sigma \times 100$	d_1 (K) d_3 (K)	d_2 (K^2) d_4 (K^2)	$\sigma \times 100$
31. *n*-Octanol (1)–*n*-heptane (2) 15–55 °C [26]						
7.6570	−3.6660	0.1581	1.1599	552.83	−64957	0.5669
−0.9057	0.9927	0.0277		108.34	−17354	
32. *n*-Octanol (1)–*n*-octane (2) 15–55 °C [26]						
8.5638	−8.8623	0.1203	0.6487	928.54	117080	0.2617
−1.4842	5.6764	0.1841		123.4	17156	
33. *n*-Octanol (1)–*n*-amylamine (2) 15–35 °C [30]						
−3.2856	−15.9490	0.1715	0.0530	195.16	3561	0.2688
−3.8600	7.2056	−1.4778		40.17	2807	
34. *n*-Decanol (1)–*n*-amylamine (2) 15–35 °C [30]						
−2.8933	−13.5908	0.1883	0.1285	80.22	21788	0.2202
−3.4425	5.2408	−1.6751		95.08	26044	
35. Methyl acetate (1)–benzene (2) 25–35 °C [31]						
0.4081	3.8988	0.7000	0.3227	−121.01	14418	0.7332
1.0758	−0.9074	6.1405		−1.56	17136	
36. Methyl acetate (1)–cyclohexane (2) 25–45 °C [31]						
6.8685	−0.1397	0.1914	0.0073	376.44	−10161	0.0096
6.0534	−0.6189	−0.0463		184.39	5104.8	
37. Methyl acetate (1)–*n*-hexane (2) 25–45 °C [27]						
5.7883	0.4083	0.1379	0.0272	709.44	−67530	0.1216
3.8410	12.3540	0.8959		8.12	28997	
38. Benzene (1)–*n*-heptane (2) 25–50 °C [32–34]						
0.3492	8.2669	0.1831	0.0153	−14.64	18254	0.0168
4.1597	−6.1086	0.8838		35.57	1217	
39. Benzene (1)–cyclohexane (2) 25–50 °C [32]						
1.5718	2.0508	0.3274	0.0142	−17.211	19497	0.0069
1.9489	1.1313	0.9931		−22.45	9282	
40. 1-Chlorohexane (1)–ethylbenzene (2) ^{d} 15–25 °C [35]						
−0.2926	−0.0194	0.6892	0.0116	−118.86	−3337	0.0073
−0.2586	−0.2169	−5.5128		84.04	17016	
41. 1-Chlorohexane (1)–*n*-propylbenzene (2) ^{d} 15–25 °C [35]						
−0.2982	−0.0245	0.6992	0.0312	13.39	−3892	0.0352
−0.2656	−0.2997	−6.9383		13.66	−2971	
42. 1-Chlorohexane (1)–toluene (2) ^{d} 15–25 °C [35]						
0.0131	−0.0772	0.1280	0.0376	−2.76	12870	0.3748
−0.7533	−0.0108	−0.1565		81.69	−27373	
43. 1,2-Dichloroethane (1)–di-*n*-butyl ether (2) 15–25 °C [36]						
0.6779	0.3288	0.4498	0.0207	104.81	−11156	0.0219
3.0573	−0.5152	0.0964		167.88	−16672	
44. 1,1,1-Trichloroethane (1)–di-*n*-butyl ether (2) 10–35 °C [36]						
−0.1889	0.0952	0.1000	0.5788	12.7	−13533	1.5734
−0.1050	−0.2460	−9.9910		14.92	9486	
45. *n*-Heptane (1)–acetic acid (2) 25–35 °C [27]						
4384.83	107.81	0.3772	0.0195	50.61	11465	0.3017
2826.63	1128.34	−0.0201		927.67	−118150	

TABLE 1 (continued)

NRTL				UNIQUAC		
c_1 (kJ mol^{-1})	c_2 (kJ K mol^{-1})	c_5	$\sigma \times 100$	d_1 (K)	d_2 (K^2)	$\sigma \times 100$
c_3 (kJ mol^{-1})	c_4 (kJ K mol^{-1})	c_6 (K)		d_3 (K)	d_4 (K^2)	
46. *n*-Heptane (1)–propionic acid (2) 25–35 °C [27]						
2.2726	0.6585	0.6041	0.1279	−83.09	9891	0.6631
2.1099	−0.0449	−0.3471		77.21	9840	
47. *n*-Heptane (1)–*n*-amylamine (2) 15–35 °C [30]						
0.9656	4.1093	0.1139	0.0042	−73.28	12608	0.0307
4.2648	−2.6466	0.4534		211.30	−6358	
48. *n*-Heptane (1)–toluene (2) 25–50 °C [32]						
1.8180	0.5350	0.4878	0.0003	−42.78	13054	0.0028
0.9647	−0.3757	−0.4824		67.31	−5149	
49. *n*-Heptane (1)–*m*-xylene (2) 25–50 °C [32]						
1.1561	0.0494	0.4386	0.0014	−13.83	5769	0.0035
0.6493	0.3015	0.2033		39.63	−1991	
50. Cyclohexane (1)–i-octane (2) 25–50 °C [32]						
−0.4742	−0.1888	0.2625	0.0127	88.47	−9262	0.0247
1.3516	0.1408	−0.4119		−63.49	9270	
51. *n*-Amylamine (1)–nonane (2) 15–35 °C [30]						
3.3354	−0.4858	0.1040	0.0020	184.97	2792	0.0218
1.8530	2.1767	0.4125		118.89	18383	
52. 2-Methylpropanoic acid (1)–water (2) [a] 20–35 °C [1]						
0.5898	14.8930	0.1152	0.2802	732.98	−106420	0.6912
7.3751	−12.4890	1.0262		529.96	69168	
53. Nitroethane (1)–2,2,4-trimethylpentane (2) [a] 20–40 °C [1]						
9.4667	3.6672	0.1649	0.2202	836.15	−39242	1.2232
8.2944	3.3758	0.2081		548.68	−48849	
54. *n*-Butylamine (1)–toluene (2) 15–35 °C [37]						
1.5872	−0.1317	0.2336	0.0191	−59.53	29749	0.9468
0.8062	0.9654	0.7693		−29.69	−1385	
55. *n*-Butylamine (1)–methylcyclohexane (2) 15–35 °C [37]						
4.7036	−4.4722	0.1010	0.0139	124.69	14165	0.0132
0.6055	6.0203	0.5107		−78.44	11653	
56. *n*-Octane (1)–2-methylpentane (2) [d] 10–40 °C [38]						
−0.2911	−3.4253	0.1099	0.2451	−81.03	335	0.3895
0.3391	3.6248	−0.1260		59.55	6948	
57. *n*-Octane (1)–3-methylpentane (2) [d] 10–40 °C [38]						
0.1144	−2.9119	0.3909	0.0923	−81.39	−1089	0.3721
−0.0905	3.0102	−1.8268		53.21	10078	

[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. [e] Temperature range for the parameters.

An analytical method due to Tassios [10] is used to determine whether or not the estimated parameters can predict the phase splitting for partially miscible systems. This consists of the following steps: (1) regress the h^E

data to estimate the parameters; (2) introduce these parameters into the expression

$$G'' = \frac{1}{RT}\left(\frac{\partial^2 g^{\mathrm{M}}}{\partial x_1^2}\right)_{T,P} \tag{10}$$

(3) determine the value of $x_1 = x_0$ for which G'' assumes its minimum value by solving the following equation

$$G''' = \frac{1}{RT}\left(\frac{\partial^3 g^{\mathrm{M}}}{\partial x_1^3}\right)_{T,P} = 0 \tag{11}$$

(4) insert the value of $x_1 = x_0$ into eqn. (10) and determine the value of G''. If $G'' > 0$, then no partial miscibility will be predicted by the estimated parameters. If $G'' < 0$, then partial miscibility will be predicted. Here g^{M} indicates the Gibbs free energy of mixing.

RESULTS AND DISCUSSION

Using data for h^{E} at more than one different isotherm, temperature dependent parameters of the NRTL and UNIQUAC models were estimated for 57 systems of binary liquid mixtures. These include associating, nearly ideal 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

$$\sigma = \frac{1}{\left(\sum^{N} n_j - NP\right)} \sum_j^N \sum_j^n \left[\left(h^{\mathrm{E}}_{i,\mathrm{exptl}} - h^{\mathrm{E}}_{i,\mathrm{calcd}}\right)/h^{\mathrm{E}}_{i,\mathrm{exptl}}\right]_j^2 \tag{12}$$

where $\sum^{N} n_j$ 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 models. The structural parameters of the UNIQUAC model are given in Table 2. These parameters are obtained from van der Waals area and volumes of the molecules [11] and the group contribution method [12].

If the model parameters are physically significant, the set of parameters used to represent g^{E} for a system should be in close agreement with the parameters used to represent h^{E}, and vice versa. This is expressed by eqn. (4). As Skjold-Jorgensen et al. [13] point out, this property is not possessed by any of the models. The confidence regions of the parameters for the models are shown in Figs. 1–5. The regions shown represent areas within which the values of the parameters can be expected to lie at a confidence level associated with the contours. The probability content of the confidence regions becomes very small as the number of parameters increases.

TABLE 2

Structural parameters for the UNIQUAC model

System	r	q	q'
Methanol	1.430	1.430	0.960
Ethanol	2.110	1.970	0.920
1-Propanol	3.249	3.128	0.890
2-Propanol	3.249	3.128	0.890
n-Butanol	3.450	3.050	0.880
n-Pentanol	4.597	4.208	1.150
n-Hexanol	4.803	4.132	1.780
n-Heptanol	5.477	4.672	2.710
n-Octanol	6.152	5.212	5.212
n-Decanol	7.501	6.292	6.292
Methyl acetate	2.800	2.580	2.580
Ethyl acetate	3.480	3.120	3.120
Ethyl formate	2.817	2.576	2.576
Ethylbenzene	4.600	3.510	3.510
n-Propylbenzene	5.272	4.048	4.048
Benzene	3.190	2.400	2.400
2-Methylpentane	4.499	3.396	3.396
3-Methylpentane	4.499	3.396	3.396
2,2,4-Trimethylpentane	5.846	5.008	5.008
n-Hexane	4.500	3.860	3.860
n-Heptane	5.170	4.400	4.400
n-Nonane	6.523	5.476	5.476
n-Octane	5.850	4.940	4.940
i-Octane	5.848	4.932	4.932
Acetone	2.570	2.340	2.340
Toluene	3.920	2.970	2.970
Cyclohexane	3.970	3.010	3.010
Methylcyclohexane	4.640	3.550	3.550
Water	0.920	1.400	1.000
Nitromethane	2.010	1.870	1.870
Nitroethane	2.680	2.410	2.410
n-Amylamine	4.294	3.704	3.704
n-Butylamine	3.620	3.164	3.164
1-Chlorohexane	5.064	4.272	4.272
1,2-Dichloroethane	2.880	2.520	2.520
1,1,1-Trichloroethane	3.541	3.032	3.032
Di-*n*-butyl ether	6.093	5.176	5.176
Acetic acid	2.230	2.040	2.040
Propionic acid	2.900	2.580	2.580
2-Methylpropanoic acid	3.778	3.460	3.460
m-Xylene	4.660	3.540	3.540

The probability statement is: the probability that all parameters take on values within the two standard deviation contour is 34%, the three standard deviation contour 66%, and the four standard deviation contour is

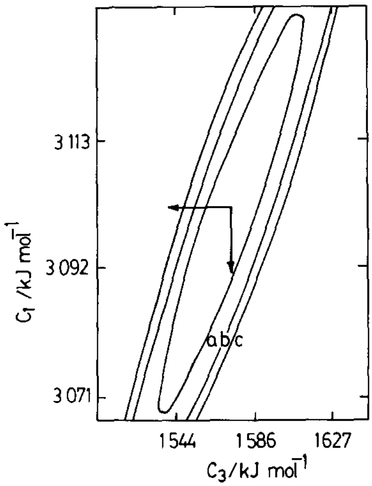

Fig. 1. Parameters c_1 and c_3 of the NRTL model, obtained from regressing h^E data only, and approximate confidence regions for the system methanol–methyl acetate: (a) 34%; (b) 66%; (c) 90%; $(g_{21}-g_{11})=c_1+c_2/(T-273.15)$; $(g_{12}-g_{22})=c_3+c_4/(T-273.15)$.

90%. The first three figures show the parameters and the confidence regions for the system methanol (1)–methyl acetate (2) obtained from the NRTL model. Figures 1 and 2 show the parameters that are obtained assuming linear temperature dependence of the parameters and using h^E data alone and h^E and g^E data simultaneously. As can be seen, the main axes, confidence regions and values of parameters are quite different.

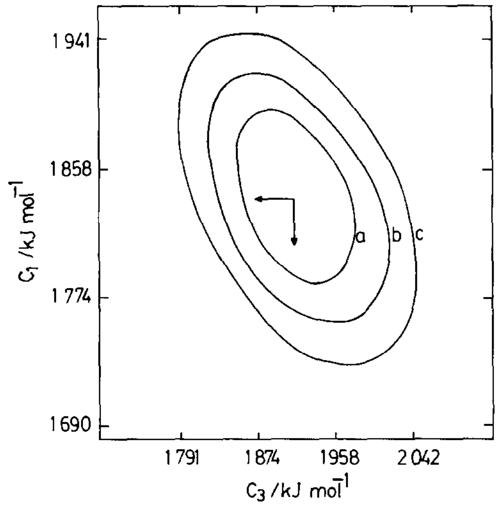

Fig. 2. Parameters c_1 and c_3 of the NRTL model, obtained from regressing h^E and g^E data and approximate confidence regions for the system methanol–methyl acetate: (a) 34%; (b) 66%; (c) 90%; $(g_{21}-g_{11})=c_1+c_2/(T-273.15)$; $(g_{12}-g_{22})=c_3+c_4/(T-273.15)$.

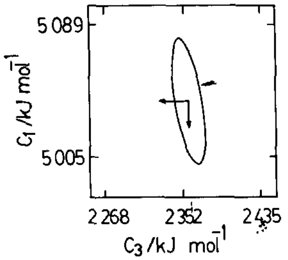

Fig. 3. Parameters c_1 and c_3 of the NRTL model, obtained from regressing h^E data only, and approximate confidence region of 90% for the system methanol–methyl acetate; $(g_{21} - g_{11}) = c_1 + c_2/(T - 273.15)$; $(g_{12} - g_{22}) = c_3 + c_4/(T - 273.15)$.

Figure 3 shows the confidence region obtained assuming non-linear temperature dependence for the parameters. In Figs. 4 and 5, confidence regions are shown for the system methyl acetate–cyclohexane obtained from the UNIQUAC model using h^E data only and h^E and g^E data simultaneously. As the figures show, the confidence regions obtained from different type of data are not similar.

Multiple roots are estimated from both of the models. However, as Tassios [10] states, the multiplicity of roots does not seem to represent a problem when all the parameters are regressed. The parameters which yield the best variance of the fit have been tabulated.

For some of the systems which do not show partial miscibility, the estimated parameters predict phase splitting, and vice versa. Physical meanings of the parameters may be lost when all of them are treated as adjustable parameters. This may cause the temperature modified version of the models to predict partial miscibility erroneously [14]. However, as Tassios [10] points out, the selection of a meaningful value of α_{ij} is ambiguous and difficult to apply, and the NRTL model performs best when

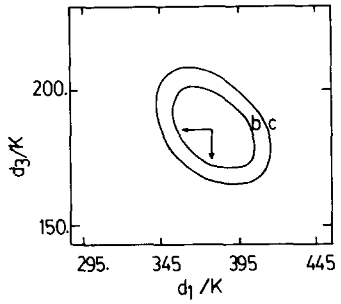

Fig. 4. Parameters d_1 and d_3 of the UNIQUAC model, obtained from regressing h^E data only, and approximate confidence regions for the system methyl acetate–cyclohexane: (b) 66%; (c) 90%.

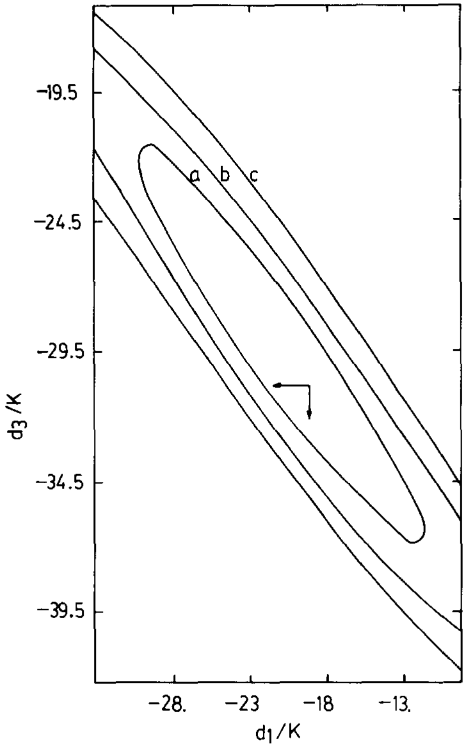

Fig. 5. Parameters d_1 and d_3 of the UNIQUAC model, obtained from regressing h^E and g^E data, and approximate confidence regions for the system methyl acetate–cyclohexane: (a) 34%; (b) 66%; (c) 90%.

all the parameters are obtained by regression of the available experimental data.

CONCLUSIONS

With the non-linear temperature dependence, the interaction energy parameters of the NRTL and UNIQUAC models are estimated using h^E data alone for 57 binary systems. These include associating and partially miscible systems. All the parameters are estimated by regression of the data at more than one different temperature.

The models produce multiple roots. Also different confidence regions are obtained from different sets of data regressed. The parameters estimated for some of the systems predict the liquid phase splitting erroneously. The parameters with the best variance of the fit have been tabulated.

ACKNOWLEDGEMENTS

The authors wish to thank the State Planning Organization, for providing financial support under project No. 90K120430, and also the Computer

Centre of the University of Çukurova for providing the computation facilities.

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