



J. Serb. Chem. Soc. 74 (5) 477–491 (2009)
JSCS–3848

AUTHORS' REVIEW

**Molecular interaction studies of the volumetric behaviour of
binary liquid mixtures containing alcohols**

BOJAN D. DJORDJEVIĆ*#, IVONA R. RADOVIĆ#, MIRJANA LJ. KIJEVČANIN#,
ALEKSANDAR Ž. TASIĆ and SLOBODAN P. ŠERBANOVIĆ#

*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,
P.O. Box 35-03, 11120 Belgrade, Serbia*

(Received 13 January 2009)

Abstract: An attempt has been made to relate the volumetric effects involved in the binary mixtures of normal and branched alcohols and various components (aromatics, halo and nitroaromatics and haloaliphatics) with the molecular interactions of unlike molecules. This review is a condensation of research activities developed in recent years as results of a better understanding of volumetric behaviour and a stronger insight into the complex structure of those mixtures. The influence of important contributions of a physical, chemical and geometrical nature that change excess molar volume, V^E (positive, sigmoidal, negative) is considered and explained in detail. It appears that the balance between these contributions is quite sensitive to the behaviour of the alcohol molecules in contact with the chosen compounds.

Keywords: molecular interactions; volumetric properties; excess volume; alcohols; binary liquid mixtures.

CONTENTS

1. INTRODUCTION
2. VOLUMETRIC PROPERTIES
3. ALCOHOL + AROMATIC SYSTEMS
 - 3.1. 1-Alcohols with aromatics
 - 3.2. Branched alcohols with aromatics
4. ALCOHOL + HALO-AROMATIC OR + NITROAROMATIC SYSTEMS
 - 4.1. 1-Alcohols with haloaromatics or nitroaromatics
 - 4.2. Branched alcohols with haloaromatics
5. ALCOHOL + HALOALIPHATIC SYSTEMS
6. CONCLUSIONS

* Corresponding author. E-mail: bojan@tmf.bg.ac.rs

Serbian Chemical Society member.

doi: 10.2298/JSC0905477D

1. INTRODUCTION

The knowledge of the structure and molecular interactions of liquid mixtures is very important from fundamental and engineering point of view.

Fundamental thermodynamic and thermophysical properties are essential sources of information necessary for a better understanding of the non-ideal behaviour of complex systems because of physical and chemical effects, which are caused by molecular interactions, intermolecular forces, *etc.*, of unlike molecules.

From a practical point of view, these properties are necessary for the development of thermodynamic models required in adequate and optimized processes of the chemical, petrochemical, pharmaceutical, and other industries. In addition, extensive information about structural phenomena of mixtures is of essential importance in the development of theories of the liquid state and predictive methods. This review is focused on the qualitative explanation of the influence of molecular structure on volumetric properties of different alcohols with some aromatics and halo-aromatics, nitro compounds or halo-aliphatics. In addition, this study also provides a better insight into the nature of the molecular interaction in the aforementioned systems. Besides their theoretical importance, these systems were chosen since they are very interesting from a practical point of view: (i) due to their diverse industrial applications, they are present as pollutants causing air, water and soil contamination, and some of them have cancerous features; (ii) alcohols and other organic compounds are employed in a variety of industrial and consumer applications, such as perfumes, cosmetics, paints, varnishes, drugs, fuels, explosives, fats, waxes, resins, plastics, rubber, detergents, DDT, *etc.*, while chloroform is applied as a solvent in the pharmaceutical industry, the paint industry, in the chemical production of pesticides, oils, alkaloids, *etc.*

Some research activities, including the modelling of volumetric properties by various models (CEOS, CEOS/ G^E and empirical models) with modern mixing rules were systematically considered in previous reviews^{1,2} and in other papers particularly concerning the correlation³⁻⁸ and prediction of volumetric and other thermodynamic properties.⁹⁻¹⁵

2. VOLUMETRIC PROPERTIES

The density (ρ) of the binary systems, the molecular behaviours of which were analyzed in this work, were measured by means of a DMA 5000 digital vibrating U-tube densimeter (with automatic viscosity correction) having a stated accuracy $\pm 5 \times 10^{-3}$ kg·m⁻³. The temperature in the cell was regulated to ± 0.001 K with a built-in solid-state thermostat. To minimize errors in composition, all mixtures were prepared by mass using the cell and the procedure described previously;^{16,17} presently, a Mettler AG 204 balance with a precision of 1×10^{-4} g was employed. The uncertainty in the mole fraction calculation was less than $\pm 1 \times 10^{-4}$. All molar quantities were based on the IUPAC Relative Atomic Mass Table. The ex-

perimental uncertainty in the density was about $\pm 1 \times 10^{-2} \text{ kg}\cdot\text{m}^{-3}$, while the average uncertainty in the excess molar volume was estimated to be $\pm 3 \times 10^{-9} \text{ m}^3\cdot\text{mol}^{-1}$.

The excess molar volumes, V^E , were calculated from the equation:

$$V^E = \sum_{i=1}^n x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (1)$$

where n represents the number of components, x_i is the mole fraction of i -th component in the mixture, M_i its molecular weight, and ρ and ρ_i the measured densities of the mixture and the pure i -th component, respectively.

Since in previous papers^{16–25} experimental measurements of the corresponding systems were presented by V^E-x_1 curves, in this work these graphs are plotted only for the systems that are suitable for a better understanding of the complex behaviour of the chosen mixtures.

The observed values of V^E can be analyzed qualitatively in terms of the following resulting effects, which predominate in some mixtures or in a certain mole fraction region:^{26–35} (i) physical, (ii) chemical and (iii) geometrical contribution. Consequently, V^E depends on the relative strength of these effects.

The physical interactions comprise mainly dispersion forces and non-specific interactions. The chemical contribution arises mainly due to hydrogen bond rupture because of the breaking up of the hydrogen bond structure, and specific interaction such as hydrogen bond formation and charge-transfer complexes. This interaction can be considered as the reaction between an alcohol, as a Lewis acid, and an aromatic compound, as a Lewis base. It should be emphasized that the hydrogen bond energy is determined by four components:^{36,37} (i) the polarization term, (ii) the electrostatic term, (iii) the exchange repulsion term and (iv) charge transfer or delocalisation term.

The geometrical contribution occurs due to packing effects arising from interstitial accommodation of one component into the other due to differences in free volumes and molar volumes between the components.

3. ALCOHOL + AROMATIC SYSTEMS

3.1. 1-Alcohols with aromatics

Numerous articles^{36,38–43} have demonstrated that alcohols are strongly self-associated (forming clusters) through H-bonded linear chains (OH...OH interactions), with restricted rotation about the H-bonds and showing variable degrees of polymeric aggregates. The degree and strength of polymerisation decrease with increasing chain length of the carbon atoms and with branching of an alcohol.

Mixing of alcohols with other organic components enables that some molecules can dissociate from the multimers to form other kinds of H-bonds with unlike molecules. This process will depend on the proton accepting ability of the functional group in the molecule.

However, aromatic hydrocarbons are potential electron donors and electron donor–acceptor interactions between benzene and the hydrogen of alcohol hydroxyl group are of importance here.

Figure 1 shows experimental points of V^E at 308.15 K for the 1-alcohol + benzene systems reported in previous papers.^{18,19,21,24,32,44,45} These data can be explained qualitatively on the basis of different aforementioned effects predominating in certain mole fraction regions.

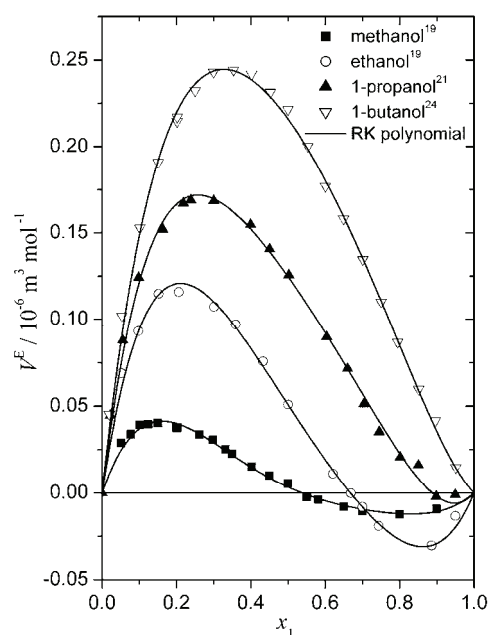


Fig. 1. Experimental values of V^E for the systems of 1-alcohols (1) with benzene (2) at 308.15 K. The symbols refer to the experimental points, while the lines present the results calculated by the Redlich–Kister polynomial.^{19,21,24}

As can be seen from this Fig. 1, the V^E of the mixtures of benzene with 1-alcohols show sigmoidal *vs.* mole fractions curves, except for the system 1-butanol + benzene for which positive V^E values were observed over the whole concentration range. When 1-alcohol molecules are added to a large amount of benzene, depolymerisation of the network of pure alcohols occurs, resulting in positive values of V^E . These V^E values indicate that there were no stronger specific interactions between the components of the mixtures but that this effect was the result of breakage of the bonds formed among the alcohol structure. This positive contribution is a consequence of hydrogen bond rupture and stretching of the self-associated molecules of the alcohols, which is insensitive to the chain length of the 1-alcohols (Fig. 1). The negative values of V^E in the alcohol-rich region indicate that complex formation occurred between the alcohols and benzene,⁴⁴ resulting in predominant electron donor–acceptor type (benzene behaves as the electron donor) of interactions between the OH group of the 1-alcohol and the π electrons of the aromatic ring of benzene. At higher mole composition of the

1-propanol + benzene mixture, the V^E values tend to be slightly negative, meaning that the breaking up of the associated alcohol aggregates is not completed and the benzene molecules are fitted into the propanol network. This situation is also clear for mixtures with methanol, where the tendency of interstitial accommodation of its molecules into benzene leads to negative values of V^E .³⁰ As can be seen from Fig. 1, the experimental data for the 1-butanol + benzene system were positive over the whole composition range at all investigated temperatures. These positive V^E values can be qualitatively explained by disruptive or stretching effects on the self-associated molecular structure of 1-butanol with physical dipole-dipole interactions between alcohol monomers and multimers, and by the disruption of the favourable orientation order of the aromatic component. The possible formation of weak intermolecular complexes between the OH group of 1-butanol and the π electron cloud of the benzene ring did not result in negative V^E values. As suggested by Assarson and Eirich,³² components of similar molecular sizes, such as 1-butanol and benzene (van der Waals volumes of 52.4 and 48.4 cm³·mol⁻¹, respectively) mix with positive values of V^E .

In addition, it is evident from the plots of 1-alcohols with benzene that, at the same temperature, the trend of increasing V^E in the positive direction in the lower alcohol region has the following order: methanol < ethanol < 1-propanol < 1-butanol. On the other hand, in the alcohol rich region, the order from negative to positive values is as follows: ethanol < methanol < 1-propanol < 1-butanol.

This behaviour of 1-alcohols can be explained in terms of the chain length of alcohols. Namely, as the mole fraction of higher 1-alcohols increases, the rupture of H-bonds of the alcohol increases from methanol to 1-butanol, and positive values of V^E become dominant. Also, interaction between the OH group of the higher 1-alcohols and the π electrons of the aromatic ring of benzene are weaker because of the decrease of their polarizability with increasing length. Structural effects leading to closer geometrical fitting of benzene into remaining structure of the higher 1-alcohols are less important. It is clear that for higher 1-alcohols, positive values of V^E are predominant. V^E measurements over a range of temperature were already performed¹⁹ and in all cases, the V^E values of the 1-alcohol + benzene systems increased with increasing temperature. It is clear that the rupture of the H-bonds of self-associated molecules of alcohols increases with increasing temperature.

1-Alcohols (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) were mixed with other aromatic hydrocarbons with increasing size and number of substituents on the benzene ring (toluene, ethylbenzene and *p*-xylene).

The results obtained in work of Munk *et al.*⁴⁵ show that the V^E values of the mixtures with the same 1-alcohol increased with increasing of size and number of substituents, while for mixtures with the same aromatic component, V^E increased with increasing chain length of the 1-alcohols.

The measured values of V^E for mixtures of benzene with higher 1-alcohols⁴⁶ were positive over whole range of concentration. This suggests that a positive contribution from the rupture of hydrogen bonds of alcohols as well as dipole–dipole interactions between alcohol monomer and polymers were dominant in all systems. The algebraic values of V^E decreased in the order: 1-decanol \approx 1-nonanol > 1-octanol > 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol > 1-propanol. In addition, it is evident that V^E increased with increasing chain length of the 1-alcohols and van der Waals interactions increased with increasing carbon chain length of the alcohols.

3.2. Branched alcohols with aromatics

Branched secondary and tertiary alcohols reflect various degrees of steric hindrance of the hydroxyl group, which directly influences the possibility of their molecules to self-associate.

First, the V^E values for the systems of benzene with 1-propanol and 2-propanol were compared.

Previously published data²¹ for the system benzene + 1-propanol at 298.15 K and those of the system benzene + 2-propanol at the same temperature⁴⁷ show that the V^E values of the former were always considerably lower at all mole fractions. This is a consequence of the branching of the alkyl group in 2-propanol, which increases the steric hindrance for the correct orientation of the benzene molecules to fit into the alcohol network.

The 1- and 2-propanol mixtures could be compared with those of other aromatic compound, for example alkylbenzenes. The introduction of two methyl groups into the benzene ring, as in the case of xylene, enhances the electron-donating power of aromatic hydrocarbons.

For 1-propanol + alkylbenzene mixtures, the V^E values have the following order: *m*-xylene > *p*-xylene \approx *o*-xylene > toluene, while for 2-propanol + alkylbenzene mixtures, the V^E values decrease in the order: *m*-xylene > *p*-xylene > toluene \approx *o*-xylene. In both cases, the V^E values in mixtures with benzene are positive over the whole composition range, having a similar magnitude as *m*-xylene in mixtures with 2-propanol, and the highest values comparing to the mixtures with 1-propanol.

From work of Singh *et al.*,⁴⁸ it is evident that alkylbenzene molecules are more or less fitted into the network of 1- and 2-propanol. This is specially the case of toluene comparing to benzene, due to its stronger electron-donating power.

On the other hand, the packing of xylene molecules is sterically hindered by the two methyl groups placed on different sites of the aromatic ring for correct orientation. Thus, a limitation of the interaction of the hydroxyl group of the alcohol with the π electron cloud of the aromatic hydrogen was realized. It is clear that the position of the methyl groups in *m*-xylene results in the maximum steric hindrance and, as a result, the maximum positive of V^E .

Finally, it can be concluded that the branching of the alkyl group in 2-propanol creates a greater geometrical contribution to fit the corresponding xylene into the alcohol network.

The V^E for all mixtures of benzene with isomeric butanols⁴⁹ are positive and follow the sequence: 1-butanol < 2-methyl-1-propanol < 2-butanol < 2-methyl-2-propanol, showing in this way that V^E becomes more positive as the branching in the alcohol molecule increases. It is the consequence of the creation of steric hindrance near the OH-group in branched alcohols, whereby it is the prevailing effect for 2-methyl-2-propanol.⁵⁰ Namely, this can be explained by postulating that steric hindrance creates the presence of one propyl group at the 1° atom in 1-butanol, one *iso*-butyl group at the 1° carbon atom in 2-methyl-1-propanol, one methyl and one ethyl group at the 2° carbon atom in 2-butanol and three methyl groups at the 3° carbon atom in 2-methyl-2-propanol.

This suggests that the appearance of steric hindrance due to the branching in an alcohol is conditioned by the strength of the interaction of unlike molecules in the order 1-butanol > 2-methyl-1-propanol > 2-butanol > 2-methyl-2-propanol. In addition, bearing in mind that the molecular sizes of the unlike components in the mixtures are similar, the packing of the molecules is not good, resulting also in positive V^E values.

In addition, it is of interest to compare the behaviour of toluene in mixtures with 1-butanol and its isomers⁴⁷ (2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol). It is known that the electron donating power of toluene is stronger than that of benzene because of the methyl group added in the benzene ring and the hydroxyl hydrogen interacts more highly with the π electron cloud of toluene than that of benzene. This results in smaller V^E values of these alcohols with toluene than those with benzene. Finally, the V^E values of the branched alcohols are higher than those for the 1-alcohols. This could be attributed explicitly to the steric hindrance caused by a change in the proportion of different structural shapes of the alcohol molecules with its changing mole fraction.

4. ALCOHOL + HALOAROMATIC OR NITROAROMATIC SYSTEMS

4.1. 1-Alcohols with haloaromatics and nitroaromatics

Methanol partially and all 1-alcohols (ethanol, 1-propanol, 1-butanol and 1-pentanol) with chlorobenzene exhibit S-shaped V^E-x_1 curves, as can be seen in Fig. 2.¹⁹ It is obvious that the maximum positive values of these systems are lower and the minimum negative values are higher than the corresponding values of 1-alcohol systems with benzene.

As in the previous cases of the systems with benzene, the positive values of V^E in the lower region of the 1-alcohols are also the result of H-bond rupture and stretching of the self-associated alcohol molecules.

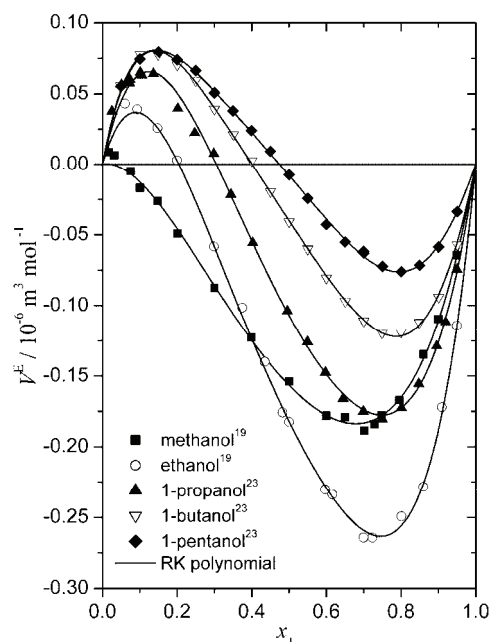


Fig. 2. Experimental values of V^E for the systems of 1-alcohols (1) with chlorobenzene (2) at 313.15 K. The symbols refer to the experimental points, while the lines present the results calculated by the Redlich–Kister polynomial.^{19,23}

Negative contributions predominate in the alcohol rich region because of dipolar complexes and changes of the free volumes in the real mixtures, as well as the geometrical fitting between unlike molecules, which are much stronger than in the systems with benzene. Here, there is an interaction between the π -electronic cloud of aromatic ring and the OH group, as in the case of the benzene mixtures, and the formation of OH–Cl hydrogen-bonded complexes between the OH group of the 1-alcohols and the electronegative Cl atom on the benzene ring.¹⁹ In addition, it is evident that the maxima of the dissociation of the polymeric aggregates of the alcohols differ slightly, since ordinary aliphatic alcohols are relatively poor proton donors. However, as the mole fraction of the higher 1-alcohol increases, the rupture of the hydrogen bonds of the alcohol increases from 1-propanol to 1-pentanol and positive volume changes appear at higher mole fraction of 1-pentanol.

The decrease in negative values of V^E with increasing chain length of the 1-alcohols could suggest that the dipole–dipole interactions are weaker in the higher 1-alcohols because of the decrease of their polarizability with increasing chain length. Bearing in mind that complexation⁵¹ is predominantly due to polarization interaction, the trend of complex formation has the following order 1-propanol > > 1-butanol > 1-pentanol, which causes the increase of V^E from lower to higher 1-alcohols. Then, the relatively high electron donor capacity of chlorobenzene, because of the introduction of a Cl atom into the benzene ring, interacts more strongly with 1-propanol than with the other higher alcohols. In addition, only a

smaller fraction of hydrogen bonds are ruptured in the higher alcohols, while the steric hindrance of 1-pentanol is higher than that of 1-propanol, giving less negative values of V^E .

It is possible to include mixtures of 1-alcohols with other chlorinated benzenes, *i.e.*, 1,2-dichlorobenzene,⁵² 1,3-dichlorobenzene⁵³ and 1,2,4-trichlorobenzene⁵⁴ for comparison with mixtures of chlorobenzene + 1-alcohols. The experimental data for binary mixtures of these haloaromatics with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol were measured at 303.15 K.²⁹

As in the case of the mixtures with chlorobenzene, V^E is negative in mixtures rich in 1-alcohols and positive in the region rich in both dichlorobenzene and 1,2,4-trichlorobenzene. The trend of V^E vs. the mole fraction x curve is similar for all mixtures of chlorobenzene, dichlorobenzenes and trichlorobenzene. This could be attributed to the dominant influence of the interactions between unlike molecules and the structure-making effect, which becomes remarkable due to the introduction of a second Cl atom, including its position in the benzene ring, and a third Cl atom.

In addition, it is necessary to consider mixtures of alcohols with nitrobenzene⁵⁵ and bromobenzene⁵⁶ and compare the obtained results with those of chlorobenzene. Namely, the V^E values become more negative due to the decrease in the π -electron density on the benzene ring when a halo or nitro group is introduced (nitro group deactivates the benzene ring).

When the Cl atom was replaced with a Br atom, no greater changes in V^E were observed,⁵⁷ which was to be expected bearing in mind the similar values of their dipole moments (chlorobenzene 1.6; bromobenzene 1.5) and the dipole moments of alcohols, as well as specific interactions like those of alcohol mixtures with chlorobenzene. However, the partial accommodation of linear alcohol molecules between the nitrobenzene molecules and interactions due to the high polarity of nitrobenzene (dipole moment 3.90) led to more negative V^E values, compared to those obtained with the halo compounds.⁵⁵

The small positive values of V^E in mixtures deficient in alcohols are due to the predominant H-bond stretching, as was already indicated in mixtures with chlorobenzene.

4.2. Branched alcohols with haloaromatics

The experimental V^E data of 1-butanol, 2-butanol and 2-methyl-2-propanol with chlorobenzene at 313.15 K are shown in Fig. 3.²³

As can be seen, the trend in the positive values of V^E is in the order 1-butanol < 2-butanol < 2-methyl-2-propanol, which indicates that the predominant effect is the steric hindrance due to branching. The OH group introduced at 2° carbon atom of 2-butanol and the globular shape and relative position of OH group on *tert*-butanol suggest that the structural effects of the steric hindrance are

predominant. The influence of the methyl, ethyl and propyl groups at various carbon atoms in these alcohols were already considered.¹⁹ An increase of temperature leads to an increase of the distance between the chains, the breaking of associates and sterically-hindered unlike molecules. In all cases, a positive change of volume occurs. In addition, as a consequence, the strength of the bond interaction $H\cdots Cl$ follows the order: 1-butanol > 2-butanol > 2-methyl-2-propanol, confirming the increase of V^E of the branched alcohols.

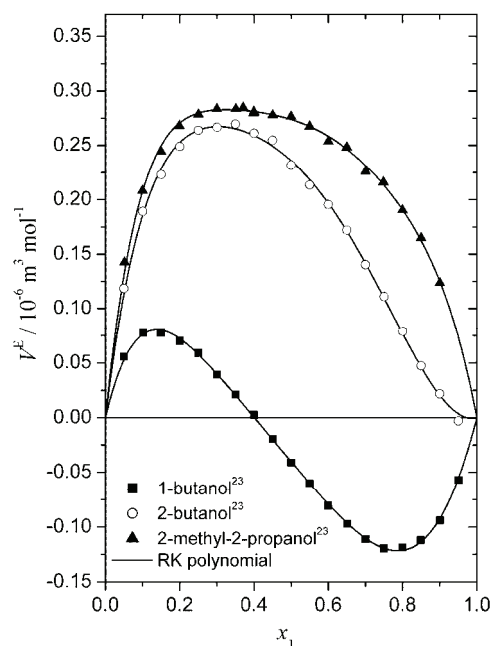


Fig. 3. Experimental values of V^E for the systems of linear or branched alcohols (1) with chlorobenzene (2) at 313.15 K. The symbols refer to the experimental points, while the lines present the results calculated by the Redlich–Kister polynomial.²³

5. ALCOHOL + HALOALIPHATIC SYSTEMS

The experimental V^E data for the 1-alcohol + chloroform systems at 308.15 K are shown in Fig. 4.^{20–22,24}

The V^E for methanol (1) + chloroform (2) mixtures are almost all negative except near the end of the dilute region for methanol. The other 1-alcohol systems with chloroform exhibit S-shaped V^E-x_1 curves with V^E positive at high mole fractions of chloroform and negative over the high mole fractions of the 1-alcohols.

For the considered systems, except methanol (1) + chloroform (2), the V^E values can be attributed qualitatively to the following contributions: (i) the positive values in the 1-alcohol lower region are caused by disruption or stretching effects on the three-dimensional, self-associated molecular structure of the alcohols; (ii) the negative values are a consequence of specific interactions between unlike molecules and (iii) the accommodation of chloroform molecules in the in-

termolecular space of 1-alcohol network structure leads to a more dense packing, affecting volume reduction in the region rich in 1-alcohols, which is, hence, a consequence of geometric factors.

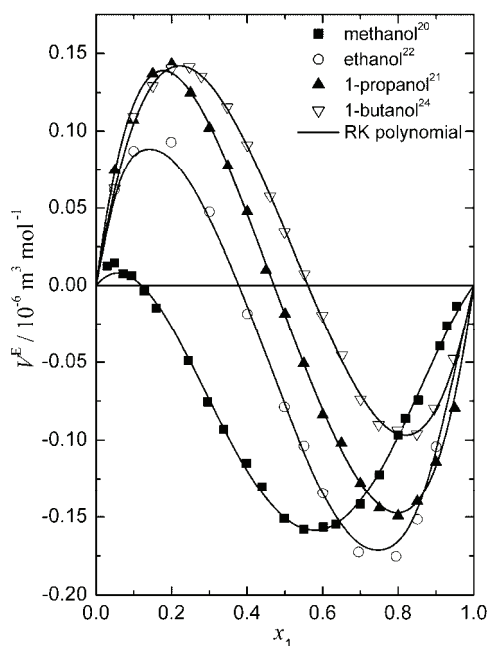


Fig. 4. Experimental values of V^E for the systems of 1-alcohols (1) with chloroform (2) at 308.15 K. The symbols refer to the experimental points, while the lines present the results calculated by the Redlich–Kister polynomial.^{20–22,24}

Concerning the alcohol mixtures with chlorobenzene (Fig. 2), unusual behaviour of the methanol + chloroform mixture was also registered. The absolute values of V^E for the same temperature at the minimum increase in the sequence ethanol > methanol > 1-propanol \approx 1-butanol. A possible explanation of this behaviour for the system with methanol could be a dominant contribution of (ii) over the factors (i) and (iii).

For the other 1-alcohol mixtures with chloroform, the positive V^E values in the 1-alcohol lower region are a consequence of the rupture of the H-bonding of the self-associated aggregates of the 1-alcohols with variable degrees of polymerization and the steric repulsion between the alkyl chain of the 1-alcohols and the Cl atom of the chloroform increasing with increasing chain length of the alcohols.

The negative V^E values in the chloroform rich region arise from changes in the free volumes in the real situation when specific interactions between unlike molecules dominate. Namely, chloroform possesses an electron-accepting hydrogen atom, which is favourable for interaction with the electron-donating oxygen atom in alcohols.

Special attention was paid to other chlorinated methanes: tetrachloromethane (CCl_4) and dichloromethane (CH_2Cl_2) in mixtures with 1-alcohols. CCl_4 is a

non-polar molecule, while the polarity of CH_2Cl_2 is larger than that of CHCl_3 . In addition, these molecules have different sizes and shapes but are structurally related, having only one C atom.⁵⁸

Comparing results for CHCl_3 with those of CCl_4 and CH_2Cl_2 mixtures with the same 1-alcohols,⁵⁹ it is evident that similar S-shaped V^E-x_1 curves were obtained for both the CH_2Cl_2 and CHCl_3 systems. It could be expected that the same three main contributions occur in the CH_2Cl_2 system as in the case when CHCl_3 was mixed with alcohols. In the case of CCl_4 , the presumption of a weak H-bond from hydroxyl group to a chlorine atom is acceptable.

The mixtures of CH_2Cl_2 with 1-alcohols showed somewhat different behaviour bearing in mind that positive values of V^E are dominant over the whole composition range, except in the region rich in some alcohols.

Two assumptions could be made for such a tendency of V^E :⁶⁰ (i) in the accommodation of CH_2Cl_2 in the H-bonded network of alcohols, the interaction of $\text{C-H}\cdots\text{H-O-R}$ is weaker than that of $\text{C-Cl}\cdots\text{H-O-R}$; (ii) it is assumed that the interaction of the C atom of CH_2Cl_2 with C-C of alcohol becomes stronger and V^E more positively increasing with increasing carbon chain length in ROH. It was concluded: (i) interaction between chlorinated methanes and R-OH are weak, except for methanol; (ii) the interactions with R-OH falls in the order $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$; (iii) the tendency of interacting with C-C in ROH ascends in the order $\text{CCl}_4 \ll \text{CHCl}_3 \ll \text{CH}_2\text{Cl}_2$ and (iv) the H-bond of $\text{C-Cl}\cdots\text{H-O}$ is weaker than that of $\text{O-H}\cdots\text{O-H}$ but stronger than the interaction of C-Cl with C-C in ROH.

Branched alcohols could be also included here. For example, mixtures of CH_2Cl_2 with isomer of butanol (2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol).⁶¹

The volume of V^E ($x = 0.5$) for mixtures of 1-butanol and these isomers with CH_2Cl_2 increases in order: 1-butanol < 2-methyl-1-propanol < 2-butanol < 2-methyl-2-propanol. It is clear that a breaking of the hydrogen bonds leads to expansion of the mixtures. The positive values of V^E for the mixtures 2-butanol + chloroform²⁵ are very explicit as opposed to the S-shape of the V^E-x curve (Fig. 4) of the mixture 1-butanol + chloroform. The positive contribution of the break-up of the alcohol structure is responsible, as in the previous cases. Namely, V^E becomes more positive as the branching in the alcohols increases and negative values for the secondary and tertiary alcohols caused by the geometrical fitting into the remaining alcohol structure is less important.

6. CONCLUSIONS

It is evident that the excess molar volume V^E in the mixtures of alcohols with various types of compounds (aromatics, halo and nitroaromatics and haloaliphatics) treated in this work, showing very complex behaviour, possesses three dominant contributions. These are: (i) the positive values are caused by the break-

ing of H-bonds in the self-associated structure of the alcohol molecules, dipole–dipole interactions between monomers and polymers of the alcohols and stretching effects in the favourable orientation order of the second component; (ii) the negative values arise from changes of the “free volumes” in these real mixtures, the presence of electron donor–acceptor ability of alcohol and the other component, and OH... π electron H-bonded complexes between unlike molecules and (iii) the fitting of the other component into the intermolecular space of the network structure of the 1-alcohols or steric hindrance of the branched alcohols leads to the dense packing of the mixtures.

For the investigated mixtures, these contributions are balanced giving the corresponding values of V^E and the explained complex behaviour of the mixtures.

Acknowledgement. The authors gratefully acknowledge the financial support received from the Research Fund of Ministry of Science and Environmental Protection, Serbia and the Faculty of Technology and Metallurgy, University of Belgrade (Project No. 142064).

ИЗВОД

СТУДИЈА МОЛЕКУЛСКИХ ИНТЕРАКЦИЈА НА БАЗИ ВОЛУМЕТРИЈСКИХ СВОЈСТАВА ТЕЧНИХ БИНАРНИХ СМЕША КОЈЕ САДРЖЕ АЛКОХОЛЕ

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

Технолошко–металуришки факултет, Универзитет у Београду, Карнегијева 4, 11120 Београд

У овом раду испитана је веза између волуметријских ефеката мешања и молекулских интеракција различитих молекула у бинарним смешама нормалних или разгранатих алкохола са различитим компонентама (ароматима, хало и нитроароматима, халогеним дериватима угљоводоника). Овај рад садржи преглед наших истраживања последњих година, као и резултате истраживања других аутора у циљу бољег разумевања волуметријских својстава и бољег увида у сложеност структура испитиваних смеша. Узети су у обзир и детаљно објашњени физички, хемијски и геометријски утицаји на промену V^E вредности (позитивне, сигмоидне, негативне). Утврђено је да на однос ових доприноса велики утицај има понашање молекула алкохола у контакту са другим компонентама.

(Примљено 13. јануара 2009)

REFERENCES

1. B. D. Djordjević, M. Lj. Kijevčanin, J. P. Orlović, S. P. Šerbanović, *J. Serb. Chem. Soc.* **66** (2001) 213
2. B. D. Djordjević, S. P. Šerbanović, I. R. Radović, A. Ž. Tasić, M. Lj. Kijevčanin, *J. Serb. Chem. Soc.* **72** (2007) 1437
3. S. P. Šerbanović, B. D. Djordjević, D. K. Grozdanić, *J. Chem. Eng. Japan* **27** (1994) 671
4. B. D. Djordjević, S. P. Šerbanović, D. K. Grozdanić, *Can. J. Chem. Eng.* **72** (1994) 171
5. M. Lj. Kijevčanin, B. D. Djordjević, P. S. Veselinović, S. P. Šerbanović, *J. Serb. Chem. Soc.* **63** (1998) 237
6. I. R. Grgurić, A. Ž. Tasić, B. D. Djordjević, M. Lj. Kijevčanin, S. P. Šerbanović, *J. Serb. Chem. Soc.* **68** (2003) 47

7. M. Lj. Kijevčanin, B. D. Djordjević, S. P. Šerbanović, I. R. Grgurić, A. Ž. Tasić, *Phys. Chem. Liquids* **42** (2004) 147
8. M. Lj. Kijevčanin, B. D. Djordjević, S. P. Šerbanović, I. R. Grgurić, A. Ž. Tasić, *Phys. Chem. Liquids* **44** (2006) 233
9. S. P. Šerbanović, B. D. Djordjević, D. K. Grozdanić, *Fluid Phase Equilib.* **57** (1990) 47
10. A. Ž. Tasić, B. D. Djordjević, D. K. Grozdanić, *J. Chem. Eng. Data* **37** (1992) 310
11. B. D. Djordjević, M. Lj. Kijevčanin, S. P. Šerbanović, *Fluid Phase Equilib.* **155** (1999) 205
12. M. Lj. Kijevčanin, A. B. Djordjević, I. R. Grgurić, B. D. Djordjević, S. P. Šerbanović, *J. Serb. Chem. Soc.* **68** (2003) 35
13. S. P. Šerbanović, I. R. Grgurić, M. Lj. Kijevčanin, A. Ž. Tasić, B. D. Djordjević, *Korean J. Chem. Eng.* **21** (2004) 858
14. M. Lj. Kijevčanin, S. P. Šerbanović, I. R. Radović, B. D. Djordjević, A. Ž. Tasić, *J. Serb. Chem. Soc.* **71** (2006) 807
15. I. R. Radović, M. Lj. Kijevčanin, M. Z. Gabrijel, S. P. Šerbanović, B. D. Djordjević, *Chem. Papers* **62** (2008) 302
16. N. Radojković, A. Tasić, B. Djordjević, D. Grozdanić, *J. Chem. Thermodyn.* **8** (1976) 1111
17. A. Ž. Tasić, D. K. Grozdanić, B. D. Djordjević, S. P. Šerbanović, N. Radojković, *J. Chem. Eng. Data* **40** (1995) 586
18. I. R. Grgurić, S. P. Šerbanović, M. Lj. Kijevčanin, A. Ž. Tasić, B. D. Djordjević, *Thermochim. Acta* **412** (2004) 25
19. S. P. Šerbanović, M. Lj. Kijevčanin, I. R. Radović, B. D. Djordjević, *Fluid Phase Equilib.* **239** (2006) 69
20. M. Lj. Kijevčanin, M. M. Djuriš, I. R. Radović, B. D. Djordjević, S. P. Šerbanović, *J. Chem. Eng. Data* **52** (2007) 1136
21. M. Lj. Kijevčanin, I. M. Purić, I. R. Radović, B. D. Djordjević, S. P. Šerbanović, *J. Chem. Eng. Data* **52** (2007) 2067
22. M. Lj. Kijevčanin, S. P. Šerbanović, I. R. Radović, B. D. Djordjević, A. Ž. Tasić, *Fluid Phase Equilib.* **251** (2007) 78
23. I. R. Radović, M. Lj. Kijevčanin, E. M. Djordjević, B. D. Djordjević, S. P. Šerbanović, *Fluid Phase Equilib.* **263** (2008) 205
24. J. D. Smiljanić, M. Lj. Kijevčanin, B. D. Djordjević, D. K. Grozdanić, S. P. Šerbanović, *Int. J. Thermophys.* **29** (2008) 586
25. J. D. Smiljanić, M. Lj. Kijevčanin, B. D. Djordjević, D. K. Grozdanić, S. P. Šerbanović, *J. Chem. Eng. Data* **53** (2008) 1965
26. J. M. Resa, C. Gonzalez, R. G. Concha, M. Iglesias, *Phys. Chem. Liquids* **42** (2004) 493
27. M. A. Saleh, Sh. Akhtar, M. Sh. Ahmed, *J. Mol. Liquids* **116** (2005) 147
28. R. Tanaka, S. Toyama, *J. Chem. Eng. Data* **42** (1997) 871
29. T. M. Letcher, J. A. Nevines, *J. Chem. Thermodyn.* **26** (1994) 697
30. A. Rodriguez, J. Canosa, J. Tojo, *J. Chem. Eng. Data* **44** (1999) 1298
31. M. C. S. Subha, K. C. Rao, G. Narayanaswamy, S. B. Rao, *Phys. Chem. Liquids* **18** (1988) 185
32. P. Assarsson, F. R. Eirich, *J. Phys. Chem.* **72** (1968) 2710
33. E. A. Muller, P. Rasmussen, *J. Chem. Eng. Data* **36** (1991) 214
34. A. J. Treszczanowicz, O. Kiyohara, G. C. Benson, *J. Chem. Thermodyn.* **13** (1981) 253
35. M. S. Contreras, *J. Chem. Eng. Data* **46** (2001) 1149
36. P. A. Kollman, L. C. Allen, *Chem. Reviews* **72** (1972) 283

37. S. Yamabe, K. Morokuma, *J. Am. Chem. Soc.* **97** (1975) 4458
38. R. K. Nigam, P. P. Singh, *Trans. Faraday Soc.* **65** (1969) 950
39. R. Mecke, *Discuss. Faraday Soc.* **9** (1950) 161
40. C. Bourderon, C. Sandorfy, *J. Chem. Phys.* **59** (1973) 2527
41. F. Smith, I. Brown, *Aust. J. Chem.* **26** (1973) 705
42. K. Nakanishi, H. Shirai, *Bull. Chem. Soc. Japan* **43** (1970) 1634
43. S. Figueroa-Gerstenmaier, A. Cabanas, M. Costas, *Phys. Chem. Chem. Phys.* **1** (1999) 665
44. K. N. Marsh, C. Burfitt, *J. Chem. Thermodyn.* **7** (1975) 955
45. P. Munk, A. Qin, D. E. Hoffman, *Collect. Czech. Chem. Commun.* **58** (1993) 2612
46. K. S. Kumar, N. V. Reddy, *Phys. Chem. Liquids* **39** (2001) 117
47. U. Bhardwaj, S. Maken, K. C. Singh, *J. Chem. Thermodyn.* **28** (1996) 1173
48. K. C. Singh, K. C. Kalra, S. Maken, B. L. Yadav *J. Chem. Eng. Data* **39** (1994) 241
49. A. Ali, A. K. Nain, B. Lal, D. Chand, *Int. J. Thermophys.* **25** (2004) 1835
50. B. Orge, M. Iglesias, G. Marino, M. Domínguez, M. M. Piñeiro, J. Tojo, *Fluid Phase Equilib.* **170** (2000) 151
51. K. Garabadu, G.S. Roy, S. Tripathy, B.B. Swain, *Czech. J. Phys.* **47** (1997) 765
52. T. S. Vijayalakshmi, P. R. Naidu, *J. Chem. Eng. Data* **34** (1989) 413
53. T. S. Vijayalakshmi, P. R. Naidu, *J. Chem. Eng. Data* **35** (1990) 338
54. T. S. Vijayalakshmi, P. R. Naidu, *J. Chem. Eng. Data* **37** (1992) 368
55. G. Dharmaraju, G. Narayanaswamy, G. K. Raman, *J. Chem. Thermodyn.* **12** (1980) 563
56. P. Venkateswarlu, G. Dharmaraju, G. K. Raman, *Proc. Indian Nat. Sci. Acad.* **48A** (1982) 265
57. K. Prasad, K. S. Kumar, G. Prabhakar, P. Venkateswarlu, *J. Mol. Liquids* **123** (2006)
58. H. L. Zhang, *J. Chem. Eng. Data* **48** (2003) 52
59. J. Nath, S. K. Mishra, *J. Chem. Eng. Data* **43** (1998) 196
60. H. L. Zhang, S. J. Han, *Phys. Chem. Liquids* **31** (1996) 49
61. J. Pardo, V. Rodriguez, C. Lafuente, P. M. Royo, J. S. Urieta, *J. Chem. Thermodyn.* **25** (1993) 373.