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MEASUREMENTS OF EXCESS MOLAR ENTHALPY AND EXCESS MOLAR HEAT CAPACITY OF (1-HEPTANOL OR 1-OCTANOL)+ (DIETHYLAMINE OR *S*-BUTYLAMINE) MIXTURES AT 298.15 K AND 0.1 MPA

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Experimental data of excess molar enthalpy (H_m^E) and excess molar heat capacity (C_{pm}^E) of binary mixtures containing (1-heptanol or 1-octanol)+(diethylamine or *s*-butylamine) have been determined as a function of composition at 298.15 K and at 0.1 MPa using a modified 1455 Parr solution calorimeter. The excess molar enthalpy data are negative and show parabolic format over the whole composition range; however, the excess molar heat capacity values, whose curves show a S-shape, are positive in the 0.0 to 0.7 molar fraction range and negative between the molar fraction values 0.7 to 1.0. The applicability of the ERAS-model to correlate the excess molar enthalpy data was tested. The calculated data values are in good agreement with the experimental ones. The experimental behavior of H_m^E is interpreted in terms of specific interactions between 1-alkanol and amine molecules.

Keywords: *1-alkanols, amines, correlation, excess properties*

Introduction

Several experimental studies on excess molar functions of binary liquid mixtures containing 1-alkanols or amines have been performed to understand the molecular interactions between these compounds in the solution, as well as to test the applicability of models of solutions: Reimann–Heintz [1] and Funke *et al.* [2] (both studied V_m^E and H_m^E of solutions containing 1-alkanol+amine), Mateolli *et al.* [3] (H_m^E of solutions containing *n*-heptane+amine), Pina–Francesconi [4], Torres–Francesconi [5], Torres *et al.* [6–7] (both studied V_m^E of solutions containing acetonitrile+1-alkanols), Gonzales *et al.* [8] (G_m^E and V_m^E of solutions containing 1-alkanols+primary or secondary amines), Torres–Francesconi [9] (V_m^E of solutions containing acetonitrile+amines), Torres *et al.* [10] (V_m^E of solutions containing acetonitrile+1-alkanols), Checoni–Francesconi [11] (H_m^E of solutions containing acetonitrile+amines), Checoni *et al.* [12], Galvão–Francesconi [13], (both studied H_m^E of solutions containing acetonitrile+1-alkanols). Kinart *et al.* [14] studied the excess molar volumes and the relative permittivities of binary solutions containing 2-methoxyethanol+(diethylamine or triethylamine) at various temperatures. Piñeiro *et al.* [15] calculated the excess molar enthalpy values for ternary liquid mixtures containing 1-propanol+3-pentanone+(*n*-hexane to *n*-octane, or 1-hexanol, or 1-heptanol) using several predictive methods [15]. Kimura *et al.* [16] studied the effect caused on the hydration Gibbs energy as well as the effects on the enthalpy, Gibbs energy and entropy of inclusion due to addition of the aliphatic 1-alkanols and butanediols on the aqueous solutions containing α-cyclodextrin. Besides V_m^E and H_m^E, another excess function of importance is the excess molar heat capacity (C_{pm}^E). According to Tamura [17] and Nashimoto *et al.* [18], experimental data of C_{pm}^E are also very important to describe the effects that molecular orientations exert on the structure of liquid mixtures. Checoni–Francesconi [19] studied the C_{pm}^E behavior of mixtures containing acetonitrile+amines and showed the influence of the intensity of the H_m^E values on the C_{pm}^E curves format.

In this work, excess molar enthalpy (H_m^E) and excess molar heat capacity (C_{pm}^E) of the binary systems (1-heptanol or 1-octanol)+diethylamine and (1-heptanol+1-octanol)+sec-butylamine have been determined as function of composition at 298.15 K and at 0.1 MPa using a solution calorimeter. The experimental results of H_m^E and C_{pm}^E were correlated by Redlich–Kister equation. The extended real association solution model (ERAS-model) [20] was used to correlate the experimental data of excess molar enthalpy. The experimental H_m^E behavior can be interpreted in terms of physical and specific interactions.

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Experimental

The reagents 1-heptanol and 1-octanol were supplied by (Avocado Research Chemicals, purity>99 mol%) and (Aldrich, purity>99.5 mol%), respectively; both were used without previous purification. Diethylamine and *s*-butylamine (Acros Organics, purity>99 mol%) was dried over molecular sieves (3 Å). To check the purity of the substances, density and refractive index measurements were performed at 293.15 K and at 0.1 MPa, whose values are showed in Table 1.

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

Compound	ρ/g cm^{-3}		n_D	
	literature[a]	measured	literature[a]	measured
1-heptanol	0.8224	0.8223	1.4249	1.4245
1-octanol	0.8253	0.8258	1.4295	1.4293
diethylamine	0.7056	0.7057	1.3864	1.3862
s-butylamine	0.7246	0.7247	1.3932	1.3934

[a]Obtained from [21]

Excess molar enthalpy and excess molar heat capacity measurements were performed using a Parr 1455 solution calorimeter with some improvements. A detailed description and performance testing of the apparatus as well as the experimental procedure are given elsewhere [11]. From pure compounds, the experimental $H^{\mathrm{E}}_{\mathrm{m}}$ values were determined from the following equation

$$H^{\mathrm{E}}_{\mathrm{m}} = \left(C_{\mathrm{pm}} + \frac{C_{\mathrm{v}}}{n}\right)\Delta T \qquad (1)$$

in which C_{pm}, C_{v}, n, ΔT represent the molar heat capacity of the mixture, heat capacity of the calorimeter, amount of mixture (mol) and temperature difference due to mixing process, respectively. For the intermediary mixture compositions, it is not possible to determine $H^{\mathrm{E}}_{\mathrm{m}}$ directly from pure reagents due to volumetric limitation of apparatus. Hence, a mixture is used, whose $H^{\mathrm{E}}_{\mathrm{m0}}$ is previously determined and the value of $H^{\mathrm{E}}_{\mathrm{m}}$ can be calculated by

$$H^{\mathrm{E}}_{\mathrm{m}} = \left(C_{\mathrm{pm}} + \frac{C_{\mathrm{v}}}{n}\right)\Delta T + \frac{n_0}{n}H^{\mathrm{E}}_{\mathrm{m}_0} \qquad (2)$$

wherein n_0 is the amount of mixture in the previous mixing process. Both n_0 and $H^{\mathrm{E}}_{\mathrm{m0}}$ values are zero when pure reagent is used. The mixtures were prepared volumetrically with an accuracy of ±5·10^{-1} cm^3 using burettes with 50 and 100 cm^3.

The quantity C_{v} is determined by reversal calorimetry, with the actuation of resistance wire, which supplies a certain amount of heat (with uncertainty of ±1·10^{-2} W) to pure compounds 1-alkanols and amines, whose mass and heat capacity (C_{pi}) are known; so, ΔT_1 and ΔT_2 values are determined; with these values it is possible to solve the equations system below and to obtain the Q and C_{v} values at experiment temperature.

$$Q = (n_1 C_{\mathrm{p1}} + C_{\mathrm{v}})\Delta T_1 \qquad (3)$$

$$Q = (n_2 C_{\mathrm{p2}} + C_{\mathrm{v}})\Delta T_2 \qquad (4)$$

The molar heat capacity of the mixture (C_{pm}) is determined by reversal calorimetry, now supplying an amount of heat to the mixture. The expression used to calculate C_{pm} is

$$C_{\mathrm{pm}} = \left(\frac{Q}{\Delta T_{\mathrm{sol}}} - C_{\mathrm{v}}\right)\frac{1}{n_{\mathrm{s}}} \qquad (5)$$

wherein n_{s} is the molar quantity of the mixture and ΔT_{sol} is the temperature variation due to heat supplied to the mixture. For the determination of the experimental data of $C^{\mathrm{E}}_{\mathrm{pm}}$ is necessary, besides the C_{pm} value, to determinate the value of the molar heat capacities of ideal solution ($C^{\mathrm{ideal}}_{\mathrm{pm}}$)

$$C^{\mathrm{ideal}}_{\mathrm{pm}} = x_1 C_{\mathrm{p1}} + x_2 C_{\mathrm{p2}} \qquad (6)$$

wherein x_1 and x_2 are the molar fraction of 1-alkanols and amines, respectively, and C_{pi} values of these components are: 1-heptanol – 271.2 J mol^{-1} K^{-1} [21], 1-octanol – 305.2 J mol^{-1} K^{-1} [21], diethylamine – 169.2 J mol^{-1} K^{-1} [21] and *s*-butylamine 174.0 J mol^{-1} K^{-1} [19], both at 298.15 K and 0.1 MPa. Finally, it is possible to calculate the experimental value of $C^{\mathrm{E}}_{\mathrm{pm}}$

$$C^{\mathrm{E}}_{\mathrm{pm}} = C_{\mathrm{pm}} - C^{\mathrm{ideal}}_{\mathrm{pm}} \qquad (7)$$

The estimated uncertainty in molar fraction is ±9·10^{-4}; for excess molar enthalpy measurements the estimated uncertainties are: ±1.5·10^{-2} $H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1}) for 0.05 to 0.16 and 0.91 to 1.00 molar fraction ranges and 2.0·10^{-2} $H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1}) for 0.17 to 0.90 molar fraction range; for excess molar heat capacity measurements, the estimated uncertainties are: ±2.2·10^{-1} $C^{\mathrm{E}}_{\mathrm{pm}}$ (J mol^{-1} K^{-1}) for 0.05 to 0.16 molar fraction range, ±1.8·10^{-1} $C^{\mathrm{E}}_{\mathrm{pm}}$ (J mol^{-1} K^{-1}) for 0.17 to 0.50 molar fraction range, 7.5·10^{-1} $C^{\mathrm{E}}_{\mathrm{pm}}$ (J mol^{-1} K^{-1}) for 0.73 to 0.90 molar fraction range and 1.2 $C^{\mathrm{E}}_{\mathrm{pm}}$ (J mol^{-1} K^{-1}) for 0.91 to 1.00 molar fraction range.

Results and discussion

The performance of the apparatus was tested by measuring excess molar enthalpy of the well-investigated system ethanol+water at 298.15 K over the whole composition range. The data show good agreement with H_m^E literature data reported by Lama–Lu [22], Boyne–Williamson [23] and Costigan *et al.* [24]; the average standard deviation between literature and measured H_m^E data is ±4.45 J mol^{-1}. The measured H_m^E data for (1-heptanol or 1-octanol)+(diethylamine or *s*-butylamine) mixtures as a function of the composition at 298.15 K at 0.1 MPa are shown in Table 2. Both H_m^E and C_{pm}^E experimental results were correlated by the Redlich–Kister type equation

$$X_m^E = x(1-x)\sum_{i=0}^{4} A_j (1-2x)^i \tag{8}$$

wherein X represents H or C_p. The parameters A_j were obtained using the method of least squares and are given in Table 3, along with the standard deviations determined from

$$\delta = [\Sigma(X_{m_{exper}}^E - X_{m_{calc}}^E)^2/(N-k)]^{0.5} \tag{9}$$

in which N is the number of data points and k is the number of the adjusted parameters of Eq. (8).

Experimental H_m^E values were correlated by means of the ERAS-model [20]; this model describes the excess molar enthalpy as the sum of a physical contribution and a chemical contribution

$$H_m^E = H_{m_{Phys}}^E + H_{m_{Chem}}^E \tag{10}$$

which are given, respectively, by

$$H_{phys}^E = (x_1V_1^* + x_2V_2^*)\left(\frac{\phi_1P_1^*}{\tilde{V}_1} + \frac{\phi_2P_2^*}{\tilde{V}_2} - \frac{P_M^*}{\tilde{V}_M}\right) \tag{11}$$

$$\begin{aligned} H_{chem}^E &= x_1K_1\Delta h_1^*(\varphi_{11}-\varphi_{11}^0) + x_2K_2\Delta h_2^*(\varphi_{21}-\varphi_{21}^0) + \\ &+ x_1K_{12}\Delta h_{12}^*\frac{\varphi_{21}(1-K_1\varphi_{11})}{(V_1/V_2)(1-K_2\varphi_{21})+K_{12}\varphi_{21}} - \\ &- \frac{P_M^*V_{chem}^E}{\tilde{V}_M^2} \end{aligned} \tag{12}$$

$$\begin{aligned} V_{chem}^E &= x_1K_1\Delta v_1^*\tilde{V}_M(\varphi_{11}-\varphi_{11}^0) + x_2K_2\Delta v_2^*\tilde{V}_M(\varphi_{21}-\varphi_{21}^0) + \\ &+ x_1K_{12}\Delta v_{12}^*\tilde{V}_M\frac{\varphi_{21}(1-K_1\varphi_{11})}{(V_1/V_2)(1-K_2\varphi_{21})+K_{12}\varphi_{21}} \end{aligned} \tag{13}$$

Table 2 Experimental excess molar enthalpy (H_m^E) for (1-heptanol or 1-octanol) (x)+(diethylamine or *s*-butylamine)(1–x) at 298.15 K and 0.1 MPa

x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}	x_1	H_m^E/J mol^{-1}
1-heptanol+diethylamine		1-octanol+diethylamine		1-heptanol+*s*-butylamine		1-octanol+*s*-butylamine	
0.0825	–556	0.0743	–558	0.0743	–598	0.0826	–592
0.1616	–1054	0.1467	–1067	0.1467	–1172	0.1618	–1153
0.2367	–1486	0.2168	–1515	0.2168	–1683	0.2370	–1646
0.3076	–1823	0.2839	–1873	0.2839	–2101	0.3080	–2042
0.3741	–2091	0.3479	–2163	0.3479	–2365	0.3745	–2282
0.4360	–2270	0.4082	–2364	0.4082	–2523	0.4364	–2418
0.4933	–2347	0.4648	–2486	0.4648	–2587	0.4937	–2462
0.5659	–2329	0.5176	–2531	0.5176	–2571	0.5464	–2430
0.5942	–2295	0.5664	–2507	0.5704	–2491	0.5934	–2368
0.6381	–2195	0.6114	–2425	0.6154	–2398	0.6339	–2288
0.6779	–2076	0.6526	–2299	0.6558	–2292	0.6747	–2177
0.7139	–1950	0.6901	–2152	0.6927	–2174	0.7114	–2064
0.7463	–1827	0.7242	–1986	0.7262	–2050	0.7444	–1952
0.7854	–1672	0.7549	–1826	0.7565	–1910	0.7739	–1833
0.8014	–1578	0.7826	–1671	0.7839	–1768	0.8003	–1715
0.8246	–1456	0.8075	–1526	0.8085	–1642	0.8238	–1598
0.8453	–1334	0.8298	–1391	0.8306	–1510	0.8447	–1492
0.8636	–1225	0.8497	–1266	0.8503	–1386	0.8632	–1388
0.8799	–1124	0.8674	–1151	0.8678	–1273	0.8796	–1267
0.8944	–1030	0.8831	–1048	0.8835	–1165	0.8941	–1149
0.9071	–944	0.8970	–956	0.8973	–1067	0.9069	–1043
0.9184	–851	0.9094	–878	0.9096	–978	0.9183	–949
0.9283	–773	0.9203	–789	0.9205	–898	0.9282	–863
0.9371	–703	0.9300	–730	0.9301	–819	0.9370	–779

Table 3 Coefficients A_j for fitting Eq. (8) for (H_m^E and C_{pm}^E) and the standard deviation σ (Eq. (9))

	Excess molar enthalpy (H_m^E)					
	A_0/J mol^{-1}	A_1/J mol^{-1}	A_2/J mol^{-1}	A_3/J mol^{-1}	A_4/J mol^{-1}	σ/J mol^{-1}
1-heptanol+diethylamine	–9393.5	931.7	2757.1	1965.6	–3985.4	8.3
1-octanol+diethylamine	–10343.2	–841.3	824.1	4005.1	–1193.1	12.4
1-heptanol+*s*-butylamine	–10136.3	762.2	3886.7	682.8	–4288.8	17.3
1-octanol+*s*-butylamine	–9829.5	–61.9	681.0	4432.6	–1741.9	7.5
	Excess molar heat capacity (C_{pm}^E)					
	A_0/J mol^{-1} K^{-1}	A_1/J mol^{-1} K^{-1}	A_2/J mol^{-1} K^{-1}	A_3/J mol^{-1} K^{-1}	A_4/J mol^{-1} K^{-1}	σ/J mol^{-1} K^{-1}
1-heptanol+diethylamine	42.9	94.1	–70.2	–62.1	50.2	0.35
1-octanol+diethylamine	53.6	62.4	–120.6	15.5	139.8	0.51
1-heptanol+*s*-butylamine	45.8	77.5	–63.3	–39.4	40.8	0.41
1-octanol+*s*-butylamine	43.2	83.2	–63.6	–32.4	58.4	0.29

Table 4 Association constant K, molar volume V_i, characteristic volume V^*, reduced volume $\tilde{V}$, surface volume ratio S, isothermal compressibility κ_i, thermal expansion coefficient α_i, characteristic pressure P^*, characteristic temperature T^*, molar enthalpy of association Δh_i^* and molar volume of association Δv_i^* for the pure compounds at 298.15 K

Compound	K_i^a	V_i/ cm^3 mol^{-1}	V^*/ cm^3 mol^{-1}	$\tilde{V}$	S_i/^{b} nm^{-1}	$10^4\alpha_i$/ K$^{-1\,b}$	$10^4\kappa_i$/ MPa$^{-1\,b}$	P^*/ J cm^{-3}	T^*/K	$-\Delta h_i^*$/^{a} kJ mol^{-1}	$-\Delta v_i^*$/^{c} cm^3 mol^{-1}
1-heptanol	69.04	141.80	119.99	1.18189	13.09	7.60	8.20	407.01	6503.48	18.99	5.60
1-octanol	51.27	158.09	131.51	1.20223	12.65	8.52	7.75	440.41	6021.47	18.85	5.60
diethylamine	6.16	104.42	78.05	1.33851	14.19	15.30	14.71	356.00	4611.37	8.50	4.70
s-butylamine	9.86	101.81	77.94	1.30184	13.09	13.11	15.90	543.20	4309.09	13.20	2.80

[a][28], [b][11] and [c][10]

Table 5 Optimized ERAS-model parameters as well as average absolute deviations (AAD) and relative deviations (RD)

Compound	K_{12}	χ_{12}/J cm^{-3}	$-\Delta h_{12}$/kJ mol^{-1}	$-\Delta v_{12}$/cm^3 mol^{-1}	AAD/J mol^{-1}	RD/%
1-heptanol+diethylamine	273.0	9.0	34.4	32.0	118.1	7.1
1-octanol+diethylamine	494.6	6.1	33.3	26.3	136.5	7.5
1-heptanol+*s*-butylamine	446.8	16.9	38.3	35.6	154.6	6.7
1-octanol+*s*-butylamine	500.0	12.3	38.1	32.5	73.5	5.1

Volumetric fractions of the monomers φ_{i1} are calculated by resolution of the following two equations system:

$$\varphi_1 = \frac{\varphi_{11}}{(1-K_1\varphi_{11})^2}\left[1+\frac{V_1K_{12}\varphi_{21}}{V_2(1-K_2\varphi_{21})}\right] \quad (14)$$

$$\varphi_2 = \frac{\varphi_{21}}{(1-K_2\varphi_{21})^2}\left[1+\frac{K_{12}\varphi_{11}}{(1-K_1\varphi_{11})}\right] \quad (15)$$

with φ_{11} equal to φ_{11}^0 if Φ_1=1 and φ_{21} equal to φ_{21}^0 if Φ_2=1; ϕ_i values are obtained by

$$\varphi_1 = 1-\varphi_2 = \frac{x_1V_1^*}{x_1V_1^*+x_2V_2^*} \quad (16)$$

The characteristic parameters V_1^* and P_1^* are obtained from experimental data of the molar volume V_i, thermal expansion coefficient (α_i) and isothermal compressibility κ_i of the pure compounds. Pure compounds parameters used in the calculations are presented in Table 4. Molar volume of pure compounds V_i were obtained experimentally using a vibrating tube densimeter (Anton Paar 4500). Cross-association equilibrium constant K_{12}, molar enthalpy of cross-association Δh_{12}^*, molar volume of cross-association Δv_{12}^*, showed in Eqs (7) and (8) and Flory's parameter χ_{12} [25], used to calculate the characteristic pressure of mixture by

$$P_M^* = P_1^*\phi_1 + P_2^*\phi_2 - \phi_1\Theta_2\chi_{12} \quad (17)$$

are the adjustable parameters of ERAS-model. The molecular surface fraction Θ_2 of component 2 is obtained by

$$\Theta_2 = 1-\Theta_1 = \frac{(S_2/S_1)\phi_2}{(S_2/S_1)\phi_2+\phi_1} \qquad (18)$$

in which S_i is the surface volume ratio of the pure compounds. A detailed description of the calculation procedure is given in [12]. Adjustable parameters values are showed in Table 5 along with the average absolute deviations (AAD) and relative deviations (RD). AAD values are calculated by Eq. (4) with one difference: K, in this case, is equal to 4; RD values are obtained by

$$\mathrm{RD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{H^{E}_{\mathrm{iexp}}-H^{E}_{\mathrm{ERAS}}}{H^{E}_{\mathrm{iexp}}}\right| \qquad (19)$$

wherein H^{E}_{ERAS} is excess molar enthalpy calculated using ERAS-model. Adjustable parameters of this model were adjusted to experimental H^{E}_{m} data using sequential search technique proposed by Rosenbrock [26], whose description of calculation routine is given in [27].

Figure 1 represents the composition dependence of experimental data of H^{E}_{m} for 1-alkanols+amines mixtures at 298.15 K. The values of H^{E}_{m} are large and negative over the whole composition range and have a parabolic form. For 1-alkanols+diethylamine mixtures is observed an increase of the H^{E}_{m} value with 1-alkanol chain length; however, for 1-alkanols+*s*-butylamine mixtures, H^{E}_{m} decreases with 1-alkanol chain length. Maximum values for H^{E}_{m} are: 1-heptanol+diethylamine (–2355 J mol^{-1} at x=0.5250), 1-octanol+diethylamine (–2563 J mol^{-1} at x=0.5250), 1-heptanol+*s*-butylamine (–2587 J mol^{-1} at x=0.4648) and 1-octanol+*s*-butylamine (–2472 J mol^{-1} at x=0.4937); these values were obtained using the Eq. (8).

The magnitude of H^{E}_{m} can be interpreted as the result of different effects which may be divided into physical and chemical contributions. Physical contributions involving nonspecific interactions such dipole-dipole and dispersion forces between 1-alkanols amines contribute positively to H^{E}_{m}; destruction of the dipole–dipole interactions as well as destruction of intermolecular hydrogen bond in these pure compounds on mixing also give a positive contribution to H^{E}_{m}. Besides this, there is a chemical contribution due to formation of the unlike intermolecular hydrogen bond between 1-alkanols and amines [2]. This specific interaction contributes negatively to H^{E}_{m}. Due to the large negative values of excess molar enthalpy data (Fig. 1), probably the chemical contribution is dominant for the studied mixtures, since the assumption of strong hydrogen bonding effects between the unlike molecules is associated to this contribution.

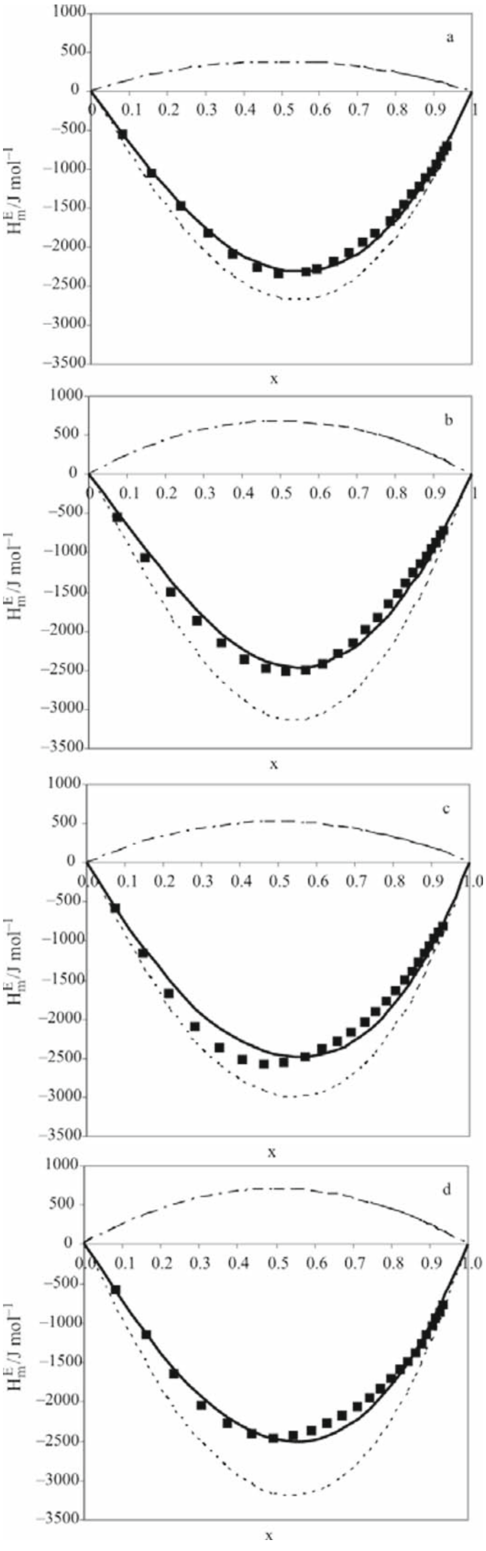

Fig. 1 Values of H^{E}_{m} as function of the mole fraction of 1-alkanol for a – (x)1-heptanol+(1–x)diethylamine, b – (x)1-octanol+diethylamine(1–x), c – (x)1-heptanol+(1–x) *s*-butylamine and d – (x)1-octanol+(1–x) *s*-butylamine, respectively, at 298.15 K and at 0.1 MPa: ■ – experimental, —– ERAS-model, – – – – physical contribution and --- – chemical contribution

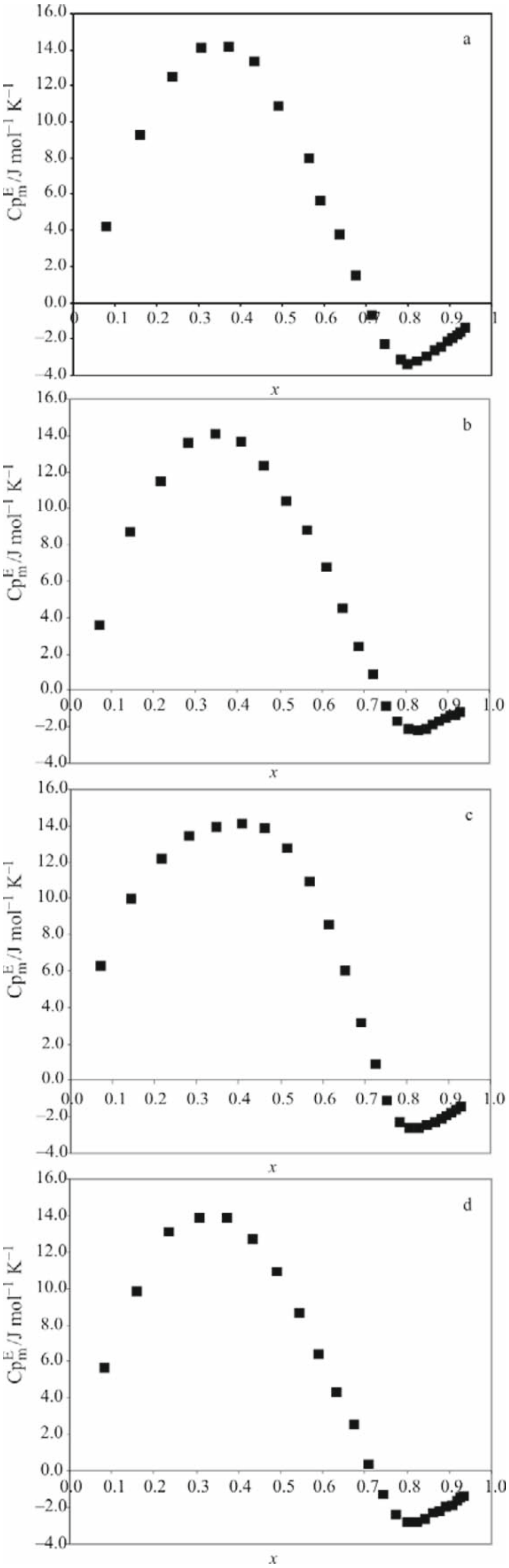

Fig. 2 Experimental values of $Cp^{\mathrm{E}}_{\mathrm{m}}$ as function of the mole fraction of 1-alkanol for a – (*x*)1-heptanol+(1–*x*) diethylamine, b – (*x*)1-octanol+diethylamine(1–*x*), c – (*x*)1-heptanol+(1–*x*)*s*-butylamine and d – (*x*)1-octanol+(1–*x*)*s*-butylamine, respectively, at 298.15 K and at 0.1 MPa

The results obtained from the ERAS-model as well as its physical and chemical contributions are also presented in Fig. 1. The physical contribution is small and positive in all mixtures; chemical contributions are dominant and take on negative values. Agreement between experimental and calculated data of $H^{\mathrm{E}}_{\mathrm{m}}$ is good. The adjustable parameters calculated in present work show good agreement with those calculated by Reimann–Heintz [1] and Funke *et al.* [2] for mixtures containing 1-alkanols+amines. According to Funke *et al.* [2], the ERAS-model is close to the physical reality and its adjustable parameters have a certain physical meaning, especially in the mixtures containing 1-alkanols+amines; this information is observed in present work: cross-association constants are higher than association constants and strong negative values of $H^{\mathrm{E}}_{\mathrm{m}}$ requires values for Δh^{*}_{12} and Δv^{*}_{12} more negative that those for molar enthalpy association and molar volume association of 1-alkanols and amines (Table 4). These results indicate that the NH-group is a weaker proton donator than the OH-group [2] as well as suggest that the free electron pair located at the N-atom has a higher polarizability, actuating as a more efficient proton OH•••N group than the OH group itself.

Figure 2 shows the experimental $C^{\mathrm{E}}_{\mathrm{pm}}$ behavior for the (1-heptanol or 1-octanol)+(diethylamine or *s*-butylamine) mixtures. In all curves it is observed the following characteristic: in the molar fraction range of 1-alkanol $0.0<x<0.7$, $C^{\mathrm{E}}_{\mathrm{pm}}$ values are positive and for $0.7<x<1.0$ range, $C^{\mathrm{E}}_{\mathrm{pm}}$ values are negative.

According to Saint-Victor and Patterson [29], Andreoli-Ball *et al.* [30] and Troncoso *et al.* [31] it is possible to establish a relation between the experimental data of $H^{\mathrm{E}}_{\mathrm{m}}$ and $C^{\mathrm{E}}_{\mathrm{pm}}$: for mixtures whose values of $H^{\mathrm{E}}_{\mathrm{m}}$ are within 1000 to 2000 J mol^{-1}, $C^{\mathrm{E}}_{\mathrm{pm}}$ curves have a W-shape and for mixtures whose values of $H^{\mathrm{E}}_{\mathrm{m}}$ are below 1000 J mol^{-1}, $C^{\mathrm{E}}_{\mathrm{pm}}$ curves has a parabolic shape [32–34]. However, for the mixtures studied here, the $C^{\mathrm{E}}_{\mathrm{pm}}$ curves have a S-shape with a positive maximum and a negative minimum. According to literature [31] local non-randomness contributes positively to $C^{\mathrm{E}}_{\mathrm{pm}}$, whereas random mixing produces negative $C^{\mathrm{E}}_{\mathrm{pm}}$. Since information about the structure of the studied mixtures are lacking, we are not able to give a satisfactory explanation for the $C^{\mathrm{E}}_{\mathrm{pm}}$ behavior of such mixtures.

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