Derived thermodynamic properties of alcohol + cyclohexylamine mixtures

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Abstract: Thermal expansion coefficients, α, excess thermal expansion coefficients, α^E, isothermal coefficients of pressure excess molar enthalpy, $(\partial H^E/\partial p)_{T,x}$, partial molar volumes, $\bar{V}_i$, partial molar volumes at infinite dilution, $\bar{V}_i^\infty$, partial excess molar volumes, $\bar{V}_i^E$, and partial excess molar volumes at infinite dilution, $\bar{V}_i^{E,\infty}$, were calculated using experimental densities and excess molar volumes, V^E, data. All calculations are performed for the binary systems of cyclohexylamine with 1-propanol or 1-butanol or 2-butanol or 2-methyl-2-propanol. The Redlich–Kister polynomial and the reduced excess molar volume approach were used in the evaluation of these properties. In addition, the aim of this investigation was to provide a set of various volumetric data in order to asses the influence of temperature, chain length and position of hydroxyl group in the alcohol molecule on the molecular interactions in the examined binary mixtures.

Keywords: binary mixtures; densities; volumetric properties; alcohols; cyclohexylamine.

INTRODUCTION

Knowledge of derived thermodynamics properties such as partial molar volumes, excess partial molar volumes, thermal expansion coefficients, excess thermal expansion and isothermal coefficient of pressure excess molar enthalpy is of practical interest and importance in the investigation of specific interactions of complex liquid mixtures, such as mixtures containing alcohols.[1]

In last few years, considerable work has been performed in order to better understand the molecular structures of solutions with strong interactions.

The densities of binary mixtures of cyclohexylamine with 1-propanol or 1-butanol or 2-butanol or 2-methyl-2-propanol or 1-pentanol were already experi-

mentally determined and details of this research were given previously.[2,3] In this paper, the results of density measurements and calculated data of excess molar volumes were used for additional analyses.

In this work, the aforementioned thermodynamic derived properties for binary systems of cyclohexylamine with 1-propanol or 1-butanol or 2-butanol or 2-methyl-2-propanol or 1-pentanol were evaluated using the Redlich–Kister Equation and the reduced excess molar volume approach.

The derived properties were used to assess the influence of temperature, chain length and position of the hydroxyl group in the alcohol molecule on molecular interactions in the examined binary mixtures.

RESULTS AND DISCUSSION

The excess molar volumes, V^E, of the binary mixtures were calculated from density data by applying Eq. (1):

$$V^E = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \qquad (1)$$

where x_1, x_2, M_1 and M_2 are the mole fraction and molar mass of components 1 and 2, while ρ, ρ_1 and ρ_2 stand for the measured densities of the mixture, and the pure components 1 and 2, respectively.

The obtained V^E values were fitted to a modified Redlich–Kister (RK) polynomial:[4]

$$V^E = x_1 x_2 \sum_{p=0}^{m} B_p (x_1 - x_2)^p \qquad (2)$$

where B_p denotes a temperature dependent parameter:

$$B_p = \sum_{q=0}^{k} B_{pq} T^q \qquad (3)$$

where T stands for the absolute temperature.

The results were also explained using the reduced excess molar volume, $V^E/x_1(1 - x_1)$, which has a better physical significance and is more sensitive than V^E to interactions which occur in dilute regions:

$$V^E/x_1(1-x_1) = \sum_{n=0}^{l} A_n x^n \qquad (4)$$

where the optimal number of parameters A_n was 3. The values of the adjustable parameters of Eq. (4), B_{pq} and A_n, were given previously.[2]

The thermal expansion coefficient, α, for a pure component and for a mixture can be computed using the expression:

$$\alpha = (\partial \ln \rho / \partial T)_{p,x} \qquad (5)$$

which takes into account the temperature dependence of the density. The expression relating the molar volume of a mixture and its excess molar volume, in accordance to Eq. (1), is:

$$V = \sum_{i=1}^{N} x_i V_i^\circ + V^E \tag{6}$$

where V_i° is the molar volume of pure component i and N is the number of components in a mixture. Differentiation of Eq. (6) and dividing by V leads to:[5]

$$\alpha = V^{-1}((\partial V^E / \partial T)_{p,x_i} + \sum_{i=1}^{N} \alpha_i x_i V_i^\circ) \tag{7}$$

where α and α_i are the thermal expansion coefficients of the mixture and the pure component, respectively. Comparison of the α values with literature data[6–8] of pure components at selected temperatures showed very good agreement up to 7×10^{-3} K^{-1}.

The excess thermal expansion coefficient, α^E, is calculated as:

$$\alpha^E = \alpha - \sum_{i=1}^{N} \phi_i \alpha_i \tag{8}$$

where ϕ_i is the volume fraction of component i:

$$\phi_i = x_i V_i^\circ / \sum_{i=1}^{N} x_i V_i^\circ \tag{9}$$

In addition, the isothermal coefficient of the pressure excess molar enthalpy, $(\partial H^E / \partial p)_{T,x}$, can be derived from volumetric measurements using the following expression:

$$(\partial H^E / \partial p)_{T,x} = V^E - T(\partial V^E / \partial T)_{p,x} \tag{10}$$

Values of α, α_i and $(\partial H^E / \partial p)_{T,x}$ for the examined binary mixtures over the entire studied temperature range are summarized in Table I (supplementary material, electronic version only at http://www.shd.org.rs/jscs/) and are graphically represented in Fig. 1 for 303.15 K. For all liquids, α increases with increasing temperature and decreases with the chain length of the 1-alcohols. The values of α for 2-butanol and 2-methyl-2-propanol are higher than those of the 1-alcohols for the same temperature. Fig 1a shows that for 1-alcohol molecules, the value of α for the mixtures slightly decreases with mole fraction of the alcohols. However, the branched alcohols behave in a rather different way, particularly for the system with 2-methyl-2-propanol where α sharply increases as the concentration of 2-methyl-2-propanol increases. For the system with 2-butanol, α is nearly constant with slight sigmoid shape. As can be seen from Fig 1b, all the excess thermal expansion coefficient, α^E, curves for the systems 1-alcohol + cyclohexylamine have sigmoid shape with small values which slightly increase with increasing temperature.
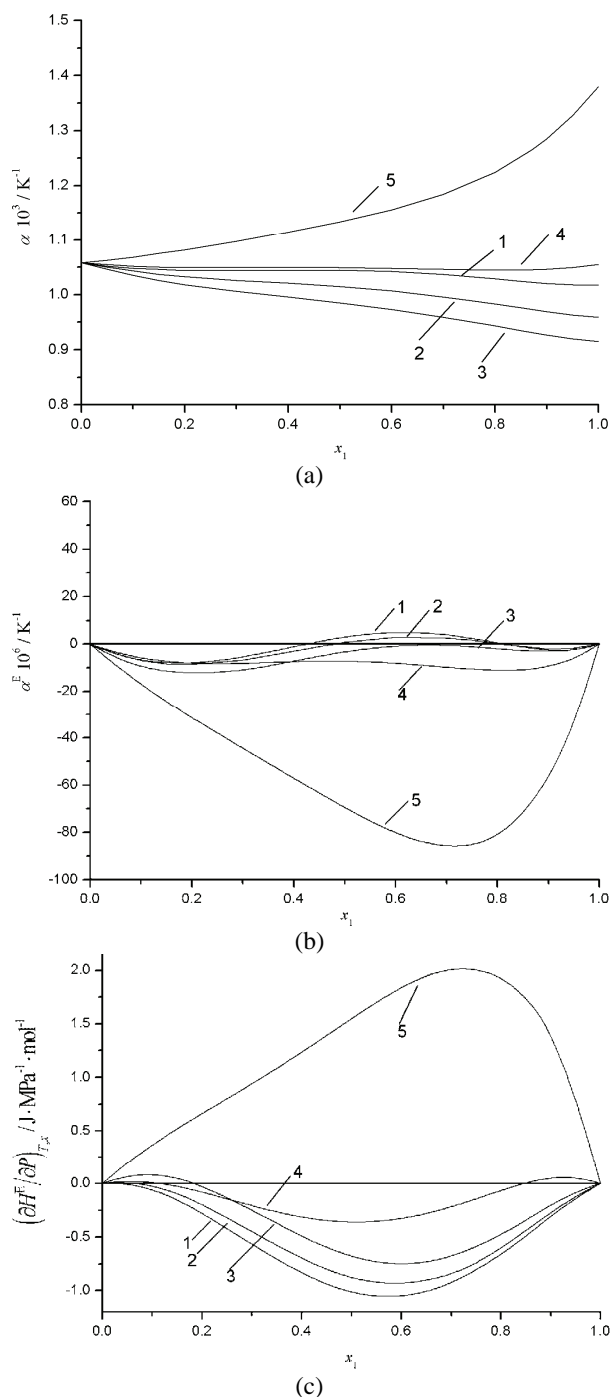
Fig. 1. Plots of a) the thermal expansion coefficient, α, b) excess thermal expansion coefficient, α^E and c) isothermal coefficient of pressure excess molar enthalpy, $(\partial H^E/\partial p)_{T,x}$, at 303.15 K for the systems: 1-propanol (1) + cyclohexylamine (2), line 1; 1-butanol (1) + cyclohexylamine (2), line 2; 1-pentanol (1) + cyclohexylamine (2), line 3; 2-butanol (1) + cyclohexylamine (2), line 4; 2-methyl-2-propanol (1) + cyclohexylamine (2), line 5.

As can be observed from Fig 1c, for all systems except for the system with 2-methyl-2-propanol, the isothermal coefficient of pressure excess molar enthalpy, $(\partial H^E/\partial p)_{T,x}$, become more negative with increasing temperature. For the system 2-methyl-2-propanol + cyclohexylamine, this quantity is positive and rises with increasing temperature.

Furthermore, the partial molar volumes, $\overline{V}_1$, and $\overline{V}_2$, of components 1 and 2, can be calculated using the equations:

$$\overline{V}_1 = V^E + V_1^\circ + (1-x_1)(\partial V^E/\partial x_1)_{p,T} \tag{11}$$

$$\overline{V}_2 = V^E + V_2^\circ - x_1(\partial V^E/\partial x_1)_{p,T} \tag{12}$$

Differentiation of Eq. (2) with respect to x_1, leads to the following equations for the partial molar volumes:

$$\overline{V}_1 = V_1^\circ + (1-x_1)^2 (\sum_{p=0}^{m} B_p(2x_1-1)^p + x_1 \sum_{p=1}^{m} 2pB_p(2x_1-1)^{p-1}) \tag{13}$$

$$\overline{V}_2 = V_2^\circ + (1-x_2)^2 (\sum_{p=0}^{m} B_p(2x_1-1)^p - x_2 \sum_{p=1}^{m} 2pB_p(2x_1-1)^{p-1}) \tag{14}$$

In Eqs. (13) and (14), B_p is the temperature dependent parameter defined by Eq. (3).

Table I (supplementary material, electronic version only at http://www.shd.org.rs/jscs/) also presents the partial molar volumes, $\overline{V}_i$, for both components in the investigated mixtures, calculated by Eqs. (13) and (14) using the RK parameters listed previously.[2]

Plots of the partial molar volumes, $\overline{V}_1$ and $\overline{V}_2$, and partial excess molar volumes, $\overline{V}_1^E$ and $\overline{V}_2^E$, are presented in Figs. 2 a–d, respectively. From Figs. 2a and 2b, it is clear that the influence of temperature on the partial molar volume $\overline{V}_1$ and $\overline{V}_2$ for all mixtures is low and that a slightly increasing trend appears when the temperature is increased. Figures 2c and 2d show that for all systems, the partial excess molar volumes, $\overline{V}_1^E$ and $\overline{V}_2^E$, over the whole concentration range are negative, indicating that the interactions of unlike molecules is stronger than those of like molecules.

A great part of investigations of volumetric behavior is related to the derived volumetric properties, $\overline{V}_i^\infty$ and $\overline{V}_i^{E,\infty}$. Setting $x_1 = 0$ and $x_1 = 1$ leads to the equations for the partial molar volumes at infinite dilution, $\overline{V}_1^\infty$ and $\overline{V}_2^\infty$:

$$\overline{V}_1^\infty = V_1^\circ + \sum_{p=0}^{m} B_p(-1)^p \tag{15}$$

$$\overline{V}_2^\infty = V_2^\circ + \sum_{p=0}^{m} B_p \tag{16}$$

Available online at www.shd.org.rs/JSCS/

In this work, the partial excess molar volumes, $\overline{V}_1^{\text{E}}$ and $\overline{V}_2^{\text{E}}$, were calculated from the equations:

$$\overline{V}_1^{\text{E}} = \overline{V}_1 - V_1^{\circ} \qquad (17)$$

$$\overline{V}_2^{\text{E}} = \overline{V}_2 - V_2^{\circ} \qquad (18)$$

where $\overline{V}_1$ and $\overline{V}_2$ are the partial molar volumes calculated from Eqs. (13) and (14), respectively. The results for $\overline{V}_i^{\text{E}}$ are also given in Table I (supplementary material, electronic version only at http://www.shd.org.rs/jscs/).

Using the values of $\overline{V}_1^{\infty}$, and $\overline{V}_2^{\infty}$ obtained from Eqs. (15) and (16), the partial excess molar volumes at infinite dilution, $\overline{V}_1^{\text{E},\infty}$, and $\overline{V}_2^{\text{E},\infty}$, were calculated by the following equations:[9]

$$\overline{V}_1^{\text{E},\infty} = \overline{V}_1 - V_1^{\circ} \qquad (19)$$

$$\overline{V}_2^{\text{E},\infty} = \overline{V}_2 - V_2^{\circ} \qquad (20)$$

The partial excess molar volumes at infinite dilution, $\overline{V}_1^{\text{E},\infty}$ and $\overline{V}_2^{\text{E},\infty}$, are of fundamental importance since they provide insight into the solute–solvent interactions independent of the composition effect, while in the limit of infinite dilution, the solute–solute interactions disappear. Bearing in mind that the RK Equation and its derivatives do not always provide the best representation of these properties, two other alternatives through the reduced excess molar volumes[10] and apparent molar volumes[9,11] were also included in this study.
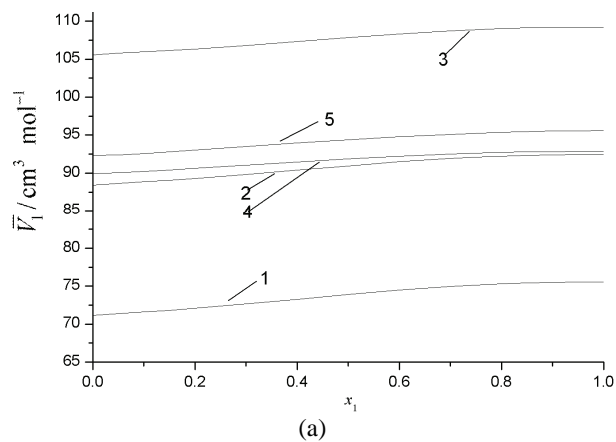

Fig. 2. Plots of partial molar volumes, a) $\overline{V}_1$ and b) $\overline{V}_2$, and partial excess molar volumes. c) $\overline{V}_1^{\text{E}}$ and d) $\overline{V}_2^{\text{E}}$ at 303.15 K for the systems: 1-propanol (1) + cyclohexylamine (2), line 1; 1-butanol (1) + cyclohexylamine (2), line 2; 1-pentanol (1) + cyclohexylamine (2), line 3; 2-butanol (1) + cyclohexylamine (2), line 4; 2-methyl-2-propanol (1) + cyclohexylamine (2), line 5.
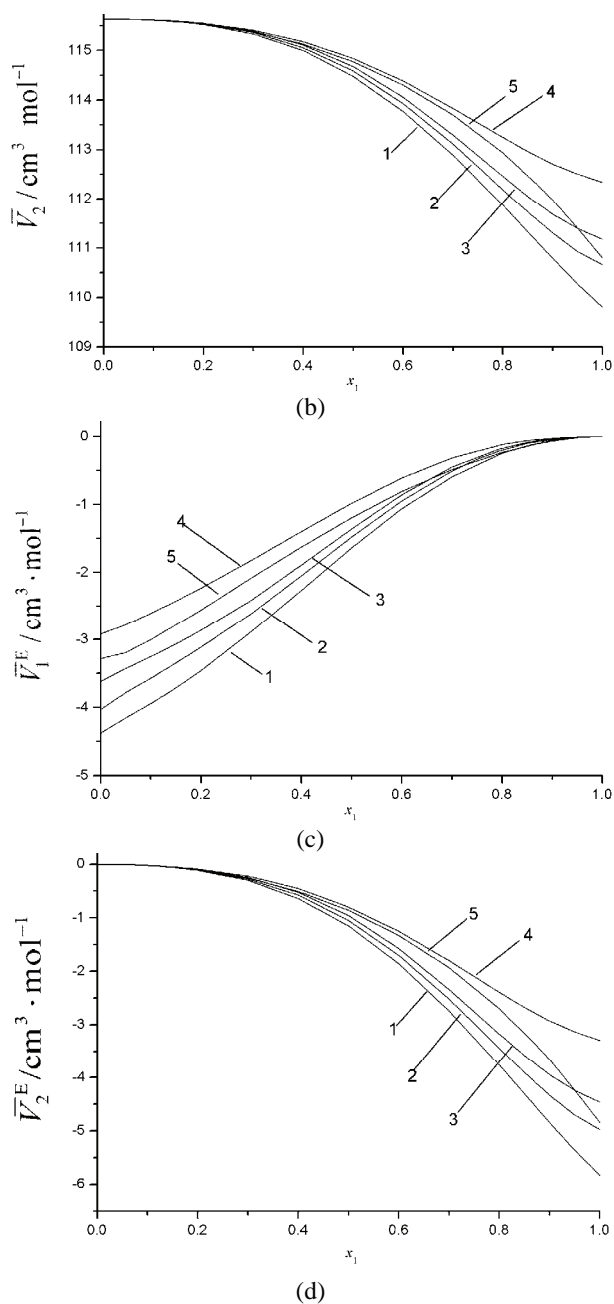
(b)

(c)

(d)

Fig. 2 continued. Plots of partial molar volumes, a) $\bar{V}_1$ and b) $\bar{V}_2$, and partial excess molar volumes. c) $\bar{V}_1^E$ and d) $\bar{V}_2^E$ at 303.15 K for the systems: 1-propanol (1) + cyclohexylamine (2), line 1; 1-butanol (1) + + cyclohexylamine (2), line 2; 1-pentanol (1) + cyclohexylamine (2), line 3; 2-butanol (1) + cyclohexylamine (2), line 4; 2-methyl-2-propanol (1) + cyclohexylamine (2), line 5.

First, the values of the partial excess molar volumes at infinite dilution, $\bar{V}_1^{E,\infty}$ and $\bar{V}_2^{E,\infty}$, were calculated by the RK Equation using the following equations:

$$\overline{V}_1^{\mathrm{E},\infty} = \sum_{p=0}^{m} B_p (-1)^p \tag{21}$$

$$\overline{V}_2^{\mathrm{E},\infty} = \sum_{p=0}^{m} B_p \tag{22}$$

Table I (supplementary material, electronic version only at http://www.shd.org.rs/jscs/) also contains the partial molar volumes at infinite dilutions, $\overline{V}_i^{\infty}$ and $\overline{V}_i^{\mathrm{E},\infty}$, for components 1 and 2 evaluated using the RK parameters.

Analytical extrapolation of Eq. (4) for the reduced excess molar volumes to $x_1 = 0$ gives $\overline{V}_1^{\mathrm{E},\infty}$, while extrapolation to $x_1 = 1$ leads to $\overline{V}_2^{\mathrm{E},\infty}$.

The apparent molar volumes of components 1 and 2 can be expressed as:

$$V_{\phi_1} = V_1^{\circ} + (V^{\mathrm{E}}/x_1) \tag{23}$$

$$V_{\phi_2} = V_2^{\circ} + (V^{\mathrm{E}}/x_2) \tag{24}$$

Graphical or analytical extrapolation of V_{ϕ_1} to $x_1 = 0$ and V_{ϕ_2} to $x_1 = 1$ leads to the values of the limiting apparent molar volumes, which are also called the partial molar volumes at infinite dilution, $\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$. The values $\overline{V}_{\phi_1}^{\mathrm{E},\infty}$ and $\overline{V}_{\phi_2}^{\mathrm{E},\infty}$ were calculated using Eqs. (19) and (20).

The results of $\overline{V}_1^{\mathrm{E},\infty}$ and $\overline{V}_2^{\mathrm{E},\infty}$ obtained from the reduced excess molar volumes extrapolation of Eq. (4) are given in Table II (supplementary material, electronic version only at http://www.shd.org.rs/jscs/). Similar results were obtained using the extrapolation of the apparent molar volume and the RK alternatives.

As can be seen from Table II (supplementary material, electronic version only at http://www.shd.org.rs/jscs/) and Fig. 3, the trends of both partial volumes, $\overline{V}_i^{\mathrm{E},\infty}$ and $\overline{V}_i^{\infty}$, at infinite dilution are the same, and increase with increasing chain length of the 1-alcohols.

The partial molar volumes at infinite dilution, $\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$, are lower than the molar volume of the pure liquids for all the investigated systems. The difference between the molar volumes of 1-propanol, as the lowest alcohol, and cyclohexylamine in their pure state was the highest, but after mixing $\overline{V}_1^{\infty}$ had the lowest value, comparing with the other 1-alcohols. The value of $\overline{V}_1^{\infty}$ increases with increasing number of C atoms in the 1-alcohols, since the difference in the molar volumes of both components is significantly lower.

This phenomenon indicates that after the mixing process, the molar volumes of both components in the mixture are smaller than the molar volumes in their pure liquid state, showing compression in volume,[2] which indicates a better packing efficiency in the mixture than in the pure state.
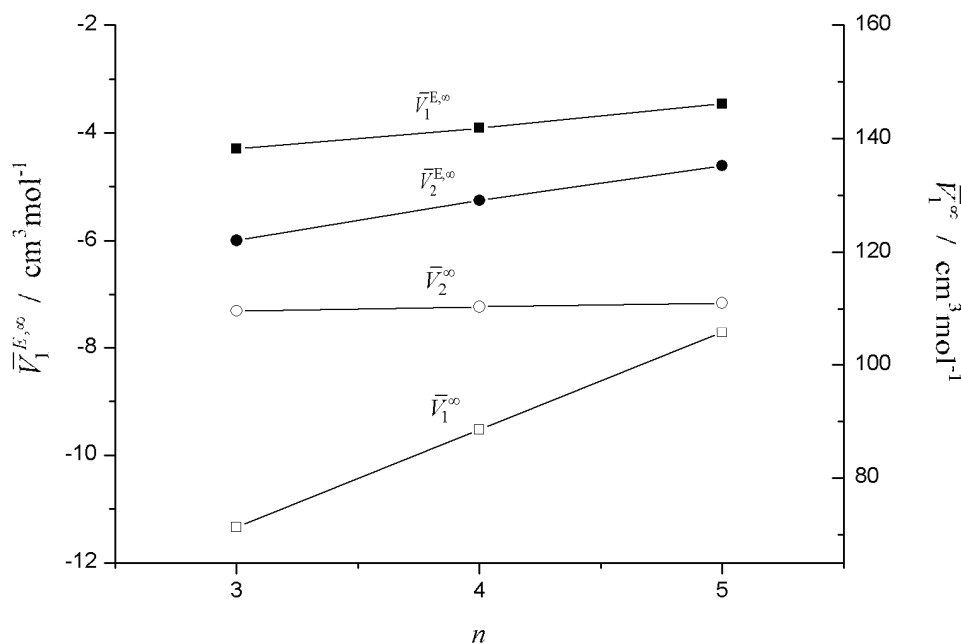
Fig. 3. Influence of increasing the number of C atoms in 1-alcohol + cyclohexylamine systems on $\bar{V}_1^{E,\infty}$ (■), $\bar{V}_1^{\infty}$ (□), $\bar{V}_2^{E,\infty}$ (●) and $\bar{V}_2^{\infty}$ (○), at 303.15 K. The symbols refer to experimental points.

Figure 3 also shows that for all systems with 1-alcohols, the $\bar{V}_1^{E,\infty}$ and $\bar{V}_2^{E,\infty}$ values are negative, increasing with increasing length of the 1-alcohols, indicating that the interactions of unlike molecules are stronger than those of like molecules, according to the previously given explanations. This also means that intermolecular hydrogen bonds are not broken in dilute regions.

The values of both properties $\bar{V}_i^{E,\infty}$ and $\bar{V}_i^{\infty}$ for the mixtures with 2-butanol and 2-methyl-2-propanol are in accordance with the explanations already given previously.

Finally, from Table II (supplementary material, electronic version only at http://www.shd.org.rs/jscs/) and Fig. 4, it is clear that the influence of temperature on $\bar{V}_i^{E,\infty}$ and $\bar{V}_i^{\infty}$ for all mixtures is low, with a slightly increasing trend with increasing temperature, because of the larger expansion capability of the molecules in the pure state compared to in the mixture in the infinite dilution regions.
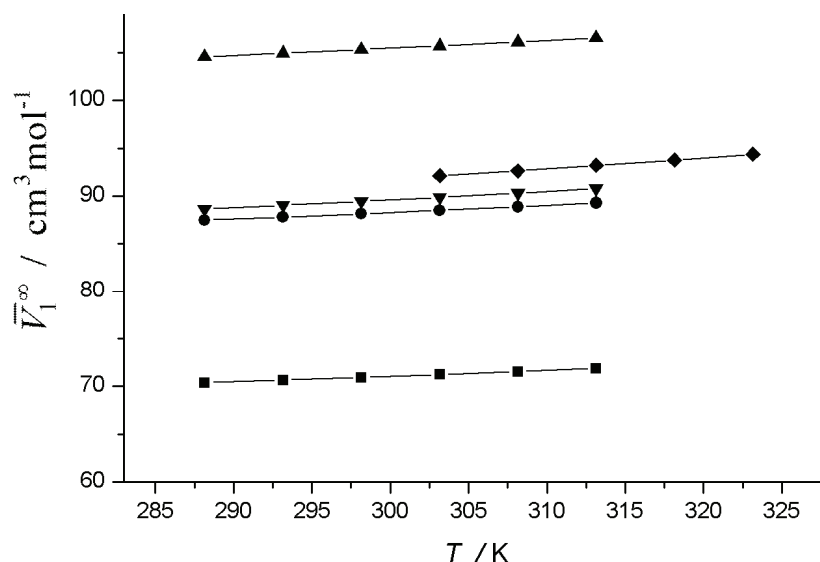
Fig. 4. Influence of temperature on $\bar{V}_1^{\infty}$ for the systems: 1-propanol (1) + cyclohexylamine (2) (■); 1-butanol (1) + cyclohexylamine (2)[2] (●); 1-pentanol (1) + cyclohexylamine (2) (▲), 2-butanol (1) + cyclohexylamine (2) (▼) and 2-methyl-2-propanol (1) + cyclohexylamine (2) (◆). The symbols refer to experimental points.

CONCLUSIONS

The aim of this work was to include thermodynamically derived properties in the analysis of the complex behavior of liquid mixtures.

For this reason, the thermal expansion coefficient, α, the excess thermal expansion coefficient, α^E, the isothermal coefficient of the pressure excess molar volumes, $(\partial H^E / \partial p)_{T,x}$, the partial molar volumes, $\bar{V}_i$, the partial molar volumes at infinite dilution, $\bar{V}_i^{\infty}$, the partial excess molar volumes, $\bar{V}_i^E$ and the partial excess molar volumes at infinite dilution, $\bar{V}_i^{E,\infty}$, were calculated using experimental densities and excess molar volumes, V^E, data of binary mixtures of cyclohexylamine with 1-propanol, or 1-butanol, or 2-butanol, or 2-methyl-2-propanol. The Redlich-Kister polynomial and the reduced excess molar volume approach were used in the determination of these properties. In this way, the influence of temperature, chain length and position of the hydroxyl group in the alcohol molecule on the molecular interactions in mixtures, including the infinite dilute region, was examined.

И З В О Д

ИЗВЕДЕНЕ ТЕРМОДИНАМИЧКЕ ОСОБИНЕ СМЕША
АЛКОХОЛ + ЦИКЛОХЕКСИЛАМИН

ИВОНА Р. РАДОВИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН, АЛЕКСАНДАР Ж. ТАСИЋ,
БОЈАН Д. ЂОРЂЕВИЋ и СЛОБОДАН П. ШЕРБАНОВИЋ

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Термички коефицијент експанзије, α, допунски термички коефицијент, α^E, изотермски коефицијент притиска допунске моларне енталпије, $(\partial H^E/\partial p)_{T,x}$, парцијалне моларне запремине, $\bar{V}_i$, парцијалне моларне запремине при бесконачном разблажењу, $\bar{V}_i^\infty$, парцијалне допунске моларне запремине, $\bar{V}_i^E$, и парцијалне допунске моларне запремине при бесконачном разблажењу, $\bar{V}_i^{E,\infty}$, су израчунате из експерименталних података за густине и података за допунске моларне запремине V^E. Сви прорачуни су извршени на бинарним смешама циклохексиламина са 1-пропанолом, или 1-бутанолом, или 2-бутанолом, или 2-метил-2-пропанолом. Полином Redlich–Kister-а и приступ редуковане допунске моларне запремине су коришћени у израчунавању ових особина. При томе, циљ овог истраживања је био да се одреди сет различитих волуметријских података да би се проценио утицај температуре, дужине ланца и положаја хидроксилне групе у молекулу алкохола на молекулске интеракције у испитиваним бинарним смешама.

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