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EXCESS ENTHALPY OF TERNARY MIXTURE FOR DIAMINE+HEPTANE+CYCLOHEXANE

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Abstract

The excess molar enthalpy of ternary mixture for 3-diethylaminopropylamine+heptane+cyclohexane were measured using a Calvet microcalorimeter at 303.15 K.

Empirical equations, Redlich-Kister, Tsao-Smith, and Kohler and group contribution models, UNIFAC (modified version) and DISQUAC have been applied. A reasonable representation of ternary data is obtained.

Keywords: Calvet microcalorimeter, diamines, enthalpy, excess functions, excess molar enthalpy data

Introduction

Diamines, a particulary interesting and technically important class of molecules [1, 2], have been investigated with a view to testing group contribution models and to analyse intramolecular effects, especially proximity effect. Recently [3, 4], the thermodynamic properties of mixtures of symmetric tertiary diamines+*n*-alkanes or cyclohexane have been measured and examined on the basis of group contribution model.

In previous work we determined the excess enthalpies of binary mixtures for unsymmetric diamine+heptane or +cyclohexane [5]. We report here data of molar excess enthalpy, H^E for ternary mixture of 3-diethylaminopropylamine (3DEPA) with heptane and cyclohexane at 303.15 K.

The excess molar enthalpy, H^E is used to test the group contribution models: UNIFAC (version modified) [6] and DISQUAC [7], and the empirical equations (Redlich-Kister [9], Tsao-Smith [9] and Kohler [10]).

Experimental

Heptane, cyclohexane and diamine (purity greater than 99 mol%) were Fluka products, and were used without further purification.

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Excess molar enthalpies were measured at 303.15 K with a C 80 calorimeter (Setaram, Lyon, France), a Calvet type microcalorimeter, with no vapour space, the mercury is used to separate the two cells which contained the liquids under study. The performance of the apparatus was checked by determining H^E of benzene+cyclohexane at 298.15 K, our results differ by less than 2% from those reported by Marsh [11].

Results and discussion

Three experimental runs were carried out for ternary mixture formed by adding 3-DEPA (1) to a binary mixture of heptane (2)+cyclohexane (3).

A ternary mixture is considered as a pseudobinary mixture composed of one binary mixture and 3-DEPA (1). The ternary molar enthalpy is given by:

$$H^E_{123}=H^E_m+(1-x_1)H^E_{23} \quad (1)$$

where H^E_m is the experimental excess enthalpy for the pseudobinary and H^E_{23} is the binary excess enthalpy of heptane (2)+cyclohexane (3).

Table 1 list the ternary excess enthalpies H^E_{123} and H^E_m at the temperature 303.15 K. Figure 1 shows the experimental excess enthalpies H^E_{123} plotted *vs*. X_i .

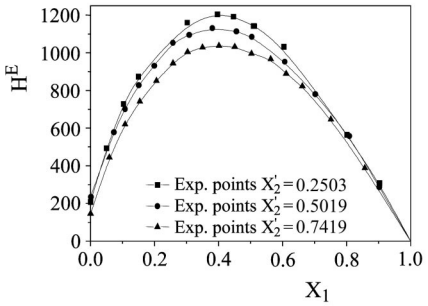

Fig. 1 Ternary excess molar enthalpy, H^E_{123}, at 303.15 K of 3-DEPA (1)+heptane (2)+cyclohexane (3)

The H^E_{123} values for 3-DEPA (1)+heptane (2)+cyclohexane (3) are positive and are of the same order that the binary mixtures.

Figure 2 shows the curves calculated using the empirical equations of Redlich-Kister [8], Tsao-Smith [9] and Kohler [10]. The three equations are adequate for correlation of the enthalpies.

The values H^E in a ternary mixture can be as the sum of a binary and a ternary contribution:

$$H^E_{123}=H^E_{12}+H^E_{23}+H^E_{13}+x_1x_2x_3(A_0+A_1x_1) \quad (2)$$

Table 2 presents the values of the A_i coefficients calculated by the least squares method. The lines of constant ternary excess molar enthalpy calculated by use of Eq. (2) are shown in Fig. 3.

Table 1 Experimental molar excess enthalpies H^E_{123} at 303.15 K of 3-DEPA (1)+*n*-heptane (2)+cyclohexane (3)

x_1	x_2	H^E_m/ J mol^{-1}	H^E_{123}/ J mol^{-1}	x_1	x_2	H^E_m/ J mol^{-1}	H^E_{123}/ J mol^{-1}	x_1	x_2	H^E_m/ J mol^{-1}	H^E_{123}/ J mol^{-1}
x_2'=0.2503 H^E_m=209 J mol^{-1}				x_2'=0.5019 H^E_m=236 J mol^{-1}				x_2'=0.7496 H^E_m=146 J mol^{-1}			
0.0499	0.2379	296	494	0.0724	0.4258	360	579	0.0588	0.7055	307	444
0.1031	0.2245	542	729	0.1072	0.4273	491	702	0.1080	0.6686	490	620
0.1494	0.2129	696	874	0.1501	0.3827	629	829	0.1538	0.6343	618	742
0.1544	0.2117	708	960	0.1990	0.3145	743	932	0.2057	0.5943	736	852
0.1807	0.2051	788	1162	0.2566	0.2600	879	1054	0.2577	0.5564	837	945
0.3016	0.1748	1016	1206	0.3079	0.2204	933	1097	0.3028	0.5226	903	1004
0.3962	0.1512	1079	1199	0.3803	0.1743	986	1133	0.3500	0.4872	934	1029
0.4463	0.1386	1084	1143	0.4555	0.1290	986	1114	0.4013	0.4488	950	1038
0.5090	0.1229	1041	1142	0.5036	0.1178	969	1086	0.4507	0.4117	952	1032
0.5119	0.1227	1040	1002	0.7019	0.11	861	954	0.5026	0.3728	932	996
0.6037	0.0992	920	813	0.8088	0.1002	711	782	0.5630	0.3275	904	967
0.8009	0.0500	524	564	0.9015	0.0608	514	559	0.6110	0.2916	832	889
0.9017	0.0246	288	309		0.0299	264	288	0.6617	0.2335	774	824
								0.7508	0.1868	610	646
								0.8571	0.1071	368	387

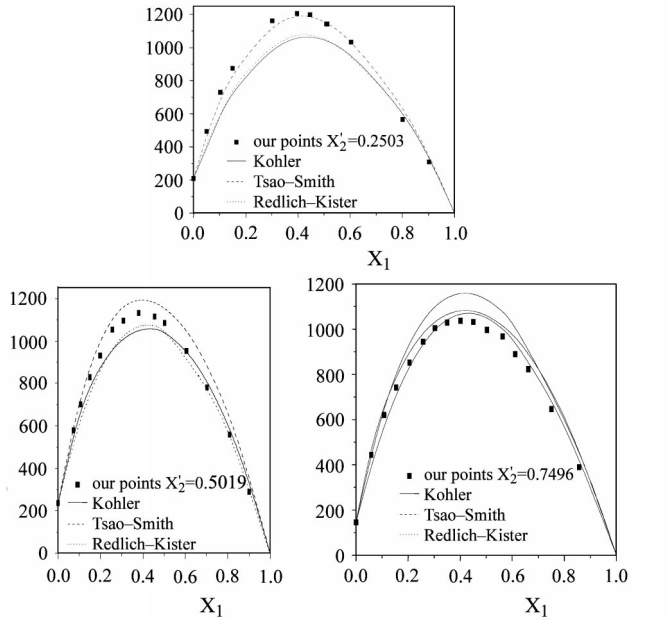

Fig. 2 Ternary excess molar enthalpy calculated by empirical equations, H^{E}_{123}, at 303.15 K of: 3-DEPA(1)+nC$_7$(2)+cC$_6$ (3)

Table 2 Values of coefficients A_0 and A_1 (Eq. (2))

System	A_0	A_1	σ/J mol^{-1}
3-DEPA (1)+nC$_7$ (2)+cC$_6$ (3)	7252.932	–12668.059	15

The original UNIFAC [12] only predicts G^E, whereas modified UNIFAC [6] can be used to predict G^E, H^E, and γ_i^∞. Using the parameters of modified UNIFAC [6], we calculated H^E for the ternary system 3-DEPA+heptane+cyclohexane.

Figure 4 shows the experimental and theoretical curves of H^{E}_{123} at 303.15 K. The modified UNIFAC model compare well with the experimental measurements. As is known, this model is an improvement which yields a good representation of data on the basis of temperature-dependent parameters and a new combinatorial term.

In DISQUAC model, the diamine is regarded as possessing three types of surfaces: type a, alkane (CH_3 or CH_2 group), type n, (–N<group) and type h, nitrogen (NH_2 group). The geometrical parameters have been calculated as before [18]. Heptane (surface type a) is regarded as a homogeneous molecule and the cyclohexane (surface type c) have been estimated previously [3]. The four types of surfaces, a, n, h and c, generate a six-pair of contact: (a, n), (a, c), (a, h), (n, h), (c, h) and (c, n). The equations used to calculate G^E and H^E are the same as previously reported [7].

Recently [3, 4], tertiary diamines+n-alkanes, or cyclohexane have been reexamined in detail in terms of the the DISQUAC model. The thermodynamic properties, G^E and H^E

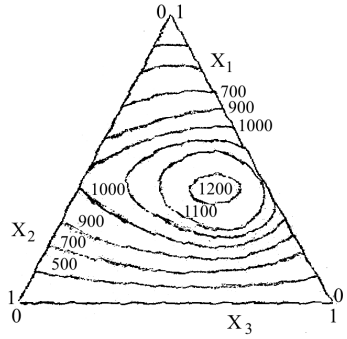

Fig. 3 Curves of constant H^E_{123} for 3-DEPA (1)+C_7 (2)+C_6 (3) at 303.15 K

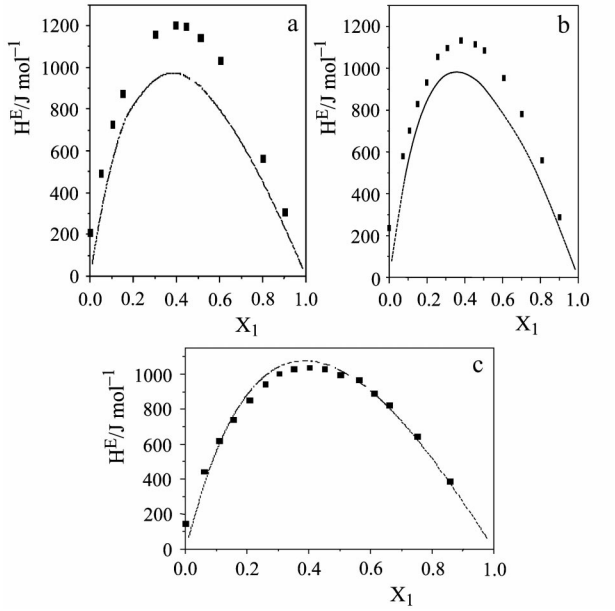

Fig. 4 Comparison of theory (modified UNIFAC) with experimental for the molar excess enthalpy H^E_{123} at 303.15 K of 3-DEPA (1)+*n*C_7 (2)+*c*C_6 (3): lines, predicted values; points, our experimentals results. a – x_2=0.2503; b – x_2=0.5019; c – x_2=0.7496

of unsymmetric diamine 3-DEPA+heptane or +cyclohexane have been investigated previously [5]. These data are used to determine the interchange parameters. The dispersive coefficients and the quasichemical coefficients have been adjusted to fit the equimolar data G^E and H^E of binary mixtures [5]. Using the same parameters of binary systems, we calculated H^E_{123} of the ternary system 3-DEPA+heptane+cyclohexane.

Figure 5 shows a good agreement between calculated and experimental curves of H^E_{123} at 303.15 K. So, good result is obtained for this complex system and with six

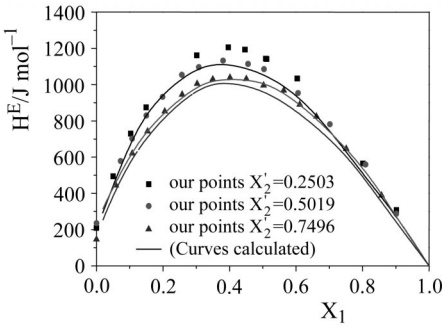

Fig. 5 Comparison of the theory DISQUAC with experiment for the molar excess enthalpy, H^E, at 303.15 K of 3-DEPA (1)+nC$_7$ (2)+cC$_6$ (3)

interactions. This is due to the fitting of the interchange parameters was adjusted to fit the data of the binary mixture.

In general, the results obtained for the mixture under study are comparable to those encountered for ternary mixtures. Finally, we can concluded that the empirical equations such as Redlich-Kister, Tsao-Smith and Kohler yields results equivalent to group contribution model. The most interesting result of our study is the confirmation that the empirical equations can be used as mentioned in literature [12].

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