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Excess molar enthalpy for methanol, ethanol, 1-propanol, 1-butanol + *n*-butylamine mixtures at 288.15 and 308.15 K at atmospheric pressure

Measurements and modeling using ERAS Model

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Abstract Experimental data of excess molar enthalpy (H_m^E) of binary liquid mixtures containing (methanol or ethanol or 1-propanol, or 1-butanol) + *n*-butylamine mixtures have been determined as a function of composition at temperatures 288.15 and 308.15 K, at atmospheric pressure, using a modified 1455 PARR mixture calorimeter. The H_m^E values are negative for both systems over the whole composition range. The applicability of the ERAS Model to correlate H_m^E of mixtures studied is tested, and the agreement between experimental and theoretical results is satisfactory. The model results are discussed in terms of the cross-association interactions with temperature variation as well as in terms of the variation of the carbon chain in the alcohols presents in the mixtures.

Keywords Alcohols · Amines · Excess molar enthalpy · ERAS Model

Introduction

Mixtures containing associating components like alcohols and amines exhibit high non-ideal behavior due to the formation of hydrogen bonds between these different species. Experimental studies on excess molar enthalpy (H_m^E) or excess molar volume (V_m^E) of mixtures containing 1-alkanol + amine have been performed contributing to understand of the molecular interactions that occur between these compounds. Excess molar properties are also used to test the predictive or correlative capability of solutions models involving such polar compounds. Heintz and Papaioannou [1] obtained the experimental excess molar enthalpy data of alcohols + propylamine and alcohols + *n*-butylamine mixtures at 298.15 K; these data were correlated to the ERAS Model. González et al. [2] studied the experimental behavior of H_m^E for mixtures containing 1-alkanols + amines, correlating the results DISQUAC model; the results were compared to UNIFAC and ERAS Model. Villa et al. [3, 4] showed the experimental V_m^E of 1-alkanols + dipropylamine and 1-alkanols + dibutylamine mixtures at 298.15 K and at atmospheric pressure and correlated the results using the ERAS Model. Funke et al. [5] and Reimann and Heintz [6] presented experimental and modeling of H_m^E and V_m^E data for 1-alkanol + amine mixtures at various temperatures. Excess molar volume of binary mixtures containing 1-alkanol + (*n*-di-propylamine or *n*-di-butylamine) and propylamine + 1-alkanol were reported by Oswal and Desai [7, 8]. Experimental H_m^E and V_m^E data for binary mixtures containing alcohols + triethylamine were presented by Kwaterski et al. [9]. Checoni and Francesconi [10] reported the excess molar enthalpy and excess molar heat capacity (Cp_m^E) for mixtures containing (1-heptanol or 1-octanol) + (diethylamine + *s*-butylamine) at 298.15 K and atmospheric pressure; the authors correlated the experimental H_m^E data to ERAS Model.

In present work, excess molar enthalpy (H_m^E) values of mixtures containing alcohols (methanol, ethanol, 1-propanol, and 1-butanol) + *n*-butylamine have been determined as a function of composition at 288.15 and 308.15 K at atmospheric pressure. The applicability of the ERAS Model [11] to correlate experimental H_m^E of these mixtures was tested.

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Experimental

Methanol, ethanol, 1-propanol, and 1-butanol, both with purity greater than 99.0 mol.%, were supplied by EM Science-Merck (USA). *n*-Butylamine was dried over molecular sieves and supplied by Across Organics (purity > 99 mol.%). The alcohols were used without previous purification. In order to check the purity of the substances, density and refractive index measurements were performed at 293.15 K using a vibrating-tube densimeter (Anton Paar, DMA 4500, resolution 10^{-5} g cm^{-3}) and an Abbé type refractometer (Atago, model 3T), respectively. The uncertainties in the refraction index and density measurements are about $\pm 1 \times 10^{-4}$ and $\pm 1 \times 10^{-4}$ g cm^{-3}, respectively. Table 1 presents a comparison of the density and refraction index measurements with literature values.

Excess molar enthalpy measurements were performed using a Parr 1455 solution calorimeter with some improvements. A detailed description and performance of the apparatus as well as the experimental procedure are given elsewhere [14]. From pure compounds, the experimental H_m^E values were determined from the following equation

$$H_m^E = -\left(\mathrm{Cp_m} + \frac{Cv}{n}\right)\Delta T + \mathrm{Cp_m^E}(T_r - T) \quad (1)$$

in which $\mathrm{Cp_m}$, Cv, n, ΔT, Cp_m^E, T_r, and T represent the molar heat capacity of the mixture, heat capacity of the calorimeter, amount of mixture (mol), temperature difference due to mixing process, excess molar heat capacity of the mixture, temperature in which the experiment effectively occurs, and reference temperature (288.15–303.15 K), respectively. The quantity Cv is determined by reversal calorimetry, with the actuation of resistance wire (with uncertainty of $\pm 1 \times 10^{-2}$ W), which supplies a certain amount of heat to pure compounds alcohols (1) and *n*-butylamine (2), whose mass and heat capacity (Cp_i) are known; so, ΔT_1 and ΔT_2 values are determined; with these values is possible to solve the equations system below and to obtain the Q and Cv values at experiment temperature

$$Q = (n_1\mathrm{Cp}_1 + Cv)\Delta T_1 \quad (2)$$

$$Q = (n_2\mathrm{Cp}_2 + Cv)\Delta T_2 \quad (3)$$

Molar heat capacity of the mixture ($\mathrm{Cp_m}$) is determined by reversal calorimetry supplying an amount of heat to the mixture. The expression used to calculate $\mathrm{Cp_m}$ is

$$\mathrm{Cp_m} = \left(\frac{Q}{\Delta T_{\mathrm{Sol}}} - Cv\right)\frac{1}{n_s} \quad (4)$$

in which n_s is the molar quantity of the mixture and ΔT_{Sol} is the temperature variation due to heat supplied to the mixture. The molar heat capacities of ideal solution ($\mathrm{Cp_m^{Ideal}}$) is obtained by

$$\mathrm{Cp_m^{Ideal}} = x_1\mathrm{Cp}_1 + x_2\mathrm{Cp}_2 \quad (5)$$

wherein x_1 and x_2 are the molar fraction of alcohols and *n*-butylamine, respectively, and $\mathrm{Cp_m^E}$ is calculated by

$$\mathrm{Cp_m^E} = \mathrm{Cp_m} - \mathrm{Cp_m^{Ideal}} \quad (6)$$

For the intermediary mixture compositions, it is not possible to determine H_m^E directly from pure reagents due to volumetric limitation of apparatus. Hence, a mixture is used, whose $H_{m_0}^E$ is previously determined and the value of H_m^E can be calculated by

$$H_m^E = \frac{n_0}{n}H_{m_0}^E - \left(\mathrm{Cp_m} + \frac{Cv}{n}\right)\Delta T + \mathrm{Cp_m^E}(T_r - T) \quad (7)$$

wherein n_0 is the amount of mixture in the previous mixing process. Both n_0 and $H_{m_0}^E$ values are zero when pure reagent is used. The mixtures were prepared gravimetrically using a Mettler Toledo PB 3002 balance (resolution, $\pm 10^{-2}$ g, uncertainty $\pm 5 \times 10^{-3}$ g). The estimated uncertainty in mole fraction is $\pm 2 \times 10^{-4}$, and in the excess molar enthalpy measurements is $\pm 1.5 \times 10^{-2}$ H_m^E for the central composition range and $\pm 2.5 \times 10^{-2}$ H_m^E for the water-rich or alkanediol-rich region.

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

Component	ρ/g cm^{-3}		n_D	
	Experimental	Literature	Experimental	Literature
Methanol	0.7915	0.7914[a]	1.3286	1.3288[b]
Ethanol	0.7894	0.7893[a]	1.3613	1.3611[b]
1-Propanol	0.8036	0.8035[a]	1.3849	1.3850[b]
1-Butanol	0.8096	0.8098[a]	1.3987	1.3988[b]
n-Butylamine	0.7413	0.7414[b]	1.4033	1.4031[b]

[a] From [12]

[b] From [13]

Results and discussion

Testing systems

The performance of the calorimeter was tested by measuring H_m^E of the well-investigated systems ethanol + water [15–17] 298.15 K over the whole composition range and atmospheric pressure. A comparison between experimental data with the plentiful literature data taken from Costigan et al. [17] shows an average difference lower than 1.0% over the whole composition range.

Alcohol + *n*-butylamine systems

Excess molar enthalpy values are negative over the complete molar fraction range. The thermal effect decreases with increasing the temperature and decreases with the number of the carbon atoms in alcohol increasing. The excess molar enthalpy behavior has a parabolic form for all systems studied with maximum values around the mol fraction 0.42 for mixtures containing methanol and 0.48 for mixtures containing ethanol, 1-propanol, and 1-butanol. Tables 2 and 3 present the experimental H_m^E values for the alcohols + *n*-butylamine mixtures at 288.15 and 303.15 K and atmospheric pressure.

The experimental results of H_m^E were correlated by the Redlich–Kister type equation

$$H_m^E = x_2(1 - x_2)\sum_{i=0}^{4} A_j(1 - 2x_2)^i \tag{8}$$

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

Table 2 Experimental H_m^E data for binary mixtures containing (methanol or ethanol) + *n*-butylamine at atmospheric pressure and 288.15 and 308.15 K

Methanol + *n*-butylamine				Ethanol + *n*-butylamine			
288.15 K		308.15 K		288.15 K		308.15 K	
$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}	$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}	$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}	$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}
0.0432	−817	0.0431	−682	0.0613	−667	0.0616	−710
0.0829	−1499	0.0827	−1310	0.1155	−1242	0.1161	−1299
0.1194	−2049	0.1191	−1851	0.1638	−1692	0.1646	−1757
0.1531	−2484	0.1528	−2299	0.2071	−2039	0.2081	−2102
0.1843	−2836	0.1840	−2662	0.2461	−2296	0.2472	−2356
0.2122	−3104	0.2123	−2945	0.2802	−2485	0.2819	−2539
0.2408	−3337	0.2412	−3187	0.3143	−2631	0.3166	−2682
0.2700	−3522	0.2707	−3387	0.3482	−2740	0.3510	−2789
0.2995	−3674	0.3006	−3543	0.3819	−2818	0.3851	−2863
0.3294	−3781	0.3308	−3659	0.4151	−2866	0.4187	−2906
0.3595	−3861	0.3612	−3737	0.4477	−2886	0.4517	−2923
0.3896	−3907	0.3915	−3780	0.4797	−2882	0.4838	−2917
0.4196	−3926	0.4217	−3794	0.5108	−2858	0.5151	−2889
0.4493	−3920	0.4517	−3781	0.5410	−2816	0.5455	−2843
0.4787	−3894	0.4812	−3747	0.5702	−2759	0.5747	−2780
0.5209	−3826	0.5236	−3664	0.6111	−2647	0.6156	−2661
0.5618	−3724	0.5645	−3546	0.6494	−2509	0.6538	−2517
0.6009	−3590	0.6036	−3399	0.6850	−2346	0.6893	−2351
0.6380	−3436	0.6407	−3225	0.7180	−2169	0.7221	−2172
0.6730	−3257	0.6757	−3029	0.7483	−1988	0.7522	−1984
0.7057	−3057	0.7083	−2813	0.7760	−1801	0.7796	−1794
0.7361	−2844	0.7385	−2584	0.8012	−1617	0.8045	−1607
0.7641	−2628	0.7664	−2348	0.8239	−1438	0.8270	−1427
0.7897	−2401	0.7919	−2110	0.8444	−1271	0.8472	−1259
0.8131	−2186	0.8151	−1878	0.8627	−1114	0.8653	−1103
0.8343	−1968	0.8361	−1656	0.8791	−973	0.8814	−962
0.8534	−1761	0.8550	−1448	0.8937	−844	0.8958	−835
0.8706	−1564	0.8720	−1257	0.9067	−731	0.9085	−722
0.8859	−1389	0.8873	−1085	0.9182	−629	0.9198	−623
0.8996	−1226	0.9008	−932	0.9283	−546	0.9297	−537
0.9118	−1079	0.9129	−797	0.9372	−468	0.9385	−462
0.9226	−946	0.9236	−680	0.9451	−401	0.9462	−397
0.9321	−826	0.9330	−579	0.9520	−346	0.9530	−342

Table 3 Experimental H_m^E data for binary mixtures containing (1-propanol or 1-butanol) + *n*-butylamine at atmospheric pressure and 288.15 and 308.15 K

1-Propanol + *n*-butylamine				1-Butanol + *n*-butylamine			
288.15 K		308.15 K		288.15 K		308.15 K	
$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}	$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}	$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}	$x_{n\text{-butylamine}}$	H_m^E/J mol^{-1}
0.0776	−952	0.0774	−864	0.0931	−925	0.0931	−880
0.1440	−1566	0.1437	−1443	0.1703	−1534	0.1703	−1478
0.2015	−1997	0.2011	−1862	0.2354	−1967	0.2354	−1910
0.2518	−2309	0.2512	−2175	0.2910	−2275	0.2911	−2220
0.2961	−2545	0.2955	−2408	0.3391	−2486	0.3392	−2434
0.3340	−2716	0.3340	−2577	0.3795	−2618	0.3802	−2572
0.3712	−2849	0.3717	−2710	0.4187	−2704	0.4199	−2660
0.4077	−2943	0.4086	−2806	0.4564	−2744	0.4581	−2703
0.4432	−2998	0.4444	−2865	0.4926	−2744	0.4946	−2701
0.4776	−3021	0.4791	−2889	0.5273	−2708	0.5295	−2667
0.5109	−3008	0.5127	−2881	0.5603	−2642	0.5628	−2602
0.5429	−2968	0.5449	−2842	0.5917	−2553	0.5943	−2514
0.5736	−2899	0.5757	−2779	0.6214	−2447	0.6241	−2408
0.6030	−2808	0.6052	−2694	0.6495	−2330	0.6522	−2292
0.6309	−2707	0.6332	−2592	0.6759	−2207	0.6786	−2169
0.6693	−2529	0.6716	−2421	0.7117	−2022	0.7145	−1986
0.7047	−2340	0.7069	−2234	0.7443	−1840	0.7469	−1806
0.7370	−2148	0.7391	−2041	0.7737	−1667	0.7761	−1635
0.7664	−1956	0.7684	−1850	0.8001	−1505	0.8024	−1475
0.7930	−1770	0.7949	−1667	0.8237	−1355	0.8259	−1328
0.8170	−1598	0.8188	−1493	0.8448	−1219	0.8468	−1193
0.8385	−1436	0.8401	−1332	0.8636	−1094	0.8654	−1070
0.8577	−1285	0.8592	−1185	0.8803	−980	0.8819	−958
0.8749	−1147	0.8762	−1050	0.8950	−877	0.8965	−856
0.8901	−1022	0.8913	−929	0.9081	−783	0.9094	−764
0.9036	−909	0.9047	−820	0.9196	−698	0.9207	−680
0.9155	−805	0.9165	−722	0.9297	−621	0.9307	−605
0.9260	−712	0.9269	−635	0.9385	−551	0.9395	−536
0.9353	−628	0.9361	−558	0.9463	−488	0.9471	−475
0.9434	−552	0.9441	−490	0.9532	−432	0.9539	−420
0.9506	−485	0.9512	−430	0.9591	−381	0.9598	−371
0.9569	−426	0.9574	−376	0.9644	−336	0.9649	−327
0.9624	−376	0.9628	−329	0.9689	−296	0.9694	−287

$$\sigma = \left[\sum \left(H^E_{m_{exper}} - H^E_{m_{calc}}\right)^2 / (N-k)\right]^{1/2}, \tag{9}$$

wherein $H^E_{m_{exp}}$ is the excess molar enthalpy obtained experimentally, $H^E_{m_{calc}}$ is the excess molar enthalpy calculated using the Redlich–Kister equation, *N* is the number of data points, and *k* is the number of the adjustable parameters of Eq. 8.

Figures 1, 2, 3 and 4 represent the composition dependence of experimental data of H_m^E for 1-alkanols + amine mixtures at 288.15 and 308.15 K.

The values of H_m^E are large and negative over the whole composition range and have a parabolic form. It is observed that the exothermic effect decreases when both the temperature and 1-alkanols chain length increases. Maximum values for H_m^E are methanol + *n*-butylamine (−3927 J mol^{-1} at 288.15 K and −3795 J mol^{-1} at 308.15 K, both at $x_{\text{butylamine}} = 0.43$), ethanol + *n*-butylamine (−2974 J mol^{-1} at 288.15 K and −2925 J mol^{-1} at 308.15 K, both at $x_{\text{butylamine}} = 0.46$), 1-propanol + *n*-butylamine (−2917 J mol^{-1} at 288.15 K and −2890 J mol^{-1} at 308.15 K, both at $x_{\text{butylamine}} = 0.48$), and

Table 4 Coefficients A_j for Redlich–Kister type equation, the standard deviation σ

Systems	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}
288.15 K						
$CH_3OH + C_4H_9NH_2$	−15463.4	−3329.5	−4801.5	−682.0	4776.1	±2.0
$C_2H_5OH + C_4H_9NH_2$	−11481.1	−1719.8	−979.5	−475.4	4190.1	±3.4
$C_3H_7OH + C_4H_9NH_2$	−12059.3	−1027.7	2377.4	−971.9	−2911.1	±3.1
$C_4H_9OH + C_4H_9NH_2$	−10956.2	−1524.3	3525.6	825.4	−3525.0	±3.6
308.15 K						
$CH_3OH + C_4H_9NH_2$	−14860.0	−3850.6	−3940.5	−840.0	−8200.1	±4.0
$C_2H_5OH + C_4H_9NH_2$	−11620.3	−1785.6	−1125.4	−842.1	3958.7	±4.6
$C_3H_7OH + C_4H_9NH_2$	−11550.2	−744.6	2541.3	−1184.6	−1987.4	±4.2
$C_4H_9OH + C_4H_9NH_2$	−10800.0	−1356.1	3658.5	965.6	−3340.7	±4.3

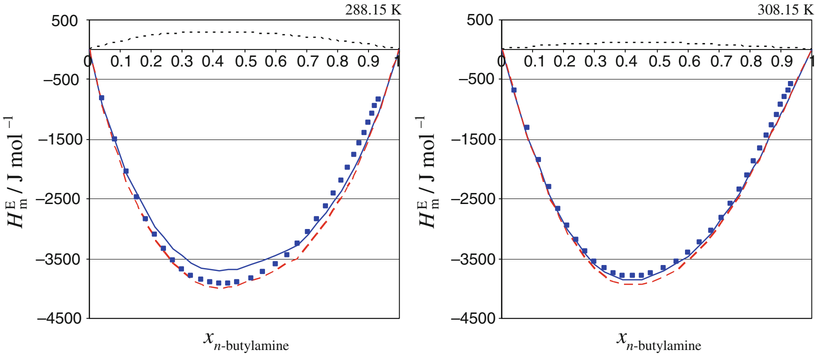


Fig. 1 Values of H_m^E as function of the mole fraction of *n*-butylamine for: methanol + *n*-butylamine at 288.15 and 308.15 K. (■) experimental data, (—) ERAS Model, (- - - -) physical contribution and (— —) chemical contribution

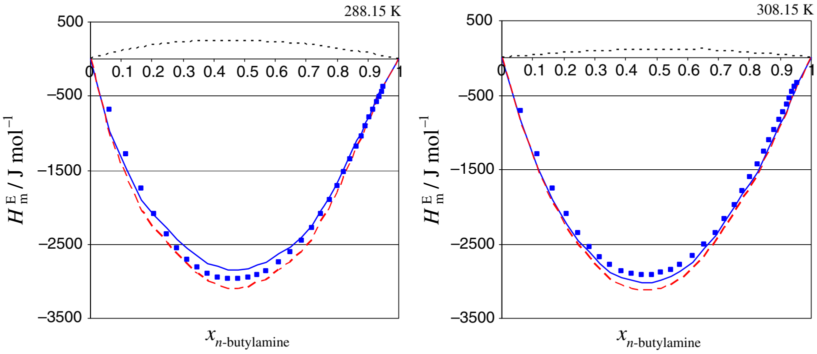


Fig. 2 Values of H_m^E as function of the mole fraction of *n*-butylamine for: ethanol + *n*-butylamine at 288.15 and 308.15 K. (■) experimental data, (—) ERAS Model, (- - - -) physical contribution and (— —) chemical contribution

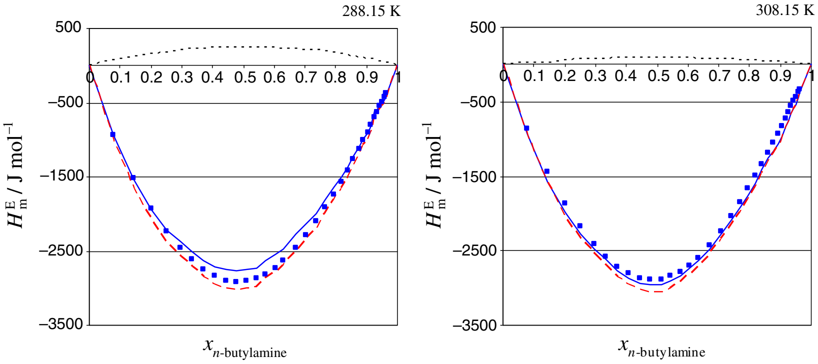


Fig. 3 Values of H_m^E as function of the mole fraction of *n*-butylamine for: 1-propanol + *n*-butylamine at 288.15 and 308.15 K. (■) experimental data, (—) ERAS Model, (- - - -) physical contribution and (— —) chemical contribution

methanol+ *n*-butylamine (−2746 J mol^{-1} at 288.15 K and −2703 J mol^{-1} at 308.15 K, both at $x_{\text{butylamine}} = 0.46$); these values were obtained using Eq. 8. The magnitude of H_m^E can be interpreted as the result of different effects which may be divided into physical and chemical contributions. Physical contributions involving non-specific interactions

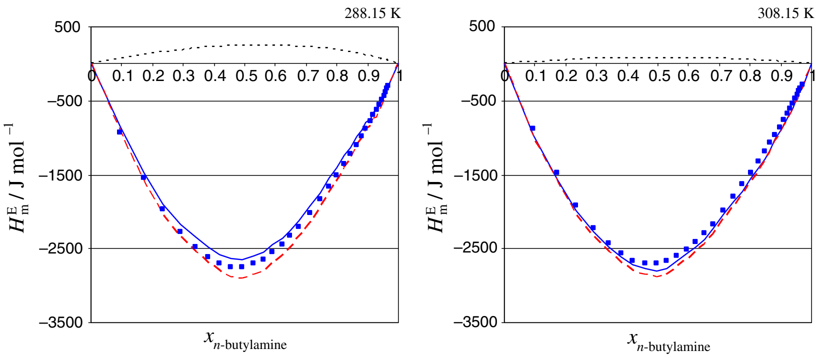


Fig. 4 Values of H^E_m as function of the mole fraction of *n*-butylamine for: 1-butanol + *n*-butylamine at 288.15 and 308.15 K. (■) experimental data, (—) ERAS Model, (- - - -) physical contribution and (— —) chemical contribution

such dipole–dipole and dispersion forces between 1-alkanols and 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 gives 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 [5]. This specific interaction contributes negatively to H^E_m. Due to the large negative values of excess molar enthalpy data, 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.

Experimental H^E_m data were correlated by means of the ERAS Model [11] which combines the real association solution model [18] with a physical term from Flory's equation of state [19]. The following equations hold for the studied systems

$$H^E_m = H^E_{m_{Phys}} + H^E_{m_{Chem}} \tag{10}$$

in which

$$H^E_{phys} = \left(x_1 \cdot V_1^* + x_2 \cdot V_2^*\right)\left(\frac{\Phi_1 p_1^*}{\tilde{V}_1} + \frac{\Phi_2 p_2^*}{\tilde{V}_2} - \frac{p_M^*}{\tilde{V}_M}\right) \tag{11}$$

$$\begin{aligned} H^E_{chem} = {} & x_1 K_1 \Delta h_1^* \left(\varphi_{11} - \varphi_{11}^0\right) + x_2 K_2 \Delta h_2^* \left(\varphi_{21} - \varphi_{21}^0\right) \\ & + x_{12} K_{12} \Delta h_{12}^* \frac{\varphi_{21}\left(1 - K_1 \cdot \varphi_{11}\right)}{(V_1/V_2)\left(1 - K_2 \cdot \varphi_{21}\right) + K_{12}\varphi_{21}} \\ & - \frac{p_M^* \cdot V^E_{Chem}}{\tilde{V}^2_M} \end{aligned} \tag{12}$$

and

$$\begin{aligned} V^E_{chem} = {} & \left(x_1 K_1 \Delta v_1^* \left(\varphi_{11} - \varphi_{11}^0\right) + x_2 K_2 \Delta v_2^* \left(\varphi_{21} - \varphi_{21}^0\right)\right. \\ & + x_1 K_{12} \Delta v_{12}^* \frac{\varphi_{21}\left(1 - K_1 \cdot \varphi_{11}\right)}{(V_1/V_2)\left(1 - K_2 \varphi_{21}\right) + K_{12}\varphi_{21}} \quad)\tilde{V}_M \end{aligned} \tag{13}$$

A detailed description of calculation procedure as well as terms significance of the Eqs. 11–13 are given in [14]. The values of parameters of the pure components used in the calculations are given in Table 5.

The association constant of pure components (K_i) is calculated using the following expression [20]

$$K_i = \exp\left[\left(\frac{s_i}{R}\right) + 1 - \left(\frac{h_i}{RT}\right)\right] \tag{14}$$

wherein s_i and h_i are the molar entropy of association of pure component and the molar enthalpy of association of pure component (both obtained from [20]), R is the universal gas constant, T is the temperature in which the association constant is obtained. The values of h_i and Δh_i^* in this study are equal due to the similarity in its significance. Cross-association equilibrium constant, K_{12}, Flory's parameter, χ_{12}, molar enthalpy of cross-association, Δh_{12}^*, and molar volume of cross-association, Δv_{12}^* are the adjustable parameters of ERAS Model, whose values are reported in Table 6, along with the average absolute deviation values, calculated using the Eq 9 with the $k = 4$, and relative deviations calculated using the following expression

$$RD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{H^E_{i\,exp} - H^E_{ERAS}}{H^E_{i\,exp}}\right| \tag{15}$$

in which HERASE is excess molar enthalpy calculated using ERAS Model.

The cross-association parameters were adjusted to excess molar enthalpy experimental data through sequential search technique proposed by Rosenbrock [21] whose description of calculation routine is given in reference [22].

The results obtained from the ERAS Model as well as its physical and chemical contributions are also presented in Figs. 1, 2, 3, and 4. 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^E_m is good. The adjustable parameters calculated in present work show good agreement with those calculated in the Funke et al. [5] and Reimann-Heintz [6] for mixtures containing

Table 5 Properties of the pure components at 288.15 and 308.15 K

Component	K_i^{a}	S_i^{b}/ nm^{-1}	V_m/ cm^3 mol^{-1}	V_m*/ cm^3 mol^{-1}	κ_i^{b}/ 10^4 MPa^{-1}	α_i^{b}/ 10^4 K^{-1}	$-s_i$/ J mol^{-1} K^{-1}	$-\Delta h_i^*$/ kJ mol^{-1}	$-\Delta v_i^*$/ cm^3 mol^{-1}
288.15 K									
Methanol	701.00	16.49	40.20	32.03	11.54	11.72	29.70	21.86	5.60
Ethanol	347.87	15.43	58.08	47.37	10.60	10.20	33.20	21.19	5.60
1-Propanol	227.58	14.90	74.83	60.92	9.04	10.20	31.80	19.77	5.60
1-Butanol	176.46	14.56	91.28	75.50	9.27	9.17	31.00	18.93	5.60
n-Butylamine	16.62	14.40	98.84	77.00	17.15	12.60	11.70	7.71	4.70
308.15 K									
Methanol	387.71	16.49	40.76	32.06	12.54	11.99	29.70	21.86	5.60
Ethanol	195.93	15.43	59.39	47.39	12.40	11.00	33.20	21.19	5.60
1-Propanol	133.20	14.90	75.85	61.20	10.40	10.25	31.80	19.77	5.60
1-Butanol	105.66	14.56	92.81	75.64	10.25	9.50	31.00	18.93	5.60
n-Butylamine	13.49	14.40	100.47	77.19	18.25	12.70	11.70	7.71	4.70

[a] Calculated from Eq. 14

[b] From [4]

Table 6 Optimized ERAS Model parameters in temperatures 288.15, 308.15 and 313.15 K as well as the deviations

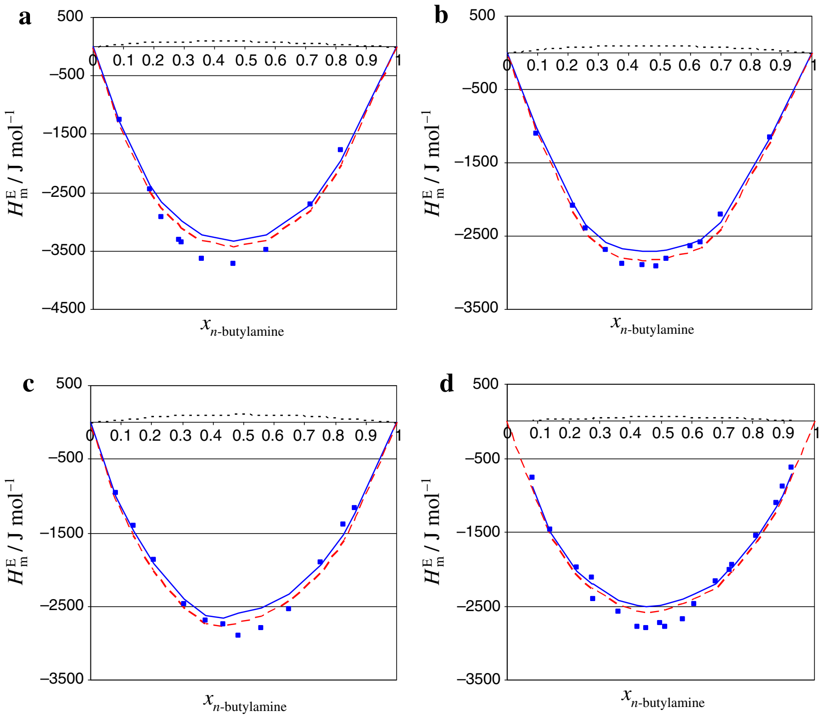
System	*T*/K	K_{12}	χ_{12}/J cm^{-3}	$-\Delta h_{12}$/kJ mol^{-1}	$-\Delta v_{12}$/cm^3 mol^{-1}	σ/J mol^{-1}	%
$CH_3OH + C_4H_9NH_2$	288.15	1632.1	17.20	48.0	13.5	308.6	11.0
	298.15[a]	1504.0	9.20	45.6	11.6	–	–
	308.15	1299.3	9.10	41.7	9.6	357.5	10.9
	313.15	1237.1	8.90	40.5	4.0	293.3	9.9
$C_2H_5OH + C_4H_9NH_2$	288.15	877.4	16.60	44.1	22.5	222.6	13.3
	298.15[a]	834.0	8.79	40.5	10.5	–	–
	308.15	711.1	8.70	38.0	9.1	202.1	12.6
	313.15	658.6	7.70	37.0	7.5	112.3	4.9
$C_3H_7OH + C_4H_9NH_2$	288.15	889.1	3.60	40.9	25.4	284.6	12.7
	298.15[a]	794.0	7.23	39.5	10.2	–	–
	308.15	480.5	5.70	36.0	8.5	159.3	10.2
	313.15	380.6	4.90	35.0	7.6	209.7	8.1
$C_4H_9OH + C_4H_9NH_2$	288.15	848.0	6.20	41.0	35.3	268.4	10.7
	298.15[a]	775.0	5.30	38.6	10.2	–	–
	308.15	461.4	5.00	33.8	9.0	136.8	8.5
	313.15	351.1	4.50	33.0	7.0	188.3	8.5

[a] Parameters at 298.15 K obtained from [1]

1-alkanols + *n*-butylamine. 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 + amine; this information is observed in present work, since association constants of 1-alkanols and amines are higher than cross-association constants and strong negative values of H_m^E requires values for Δh_{12}^* and Δv_{12}^* more negative that those for molar enthalpy association and molar volume association of 1-alkanols and *n*-butylamine (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.

Heintz and Papaioannou [1] present the experimental data for mixtures containing (methanol, ethanol, 1-propanol, 1-butanol) + *n*-butylamine at 298.15 K and

Fig. 5 Values of H_m^E as function of the mole fraction of *n*-butylamine for: **a** methanol + *n*-butylamine, **b** ethanol + *n*-butylamine, **c** 1-propanol + *n*-butylamine and **d** 1-butanol + *n*-butylamine at 313.15 K. (■) experimental data [23], (—) ERAS Model, (- - - -) physical contribution and (— —) chemical contribution



atmospheric pressure. These data were correlated to the ERAS Model by the researchers and K_{12}, Δv_{12}^*, Δh_{12}^*, and χ_{12} are compared to those presented in Table 4. It is possible to verify that their value belongs to parameters interval calculated at 288.15 and 308.15 K. Furthermore, if the experimental data obtained by Duttachoudhury and Mathur [23] are correlated to the ERAS Model, the obtained adjustable parameters are lower than those at 308.15 K, even though the agreement between experimental and calculated H_m^E to be only qualitatively satisfactory at this temperature (see Table 4; Fig. 5).

Conclusions

Experimental data of excess molar enthalpy for mixtures containing (methanol or ethanol or 1-propanol, or 1-butanol) + *n*-butylamine were determined at 288.15 and 308.15 K. The ERAS Model allows a good theoretical interpretation of these experimental H_m^E data. The chemical contribution to the H_m^E values is negative and dominant in relation to the physical contribution (positive and small) in all mixtures. The negatives values of H_m^E values for the systems studied may be attributed to structural effects arising from the geometrical fitting of *n*-butylamine molecules in the hydrogen bonded network of alcohols and to complex formation between alcohols and *n*-butylamine. Such negative contributions overweigh the positive contributions due to physical interactions (mainly dipole–dipole and dispersion interactions) and to the disruption of the associated alcohols molecules structure by amine.

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