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CALCULATION OF ENTHALPY OF MIXING AT INFINITE DILUTION BY THE NRTL AND UNIQUAC MODELS

YAŞAR DEMİREL

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

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ABSTRACT

Enthalpies of mixing at infinite dilution have been calculated for 42 binary systems of liquid mixtures using the NRTL and UNIQUAC models. Temperature-dependent parameters of the models are used in the calculations. These parameters have been estimated by regressing excess Gibbs energy, g^E, and enthalpy of mixing, h^E, data simultaneously. The calculated values are compared with experimental infinite dilution enthalpy of mixing obtained by extrapolation of finite concentration h^E data published in the literature. The performance of the models is satisfactory for only slightly non-ideal and polar systems and the choice of the best model is mainly system dependent.

INTRODUCTION

Heat of mixing data are extremely valuable for testing solution models and understanding the effect of molecular structure on thermodynamic properties of solutions. It is well known that the measurement of the heats of mixing of associated solutions is significant in investigation of the interaction energy in a single component and between the different components. Such thermochemical treatments have revealed the energy of intermolecular hydrogen bonding between alcohol molecules [1,2], alcohol–ketones [3,4] and alcohol–polar molecules [5], and the enthalpy of OH–π type hydrogen bonds for aromatic alcohol–aromatic hydrocarbons [6] by means of an enthalpy cycle [3]. Studies on the heats of mixing also help in investigating the effect of the substituent hydrocarbon groups on the thermodynamic properties of a mixture of highly polar liquids [7].

The NRTL and UNIQUAC models are not capable of correlating both g^E and h^E data for a system where the value of the heat of mixing is greater than a certain maximum value of h^E at any given temperature [8,9]. However, limitations can be overcome by treating the parameters of the models as functions of temperature and using experimental h^E data together with vapour–liquid equilibrium data [8–11]. Hence temperature-dependent parameters (a list of parameters is available on request from the author) of

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the NRTL and UNIQUAC models have been estimated recently for 42 systems by regressing finite concentration data of g^E and h^E simultaneously, and these are partly presented in ref. 9. 23 of these systems include data at more than one different isotherm.

Recently Cairns and Furzer [12] have pointed out that, in the separation calculations, the performance of the NRTL and UNIQUAC models varies greatly, and it is very difficult to choose the best model, especially for highly non-ideal systems. This aspect of these semi-empirical models needs further investigation, as the authors' conclusions are based on a limited number of systems. Therefore this study aims to test the NRTL and UNIQUAC models with temperature-dependent parameters in representing the enthalpy of mixing at infinite dilution and the effect of temperature on them for various types of binary system.

CALCULATION OF ENTHALPY OF MIXING AT INFINITE DILUTION

The values of h^E/x_1x_2 at liquid compositions $x_1 = 0$ and $x_2 = 0$ are identical with the partial molal heat of mixing of components 1 and 2, $\Delta\overline{H}_1$ $\Delta\overline{H}_2$ respectively, at infinite dilution. The value of h^E/x_1x_2 at $x_1 = 0$ corresponds to the energy changes associated with the transfer of 1 mol from the pure component 1 state to that in which each component 1 molecule takes part in an interaction, such as hydrogen bonding, with a component 2 molecule and in which such complexes of components 1 and 2 are surrounded by a large number of component 2 molecules [7].

Using the two models, enthalpies of mixing at infinite dilution are expressed as follows.

For the NRTL model,

$$\Delta\overline{H}_1 = \left(\frac{h^E}{x_1x_2}\right)_{x_1=0}$$

$$= c_1 - 273.15c_2 + G_{12}\left[(1-\alpha_{12}\tau_{12})(c_3 - 273.15c_4) + \tau_{12}c_6RT^2\right] \qquad (1)$$

$$\Delta\overline{H}_2 = \left(\frac{h^E}{x_1x_2}\right)_{x_2=0}$$

$$= c_3 - 273.15c_4 + G_{21}\left[(1-\alpha_{12}\tau_{21})(c_1 - 273.15c_2) + \tau_{21}c_6RT^2\right] \qquad (2)$$

where

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

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

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

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

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

Here $g_{21} - g_{11}$, $g_{12} - g_{22}$ and α_{12} are the energies of interaction in J mol^{-1} and non-randomness parameters respectively for the NRTL model [13]. The terms c_1, c_3 and c_5 are the values of the parameters at 0 °C, while c_2 and c_4 in J mol^{-1} K^{-1} and c_6 in K^{-1} are the coefficients of temperature.

For the UNIQUAC model,

$$\Delta\overline{H}_1 = Rq_1'[(d_1 + 2d_2/T) + \tau_{12}^{\star}(d_3 + 2d_4/T)] \tag{3}$$

$$\Delta\overline{H}_2 = Rq_2'[(d_3 + 2d_4/T) + \tau_{21}^{\star}(d_1 + 2d_2/T)] \tag{4}$$

where

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

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

Here a_{21} and a_{12} are the interaction parameters in K for the UNIQUAC model [14]. 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}. R and q_i' are the gas constant in J mol^{-1} K^{-1} and molecular interaction area parameter for pure component i.

RESULTS AND DISCUSSION

The values of h^E/x_1x_2 at $x_1 = 0$ and $x_1 = 1$ are finite but indeterminate. Hence experimental values of enthalpy of mixing at infinite dilution were determined by graphical extrapolation of finite concentration data. Although necessary care has been exercised in the extrapolation stage, the values of the enthalpy of mixing at infinite dilution are subject to some uncertainty, especially for those systems where the values of h^E/x_1x_2 exhibit a steep change in the dilute region. This is pointed out clearly by Savini et al. [15] and Nguyen and Ratcliff [16]. Data for h^E have been fitted by the Redlich–Kister polynomial

$$h^E = x_1x_2\sum A_k(x_1 - x_2)^k, \qquad k = 0, 1, \ldots, m \tag{5}$$

and the parameters, A_k have been supplied together with published experimental h^E data for some of the systems considered. For such systems, the polynomial expressions have also been used to determine the values of h^E/x_1x_2 at $x_1 = 0$ and $x_1 = 1$. The percentage uncertainties, U_i, based on the average absolute deviation in the extrapolation have been expressed as

$$U_i = \left| \frac{\Delta\overline{H}_{i,\max} - \Delta\overline{H}_{i,\min}}{2\,\Delta\overline{H}_i} \right| \times 100 \tag{6}$$

Here the deviation is taken as one-half of the difference between the maximum, $\Delta\overline{H}_{i,\max}$, and minimum, $\Delta\overline{H}_{i,\min}$, values of the extrapolations. Comparisons of experimental, $\Delta\overline{H}_{i,\text{exptl}}$, and calculated, $\Delta\overline{H}_{i,\text{calc}}$, enthalpies of mixing at infinite dilution by the NRTL and UNIQUAC models are

TABLE 1

Comparison of experimental and calculated enthalpy of mixing at infinite dilution obtained from the NRTL and UNIQUAC models with temperature-dependent parameters

Temperature for h^E data (°C)	Experimental values (J mol^{-1})		Estimated values (J mol^{-1})				Uncertainty and error (%)					
			NRTL		UNIQUAC		Extrapolation		NRTL		UNIQUAC	
	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	U_1	U_2	D_1	D_2	D_1	D_2
(1) Methanol–ethyl acetate [17]												
25	6277	3599	6037	3874	6080	3763	5.1	5.0	3.8	7.6	3.1	4.5
35	6235	4771	6120	4104	5918	3623	6.2	5.4	1.8	13.9	5.1	24.1
(2) Ethanol–ethyl acetate [17]												
25	7951	5440	7576	5393	7723	5299	6.2	4.5	4.7	0.8	2.8	2.6
35	8370	6152	7782	5677	7432	5051	7.1	5.3	7.0	7.7	11.2	17.9
(3) 2-propanol–ethyl acetate [17]												
25	8663	7616	7724	6481	8030	6578	4.3	2.2	10.8	14.9	7.3	13.6
35	8956	7533	7778	6808	7610	7028	4.2	7.2	13.1	9.6	15.0	6.7
(4) 1-propanol–ethyl acetate [17]												
25	8077	6947	7007	5496	7981	6279	6.1	5.2	13.2	20.8	1.2	9.6
35	7868	6445	7041	5655	7610	6260	4.1	3.0	10.5	12.2	3.2	2.8
45	8119	6779	7076	5831	7260	6246	5.0	2.2	12.8	13.9	10.5	7.8
(5) Ethyl formate–methanol [18]												
25	2678	4017	2861	4435	2884	4767	2.1	2.5	6.8	10.4	7.6	18.6
35	2992	4833	3004	4623	2792	4696	2.0	2.0	0.4	4.3	6.7	2.8
45	3118	5001	3142	4800	2712	4627	2.1	2.1	0.7	4.0	12.9	7.5
(6) Ethyl formate–ethanol [18]												
25	4227	5901	4610	6305	4562	6838	4.1	6.3	9.1	6.8	7.9	15.9
35	4854	6654	4812	6540	4358	6635	4.4	3.7	0.8	1.7	10.2	0.3
45	5022	6738	5008	6763	4174	6438	2.6	3.0	0.3	0.4	16.8	4.4

(7) Ethyl formate–1-propanol [18]												
25	5880	6507	5941	6682	6368	7444	3.1	4.2	1.0	2.6	8.3	14.4
35	6445	7344	6099	7031	6031	7195	3.2	6.3	5.3	4.2	6.4	2.0
45	6570	7449	6252	7361	5721	6949	3.2	3.0	4.8	1.2	12.9	6.7
(8) Ethyl formate–2-propanol [18]												
25	7533	7240	7621	7623	7597	8102	5.1	5.3	1.2	5.3	0.8	11.9
35	7637	7700	7738	7964	7153	7857	5.4	5.0	1.3	3.4	6.3	2.0
45	8119	8286	7852	8303	6745	7607	3.1	4.1	3.3	0.2	16.9	8.2
(9) Methyl acetate–methanol [19]												
25	3557	5649	3765	5770	3513	5748	3.2	2.1	5.8	2.1	1.2	1.7
35	3683	5817	3988	5782	3572	5576	5.0	3.0	8.3	0.6	3.0	4.1
45	3871	6194	4208	5794	3629	5414	3.1	5.1	8.7	6.4	6.2	12.6
(10) Methyl acetate–ethanol [19]												
25	5398	7449	4108	7171	5716	8322	6.2	6.1	23.9	3.7	5.8	11.7
35	5859	7386	4529	7188	5534	7987	4.0	5.2	22.7	2.7	5.5	8.1
45	6047	8140	4406	7204	5370	7665	5.0	5.0	27.1	11.5	11.2	5.8
(11) Ethanol–toluene [a] [20]												
25	14940	1490	13762	2054	17254	1813	3.5	5.7	7.8	37.8	15.5	21.7
45	14250	2520	13828	2957	15942	2177	4.6	4.6	2.9	17.3	11.8	13.6
60	14150	3495	13874	3707	15061	2550	5.7	3.5	1.9	6.0	6.4	27.0
(12) 2-propanol–*n*-heptane [a] [20]												
30	23300	3070	18707	4024	24593	3931	6.8	6.9	19.7	31.0	5.5	28.0
45	22840	3880	18799	4582	23059	3742	3.4	5.7	17.7	18.1	0.9	3.5
60	22600	5060	18887	5267	21657	3792	4.5	4.6	16.4	4.1	4.1	25.0
(13) *n*-pentanol–*n*-hexane [15,21]												
25	19250	1100	9520	1323	6760	1108	14.1	5.6	50.5	20.2	64.8	0.7
30	22300	1210	9566	1402	6720	959	14.2	4.5	57.1	15.8	69.8	20.7
45	22750	1690	9696	1647	6609	560	13.2	5.6	57.3	2.5	70.9	66.7

(continued)

TABLE 1 (continued)

Temperature for h^E data (°C)	Experimental values (J mol^{-1})		Estimated values (J mol^{-1})				Uncertainty and error (%)					
			NRTL		UNIQUAC		Extrapolation		NRTL		UNIQUAC	
	$\Delta\bar{H}_1$	$\Delta\bar{H}_2$	$\Delta\bar{H}_1$	$\Delta\bar{H}_2$	$\Delta\bar{H}_1$	$\Delta\bar{H}_2$	U_1	U_2	D_1	D_2	D_1	D_2
(14) *n*-pentanol–2,3-dimethylbutane [21]												
25	18500	930	8994	1279	8588	964	15.6	5.7	51.4	37.5	53.5	3.6
(15) *n*-pentanol–2-methylpentane [21]												
25	17600	1050	8045	1399	7803	1063	16.1	5.6	54.3	33.3	55.6	1.1
(16) Isopentanol–*n*-hexane [21]												
25	19700	1225	6370	1674	8091	1310	14.1	6.8	67.6	36.6	58.9	6.9
(17) *n*-pentanol–3-methylpentane [21]												
25	18100	950	6188	1680	7951	1008	14.1	5.6	52.3	56.0	65.8	76.9
(18) *n*-pentanol–2,2-dimethylbutane [21]												
25	17500	950	8998	1301	8738	869	14.2	5.7	48.8	36.9	50.3	8.5
(19) *n*-butanol–*n*-heptane [15,16]												
15	17100	1150	8020	1859	32648	1949	14.5	6.8	53.1	61.7	90.9	69.5
30	22250	1700	8381	2272	30435	1555	13.4	6.7	62.3	33.7	36.8	8.5
45	23350	2360	8719	2964	28429	1447	12.1	4.5	62.6	25.6	21.7	38.6
55	27900	2900	8932	2978	27192	1549	11.2	3.5	67.9	2.7	2.6	46.5
(20) *n*-butanol–*n*-hexane [16]												
15	17300	1200	6492	1313	9121	1238	15.1	9.8	62.5	9.4	47.2	3.2
(21) Methyl acetate–benzene [22]												
25	1728	1774	1318	1520	1469	1771	7.5	3.5	23.7	14.3	14.9	0.2
35	1464	1778	1216	1538	1377	1670	4.1	11.2	16.5	14.5	4.5	7.2

(22) Methyl acetate–cyclohexane [22]												
25	9249	8098	9048	8388	8190	7221	5.5	4.6	2.1	2.9	11.4	10.8
35	8956	8035	9120	8483	7913	7091	4.1	4.5	1.8	4.9	11.6	11.7
45	9165	8328	9190	8632	7652	6959	5.2	5.0	0.3	3.6	16.5	16.4
(23) Acetonitrile–benzene [23]												
45	1716	2678	1162	3504	1425	2534	6.8	2.1	32.2	30.8	16.9	5.4
(24) Benzene–*n*-heptane [23,24]												
25	3220	4916	3157	4996	2926	4920	2.0	3.4	1.9	1.6	9.1	0.1
45	2720	5043	2968	5230	2692	4874	3.5	3.4	9.1	3.7	1.0	3.3
50	2920	4600	2918	5267	2636	4847	3.4	4.7	0.1	14.5	9.7	5.3
(25) Acetonitrile–*n*-heptane [23]												
45	11299	12764	18328	8495	12034	12529	7.5	3.8	62.2	33.4	6.5	1.8
(26) 1,4-dioxane–acetonitrile [25]												
40	−146	648	−25	681	−269	502	13.5	4.5	82.2	5.1	83.9	22.5
(27) Carbon tetrachloride–diethyl sulphide [26]												
25	−2260	−2281	−2942	−2926	−2478	−2582	6.7	5.3	30.1	28.3	9.6	13.2
(28) Chloroform–diethyl sulphide [26]												
25	−4729	−6758	−4860	−10255	−5108	−7780	4.8	3.5	2.7	51.7	8.0	15.1
(29) Toluene–1-chlorohexane [a] [27]												
15	−784	−821	−930	−812	−832	−898	3.5	2.3	18.6	1.0	6.2	9.4
25	−711	−776	−566	−963	−759	−823	3.5	3.4	20.4	24.1	6.7	6.1
(30) 1-chlorohexane–ethylbenzene [a] [27]												
15	−654	−583	−612	−419	−624	−679	3.7	3.6	6.4	28.1	4.6	16.5
25	−619	−592	−616	−524	−632	−688	2.6	4.3	0.5	11.4	2.1	16.4
(31) 1-chlorohexane–*n*-propylbenzene [a] [27]												
15	−712	−658	−649	−649	−641	−754	3.4	4.5	8.8	1.4	9.9	14.6
25	−598	−567	−654	−674	−614	−702	3.6	3.6	9.4	18.8	4.1	28.1

(continued)

TABLE 1 (continued)

Temperature for h^E data (°C)	Experimental values (J mol^{-1})		Estimated values (J mol^{-1})				Uncertainty and error (%)					
			NRTL		UNIQUAC		Extrapolation		NRTL		UNIQUAC	
	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	U_1	U_2	D_1	D_2	D_1	D_2
(32) 1,3-dioxalane–methylcyclohexane [a] [28]												
40	7888	8412	9519	9882	7203	8164	3.4	3.6	20.6	17.5	8.7	2.9
(33) 1-chloropentane–di-*n*-butyl ether [a] [29]												
5	100	49	129	36	106	16	12.5	12.1	29.5	26.8	6.0	67.1
25	160	77	210	94	137	60	13.1	11.1	31.0	20.8	14.6	22.6
40	265	155	279	147	157	89	6.1	6.2	4.9	4.9	40.9	42.4
(34) 1,2-dichloroethane–di-*n*-butyl ether [a] [29]												
5	1276	3306	1504	3152	1511	2863	8.1	3.5	17.8	4.6	18.4	13.4
25	1360	3557	1569	3185	1457	2898	8.2	6.9	15.4	10.5	7.1	18.5
(35) 1,1,1-trichloroethane–di-*n*-butyl ether [a] [29]												
10	−479	−427	−348	−363	−288	−479	12.5	7.5	27.5	14.9	39.8	12.3
25	−399	−351	−281	−306	−256	−424	11.1	6.9	29.7	12.8	35.8	20.7
35	−350	−284	−234	−266	−236	−390	12.5	4.5	33.1	6.3	32.4	37.5

(36) Ethanol–acetone [a] [30]												
25	5070	4645	5029	4375	5543	4699	2.0	1.0	0.8	5.8	9.3	1.2
50	5300	5272	4907	5197	4983	4506	1.0	2.0	7.4	1.4	5.9	14.5
(37) Acetone–water [a] [31]												
50	−6832	3964	−6820	4012	−5676	3475	2.3	8.1	0.2	1.2	16.9	12.3
(38) Cyclohexane–methyl methacrylate [a] [32]												
25	4350	6550	4364	6491	4193	6286	3.5	5.7	0.3	0.9	3.6	4.0
(39) Isobutyric acid–cyclohexane [33]												
35	1650	1945	1488	2324	1574	1957	3.5	3.5	9.8	19.5	4.5	0.6
(40) Trimethylacetic acid–cyclohexane [33]												
35	1038	933	1028	1086	1108	1061	3.3	3.4	0.9	16.4	6.8	13.7
(41) Isobutyric acid–*n*-heptane [33]												
35	1661	1716	1539	2352	1692	1632	2.0	2.0	7.3	37.1	3.4	4.8
(42) Trimethylacetic acid–*n*-heptane [33]												
35	1201	1209	1167	1187	1357	1294	2.3	2.0	2.8	1.1	13.0	7.8

The first component is component 1, the second is component 2.

[a] Redlich–Kister polynomial or a similar expression is also used in the extrapolation.

given in Table 1. Discrepancies between the experimental and the calculated values of the enthalpy of mixing at infinite dilution for each isotherm were assessed in terms of

$$D_i = \left| \frac{\Delta \overline{H}_{i,\text{exptl}} - \Delta \overline{H}_{i,\text{calc}}}{\Delta \overline{H}_{i,\text{exptl}}} \right| \times 100 \tag{7}$$

The values of D_i indicate the percentage error for each component. As Table 1 shows, the values of D_i vary between 0.1% and 91.0%. The values of the arithmetic mean error for over 82 data points are 19.4% and 17.6% for ΔH_1, while they are 14.1% and 14.6% for ΔH_2 obtained from the NRTL and UNIQUAC models respectively. The discrepancies are due to the uncertainties of extrapolation as well as the ability of the models. Uncertainties are especially high for the systems (13)–(20), (25)–(27) and (32)–(35). Also, the uncertainty involved in estimating the temperature-dependent parameters should also be taken into account, although the quality and quantity of the data regressed [9] are the same for both of the models.

Discrepancies for most of the systems, i.e. (11)–(22) and (24)–(34), are large, which demonstrates the poor performance of the models. They are only acceptable for the slightly polar and non-ideal systems (1)–(10), (29)–(31) and (37)–(42). Discrepancies are especially large for alcohol–hydrocarbon systems (1)–(20) at $x_{\text{alcohol}} \to 0$ averaging 22.6% and 21.6% using the NRTL and UNIQUAC models respectively, while they are 16.7% and 16.0% for the NRTL and UNIQUAC models at $x_{\text{hydrocarbon}} \to 0$. For the highly non-ideal alcohol–hydrocarbon systems (12)–(20), percentage errors are smaller for $\Delta \overline{H}_2$ compared with those for $\Delta \overline{H}_1$ obtained from both of the models, although only the performance of the UNIQUAC model seems satisfactory. For the carboxylic acids–hydrocarbon systems (39)–(42), performance of the UNIQUAC model is better than that of the NRTL model, since the average errors are 13.6% and 23.7% respectively.

The UNIQUAC model fails to represent the correct temperature dependence of ΔH_2 for systems (1)–(3), (5)–(10), (12), (13), (19), (21), (22), (31) and (36), while the NRTL model fails only for systems (3), (4), (24) and (29). For highly non-ideal systems at low temperatures in particular, the dependence on temperature may be rather important in physical separation processes.

As seen from Table 1, among the same types of systems, e.g. (9) and (10), (12)–(18), and at different temperatures in the same system, e.g. (1), (4)–(8), (10), (12), (22), (25)–(29), the performances of the models vary greatly. For example, for the systems methyl acetate–benzene and methyl acetate–cyclohexane, average errors for $\Delta \overline{H}_1$ and $\Delta \overline{H}_2$ using the NRTL model are 34.5% and 5.3% respectively. A somewhat reversed situation occurs using the UNIQUAC model, as the average errors are 13.4% are 26.1% respectively.

CONCLUSIONS

The NRTL and UNIQUAC models with temperature-dependent parameters are capable of calculating the enthalpy of mixing at infinite dilution, although they have not been designed for calculating heats of mixing. However, the performances of the models are acceptable only for slightly non-ideal and polar systems. The representation of the temperature dependence of the enthalpy of mixing at infinite dilution by the NRTL model seems better than that of the UNIQUAC model. The choice of the best model is mainly system dependent.

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