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# Experimental Solid + Liquid Equilibria and Excess Molar Volume of Alkanol + Octylamine Mixtures. Analysis in Terms of ERAS, DISQUAC, and Modified UNIFAC[†]

**Urszula Domańska* and Małgorzata Głoskowska**

Warsaw University of Technology, Faculty of Chemistry, Physical Chemistry Division, 00-664 Warsaw, Poland

(Solid + liquid) phase diagrams have been determined for (1-octanol or 1-nonanol or 1-decanol or 1-undecanol + octylamine) mixtures. Solid addition compounds form with the empirical formulas $C_8H_{17}OH{\cdot}C_8H_{19}N$, $C_9H_{19}OH{\cdot}C_8H_{19}N$, $C_{10}H_{21}OH{\cdot}C_8H_{19}N$, and $C_{11}H_{23}OH{\cdot}C_8H_{19}N$. All are congruently melting compounds. Compound formation is attributed to a strong A−B interaction. The excess molar volumes, $V_m^E$, have been determined for an alcohol (1-octanol, 1-nonanol, 1-decanol, or 1-undecanol) + octylamine at 298.15 K and atmospheric pressure. The systems exhibit very large negative molar excess volumes, $V_m^E$, and molar excess enthalpies, $H_m^E$. The $V_m^E$ curves are nearly symmetrical. Strong cross-association between hydroxyl and amine groups ($OH{\cdots}NH_2$) is a dominant effect, and it causes high negative values of $V_m^E$ and $H_m^E$ and a 1:1 congruently melting solid compound at lower temperatures. Our experimental data of $V_m^E$ and the literature data of $H_m^E$ were treated in terms of the ERAS, DISQUAC, and modified UNIFAC models. The ERAS model consistently describes $V_m^E$ values and excess molar enthalpies, $H_m^E$, of the studied mixtures.

## Introduction

In this series of papers[1] our general aim is to confirm from solid + liquid equilibria measurements the interactions between unlike molecules in systems which exhibit very strong negative deviations from Raoult's law. Mixtures of alcohols and amines show large negative values of molar excess volumes, $V_m^E$, and molar excess enthalpies, $H_m^E$. Strong intermolecular interactions between the hydroxyl group and the amine group lead to the largest negative values found for organic mixtures in the literature and were very well described by the ERAS model.[2−6] New systematic characterization, using different models of interactions between unlike molecules and new experimental data of molar excess volumes, was shown for *n*-alkane + triethylamine or tributylamine[7] or methylbutylamine[8] systems and alcohols + primary or secondary amines.[9] In the systems under study, the strong intermolecular hydrogen bonds $O{-}H{\cdots}N$ predominate the $O{-}H{\cdots}O$ and $N{-}H{\cdots}N$ bonds. Thus, the dominant effect in this kind of mixtures is cross-association but not self-association. Values of a cross-hydrogen-bonding energy between −32 $kJ{\cdot}mol^{-1}$ and −45 $kJ{\cdot}mol^{-1}$ have been determined, exceeding significantly the corresponding values of the self-association of alcohols and amines.[2] In the present work we extended the thermodynamic study to low temperatures, where solid + liquid equilibria were measured. In this work 1-octanol, 1-nonanol, 1-decanol, and 1-undecanol were chosen in mixtures with octylamine. The experimental data of the excess molar volumes of these four mixtures at 298.15 K and atmospheric pressure were also measured. The data of $V_m^E$ together with the literature values of the excess molar enthalpies for two of these systems published previously[6] were used for testing the extended real associated solution model, the ERAS model, the DISQUAC model, and the modified UNIFAC model. The ERAS model combines the real association solution model[2,10−13] with a physical term from the Flory's equation of state.[14] The DISQUAC model[15,16] and the modified UNIFAC model[17] were examined for the alkanol + amine mixtures in earlier papers.[1,7−10]

The ERAS model has already been applied to many binary mixtures, not only an alcohol + an amine mixtures (see ref 1 and the literature cited within).

## Experimental Section

The origins of the chemicals and their mass fraction purities were as follows: octylamine (Fluka, >98%), 1-octanol (Aldrich Chemical Co., 99+%), 1-nonanol (Fluka, >98%), 1-decanol (Aldrich Chemical Co., 99%), and 1-undecanol (Fluka, >98%). Octylamine and alcohols were fractionally distilled over different drying reagents to a mass fraction purity better than 99.8 mass % determined by GLC. Liquids were stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The physical properties of the reagents used in this work are listed in Table 1 together with the literature values.

The (solid + liquid) equilibrium (SLE) temperatures were determined using a dynamic method.[24] Appropriate mixtures of solute and solvent were heated very slowly ($<1.0 \times 10^{-3}$ $K{\cdot}h^{-1}$ near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell which was placed in a glass thermostat filled with acetone and dry ice. The temperature at which the last crystals disappeared (or disappearance of solution cloudiness) was taken as the temperature of the (solid + liquid) equilibrium. The crystal disappearance temperatures, detected visually, were measured with an electronic thermometer P 550 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostating liquid. The thermometer was calibrated on

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* Corresponding author. E-mail: Ula @ ch.pw.edu.pl.

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**Table 1. Physical Properties of the Pure Substances: $V^{298.15}$, Molar Volume; $T_m$, Melting Temperature (Experimental and Literature Values); and $\rho^{298.15}$, Density (Experimental and Literature Values)**

| | $V_m(298.15)$ | $T_m$ | $T_m^{(lit)}$ | $\rho(298.15)$ | $\rho(298.15)^{(lit)}$ |
|---|---|---|---|---|---|
| compd | $cm^3 \cdot mol^{-1}$ | K | K | $g \cdot cm^{-3}$ | $g \cdot cm^{-3}$ |
| 1-octanol | 158.41 | 258.03 | 258.35[a] | 0.822 21 | 0.822 50[b] |
| 1-nonanol | 174.95 | 268.10 | | 0.824 60 | 0.823 84[c] |
| 1-decanol | 191.49 | 278.67 | 279.14[d] | 0.826 64 | 0.826 23[e] |
| 1-undecanol | 207.77 | 289.63 | 289.65[f] | 0.829 34 | 0.828 98[c] |
| octylamine | 165.70 | 273.37 | 273.15[g] | 0.779 95 | 0.779 35[h] |

[a] Reference 18. [b] Reference 11. [c] Reference 19. [d] Reference 20. [e] Reference 6. [f] Reference 21. [g] Reference 22. [h] Reference 23.

**Table 2. Experimental (Solid + Liquid) Phase Equilibria, Where $T$ Denotes the Equilibrium Temperature and $\delta T$ Is the Deviation of the Experimental Temperature from the Temperature Calculated from Eq 1**

| $x_1$ | $T$/K | $\delta T$/K | $x_1$ | $T$/K | $\delta T$/K |
|---|---|---|---|---|---|
| | | 1-Octanol (1) + Octylamine (2) | | | |
| 0.0000 | 273.37 | 0.00 | 0.5161 | 267.32 | 0.12 |
| 0.0285 | 273.26 | 0.09 | 0.5462 | 267.18 | 0.08 |
| 0.0535 | 272.93 | 0.05 | 0.5778 | 266.77 | −0.03 |
| 0.0847 | 272.20 | −0.19 | 0.6034 | 266.36 | −0.06 |
| 0.1097 | 271.87 | −0.05 | 0.6338 | 265.71 | −0.09 |
| 0.1427 | 271.10 | −0.10 | 0.6673 | 264.83 | −0.05 |
| 0.1709 | 270.72 | 0.20 | 0.6892 | 264.10 | −0.04 |
| 0.1876 | 270.17 | 0.07 | 0.7170 | 263.14 | 0.09 |
| 0.2277 | 269.27 | 0.21 | 0.7437 | 261.93 | 0.11 |
| 0.2368 | 268.79 | −0.03 | 0.7710 | 260.35 | −0.02 |
| 0.2486 | 268.45 | −0.06 | 0.8031 | 258.35 | −0.05 |
| 0.2800 | 267.70 | 0.01 | 0.8369 | 255.98 | −0.03 |
| 0.2934 | 267.27 | −0.09 | 0.8665[a] | 253.65 | 0.02, 0.06[b] |
| 0.3110 | 266.85 | −0.08 | 0.8713 | 253.88 | 0.06 |
| 0.3395 | 266.17 | −0.11 | 0.8844 | 254.45 | 0.01 |
| 0.3655 | 265.88 | 0.13 | 0.9022 | 255.15 | −0.05 |
| 0.3773[a] | 265.55 | 0.02, 0.01[b] | 0.9221 | 255.98 | 0.01 |
| 0.3949 | 266.03 | 0.09 | 0.9381 | 256.60 | 0.09 |
| 0.4299 | 266.40 | −0.18 | 0.9686 | 257.45 | 0.07 |
| 0.4567 | 266.85 | −0.06 | 1.0000 | 258.03 | 0.00 |
| 0.4874 | 267.22 | 0.08 | | | |
| | | 1-Nonanol (1) + Octylamine (2) | | | |
| 0.0000 | 273.37 | 0.00 | 0.5347 | 271.12 | 0.03 |
| 0.0964 | 271.21 | 0.00 | 0.6054 | 270.68 | −0.21 |
| 0.1339 | 269.53 | 0.00 | 0.6408 | 270.15 | −0.28 |
| 0.2017[a] | 265.30 | 0.00, −0.01[b] | 0.6852 | 268.99 | −0.26 |
| 0.2182 | 266.49 | 0.18 | 0.7423 | 266.92 | 0.68 |
| 0.2712 | 268.26 | −0.29 | 0.8157 | 258.35 | −0.20 |
| 0.3384 | 269.85 | −0.11 | 0.8342[a] | 255.68 | −0.01, 0.05[b] |
| 0.3888 | 270.57 | 0.11 | 0.8594 | 258.68 | −0.04 |
| 0.4284 | 270.86 | 0.15 | 0.9446 | 266.04 | 0.04 |
| 0.4837 | 271.05 | 0.09 | 1.0000 | 268.10 | 0.00 |
| 0.5079 | 271.15 | 0.11 | | | |
| | | 1-Decanol (1) + Octylamine (2) | | | |
| 0.0000 | 273.37 | 0.00 | 0.5173 | 277.37 | 0.00 |
| 0.0239 | 272.43 | −0.06 | 0.5342 | 277.26 | −0.03 |
| 0.0467 | 271.83 | 0.04 | 0.5504 | 277.08 | −0.08 |
| 0.0655 | 271.27 | −0.01 | 0.5715 | 276.87 | −0.06 |
| 0.0932 | 270.53 | −0.05 | 0.5875 | 276.66 | −0.05 |
| 0.1260 | 269.75 | 0.01 | 0.6087 | 276.32 | −0.03 |
| 0.1448 | 269.17 | −0.02 | 0.6318 | 275.83 | −0.04 |
| 0.1573[a] | 268.78 | −0.01, 0.02[b] | 0.6589 | 275.32 | 0.11 |
| 0.1620 | 269.04 | 0.03 | 0.6860 | 274.47 | 0.06 |
| 0.1797 | 269.85 | −0.04 | 0.7177 | 273.41 | 0.08 |
| 0.2119 | 271.35 | −0.01 | 0.7526 | 271.85 | −0.08 |
| 0.2543 | 273.10 | 0.05 | 0.7697[a] | 271.15 | −0.01, 0.00[b] |
| 0.2700 | 273.57 | −0.04 | 0.7706 | 271.20 | 0.01 |
| 0.2928 | 274.22 | −0.13 | 0.7856 | 271.76 | −0.02 |
| 0.3139 | 274.95 | −0.01 | 0.8071 | 272.72 | 0.15 |
| 0.3342 | 275.55 | 0.06 | 0.8392 | 273.64 | 0.01 |
| 0.3646 | 276.20 | 0.04 | 0.8717 | 274.50 | −0.11 |
| 0.3903 | 276.67 | 0.05 | 0.8919 | 275.21 | 0.00 |
| 0.4139 | 276.98 | 0.03 | 0.9148 | 275.97 | 0.09 |
| 0.4462 | 277.28 | 0.02 | 0.9433 | 276.76 | 0.02 |
| 0.4743 | 277.45 | 0.05 | 0.9655 | 277.48 | 0.03 |
| 0.5009 | 277.42 | 0.00 | 1.0000 | 278.67 | 0.00 |
| | | 1-Undecanol (1) + Octylamine (2) | | | |
| 0.0000 | 273.37 | 0.00 | 0.5109 | 279.01 | 0.05 |
| 0.0370 | 271.97 | 0.00 | 0.5609 | 278.69 | −0.04 |
| 0.0642 | 271.31 | 0.00 | 0.5965 | 278.20 | −0.12 |
| 0.1033 | 270.30 | 0.00 | 0.6561 | 277.03 | 0.06 |
| 0.1290[a] | 269.20 | 0.00, 0.02[b] | 0.6855[a] | 275.90 | 0.00, −0.12[b] |
| 0.1332 | 269.44 | −0.06 | 0.7002 | 276.75 | −0.06 |
| 0.1933 | 273.23 | 0.05 | 0.7411 | 278.71 | −0.23 |
| 0.2519 | 275.68 | 0.13 | 0.7727 | 280.57 | 0.07 |
| 0.3184 | 277.13 | −0.13 | 0.8580 | 284.10 | −0.27 |
| 0.3652 | 277.74 | −0.30 | 0.8974 | 286.12 | 0.15 |
| 0.4016 | 278.65 | 0.19 | 0.9537 | 287.72 | −0.35 |
| 0.4425 | 278.94 | 0.15 | 1.0000 | 289.63 | 0.00 |

[a] Eutectic composition. [b] The two $\delta T$ values are the deviations from the intersecting equations at the invariant point. The deviation from the equation for the lower-$x_1$ region is given first.

the basis of the ITS-90 scale. The accuracy of the temperature measurements was judged to be ±0.01 K. Mixtures were prepared by mass, and the errors did not exceed $\delta x_1 = 0.0005$ and $\delta T_1/K = 0.1$ in the mole fraction and temperature, respectively.

The densities of all the chemicals were measured using an Anton Paar DMA 602 vibrating-tube densimeter thermostated at $T = (298.15 \pm 0.01)$ K. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, specially purified benzene (CHEMIPAN, Poland 0.999), and dried air. The vibrating-tube temperature was measured with an Anton Paar DM 100-30 digital thermometer and was regulated to within better than ±0.01 K using a UNIPAN 60 thermostat and 202 temperature control system (UNIPAN, Poland). Mixtures were prepared by mass with the error in mole fraction being estimated as $< 5 \times 10^{-5}$. The densities of octylamine and the alcohols are in satisfactory agreement with the literature values, which is shown in Table 1.

## Results and Discussion

***SLE.*** Experimental (solid + liquid) equilibrium temperatures of an alcohol (1) + octylamine (2) are recorded in Table 2 and are shown in Figures 1−4. Molecular addition compounds melting congruently were observed, which was attributed to compound formation because of strong intermolecular interactions between an alcohol and octylamine. Solid compounds with the empirical formulas (ROH·octylamine) were formed by one OH group from the alcohol and one $NH_2$ group from the amine. The equilibrium temperatures $T$ were fitted using a least-squares method to the Ott equation:[25]

$$T/\mathrm{K} = T^*/\mathrm{K}\{1 + \sum_{j=1}^{n} a_j (x - x^*)^j\} \qquad (1)$$

where $x^*$ and $T^*$ were taken as the stoichiometric composition and melting temperature for the congruently melting compounds and as the melting temperature $T_m$ of pure substances ($x^*$ for pure substances is the value of $x$ at $T_m$). The deviation of the experimental temperature $\delta T$ from the temperature calculated by eq 1 is also shown in Table 2. The parameters of the fitting equation together with the standard deviation ($s$) are given in Table 3. Excellent fits were obtained for all mixtures. The curves in Figures 1−4 were drawn using the fitting equation. It is evident from the phase diagrams that congruently melting solid addition compounds with the empirical formulas 1:1 for all mixtures under study were detected. The eutectic compositions were obtained from the intersection of the liquidus lines. The invariant temperatures of (solid + liquid) diagrams are listed in Table 4. An increase

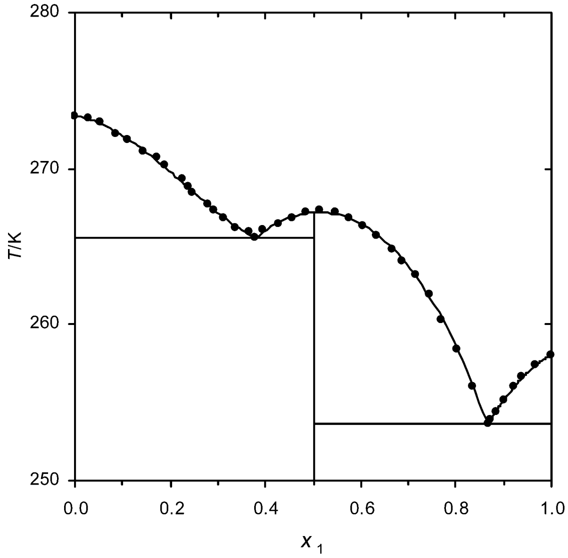

**Figure 1.** (Solid + liquid) phase diagram for 1-octanol (1) + octylamine (2): points, experimental equilibrium temperatures; solid lines, calculated from Ott's eq 1.

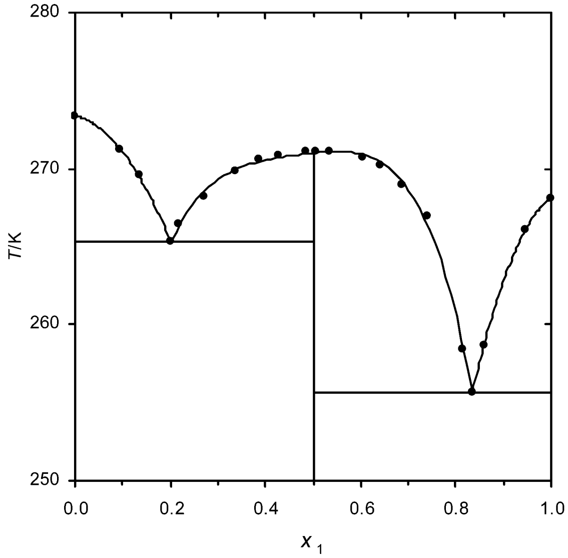

**Figure 2.** (Solid + liquid) phase diagram for 1-nonanol (1) + octylamine (2): points, experimental equilibrium temperatures; solid lines, calculated from Ott's eq 1.

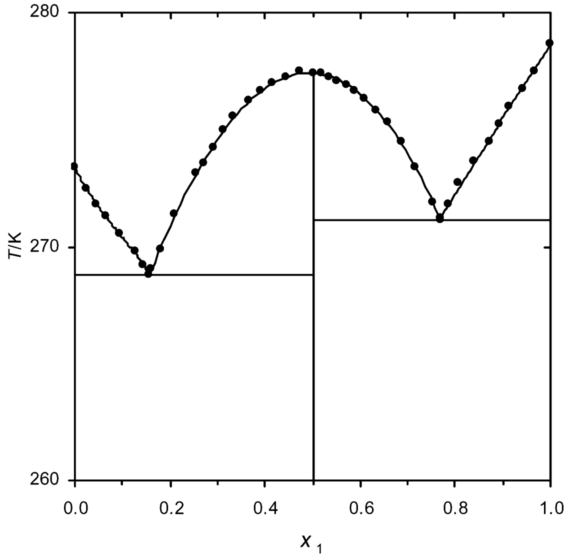

**Figure 3.** (Solid + liquid) phase diagram for 1-decanol (1) + octylamine (2): points, experimental equilibrium temperatures; solid lines, calculated from Ott's eq 1.

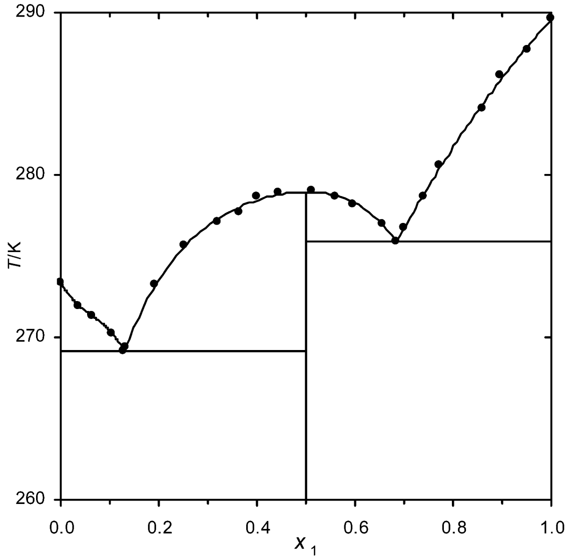

**Figure 4.** (Solid + liquid) phase diagram for 1-undecanol (1) + octylamine (2): points, experimental equilibrium temperatures; solid lines, calculated from Ott's eq 1.

in the number of carbon atoms in the alcohol chain length results in higher temperatures for the melting temperatures of compounds and eutectic points; the eutectic compositions were shifted to the higher concentration of amine in the binary mixture. The obtained results are very similar to those previously published for the alkanol + hexylamine mixtures.[1]

***Excess Molar Volumes***. Experimental data of the $V_m^E$ values of an (alcohol + octylamine) mixture are recorded in Table 5 together with the deviations $\delta V_m^E$, calculated from the smoothing Redlich−Kister equation:

$$\delta V_m^E = V_m^E - x_1(1 - x_1)\sum_{r=0}^{r=3} B_r\ (\mathrm{cm^3 \cdot mol^{-1}})(2x_1 - 1)^r \quad (2)$$

where $x_1$ is the mole fraction of the alcohol and $V_m^E$/cm$^3$·mol$^{-1}$ is the molar excess volume. The values of the parameters ($B_r$) have been determined using a method of least-squares. The parameters are given in Table 6 together with the standard deviation $\sigma$:

$$\sigma = \{\sum_{i=1}^{n}(V^E_{m(expt)} - V^E_{m(calc)})_i^2/(n - k)\}^{1/2} \quad (3)$$

where $n$ is the number of experimental points and $k$ is the number of coefficients.

The $V_m^E$ is negative for all mixtures over the entire composition range, which is presented in Figure 5. The minimum of $V_m^E$ occurs over the mole fraction range 0.51 $< x_1 <$ 0.52. The excess molar volume data become less negative in the following order: 1-octanol < 1-nonanol < 1-decanol < 1-undecanol. The $V^E_{m(min)}$ values were −1.07 cm$^3$·mol$^{-1}$ for $x_1 = 0.5223$, −1.05 for $x_1 = 0.5153$, −1.04 cm$^3$·mol$^{-1}$ for $x_1 = 0.5122$, and −1.01 cm$^3$·mol$^{-1}$ for $x_1 =$ 0.5138 for 1-octanol, 1-nonanol, 1-decanol, and 1-undecanol, respectively. These results show that the differences are very small. From our literature analysis of alcohol + amine

**Table 3. Coefficients $A_i$ for Eq 1**[a]

| $x_{\min}$ | $x_{\max}$ | $x^*$ | $T^*$/K | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $s^b$/K |
|---|---|---|---|---|---|---|---|---|
| | | | | 1-Octanol (1) + Octylamine (2) | | | | |
| 0.0000 | 0.3773 | 0.0000 | 273.37 | −0.016 48 | −0.345 02 | 0.496 22 | | 0.12 |
| 0.3773 | 0.8665 | 0.5000 | 267.19 | 0.008 80 | −0.342 00 | −0.074 20 | −0.243 06 | 0.09 |
| 0.8665 | 1.0000 | 1.0000 | 258.03 | 0.065 99 | −0.471 13 | | | 0.06 |
| | | | | 1-Nonanol (1) + Octylamine (2) | | | | |
| 0.0000 | 0.2017 | 0.0000 | 273.37 | −0.023 03 | −0.611 47 | | | 0.00 |
| 0.2017 | 0.8342 | 0.5000 | 271.01 | 0.011 64 | −0.072 71 | −0.439 57 | −2.876 68 | 0.28 |
| 0.8342 | 1.0000 | 1.0000 | 268.10 | 0.071 99 | −1.257 48 | | | 0.05 |
| | | | | 1-Decanol (1) + Octylamine (2) | | | | |
| 0.0000 | 0.1573 | 0.0000 | 273.37 | −0.148 36 | 0.636 62 | −2.353 60 | | 0.04 |
| 0.1573 | 0.7697 | 0.5000 | 277.42 | −0.004 39 | −0.282 76 | −0.028 34 | −0.046 00 | 0.06 |
| 0.7697 | 1.0000 | 1.0000 | 278.67 | 0.136 11 | 0.295 36 | 0.924 47 | | 0.08 |
| | | | | 1-Undecanol (1) + Octylamine (2) | | | | |
| 0.0000 | 0.1290 | 0.0000 | 273.37 | −0.189 76 | 1.703 83 | −8.909 90 | | 0.01 |
| 0.1290 | 0.6855 | 0.5000 | 278.97 | 0.000 36 | −0.206 75 | −0.369 02 | −1.337 21 | 0.15 |
| 0.6855 | 1.0000 | 1.0000 | 289.63 | 0.110 39 | −0.124 09 | | | 0.22 |

[a] Columns 1 and 2 give the range of $x_1$ over which the equation applies; $s$ is the standard deviation of $T$. [b] Given by the equation $s = [\sum_{i=1}^{n}\{(T_{\exp} - T_{\mathrm{calc}})_i^2/(n - k)\}]^{1/2}$; here $n$ is the number of experimental points, and $k$ is the number of parameters.

**Table 4. Summary of Invariant Points**

| type of invariant point | $x_1$ | $T$/K |
|---|---|---|
| 1-Octanol (1) + Octylamine (2) | | |
| eutectic | 0.3773 | 265.55 |
| compd ($C_8H_{17}OH{\cdot}C_8H_{19}N$) | 0.5000 | 267.19[a] |
| eutectic | 0.8665 | 253.65 |
| 1-Nonanol (1) + Octylamine (2) | | |
| eutectic | 0.2017 | 265.30 |
| compd ($C_9H_{19}OH{\cdot}C_8H_{19}N$) | 0.5000 | 271.01[a] |
| eutectic | 0.8342 | 255.68 |
| 1-Decanol (1) + Octylamine (2) | | |
| eutectic | 0.1573 | 268.78 |
| compd ($C_{10}H_{21}OH{\cdot}C_8H_{19}N$) | 0.5000 | 277.42[a] |
| eutectic | 0.7697 | 271.15 |
| 1-Undecanol (1) + Octylamine (2) | | |
| eutectic | 0.1290 | 269.20 |
| compd ($C_{11}H_{23}OH{\cdot}C_8H_{19}N$) | 0.5000 | 278.97[a] |
| eutectic | 0.6855 | 275.90 |

[a] Melting temperature of congruently melting molecular addition compound.

systems it may be concluded that interactions between longer alkanols and amines are weaker than those between methanol or ethanol and an amine.[9]

## Theories

***ERAS Model.*** The ERAS model pure components' parameters—association constants $K_A$ and $K_B$ and enthalpies $\Delta h_A^*$ and $\Delta h_B^*$—are very well-known for alcohols and amines from spectroscopic and thermodynamic measurements. The changes of volumes $\Delta v_A^*$ and $\Delta v_B^*$ are also known from thermodynamic descriptions of (an alcohol or an amine + an alkane) mixtures, as they were fitted to $V_m^E$ values of (alcohol or amine + alkane) systems. The interaction parameter $\chi_{AB}$ is the only adjustable parameter of the physical part of $V_m^E$ and $H_m^E$.[6,26] The remaining parameters $K_{AB}$, $\Delta h_{AB}^*$, $\Delta v_{AB}^*$, and $\chi_{AB}$ are usually simultaneously adjusted parameters to $V_m^E$ and $H_m^E$ experimental data. More details are given in the literature.[2,6,26]

Parameters for pure compounds and those corresponding to the mixtures analyzed in this work are listed in Tables 7 and 8. As in our first work of this series,[1] in this work the values of the hydrogen bond enthalpies for longer chain alcohols were assumed (see Table 7) having in mind the discussions of the association constants provided by Nagata.[29,31]

**Table 5. Experimental Data of Excess Molar Volume $V_m^E$ and Deviations $\delta V_m^E$ at 298.15 K**

| $x_1$ | $V_m^E$ $\mathrm{cm^3{\cdot}mol^{-1}}$ | $10^{-3}\delta V_m^E$ $\mathrm{cm^3{\cdot}mol^{-1}}$ | $x_1$ | $V_m^E$ $\mathrm{cm^3{\cdot}mol^{-1}}$ | $10^{-3}\delta V_m^E$ $\mathrm{cm^3{\cdot}mol^{-1}}$ |
|---|---|---|---|---|---|
| | | 1-Octanol (1) + Octylamine (2) | | | |
| 0.0430 | −0.1921 | −30.7 | 0.5540 | −1.0682 | −2.1 |
| 0.1300 | −0.4625 | −11.3 | 0.5877 | −1.0515 | 0.3 |
| 0.2358 | −0.7264 | 7.1 | 0.6385 | −1.0123 | −1.4 |
| 0.3041 | −0.8581 | 14.4 | 0.7090 | −0.9034 | 11.4 |
| 0.3470 | −0.9393 | 2.4 | 0.7589 | −0.8079 | 10.3 |
| 0.4158 | −1.0244 | −2.1 | 0.8750 | −0.5102 | −11.3 |
| 0.4571 | −1.0621 | −9.8 | 0.9290 | −0.3207 | −17.1 |
| 0.5174 | −1.0712 | −0.8 | 0.9920 | −0.0724 | −35.5 |
| | | 1-Nonanol (1) + Octylamine (2) | | | |
| 0.0489 | −0.1701 | −21.5 | 0.5326 | −1.0570 | −3.3 |
| 0.1572 | −0.4742 | −0.6 | 0.5732 | −1.0490 | −11.1 |
| 0.2155 | −0.6354 | −2.5 | 0.6064 | −1.0157 | −3.3 |
| 0.2763 | −0.7661 | 12.5 | 0.6370 | −0.9761 | 2.9 |
| 0.3283 | −0.8704 | 12 | 0.6602 | −0.9511 | −3.6 |
| 0.3560 | −0.9277 | 0.9 | 0.7321 | −0.8074 | 9.7 |
| 0.4125 | −1.0052 | −3.5 | 0.7905 | −0.6629 | 14.8 |
| 0.4566 | −1.0434 | −5.8 | 0.8753 | −0.4313 | −1.2 |
| 0.4998 | −1.0553 | −1.3 | 0.9610 | −0.1661 | −26.2 |
| | | 1-Decanol (1) + Octylamine (2) | | | |
| 0.0791 | −0.2401 | −4.7 | 0.5525 | −1.0393 | −5.3 |
| 0.1302 | −0.3963 | −8.8 | 0.5811 | −1.0231 | −5.4 |
| 0.2056 | −0.6005 | −2 | 0.6153 | −0.9952 | −7.9 |
| 0.2788 | −0.7660 | 9.1 | 0.6452 | −0.9534 | −2.4 |
| 0.3263 | −0.8612 | 8.4 | 0.6956 | −0.8646 | 5.6 |
| 0.3863 | −0.9584 | 3.2 | 0.7565 | −0.7349 | 7.2 |
| 0.4220 | −1.0023 | −1.7 | 0.8463 | −0.4965 | 4.7 |
| 0.4623 | −1.0302 | −0.7 | 0.9025 | −0.3208 | 5.7 |
| 0.5138 | −1.0425 | −0.1 | 0.9700 | −0.1278 | −25.8 |
| | | 1-Undecanol (1) + Octylamine (2) | | | |
| 0.0752 | −0.2147 | −2.4 | 0.5463 | −1.0078 | −3 |
| 0.1043 | −0.2984 | −2.4 | 0.5958 | −0.9803 | −4.3 |
| 0.1334 | −0.3833 | −4.6 | 0.6390 | −0.9391 | −8.3 |
| 0.2069 | −0.5724 | 4.8 | 0.6894 | −0.8580 | −2.6 |
| 0.3217 | −0.8290 | 1.4 | 0.7458 | −0.7411 | 3 |
| 0.4007 | −0.9437 | 2.6 | 0.7961 | −0.6060 | 17.4 |
| 0.4491 | −0.9846 | 4.5 | 0.8730 | −0.4122 | −5.2 |
| 0.4941 | −1.0081 | 0.1 | 0.9158 | −0.2804 | −6.3 |

The ERAS parameters for A + B interactions, presented in Table 7, exhibit a quite small value of the enthalpy of interaction for all (alcohol + amine) mixtures, $\Delta h_{AB}^*$ −40.8 kJ·mol$^{-1}$, which is very close to the results published previously (the constant value −41.6 kJ·mol$^{-1}$).[6] Values of association constants for 1-octanol and 1-decanol were taken to be the same as previously,[6] and for all alcohols, they differ more or less for each system. The values of $K_{AB}$

**Table 6. Coefficients of the Redlich–Kister Equation and Standard Deviation $\sigma$ for $V_m^E$ of Binary Mixtures of Alcohol (1) + Octylamine (2) at 298.15 K**

| | $B_0$ | $B_1$ | $B_2$ | $10^3\sigma$ |
|---|---|---|---|---|
| component | $cm^3\cdot mol^{-1}$ | $cm^3\cdot mol^{-1}$ | $cm^3\cdot mol^{-1}$ | $cm^3\cdot mol^{-1}$ |
| 1-octanol | −4.2733 | −0.3837 | | 15.5 |
| 1-nonanol | −4.2161 | −0.3139 | 0.9075 | 11.5 |
| 1-decanol | −4.1666 | −0.2535 | 1.0187 | 8.9 |
| 1-undecanol | −4.0369 | −0.2801 | 1.0333 | 6.6 |

**Table 7. ERAS Model Parameters of Pure Components at 298.15 K**

| | α | $\kappa_T$ | $\Delta h^*$ | $\Delta v^*$ | |
|---|---|---|---|---|---|
| component | $10^{-4}\ K^{-1}$ | $10^{-7}\ kPa^{-1}$ | $kJ\cdot mol^{-1}$ | $cm^3\cdot mol^{-1}$ | $K_A$ |
| octylamine | 9.67[a] | 8.70[b] | −13.2[b] | −2.8[b] | 0.620[c] |
| 1-octanol | 8.27[d] | 7.77[e] | −21.9[f] | −5.6[b] | 98[e] |
| 1-nonanol | 8.18[g] | 7.40[g] | −21.9[f] | −5.6[b] | 91.85[h] |
| 1-decanol | 8.12[d] | 7.33[e] | −21.8[f] | −5.6[b] | 88[e] |
| 1-undecanol | 8.06[g] | 7.34[g] | −21.8[i] | −5.6[b] | 82.2[h] |

[a] Reference 23. [b] Reference 6. [c] Reference 27. [d] Reference 28. [e] Reference 11. [f] Recalculated for 298.15 K from ref 29. [g] Reference 30. [h] Values interpolated or extrapolated for alcohols from $C_3$ to $C_{16}$, according to ref 29. [i] Reference 31.

lie between 51 and 80, while those for lower alcohols were much higher.[6] Our new measurements of the excess molar volumes have changed the values of $\Delta v_{AB}^*$ for two alcohols ($C_8$, $C_{10}$) and were defined for two others ($C_9$, $C_{11}$). Our value is between −11.0 $cm^3\cdot mol^{-1}$ and −10.1 $cm^3\cdot mol^{-1}$.[6] The description by the ERAS model was made more precisely compared with the discussion in the literature.[6] The general agreement is good, but as is presented in Figures 5 and 6, the symmetry of $V_m^E$ and $H_m^E$ is not described properly by the ERAS model. The strongly negative $H_m^E$ curves are dominated by the chemical contribution, and the curves are strongly shifted to the higher alcohol concentration range. One may assume that this is attributed to a pure alcohol or to an amine overdescribed association constant or enthalpy or volume. The strongest O−H···N hydrogen bond exceeds by −40.8 $kJ\cdot mol^{-1}$ the −21.8 to −21.9 $kJ\cdot mol^{-1}$ of the O−H···O hydrogen bond between the alcohol molecules. The $V_{m(min)}^E$ values are very similar for the measured mixtures. This is evidence of the structural implications of the long chain alcohols and amines, where the intermolecular interactions and packing effects are very similar.

***DISQUAC.*** It was shown that DISQUAC,[7−10,15,16] a purely physical model based on the rigid lattice theory, is

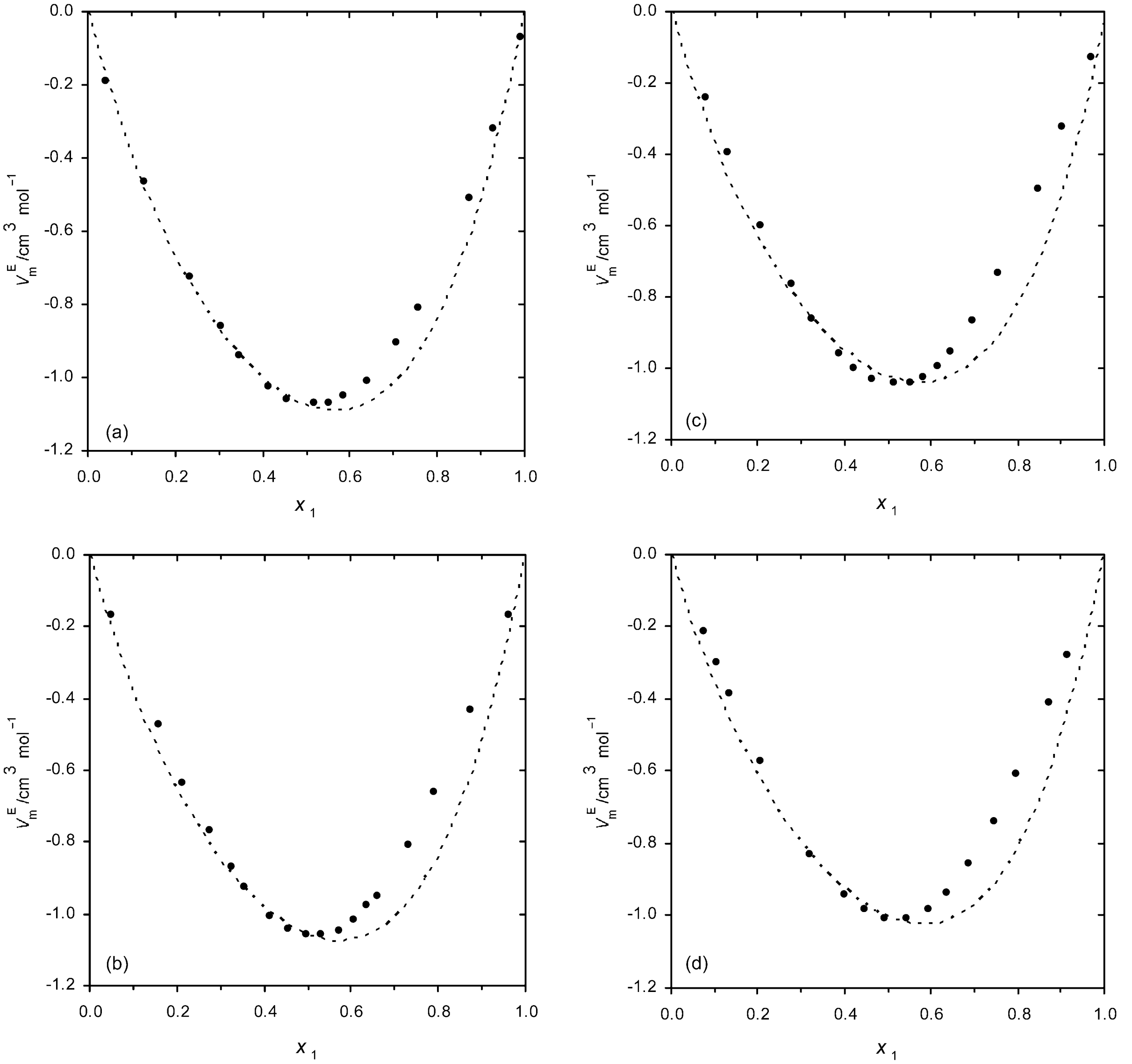

**Figure 5.** $V_m^E$ for alcohol (1) + octylamine (2) mixtures at 298.15 K for (a) 1-octanol, (b) 1-nonanol, (c) 1-decanol, and (d) 1-undecanol: points, experimental results; dotted line, ERAS calculations.

**Table 8. ERAS Model Parameters for Binary Mixtures at 298.15 K**

| mixture: alkanol + octylamine | $K_{AB}$ | $\Delta h^*_{AB}$ kJ·mol$^{-1}$ | $\Delta v^*_{AB}$ cm$^3$·mol$^{-1}$ | $\chi_{AB}$ J·cm$^{-3}$ |
|---|---|---|---|---|
| 1-octanol | 80 | −40.8 | −11.0 | 9 |
| 1-nonanol | 66 | −40.8 | −11.0 | 9 |
| 1-decanol | 55 | −40.8 | −11.0 | 8 |
| 1-undecanol | 51 | −40.8 | −11.0 | 8 |

**Table 9. Relative Group Increments for Molecular Volumes, $r_G = R_G/R_{CH_4}$, and Areas, $q_G = Q_G/Q_{CH_4}$, Calculated Using Bondi's Method[32]**

| group | $r_G$ | $q_G$ | ref |
|---|---|---|---|
| $CH_3$ | 0.798 48 | 0.731 03 | 33 |
| $CH_2$ | 0.597 55 | 0.465 52 | 33 |
| OH | 0.469 63 | 0.503 45 | 34 |
| $NH_2$ | 0.615 65 | 0.600 00 | 35 |

a powerful tool to describe thermodynamic properties of the mentioned solutions assuming structure-dependent interaction parameters. It is remarkable that the DISQUAC model gives similar results to those obtained using association models.

In the framework of the DISQUAC model, a mixture of an alkan-1-ol with a primary linear amine is regarded as possessing three types of surfaces: (i) type a (aliphatic: $CH_3$, $CH_2$ in alcohols or amines); (ii) type n ($NH_2$ in primary amines); (iii) type h (hydroxyl, OH in alcohols). When the DISQUAC model is applied, the total relative molecular volumes $r_i$, the surface areas $q_i$, and the molecular surface fractions $\alpha_{si}$ of the compounds present in the mixture are usually calculated additively on the basis of the group volumes $r_G$ and surface areas $q_G$ recommended by Bondi.[32] The geometrical parameters referred to in this work are listed in Table 9.

The equation to calculate $H^E_m$/J·mol$^{-1}$ is the same as that in other applications.[34] For the QUAC part, as coordination number, the reference value was chosen, that is $z = 4$. The temperature dependence of the interaction parameters $g_{st}$, $h_{st}$, and $c_{pst}$ has been expressed in terms of the DIS and QUAC interchange coefficients[15] $C^{DIS}_{st,l}$ and $C^{QUAC}_{st,l}$, where s and t = a, h, and n and $l = 1$ (Gibbs energy; $C^{DIS/QUAC}_{st,1} = g^{DIS/QUAC}_{st}(T_0)/RT_0$); $l = 2$ (enthalpy; $C^{DIS/QUAC}_{st,2} = h^{DIS/QUAC}_{st}(T_0)/RT_0$); and $l = 3$ (heat capacity; $C^{DIS/QUAC}_{st,3} = c^{DIS/QUAC}_{pst}(T_0)/R$). $T_0 = 298.15$ K is the scaling temperature.

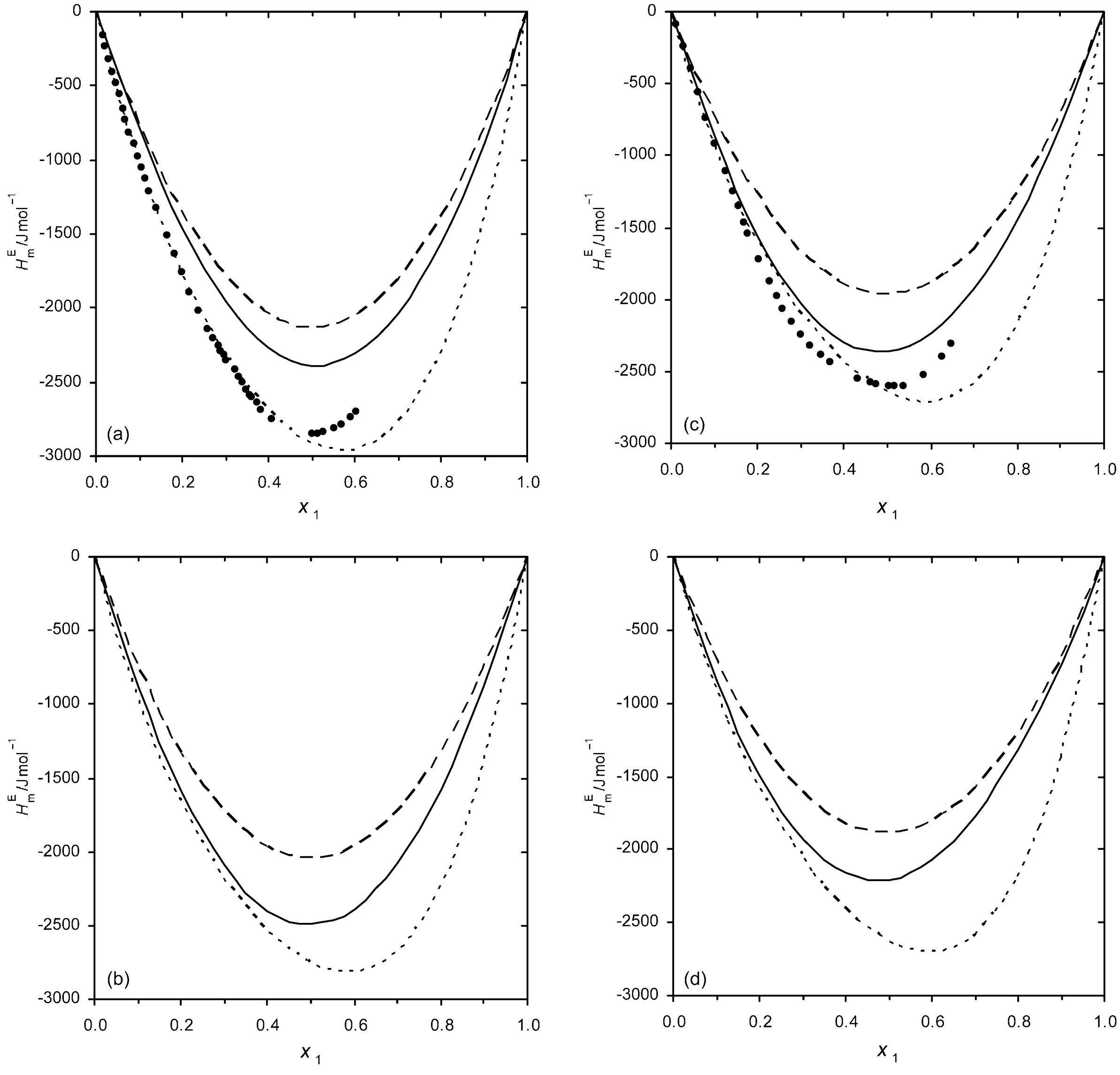

**Figure 6.** $H^E_m$ for alcohol (1) + octylamine (2) mixtures at 298.15 K (ref 6) for (a) 1-octanol, (b) 1-nonanol, (c) 1-decanol, and (d) 1-undecanol; points, experimental results; dotted lines, ERAS calculations; solid lines, DISQUAC results; dashed lines, modified UNIFAC results.

**Table 10. Interchange Coefficients, $C_{\mathrm{st},l}^{\mathrm{DIS}}$ and $C_{\mathrm{st},l}^{\mathrm{QUAC}}$ [a]**

| system | $C_{\mathrm{hn},1}^{\mathrm{DIS}}$ | $C_{\mathrm{hn},2}^{\mathrm{DIS}}$ | $C_{\mathrm{hn},3}^{\mathrm{DIS}}$ | $C_{\mathrm{hn},1}^{\mathrm{QUAC}}$ | $C_{\mathrm{hn},2}^{\mathrm{QUAC}}$ | $C_{\mathrm{hn},3}^{\mathrm{QUAC}}$ | ref |
|---|---|---|---|---|---|---|---|
| 1-octanol + octylamine | −11.4 | −73 | 8.0 | 1.5 | 3.25 | 6.0 | 9 |
| 1-nonanol or 1-decanol or 1-undecanol + octylamine | −11.4 | −80 | 8.0 | 1.5 | 3.25 | 6.0 | 9 |

| system | $C_{\mathrm{an},1}^{\mathrm{DIS}}$ | $C_{\mathrm{an},2}^{\mathrm{DIS}}$ | $C_{\mathrm{an},3}^{\mathrm{DIS}}$ | $C_{\mathrm{an},1}^{\mathrm{QUAC}}$ | $C_{\mathrm{an},2}^{\mathrm{QUAC}}$ | $C_{\mathrm{an},3}^{\mathrm{QUAC}}$ | ref |
|---|---|---|---|---|---|---|---|
| alcohol + octylamine | 1.2 | 2.4 | 0 | 3.51 | 7.2 | 0 | 35 |

| system | $C_{\mathrm{ah},1}^{\mathrm{DIS}}$ | $C_{\mathrm{ah},2}^{\mathrm{DIS}}$ | $C_{\mathrm{ah},3}^{\mathrm{DIS}}$ | $C_{\mathrm{ah},1}^{\mathrm{QUAC}}$ | $C_{\mathrm{ah},2}^{\mathrm{QUAC}}$ | $C_{\mathrm{ah},3}^{\mathrm{QUAC}}$ | ref |
|---|---|---|---|---|---|---|---|
| 1-octanol or 1-nonanol + octylamine | 8.16 | 2.9 | −27.5 | 12.2 | 13.2 | 71.1 | 37, 38 |
| 1-decanol or 1-undecanol + octylamine | 12.8 | 5.0 | −33.5 | 12.2 | 12.0 | 71.1 | 37, 38 |

[a] s, t = a, h, n; $l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity for contacts (h,n), (a,n), (a,h) (type h, OH in alkanols; type n, $NH_2$ in amine; type s = a, aliphatic).

**Table 11. Molar Excess Enthalpies, $H_{\mathrm{m}}^{\mathrm{E}}$, at 298.15 K and Equimolar Composition for Alkanol + Octylamine Mixtures**

| | | $H_{\mathrm{m}}^{\mathrm{E}}$/J·mol$^{-1}$ | | | | $\sigma(H_{\mathrm{m}}^{\mathrm{E}})^{a}$/J·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| system | $n^{b}$ | exp$^{c}$ | ERAS | DQ | UNIF | exp$^{c}$ | ERAS | DQ | UNIF |
| 1-octanol | 42 | −2848 | −2912 | −2387$^{d}$ | −2134$^{d}$ | 9$^{d}$ | 70 | 335$^{d}$ | 487$^{d}$ |
| 1-nonanol$^{e}$ | | | −2757 | −2494 | −2047 | | | | |
| 1-decanol | 29 | −2606 | −2648 | −2360$^{d}$ | −1965$^{d}$ | 21$^{d}$ | 125 | 164$^{d}$ | 472$^{d}$ |
| 1-undecanol$^{e}$ | | | −2632 | −2208 | −1888 | | | | |

[a] See eq 4. [b] $n$ = number of experimental points. [c] Reference 6. [d] Calculated earlier with small differences in ref 9. [e] Direct experimental data not available.

The three types of surfaces generate three pairs of contacts: (a,n), (a,h), and (h,n). The aliphatic/amine (a,n) interactions are represented by DIS and QUAC coefficients. DISQUAC interaction parameters were calculated on the basis of experimental data for these systems.[36,37] Similarly, the aliphatic/hydroxyl contacts (a,h) are also described by both DIS and QUAC interchange coefficients, obtained from data for alkan-1-ols + $n$-alkanes systems.[34,38] The aliphatic/amine (a,n), aliphatic/hydroxyl (a,h), and hydroxyl/amine (h,n) interactions were taken from the literature. The DISQUAC interaction parameters are listed in Table 10.

***Modified UNIFAC Model (Dortmund Version).*** Changing of the combinatorial term from the original UNIFAC model[39] and including the temperature dependence of the group interaction parameters made the modified UNIFAC model an important tool for the prediction of the thermodynamic properties of the presented mixtures. The corresponding published geometrical and interaction parameters were used without modification.[17] Equations were given in ref 9.

In the modified UNIFAC model, alcohols are characterized by two main groups, OH and $CH_3OH$. The former is subdivided in subgroups: OH(p), OH(s), and OH(t), which represent the hydroxyl group in primary, secondary, and tertiary alcohols. Primary amines are characterized by the main group $CNH_2$, which is subdivided into four subgroups: $CH_3NH_2$, $CH_2NH_2$, $CHNH_2$, and $CNH_2$. The subgroups have different geometrical parameters, but the subgroups within the same main group are assumed to have identical group energy-interaction parameters. The interaction parameters were taken from the literature.[17]

The comparison between the experimental data of $H_{\mathrm{m}}^{\mathrm{E}}$ and the results obtained using the ERAS model, the DISQUAC model, and the modified UNIFAC model is presented in Table 11 and in Figure 6. The standard deviations for $H_{\mathrm{m}}^{\mathrm{E}}$ defined by eq 7 and the equimolar values of $H_{\mathrm{m}}^{\mathrm{E}}$ calculated by different models in comparison with the experimental values are presented in Table 11:

$$\sigma(H_{\mathrm{m}}^{\mathrm{E}})/\mathrm{J{\cdot}mol^{-1}} = [(1/n)\sum(H_{\mathrm{m(exp)}}^{\mathrm{E}} - H_{\mathrm{m(calc)}}^{\mathrm{E}})^2]^{1/2} \quad (4)$$

In eq 4, $n$ is the number of data points of each system. From the standard deviation values we can conclude that the DISQUAC model provides the best results of the prediction. Comparing the results from Table 11 with the data of exact, full analyses made by Gonzalez et al.,[9] the results for 1-octanol and 1-decanol are close to the same with better description with the ERAS model. Two new mixtures were added to the discussion: (1-nonanol and 1-undecanol + octylamine).

## Conclusions

The results obtained from our study reveal that strong negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ and $H_{\mathrm{m}}^{\mathrm{E}}$, observed for (an alcohol + an amine) mixtures, were perfectly confirmed by the solid + liquid equilibria measurements. Solid, congruently melting addition compounds, formed with the empirical formulas 1:1, were described only by the Ott equation and to our knowledge were never discussed in the frame of the other models used in this work.

The $V_{\mathrm{m}}^{\mathrm{E}}$ results for the mixtures (an alcohol + octylamine) indicate that as the aliphatic chain length of an alcohol increases from $C_8$ to $C_{11}$, the level of the interaction effects between A and B molecules is not significantly different. Besides the new $V_{\mathrm{m}}^{\mathrm{E}}$ data measured for four mixtures, the values of $H_{\mathrm{m}}^{\mathrm{E}}$ were predicted by three models for (1-nonanol and 1-undecanol + octylamine) systems. For two mixtures the description by the ERAS model, discussed in the literature,[9] was improved.

The negative values of the excess molar functions of these systems may be interpreted in terms of two opposing effects: (a) In the pure state, both the alkanol and amine are self-associated by the formation of O−H···O and N−H···N bonds, respectively. The disruption of that association leads to a positive contribution to $H_{\mathrm{m}}^{\mathrm{E}}$. (b) Strong intermolecular interactions between the hydroxyl and amine groups upon mixing contribute negatively to $H_{\mathrm{m}}^{\mathrm{E}}$. Thus, $H_{\mathrm{m}}^{\mathrm{E}} < 0$ means that, even for longer chain molecules of alkanol and amine, the O−H···N bonds are stronger than the O−H···O and N−H···N bonds.

Finally, it should be noted that, as it is known, the main advantage of the ERAS model, which combines the real association theory[1−11] with a physical contribution, the Flory's equation of state,[14] is its ability to describe simultaneously $V_m^E$ and $H_m^E$. In contrast, in the framework of the DISQUAC model, $V_m^E = 0$, since DISQUAC is a rigid lattice theory. On the other hand, the ERAS model is only applicable to those systems where association is expected. The DISQUAC and modified UNIFAC models, the purely physical models, can be applied to any type of binary mixtures. In our work the DISQUAC model describes the $H_m^E$ (see Figure 6 and Table 11) better than the modified UNIFAC model but worse than ERAS model.

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