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Excess enthalpies and excess volumes of mixing for mixtures of isomeric butyl amines and acetonitrile [1]

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Abstract

The excess enthalpies and excess volumes of 1-aminobutane, 1-amino-2-methylpropane, 2-aminobutane and 2-amino-2-methylpropane with acetonitrile were determined at 303.15 and 298.15 K, respectively, using a microcalorimeter and a densimeter. Dissociation of self-associated amine species and formation of amine–acetonitrile complexes were expected to take place in solution. The excess enthalpies were positive and the excess volumes were negative for all four systems. The enthalpies of complex formation were calculated from the partial molar enthalpies. The endothermic heats of mixing and negative volume change on mixing are explained in terms of the extent of formation of amine–acetonitrile complexes in the liquid mixtures.

INTRODUCTION

In a systematic study of molecular interactions in liquids with particular attention to the energies of complex formation between different functional groups, binary mixtures of isomeric butanols with amines, acetone, dibutyl ether, and acetonitrile, and of isomeric butyl amines with primary alcohols, and chloroform, have been studied [1–6]. In the present communication, we report results for the excess enthalpies and excess volumes on mixing isomeric butyl amines with acetonitrile. Work on these systems has not been reported before in the literature.

EXPERIMENTAL

1-Aminobutane, 1-amino-2-methylpropane, 2-aminobutane and 2-amino-2-methylpropane, all Fluka 99%, and acetonitrile (S.D. Chem. AnalaR) were further purified by fractional distillation and then dried over activated molecular sieve.

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The excess enthalpies were determined by means of a heat flux Calvet-type microcalorimeter (Setaram C-80) at 303.15 K, using cells of the mixing type. Weighed quantities of two compounds, accurate to ±0.1 mg, were placed in two compartments of the cell. Mixing was carried out after attainment of thermal equilibrium. The accuracy of the data is of the order of ±1%.

The excess volumes were determined by the density method. Binary mixtures were made by placing weighed quantities of two compounds accurate to ±0.1 mg in a stoppered conical flask and thoroughly mixing them. With this procedure the uncertainty in the mole fraction was less than 10^{-4}. The densities were determined at 298.15 K by means of an Anton Paar densimeter (D.M.A. 60/80) using a differential cell arrangement. One of the cells was filled with distilled water and the other with the sample mixture. The temperatures of the cells were kept constant to +0.005°C. The densities were determined at least three times for each concentration and were reproducible to within 10^{-5} g cm^{-3} and the V^E values were accurate to $\pm 10^{-3}$ ml mol^{-1}.

RESULTS AND DISCUSSION

Excess enthalpies of mixing

Excess enthalpy data for isomeric butylamine–acetonitrile systems are reported in Table 1. Data for each system were fitted to the equation

$$H^E = x_1 x_2 \sum_{i=0}^{3} A_i (x_1 - x_2)^i \qquad (1)$$

using the method of least-squares, with all points weighted equally. The least-squares parameters, along with the standard deviations, are given in Table 2. The H^E versus x_1 plots for these systems are given in Fig. 1.

The enthalpies of mixing are positive for all four systems. The isomers of butylamine are self-associated to different degrees in the liquid state, and acetonitrile is a polar liquid with a proton-acceptor nitrogen atom. It has been established by spectroscopy that amine and acetonitrile form hydrogen-bonded complexes in liquid mixtures [7]. The mixing of amine and acetonitrile leads to four types of molecular interactions, with different thermal effects.

(i) Disruption of hydrogen-bonded self-associated amine species by acetonitrile molecules, which is an endothermic interaction.

(ii) Hydrogen bond formation between amine and acetonitrile, which is an exothermic interaction.

(iii) Disruption of dipole–dipole or specific interactions between the acetonitrile molecules, which is an endothermic interaction.

TABLE 1

Excess enthalpies of mixing of isomeric butylamine(1) with acetonitrile(2) at 303.15 K

X_1	H^E/J mol^{-1}	X_1	H^E/J mol^{-1}
1-Aminobutane(1) + acetonitrile(2)			
0.0985	236	0.5397	546
0.1470	326	0.6549	472
0.2766	509	0.7548	382
0.4226	572	0.8353	264
1-Amino-2-methylpropane(1) + acetonitrile(2)			
0.0580	120	0.5818	542
0.1298	255	0.6161	512
0.2045	372	0.7379	383
0.3660	538	0.8176	276
0.5080	573	0.8495	230
2-Aminobutane(1) + acetonitrile(2)			
0.0425	73	0.5267	476
0.0645	118	0.6528	422
0.0905	152	0.6899	400
0.2168	353	0.7935	308
0.2977	429	0.8507	235
0.4434	486		
2-Amino-2-methylpropane(1) + acetonitrile(2)			
0.0817	136	0.4754	494
0.0874	151	0.5772	490
0.1517	240	0.6770	438
0.1810	275	0.7256	404
0.2410	340	0.7981	304
0.3663	451	0.8863	183
0.4380	474		

(iv) Dipole–dipole interactions between amine and acetonitrile molecules without hydrogen bonding.

It is not possible to calculate the contributions of the endothermic and exothermic interactions to the overall effect but, obviously, the endothermic

TABLE 2

The least-squares coefficients of eqn. (1) for the excess enthalpies of mixing of isomeric butyl amines with acetonitrile

System	A_0/ J mol^{-1}	A_1/ J mol^{-1}	A_2/ J mol^{-1}	A_3/ J mol^{-1}	Std.dev./ J mol^{-1}
1-Aminobutane	2257.02	−640.34	17.01	264.89	3.0
1-Amino-2-methylpropane	2277.78	−319.58	514.61	−51.46	2.0
2-Aminobutane	1953.17	−339.62	−36.27	528.46	4.7
2-Amino-2-methylpropane	1971.81	117.48	−245.70	−252.35	4.8

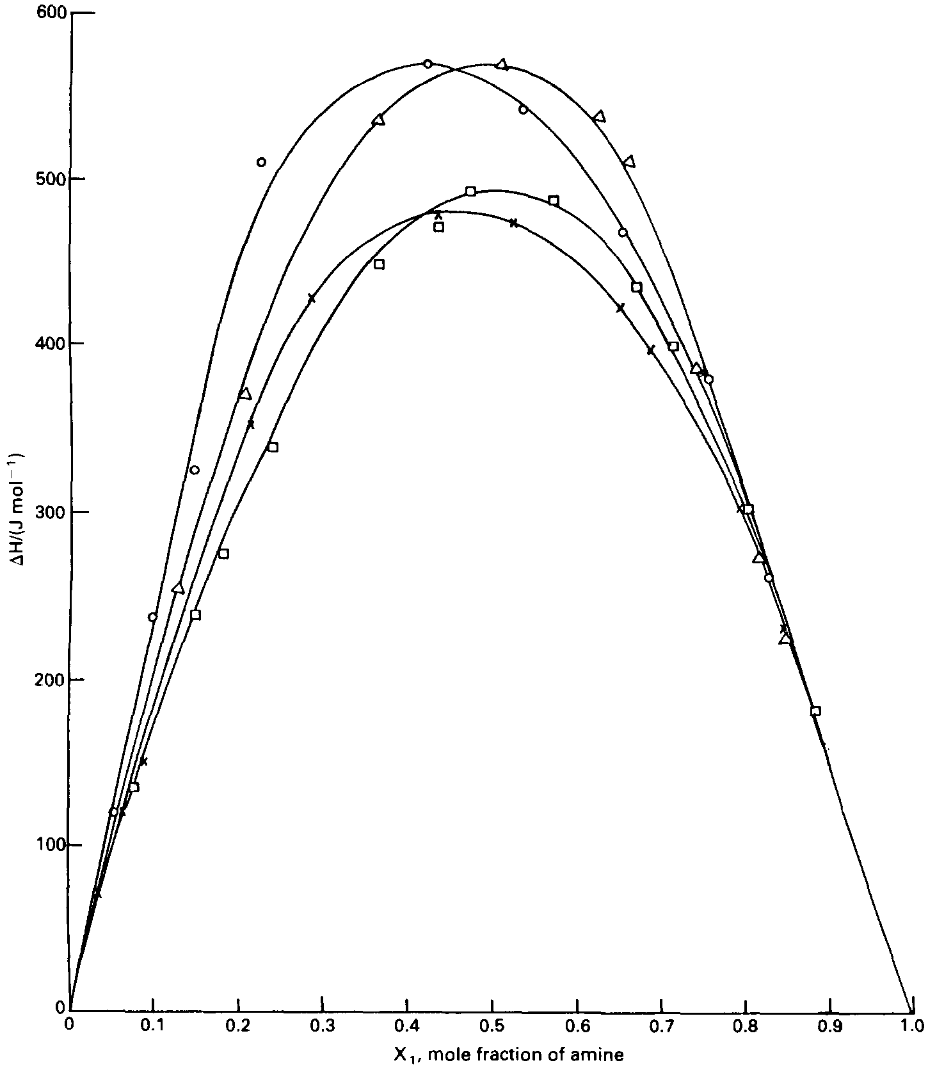

Fig. 1. H^E vs. X_1 plots for isomeric butylamine(1)–acetonitrile(2) systems: ○, 1-aminobutane; △, 1-amino-2-methylpropane; ×, 2-aminobutane; □ 2-amino-2-methylpropane.

effect dominates over the exothermic effect. From the calorimetric data alone, the formation of complex species in liquid mixtures of amine and acetonitrile is indicated qualitatively when the enthalpy data of these systems are compared with the enthalpy data for amine–non-polar systems. The H^E_{max} values for 1-aminobutane, 1-amino-2-methylpropane, 2-aminobutane and 2-amino-2-methylpropane in acetonitrile are 575, 575, 485 and 495 J mol^{-1}, respectively, whereas the H^E_{max} for these four butylamine isomers in n-hexane are 1015, 870, 870 and 915 J mol^{-1}, respectively. The marked decrease in endothermicity of the amine–acetonitrile systems indi-

TABLE 3

Enthalpies of hydrogen bonding between isomeric butyl amines and acetonitrile calculated by eqn. (2)

System	ΔH_1/ kJ mol^{-1}	ΔH_2/ kJ mol^{-1}	ΔH_3/ kJ mol^{-1}	ΔH_c/ kJ mol^{-1}
1-Aminobutane	2.6	8.4		−18.4
1-Amino-2-methylpropane	2.3	7.5		−17.8
2-Aminobutane	2.9	6.6		−16.3
2-Amino-2-methylpropane	1.8	4.9		−15.7
Acetonitrile			12.6 [a]	

[a] From ref. 4.

cates the strong specific interaction in the liquid mixture. The enthalpy of complex formation can be obtained from the partial molar enthalpies [8] by the equation

$$\Delta H_c = \Delta H_1 - \Delta H_2 - \Delta H_3 \tag{2}$$

where ΔH_c is the enthalpy of complex formation, ΔH_1 is the partial molar enthalpy of amine in acetonitrile, ΔH_2 is the partial molar enthalpy of amine in a non-polar solvent, and ΔH_3 is the partial molar enthalpy of acetonitrile in a non-polar solvent.

The partial molar enthalpies of mixing were obtained by extrapolating the $\Delta H/x_1x_2$ versus x_1 plots to zero mole fraction [9]. The enthalpies of complex formation thus calculated, along with the relevant data, are reported in Table 3. The branching of the alkyl chain has a small effect on the enthalpy of complex formation and shows the trend: 1-aminobutane > 1-amino-2-methylpropane > 2-aminobutane > 2-amino-2-methylpropane.

Volume change on mixing

Data on the volume change on mixing are reported in Table 4 and are plotted in Fig. 2. The data were fitted to eqn. (1) by the least-squares method and the parameters of the equation, along with the standard deviations for the systems, are reported in Table 5.

The volume change on mixing is negative for all four systems, which indicates that the binary mixtures of butylamine and acetonitrile are in a more ordered state. Three factors contribute to volume change on mixing.

(i) Specific interactions, such as formation of complexes, hydrogen bond formation, or dissociation of associated species.

(ii) Molecular orientation leading to a particular orientation of molecules in the liquid mixture.

TABLE 4

Excess volumes on mixing isomeric butylamine(1) with acetonitrile(2) at 298.15 K

X_1	d_{12}	V^E/ml mol^{-1}	X_1	d_{12}	V^E/ml mol^{-1}
1-Aminobutane(1) + acetonitrile(2)			2-Aminobutane(1) + acetonitrile(2)		
0.0445	0.77311	−0.018	0.0493	0.77158	−0.058
0.0709	0.77121	−0.026	0.1003	0.76700	−0.102
0.0965	0.76944	−0.034	0.1403	0.76367	−0.136
0.1146	0.76609	−0.043	0.1945	0.75921	−0.160
0.1910	0.76339	−0.055	0.2328	0.75622	−0.172
0.2805	0.75833	−0.068	0.2784	0.75294	−0.191
0.3520	0.75472	−0.077	0.2856	0.75245	−0.194
0.4094	0.75202	−0.081	0.3550	0.74778	−0.212
0.4494	0.75024	−0.081	0.3915	0.74545	−0.216
0.4909	0.74849	−0.083	0.4490	0.74199	−0.221
0.5084	0.74778	−0.083	0.4674	0.74094	−0.223
0.5446	0.74634	−0.083	0.5073	0.73873	−0.225
0.6312	0.74314	−0.081	0.5463	0.73663	−0.223
0.6701	0.74179	−0.079	0.6125	0.73332	−0.222
0.7424	0.73942	−0.074	0.6184	0.73303	−0.221
0.7651	0.73869	−0.070	0.6728	0.73049	−0.217
0.8690	0.73558	−0.052	0.7427	0.72737	−0.202
0.9083	0.73444	−0.039	0.8065	0.72467	−0.181
0.9600	0.73301	−0.023	0.8327	0.72360	−0.171
1-Amino-2-methylpropane(1) + acetonitrile(2)			0.9110	0.72036	−0.112
			0.9424	0.71906	−0.078
0.0506	0.77244	−0.033	2-Amino-2-methylpropane(1) + acetonitrile(2)		
0.1036	0.76827	−0.059	0.0626	0.76800	−0.153
0.1219	0.76693	−0.069	0.1078	0.76201	−0.236
0.1869	0.76229	−0.090	0.1555	0.75596	−0.304
0.2394	0.75886	−0.106	0.2024	0.75033	−0.360
0.2871	0.75590	−0.115	0.2551	0.74455	−0.426
0.3309	0.75334	−0.122	0.3051	0.73926	−0.467
0.3810	0.75058	−0.128	0.3561	0.73412	−0.494
0.4103	0.74905	−0.132	0.4078	0.72915	−0.508
0.4389	0.74762	−0.136	0.4558	0.72481	−0.515
0.4520	0.76497	−0.137	0.4912	0.72179	−0.521
0.4955	0.74489	−0.139	0.5470	0.71723	−0.520
0.5230	0.74360	−0.138	0.5804	0.71461	−0.514
0.5877	0.74075	−0.135	0.6216	0.71149	−0.501
0.6133	0.73968	−0.134	0.6928	0.70643	−0.476
0.6681	0.73748	−0.130	0.7103	0.70515	−0.456
0.7237	0.73536	−0.124	0.7699	0.70110	−0.405
0.7896	0.73297	−0.111	0.8072	0.69854	−0.351
0.8457	0.73106	−0.100	0.8703	0.69462	−0.283
0.8929	0.72948	−0.083	0.8868	0.69354	−0.251
0.9213	0.72852	−0.067	0.9275	0.69096	−0.171
0.9523	0.72752	−0.051			

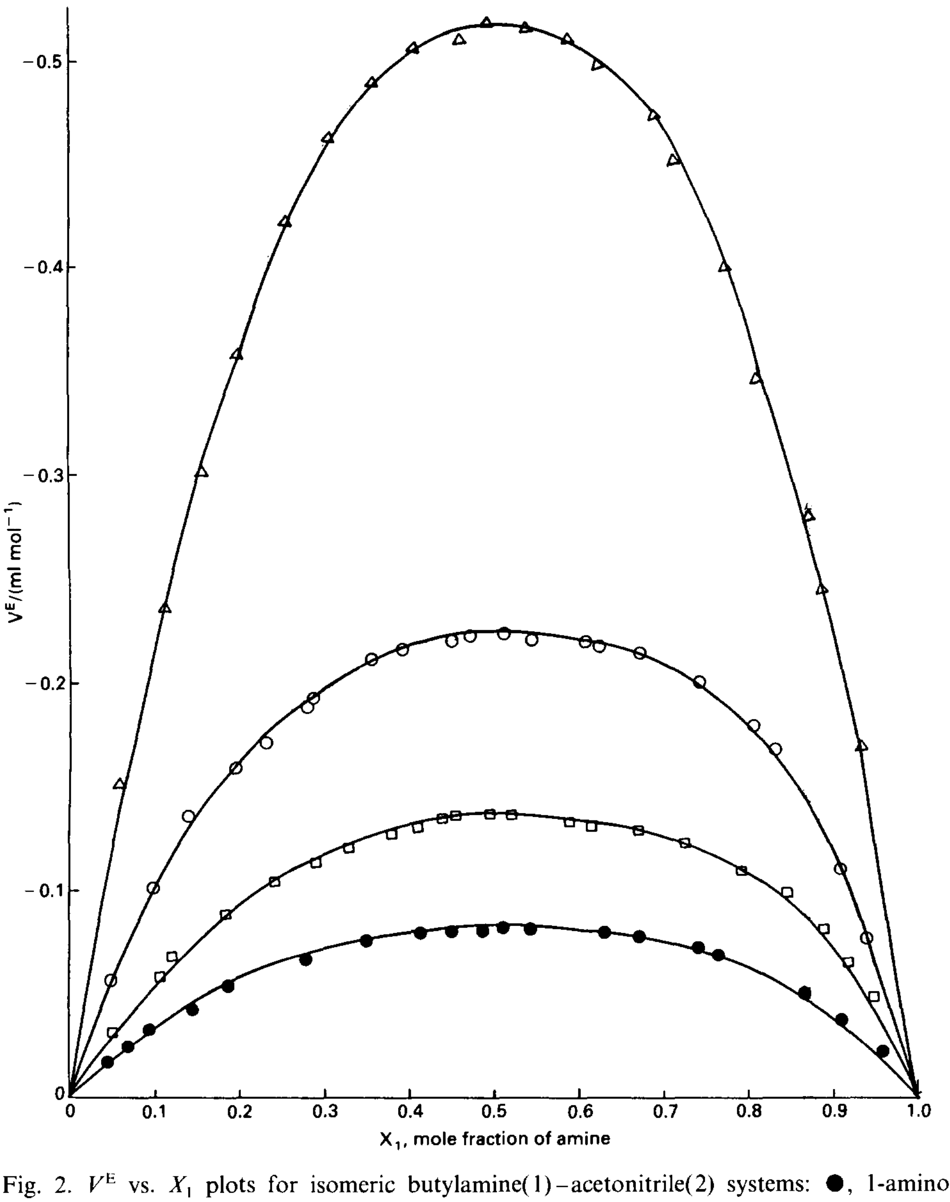

Fig. 2. V^E vs. X_1 plots for isomeric butylamine(1)-acetonitrile(2) systems: ●, 1-aminobutane; □, 1-amino-2-methylpropane; ○, 2-aminobutane; △, 2-amino-2-methylpropane.

(iii) The situation of small molecules in the vacant spaces of the liquid [10].

The excess enthalpy data and the excess volume data indicate that in the present systems, the energetic breaking of associated species of butylamine predominates over the specific interactions between amine and acetonitrile molecules, but specific interactions make a more compact molecular arrangement in a mixture. It may be noted that amongst the four systems, the

TABLE 5

The least-squares coefficients of eqn. (1) for the excess volumes on mixing isomeric butyl amines with acetonitrile

System	A_0/ ml mol^{-1}	A_1/ ml mol^{-1}	A_2/ ml mol^{-1}	A_3/ ml mol^{-1}	Std.dev./ ml mol^{-1}
1-Aminobutane	−0.3260	−0.0097	−0.190	−0.0734	0.0017
1-Amino-2-methylpropane	−0.5302	0.0124	−0.3836	−0.2801	0.0037
2-Aminobutane	−0.8892	−0.0907	−0.5616	−0.0426	0.0024
2-Amino-2-methylpropane	−2.0873	−0.0546	−0.6291	−0.0549	0.0055

1-aminobutane, and 1-amino-2-methylpropane systems are more endothermic, although the enthalpies of complex formations are higher for these two systems.

The observed enthalpy of mixing is governed by the number of associated species broken and the number of complexes formed on mixing the two liquids. In other words, the equilibrium constants of complex formation determine the net enthalpy of mixing. The equilibrium constant is independent of the enthalpy of complex formation [11]. The observed larger endothermic enthalpies of mixing of the 1-aminobutane and 1-amino-2-methylpropane systems may therefore be attributed to formation of fewer amine–acetonitrile complexes than in the other two systems in the liquid mixtures; consequently, the excess volumes are less negative.

However, the 2-aminobutane–acetonitrile and 2-amino-2-methylpropane–acetonitrile systems show a less endothermic behaviour due to larger specific interactions, and more negative excess volumes. So the trends of excess enthalpies and excess volumes, in terms of the number of complex species formed in the liquid mixtures, are consistent with each other.

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