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MEASUREMENT AND CORRELATION OF EXCESS MOLAR ENTHALPY AT VARIOUS TEMPERATURES

Acetonitrile + diethylamine or *s*-butylamine mixtures

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As a continuation of our studies on excess functions of binary systems containing acetonitrile-amines mixtures, in this work excess molar enthalpy (H_m^E) of acetonitrile+diethylamine or *s*-butylamine mixtures have been determined as a function of composition at 288.15, 293.15, 298.15 and 303.15 K at atmospheric pressure using a modified 1455 Parr adiabatic calorimeter. The excess enthalpy data are positive for both systems over the whole composition range. ERAS-Model calculations allowing for self-association and cross-association of the components were performed. The results of the calculations and the influence of temperature and isomers chains on the excess enthalpy behavior are discussed.

Keywords: *acetonitrile, amines, correlation, data, excess enthalpy*

Introduction

Studies on excess functions, especially on excess enthalpy, of binary liquid acetonitrile or amine containing mixtures (Reimann–Heintz [1], Funke *et al.* [2], Matteoli *et al.* [3], Pina–Francesconi [4]), have been performed to understand the molecular interactions between the components of the solution. As a continuation of our studies on excess functions of binary systems containing acetonitrile+amines mixtures [5], in this work new excess molar enthalpy (H_m^E) values of acetonitrile+diethylamine or s-butylamine mixtures have been determined as a function of composition at 288.15, 293.15, 298.15 and 303.15 K at atmospheric pressure. The applicability of the ERAS-Model to correlate (H_m^E) of (acetonitrile+diethylamine or s-butylamine) mixtures was tested. Previous excess molar enthalpy values for some acetonitrile+amines mixtures are reported by Pathak *et al.* [6].

Experimental

The reagents acetonitrile, diethylamine and s-butylamine are analytical grade and were supplied by EM Science–Merck (USA, purity >99.99 mol%), diethylamine and *s*-butylamine (Acros Organics, purity >99 mol%), were dried over molecular sieves (3Å). To check the purity of the substances, density and refractive index measurements were performed using a vibrating-tube densimeter (Anton Parr, model 55) and an Abbé type refractometer (Atago, model 3T), respectively. Table 1 presents a comparison of the density and refractive index measurements with literature values.

Excess enthalpy measurements were performed using a Parr 1455 solution calorimeter similar to that described by Venkatesulu *et al.* [7] with some improvements. Figure 1 shows a schematic view of the apparatus.

A Teflon cover (1) was fitted on the top of the Dewar flask (2) to reduce the influence of evaporation and a resistance wire (3) was placed in the Dewar flask to perform calibration measurements. Another modification was to place the calorimeter in a thermostatic bath (4) so that heat losses between the calorimeter and its surrounding were kept as small as possible. The operating procedure of the calorimeter is the following. One of the pure substances is loaded with

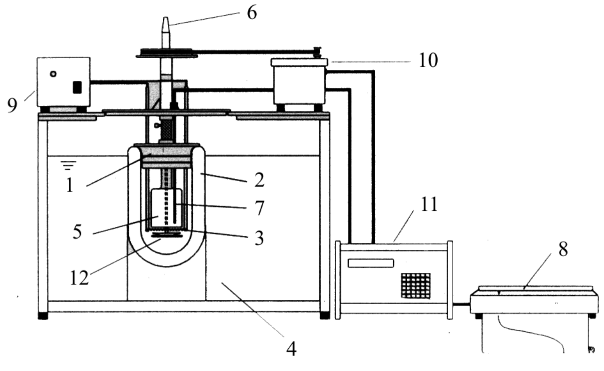

Fig. 1 Schematic views of the apparatus

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Table 1 Comparison of measured values with literature values of refractive index (n_D) and density (ρ) at 293.15 K.

Component	ρ/g cm^{-3}		n_D	
	Literature[a]	Measured	Literature[b]	Measured
acetonitrile	0.7822	0.78209	1.3442	1.3443
diethylamine	0.7056	0.70472	1.3864	1.3862
s-butylamine	0.7246	0.72260	1.3946	1.3947

[a]from [15] and [b]from [1]

Table 2 Experimental excess molar enthalpies H_m^E for acetonitrile+diethylamine at four temperatures

x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}
$(1–x)CH_3CN+x(C_2H_5)2NH$							
288.15 K		293.15 K		298.15 K		303.15 K	
0.0247	70	0.0246	71	0.0246	73	0.0246	74
0.0494	135	0.0492	136	0.0492	142	0.0492	142
0.0739	196	0.0736	199	0.0737	205	0.0737	208
0.0984	250	0.0980	253	0.0980	261	0.0982	267
0.1228	301	0.1223	302	0.1223	317	0.1224	322
0.1699	382	0.1693	392	0.1693	414	0.1694	416
0.2161	449	0.2156	467	0.2155	495	0.2156	498
0.2614	498	0.2608	517	0.2607	551	0.2608	556
0.3056	531	0.3049	553	0.3048	593	0.3049	602
0.3484	549	0.3478	576	0.3476	617	0.3477	630
0.3898	558	0.3892	586	0.3890	632	0.3891	642
0.4297	561	0.4290	590	0.4289	637	0.4289	649
0.4679	559	0.4673	589	0.4671	636	0.4671	648
0.5044	549	0.5038	581	0.5036	625	0.5037	638
0.5392	535	0.5386	569	0.5385	613	0.5385	625
0.5871	516	0.5865	546	0.5863	584	0.5866	596
0.6312	488	0.6306	516	0.6304	552	0.6308	566
0.6715	459	0.6709	482	0.6708	516	0.6712	528
0.7081	420	0.7077	448	0.7075	479	0.7080	488
0.7414	386	0.7409	411	0.7408	439	0.7413	445
0.7713	352	0.7709	374	0.7707	401	0.7712	405
0.7981	322	0.7978	339	0.7977	364	0.7981	368
0.8222	292	0.8218	308	0.8217	329	0.8222	334
0.8436	262	0.8433	278	0.8432	296	0.8436	301
0.8626	234	0.8623	249	0.8622	265	0.8626	271
0.8794	210	0.8792	223	0.8791	238	0.8795	243
0.8944	189	0.8941	200	0.8941	214	0.8944	219
0.9075	169	0.9073	179	0.9072	193	0.9076	197
0.9191	151	0.9189	161	0.9189	173	0.9191	176
0.9293	134	0.9291	144	0.9291	156	0.9293	155
0.9382	118	0.9381	127	0.9380	138	0.9383	137
0.9461	104	0.9459	111	0.9459	121	0.9461	120
0.9529	91	0.9528	97	0.9528	106	0.9530	105

the aid of a burette into the cell (5) (volume 20 cm³) which also acts as stirrer; the other reagent is set in the Dewar vessel (approximate 120 cm³), both immersed in the thermostatic bath. Measurements are performed by depressing a push rod (6), which drops the content of the cell into the vessel. Under the stirring action of the rotating cell, the mixing proceeds to completion when the thermal equilibrium is reached. Temperature in the calorimeter is sensed by a thermistor (7) and read from a microprocessor (11) based thermometer which is built into the calorimeter case. An auxiliary potentiometric strip chart recorder connected to the thermometer produces a thermogram (8) (uncertainty $\pm 1\cdot 10^{-3}$ K) showing the temperature change in the calorimeter produced by the mixing of the components. The experimental H_m^E values were determined from the following equation

$$H_m^E = -\left(C_p + \frac{C_v}{n}\right)\Delta T$$

in which C_p, C_v, n, ΔT represent the molar heat capacity of the mixture, heat capacity of the calorimeter, temperature difference, due to mixing process, respectively,

Table 3 Experimental excess molar enthalpies H_m^E for acetonitrile+*s*-butylamine at four temperatures

x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}
$(1-x)$ CH_3CN+$x(C_2H_5)CH(NH_2)CH_3$							
288.15 K		293.15 K		298.15 K		303.15 K	
0.0253	56	0.0253	59	0.0253	65	0.0253	67
0.0505	110	0.0506	116	0.0505	125	0.0505	130
0.0757	162	0.0758	170	0.0757	182	0.0757	191
0.1007	209	0.1008	218	0.1007	233	0.1006	251
0.1255	249	0.1256	262	0.1255	279	0.1255	300
0.1723	333	0.1723	346	0.1721	365	0.1721	386
0.2183	400	0.2182	416	0.2180	442	0.2180	464
0.2633	454	0.2632	474	0.2630	497	0.2630	527
0.3073	491	0.3070	511	0.3068	535	0.3068	564
0.3499	520	0.3496	543	0.3494	562	0.3494	596
0.3911	536	0.3908	560	0.3905	579	0.3905	617
0.4308	545	0.4304	571	0.4302	589	0.4302	629
0.4689	552	0.4685	574	0.4683	592	0.4682	629
0.5053	549	0.5049	570	0.5047	589	0.5046	627
0.5400	544	0.5396	563	0.5393	581	0.5393	616
0.5877	527	0.5873	543	0.5870	559	0.5872	590
0.6316	499	0.6312	514	0.6310	531	0.6313	561
0.6718	468	0.6714	482	0.6712	500	0.6716	524
0.7084	435	0.7080	449	0.7079	465	0.7083	487
0.7416	401	0.7412	418	0.7410	431	0.7415	449
0.7715	366	0.7711	382	0.7710	395	0.7715	413
0.7983	332	0.7980	346	0.7978	361	0.7983	379
0.8223	298	0.8220	314	0.8219	330	0.8223	348
0.8437	268	0.8434	284	0.8433	298	0.8437	317
0.8627	240	0.8624	256	0.8623	270	0.8627	286
0.8795	216	0.8793	231	0.8792	244	0.8796	259
0.8944	193	0.8942	209	0.8941	221	0.8945	233
0.9075	173	0.9074	188	0,9073	200	0.9076	209
0.9191	154	0.9189	168	0.9189	180	0.9192	185
0.9293	135	0.9291	149	0.9291	161	0.9294	164
0.9382	119	0.9381	132	0.9381	143	0.9383	145
0.9461	104	0.9460	116	0.9459	125	0.9461	128
0.9529	91	0.9528	101	0.9528	109	0.9530	112

and n is the amount of substance (unit mol) of mixture in the Dewar flask after the mixture process. C_p and C_v are determined by reversal calorimetry using an electrical resistance (3) which supplies a certain amount of heat with uncertainty of $\pm 1\cdot 10^{-2}$ W. For the intermediary mixture compositions, it is not possible to determine H_m^E directly from pure reagents due to limited volume of the cell and vessel. Hence, a mixture is used in Dewar vessel whose H_m^E can be previously determined, and the value of H_m^E is calculated by

$$H_m^E = -\left(C_p + \frac{C_v}{n}\right)\Delta T + \frac{n_0}{n} H_{m_0}^E$$

where n_0 and $H_{m_0}^E$ are the amount of substance in the previous mixing process and its excess molar enthalpy inside the Dewar vessel respectively. Their values are zero when pure reagent is used. The mixtures were prepared volumetrically with an accuracy of $\pm 1\cdot 10^{-2}$ cm³ using burettes with 50 and 100 cm³. The relative uncertainty of H_m^E measurements is about 0.5% for the central composition range.

The measured H_m^E data for acetonitrile+diethylamine or *s*-butylamine mixtures as a function of the composition at 288.15, 293.15, 298.15 and 303.15 K at atmospheric pressure are shown in Tables 2 and 3.

Results and discussion

Testing systems

The performance of the calorimeter was tested by measuring H_m^E of the well-investigated systems ethanol+water and acetone+water at 298.15 K over the whole composition range. The data show good agreement with literature data reported by Lama, Lu [8], Boyne, Williamnson [9], Costigan *et al.* [10], French [11], Coomber, Wormald [12] and Piñheiro *et al.* [13].

The experimental results were correlated by the Redlich–Kister type equation:

$$H_m^E = x(1-x)\sum_{i}^{4} A_j (1-2x)^i$$

The parameters A_j were obtained using the method of least squares and are given in Table 4, along with the standard deviations determined from

$$\sigma = [\sum (H_{m_{\mathrm{exp\,er}}}^E - H_{m_{\mathrm{calc}}}^E)^2 / (N-k)]^{1/2}$$

where N is the number of data points and k is the order of the fitting polynomial.

A comparison with literature data [6] can be made for the system acetonitrile+*s*-butylamine at 303.15 K. Our H_m^E values, at the whole composition range, are greater than values reported by Pathak *et al.* [6] (for the composition range of *s*-butylamine 0.35 to 0.60 a maximum deviation of +150 J mol^{-1} at x=0.47 has been found, which corresponds approximately to +30% of Pathak's H_m^E value at this composition). We cannot explain this large discrepancy. A systematic error in our measurements is unlikely in view of the good agreement between our data and literature data for two test systems.

The experimental H_m^E values was correlated by means of the ERAS-Model proposed by Heintz [14]. The following equations hold for the studied systems

$$H_m^E = H_{m_{\mathrm{Phys}}}^E + H_{m_{\mathrm{Chem}}}^E$$

with

$$h_{\mathrm{phys}}^E = (x_A V_A^* + x_B V_B^*)\left(\frac{\Phi_A p_A^*}{\tilde{V}_A} + \frac{\Phi_B p_B^*}{\tilde{V}_B} - \frac{p_M^*}{\tilde{V}_M}\right),$$

$$\begin{aligned} h_{\mathrm{chem}}^E &= x_A K_A \Delta h_A^* \tilde{V}_M (\varphi_{A1} - \varphi_{A1}^0) + \\ &+ x_B K_B \Delta h_B^* \tilde{V}_M (\varphi_{B1} - \varphi_{B1}^0) + \\ &+ x_{AB} K_{AB} \Delta h_{AB}^* \tilde{V}_M \frac{\phi_{B1}(1 - K_A \phi_{A1})}{(V_A / V_B)(1 - K_B \phi_{B1}) + K_{AB}\phi_{AB1}} - \\ &- \frac{p_M^* V_{\mathrm{chem}}^E}{\tilde{V}_M^2} \end{aligned}$$

and

$$\begin{aligned} V_{\mathrm{chem}}^E &= x_A K_A \Delta v_A^* \tilde{V}_M (\varphi_{A1} - \varphi_{A1}^0) + \\ &+ x_B K_B \Delta v_B^* \tilde{V}_M (\varphi_{B1} - \varphi_{B1}^0) + \\ &+ x_A K_{AB} \Delta v_{AB}^* \tilde{V}_M \frac{\phi_{B1}(1 - K_A \phi_{A1})}{(V_A / V_B)(1 - K_B \phi_{B1}) + K_{AB}\phi_{B1}} \end{aligned}$$

According to literature [15–16] the self-association of acetonitrile was neglected. The value of $\tilde{V}_M$ is obtained by solution of the equation

$$T_M^* = T_M \frac{\tilde{V}_M^{4/3}}{(\tilde{V}_M^{1/3} - 1)}$$

with

$$T_M^* = \frac{p_M^*}{\frac{p_A^* \Phi_A}{T_A^*} + \frac{p_B^* \Phi_B}{T_B^*}}$$

and

$$p_M^* = p_A^* \Phi_A + p_B^* \Phi_B - \Phi_A \Theta_B \chi_{AB}$$

with the hard-core volume fractions defined by

$$\phi_A = \frac{x_A V_A^*}{x_A V_A^* + x_B V_B^*} = 1 - \phi_B$$

The molecular surface fraction is given by

$$\theta_B = 1 - \theta_A = \frac{\left(\frac{S_B}{S_A}\right)\phi_B}{\left(\frac{S_B}{S_A}\right)\phi_B + \phi_A}$$

A detailed description of calculation procedure is given in [14].

Table 4 Coefficients A_j for fitting Eq. (2) and the standard deviation σ

T/K	A_0	A_1	A_2	A_3	A_4	σ/J mol^{-1}
			$x(C_2H_5)_2NH+(1–x)CH_3CN$			
288.15	2208.3	598.5	399.5	–127.3	–121.7	±2.28
293.15	2332.9	602.5	328.3	–208.3	–108.9	±2.58
298.15	2447.6	655.3	221.8	–349.0	–52.4	±2.60
303.15	2565.4	655.3	154.8	–333.8	9.8	±2.42
			$x(C_2H_5)CH(NH_2)CH_3+(1–x)CH_3CN$			
288.15	2228.5	242.9	13.6	–155.3	–93.9	±2.53
293.15	2317.0	315.1	–10.4	–344.5	68.7	±2.18
298.15	2389.4	365.0	93.0	–386.0	120.5	±2.80
303.15	2534.8	417.1	24.3	–428.3	182.2	±2.14

Table 5 Association constant K, surface volume ratio S, molar volume V_m, isothermal compressibility κ, thermal expansion coefficient α, molar enthalpy of association Δh^* and molar volume of association Δv^* for the pure components in the temperature range studied

Component	T/K	K^a	S^d/ nm^{-1}	V_m/ cm^3 mol^{-1}	κ^b/ 10^4 Mpa^{-1}	α^b/ *10^4 K^{-1}	$-\Delta h^{*c}$/ kJ.mol^{-1}	$-Dv^{*c}$/ cm^3 mol^{-1}
acetonitrile	288.15	–	15.19	52.08	9.76	13.53	–	–
	293.15	–	15.19	52.45	10.23	13.60	–	–
	298.15	–	15.19	52.78	10.70	13.68	–	–
	303.15	–	15.19	53.20	11.17	13.75	–	–
diethylamine	288.15	6.56	14.19	102.88	13.27	15.10	8.50	4.70
	293.15	6.35	14.19	103.69	13.99	15.20	8.50	4.70
	298.15	6.16	14.19	104.42	14.71	15.30	8.50	4.70
	303.15	5.97	14.19	105.26	15.49	15.40	8.50	4.70
s-butylamine	288.15	10.72	14.41	100.19	14.14	13.04	13.20	2.80
	293.15	10.26	14.41	101.01	15.02	13.07	13.20	2.80
	298.15	9.86	14.41	101.81	15.90	13.11	13.20	2.80
	303.15	9.46	14.41	102.62	16.78	13.14	13.20	2.80

[a]Calculated from [17], [b]from [1], [c]from [5] and [d]from [18].

The values of parameters of the pure components used in the calculations are given in Table 5. Figures 1 and 2 show the composition dependence of H_m^E for the mixtures. Dashed lines represent calculated results obtained from ERAS-Model. The results of the calculation are shown in Table 6. The agreement between theoretical values using the ERAS-Model and the experimental values obtained in this work at all temperatures is excellent.

The curves of H_m^E plotted against the mole fraction show positive values over the whole composition range in the temperature range studied H_m^E values increase with increasing temperature probably indicating weakening of cross-association between amine and acetonitrile molecules. Owing to the presence of isomers in the two systems, the H_m^E curves exhibit a similar behavior, the main difference lying in the acetonitrile-rich region.

The excess enthalpy behavior has a parabolic form for all the systems studied with maximum values around the mol fraction 0.43 for mixtures containing diethylamine (at temperatures 288.15, 293.15, 298.15 and 303.15 K, the maximum H_m^E values are 561, 590, 620 and 649 J mol^{-1}, respectively) and 0.47 for mixtures containing *s*-butylamine (at temperatures 288.15, 293.15, 298.15 and 303.15 K, the maximum H_m^E values are 557, 580, 598 and 636 J mol^{-1}, respectively).

The results can be interpreted in terms of physical and chemical interactions between the molecules:

- physical interactions consisting mainly of dispersion, dipole-dipole and induction forces making a positive contribution to H_m^E values, and

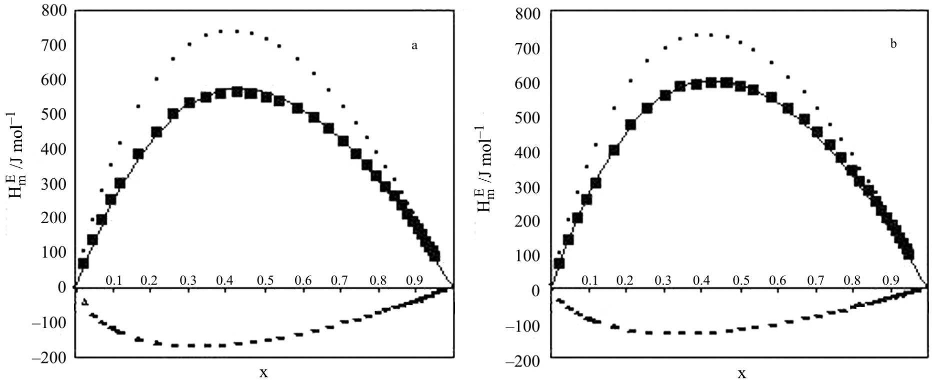
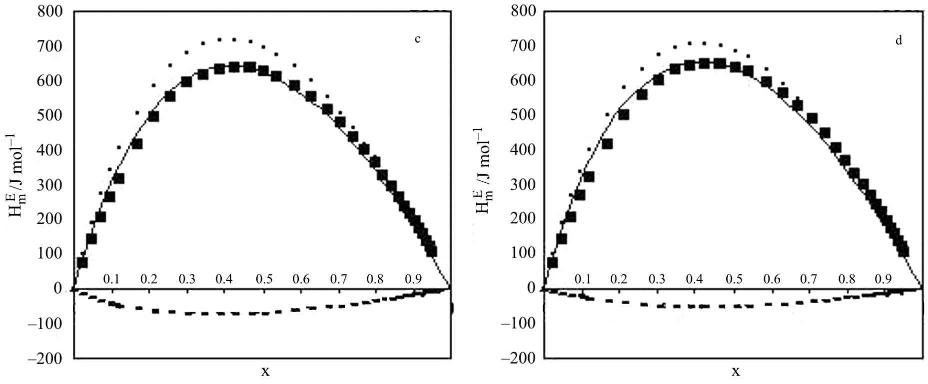

Fig. 2 Values of H_m^E as function of the mole fraction of amine(x) for (acetonitrile + diethylamine) mixtures at a – 288.15, b – 293.15, c – 298.15 and d – 303.15 K, respectively. ■ – experimental, —— – ERAS-Model, – – – chemical contribution and ····· – physical contribution

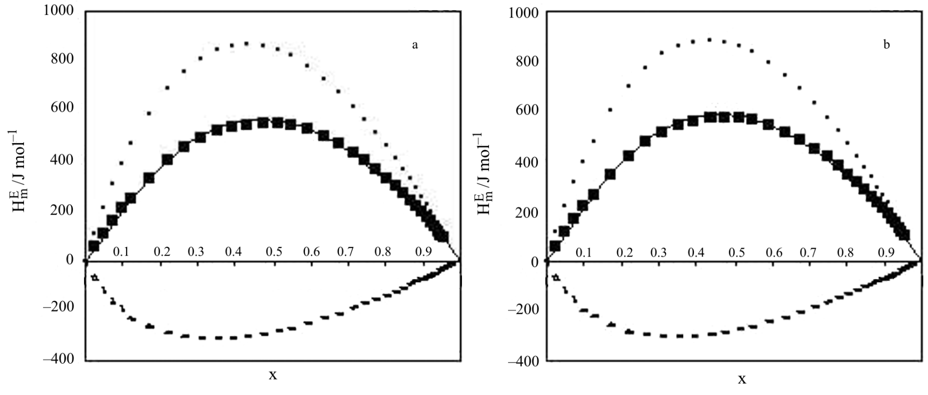
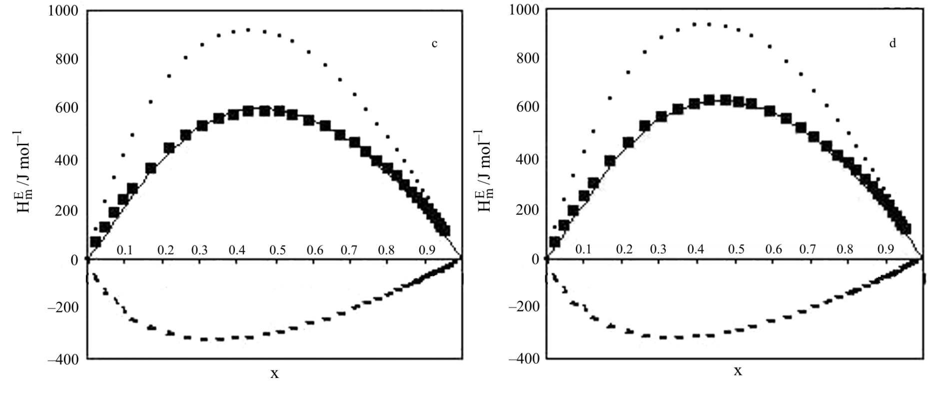

Fig. 3 Values of H_m^E as function of the mole fraction of amine(x) for (acetonitrile + *s*-butylamine) mixtures at a – 288.15, b – 293.15, c – 298.15 and d – 303.15 K, respectively. ■ – experimental, —— – ERAS-Model, – – – chemical contribution and ····· – physical contribution

Table 6 Optimized ERAS-Model parameters in the temperature range studied

System	T/K	χ_{AB}/J cm^{-3}	K_{AB}	$-\Delta h_{AB}$/kJ mol^{-1}	$-\Delta v_{AB}$/cm^3 mol^{-1}
$x(C_2H_5)_2NH+(1-x)CH_3CN$	288.15	65	2.920	4.05	3.17
	293.15	64	2.840	3.95	3.43
	298.15	63	2.765	3.65	3.63
	303.15	62	2.695	2.60	3.82
$x(C_2H_5)CH(NH_2)CH_3+(1-x)CH_3CN$	288.15	90	1.700	8.50	1.48
	293.15	89	1.610	8.35	1.77
	298.15	88	1.523	8.30	2.09
	303.15	87	1.435	8.05	2.36

- chemical contributions consisting of self-association of the amines resulting in a positive contribution to H_m^E results and cross-association of the components resulting in a negative contribution to H_m^E values.

Since the H_m^E values are typically positive, physical interactions are probably dominant. This is in agreement with the interpretation of the results in terms of intermolecular forces.

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