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EXCESS ENTHALPIES FOR KETONE–ALCOHOL SYSTEMS *

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ABSTRACT

Excess enthalpy data for two binary systems, acetone(1) + *n*-propanol(2) and acetone(1) + *n*-butanol(2), were measured with a low-temperature Calvet microcalorimeter at ambient pressure and temperatures of 30 and 35 °C.

Based on the association solution theory, a temperature-dependent association model (TDA model) was established to describe the excess enthalpy, H^E, for the ketone–alcohol systems. For a particular system, the system-dependent parameters, A and B, are related to H^E by

$$H^E = x_1x_2[A + B(x_2 - x_1)] + \frac{x_1x_2k\,\Delta H}{[1+(k-1)x_1]}$$

The relationship between the association heat difference, ΔH, and temperature is expressed as

$$\frac{\Delta H}{T} = \frac{\Delta H_0}{T_0} + \Delta H'\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

where only three parameters, A, B and $\Delta H'$, are needed. By interpolating the H^E data of two temperatures, the H^E data for the other temperatures can be predicted.

The agreement between calculated and experimental data is satisfactory. The results correlated by the TDA model were compared with those by the QCS and Wilson models.

INTRODUCTION

The excess properties of ketone–alcohol binary systems, which are typically associated solutions, are of importance in both theoretical and practical application. A lot of researchers have measured excess enthalpy, H^E, data for some ketone–alcohol systems at 25 °C [1] and correlated the data by the Redlich–Kister equation. For lack of H^E data at other temperatures and no satisfactory excess enthalpy model to describe H^E data at different tempera-

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tures, we have measured the H^E data for acetone(1)–n-propanol(2) and acetone(1)–n-butanol(2) at 30 and 35 ° C, and presented the temperature-dependent association model (TDA model). Agreement between calculated results by the TDA model and experimental data is satisfactory. Furthermore, in addition to the ketone–alcohol binary systems, the TDA model has been tested for many other alcohol-containing systems.

EXPERIMENTAL

Apparatus. A low-temperature Calvet microcalorimeter

Materials

The analytical reagents acetone and n-propanol and the high-quality reagent n-butanol were treated by 5 Å zeolite and dewatered. The purity of the materials was higher than 99.5%. The refractive indices and densities at 20 ° C were determined and compared with the published values [2] shown in Table 1.

Data

Experimental excess enthalpy data for two binary systems, acetone–n-propanol and acetone–n-butanol, at 303.15 and 308.15 K are presented in Tables 2 and 3.

THE TEMPERATURE-DEPENDENT ASSOCIATION MODEL

The Gibbs free energy of mixing consists of both the physical and chemical contributions

$$\Delta G = \Delta G_{\mathrm{ph}} + \Delta G_{\mathrm{ch}} \tag{1}$$

Furthermore, the physical term can be divided into enthalpic and entropic parts under isothermal conditions

$$\Delta G_{\mathrm{ph}} = \Delta H_{\mathrm{ph}} - T\Delta S_{\mathrm{ph}} \tag{2}$$

TABLE 1

Physical properties of the chemicals used

	Density (20 ° C) (g cm^{-3})		Refractive index (20 ° C)	
	Exptl.	Lit.	Exptl.	Lit.
Acetone	0.80365	0.8035	1.38487	1.3850
n-Propanol	0.79023	0.7899	1.35892	1.3588
n-Butanol	0.80960	0.8098	1.39971	1.3993

TABLE 2

Experimental H^E data for the acetone(1)–*n*-propanol(2) system at 303.15 and 308.15 K

303.15 K			308.15 K		
No.	x_1	H^E (J mol^{-1})	No.	x_1	H^E (J mol^{-1})
1	0.0769	551.88	1	0.0810	454.85
2	0.1396	845.78	2	0.1018	547.99
3	0.2141	1055.40	3	0.1596	812.59
4	0.2910	1364.65	4	0.1746	862.91
5	0.3276	1320.80	5	0.1959	937.91
6	0.4286	1474.93	6	0.2571	1100.17
7	0.5040	1436.43	7	0.3381	1320.86
8	0.5390	1403.55	8	0.4192	1448.27
9	0.5997	1373.55	9	0.4526	1479.56
10	0.6561	1313.73	10	0.5002	1458.53
11	0.7312	1169.70	11	0.5485	1438.95
12	0.7992	919.51	12	0.5936	1414.53
13	0.8769	672.40	13	0.6798	1290.55
14	0.8963	596.91	14	0.7273	1212.69
15	0.9203	459.89	15	0.7918	1040.52
			16	0.8374	830.32
			17	0.8631	737.22
			18	0.9039	575.13
			19	0.9229	469.49

TABLE 3

Experimental H^E data for the acetone(1)–*n*-butanol(2) system at 303.15 and 308.15 K

303.15 K			308.15 K		
No.	x_1	H^E (J mol^{-1})	No.	x_1	H^E (J mol^{-1})
1	0.1941	800.35	1	0.0688	381.84
2	0.2226	964.98	2	0.1425	689.60
3	0.3031	1216.17	3	0.2288	991.72
4	0.3723	1401.97	4	0.3187	1314.54
5	0.3961	1385.31	5	0.3688	1398.59
6	0.4654	1459.58	6	0.4314	1498.35
7	0.5476	1498.24	7	0.4764	1521.22
8	0.5660	1505.33	8	0.4806	1542.07
9	0.6432	1444.35	9	0.5257	1552.80
10	0.7069	1297.86	10	0.5641	1507.23
11	0.7471	1225.73	11	0.6147	1469.53
12	0.7854	1130.82	12	0.7041	1342.78
13	0.8169	1025.44	13	0.7434	1278.22
14	0.8828	737.06	14	0.7856	1103.13
15	0.9283	464.03	15	0.8350	932.64
			16	0.8913	703.88
			17	0.9354	428.14

For the ideal mixing process, the entropy of mixing for a binary solution is

$$\Delta S_{\mathrm{ph}} = -R(x_1 \ln x_1 + x_2 \ln x_2) \tag{3}$$

The enthalpy of mixing is related to composition

$$\Delta H_{\mathrm{ph}} = x_1 x_2 [A + B(x_2 - x_1)] \tag{4}$$

A and B in eqn. (4) are constants, and x_1 and x_2 are the mole fractions of ketone(1) and alcohol(2), respectively.

We postulate that the relation between the association constant K and the composition x_1 of the system is linear, i.e.

$$K = K^{\circ} + (K^{\infty} - K^{\circ}) x_1 \tag{5}$$

where K° is the association constant for the pure alcohol and K^{∞} that for the infinitely dilute alcoholic solution. Then, the Gibbs free energy of mixing caused by association is given by

$$\Delta G_{\mathrm{ch}} = x_1\, \Delta G_1^{\circ} + x_2\, \Delta G_2^{\circ} - x_2 RT \ln\left[1 + \left(\frac{K^{\infty}}{K^{\circ}} - 1\right) x_1\right] \tag{6}$$

The expression for the excess Gibbs free energy, G^{E}, for the ketone–alcohol systems is

$$G^{\mathrm{E}} = x_1 x_2 [A + B(x_2 - x_1)] - x_2 RT \ln[1 + (k - 1) x_1] \tag{7}$$

where $k = K^{\infty}/K^{\circ}$.

From eqn. (7) and the Gibbs–Helmholtz relation, we obtain the excess enthalpy H^{E}

$$H^{\mathrm{E}} = x_1 x_2 [A + B(x_2 - x_1)] + \left[\frac{x_2 RT}{1 + (k-1) x_1}\right] x_1 \frac{\mathrm{d}k}{\mathrm{d}T} \tag{8}$$

Assuming that the relation between the association constant and temperature follows the Van 't Hoff equation

$$\frac{\mathrm{d} \ln K^{\circ}}{\mathrm{d}T} = \frac{\Delta H^{\circ}}{RT^2} \tag{9}$$

and

$$\frac{\mathrm{d} \ln K^{\infty}}{\mathrm{d}T} = \frac{\Delta H^{\infty}}{RT^2} \tag{10}$$

where ΔH° is the association heat of the pure alcohol and ΔH^{∞} that of the infinitely dilute alcoholic solution. Therefore, the temperature-independent association heat difference, ΔH, is related to the parameter $\Delta H'$ by

$$\frac{\Delta H}{T} = \frac{\Delta H_0}{T_0} + \Delta H' \left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{11}$$

where $\Delta H = \Delta H^{\infty} - \Delta H^{\circ}$ is the association heat difference, ΔH_0 is the association heat difference at the reference temperature (T_0), and $\Delta H'$ is a constant independent of T.

TABLE 4

The values of ΔH_0 and k_0 for the ketone–alcohol systems

System	T_0 (K)	ΔH_0 (J mol^{-1})	k_0	Ref.
Acetone–methanol	298.15	3231.00	0.7196	1
Acetone–ethanol	298.15	3592.00	0.8907	1
Acetone–*n*-propanol	298.15	3216.00	0.0612	3
Acetone–*n*-butanol	298.15	3439.00	0.2837	3
Cyclohexanone–cyclohexanol	303.15	1312.00	0.0223	4

Combining the previous equations we propose the working equations for the TDA model to be

$$G^{\mathrm{E}} = x_1x_2[A + B(x_2 - x_1)] - x_2RT \ln[1 + (k-1)x_1] \tag{12}$$

$$H^{\mathrm{E}} = x_1x_2[A + B(x_2 - x_1)] + \frac{x_1x_2k\,\Delta H}{1 + (k-1)x_1} \tag{13}$$

$$\Delta H = \Delta H_0 \frac{T}{T_0} + \Delta H'\left(1 - \frac{T}{T_0}\right) \tag{14}$$

$$k = k_0 \exp\left[\frac{(\Delta H_0 - \Delta H')\ln\left(\frac{T}{T_0}\right) + \Delta H'\left(1 - \frac{T_0}{T}\right)}{RT_0}\right] \tag{15}$$

where k_0 is the association constant ratio at the reference temperature, and A, B, $\Delta H'$ are three adjustable model parameters. The association heat difference, ΔH_0, and association constant ratio, k_0, can be obtained from the accurate H^{E} data at the reference temperature. ΔH_0 and k_0 for ketone–alcohol systems correlated by means of the complex optimization method are given in Table 4.

RESULTS AND DISCUSSION

Table 5 presents the calculated excess enthalpy, H^{E}, obtained by the TDA model and the constants in Table 4. For comparison, results from the Wilson equation and the quasi-chemical solution model (QCS model) [5] are also listed.

The experimental data for the acetone–*n*-propanol and acetone–*n*-butanol binary systems and the data calculated by the TDA model are compared in Figs. 1 and 2, respectively.

The values of three adjustable model parameters, A, B and $\Delta H'$, were determined from ΔH_0 and k_0 in Table 4 and a set of known H^{E} data other

TABLE 5

The correlated results of the H^E data for the ketone(1)–alcohol(2) systems by the TDA, QCS and Wilson models

System	*T* (K)	*N*	TDA		QCS		Wilson	
			AVDH	AVEH	AVDH	AVEH	AVDH	AVEH
Acetone–methanol	303.15	6	2.87	0.684	3.66	1.094	10.95	4.337
	323.15	20	4.42	1.043	6.26	1.609	7.23	2.275
Acetone–ethanol	282.28	9	18.48	1.825	16.92	1.709	414.69	40.641
	323.15	13	9.75	1.804	6.90	1.252	299.67	32.171
Acetone–*n*-propanol	303.15	16	39.20	4.264	54.22	5.946	591.97	49.758
	308.15	19	13.12	1.335	16.54	1.744	587.46	49.367
Acetone–*n*-butanol	303.15	15	19.63	2.045	20.01	1.851	532.47	48.886
	308.15	17	17.07	1.713	17.41	1.738	490.71	46.542
Cyclohexanone–cyclohexanol	313.15	13	16.70	1.733	19.83	2.052	486.49	44.361
	323.15	14	16.58	2.494	27.77	3.909	381.01	37.344

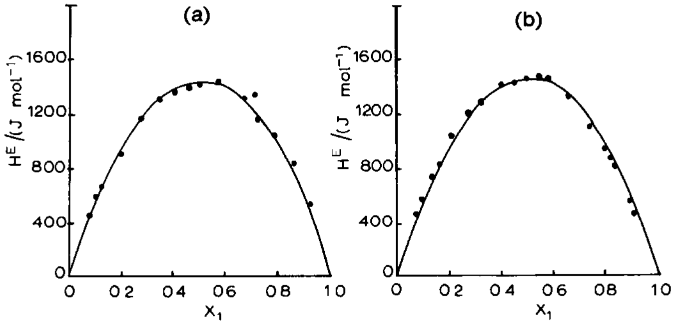

Fig. 1. Excess molar enthalpies for acetone(1)–*n*-propanol(2) at (a) 303.15 and (b) 308.15 K. ●, Experimental; ———, calculated by the TDA model.

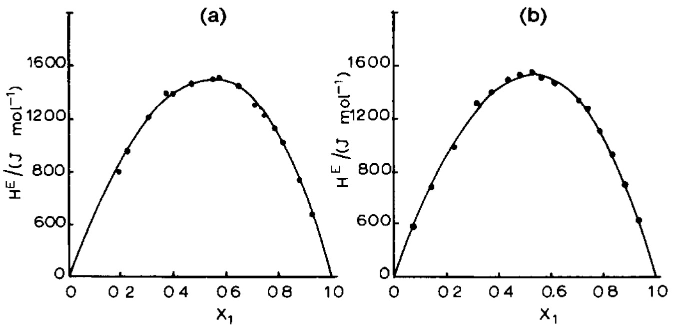

Fig. 2. Excess molar enthalpies for acetone(1)–*n*-butanol(2) at (a) 303.15 and (b) 308.15 K. ●, Experimental; ———, calculated by the TDA model.

TABLE 6

Prediction of H^E data for ketone(1)–alcohol(2) systems at different temperatures

System	Corr. temp. (K)	Model parameters			Pred. temp. (K)	AVDH	AVEH
		A	B	$\Delta H'$			
Acetone–methanol	303.15	198.0	−107.9	2877.0	323.15	4.4950	1.105
Acetone–ethanol	282.28	1435.0	−21.33	3981.0	323.15	10.582	1.888
Acetone–*n*-propanol	303.15	5419.0	729.4	−23220.0	308.15	21.706	2.327
Acetone–*n*-butanol	303.15	4353.0	172.0	−7010.0	308.15	21.730	2.168
Cyclohexanone–cyclohexanol	313.15	5790.0	−265.6	75160.0	323.15	17.954	2.654

than at the reference temperature. As a result, H^E at the other temperatures can be predicted from A, B and $\Delta H'$ by eqn. (13).

A comparison between the experimental H^E data and those predicted by the TDA model for the ketone–alcohol binary system, as well as the parameters in this model, are shown in Table 6.

AVDH and AVEH in Tables 5 and 6 are the average absolute and relative deviations of the excess enthalpy, respectively. They are expressed as

$$\text{AVDH} = \sum_i \frac{\text{ABS}\left(H^E_{\text{exptl}} - H^E_{\text{calc}}\right)_i}{N} \quad (\text{J mol}^{-1}) \tag{16}$$

$$\text{AVEH} = \sum_i \frac{\text{ABS}\left[\left(H^E_{\text{exptl}} - H^E_{\text{calc}}\right)/H^E_{\text{exptl}}\right]_i}{N} \times 100(\%) \tag{17}$$

where N is the number of points.

SUMMARY AND CONCLUSION

Based on the discussion above, the excess enthalpies for the ketone–alcohol systems at different temperatures obtained from the TDA model are more accurate than those obtained from the Wilson equation and the QCS model. The model constants and parameters are determined from two sets of H^E data at two known temperatures. The agreement between the experimental and predicted H^E values for the other temperatures obtained from eqn. (13) is satisfactory. Since the extrapolated temperature covered a wide range, we can conclude that the function between the association heat and the temperature put forward in the TDA model is reasonable. In contrast, the other models mentioned above fail to predict H^E at different temperatures.

In our other article, the TDA model has been extended to describe the excess properties for the other alcohol-containing systems and to correlate and predict the vapour–liquid equilibria using the parameters determined from the H^E data. The results are also satisfactory.

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