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REVIEW

**Physical, chemical and structural effects as important factors for  
the determination of thermodynamic and transport properties  
and the modelling of non-electrolyte solutions**

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*Abstract:* In our previous review, an attempt was made to relate the volumetric effects involved in binary mixtures of normal and branched alcohols. The present paper summarizes some selected research activities related to complex molecular structure of various authors that appeared in leading international journals. The main aim was a better understanding of the complex structure of different non-electrolyte mixtures with no alcohols, which are most frequently present in the chemical, petrochemical and related industries. The influences of the basic physical, chemical and structural effects of the most often chosen types of various binary and ternary mixtures were analyzed. These contributions are of primary importance for the determination and modelling of thermodynamic, transport and other properties.

*Keywords:* thermophysical properties; transport properties; non-electrolyte systems; structural effect.

CONTENTS

1. INTRODUCTION
2. INTERACTIONS IN DIFFERENT TYPES OF MIXTURES
  - 2.1. Systems containing amines
  - 2.2. Systems containing esters
  - 2.3. Systems containing amides
  - 2.4. Systems containing chloro-alkanes
3. CONCLUSIONS

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## INTRODUCTION

Increasing use of many non-electrolyte mixtures in various industrial processes, such as in the chemical, petrochemical and related industries, has greatly stimulated need for extensive data on the thermodynamic and transport properties. These properties play an important role in the comprehension of the nature of the complex molecular structures that exists in binary and ternary mixtures.

Knowledge of adequate structures forms the basis for the development of new theoretical and empirical models. Herein, excess molar volumes,  $V^E$ , viscosity deviations,  $\Delta\eta$ , speed of sound deviations,  $\Delta u$ , changes of isentropic compressibility,  $\Delta\kappa_s$ , molar refraction changes of mixing,  $\Delta R$ , changes in the refractive indices on mixing,  $\Delta n_D$ , *etc.*, are considered, bearing in mind that their values are the consequence of molecular motion, molecular packing and various types of molecular interactions caused by the chemical nature and the size and shape of different molecules.

Thermodynamic and transport properties are attributed to a balance between physical, chemical and structural effects. Physical contributions represent non-specific interactions between the actual species present in the solution. The chemical contributions function as specific intermolecular interactions, which include charge-transfer type forces and other complex forming interactions. The structural contributions arise from several effects, especially from interstitial accommodation and changes in free volume. Namely, geometrical fitting of one component into another might occur due to differences in size and shape of components. More information about these contributions can be found in the literature.<sup>1-7</sup> Additionally, an in detail definition<sup>8,9</sup> and theory<sup>10</sup> of the hydrogen bond are given.

Mixtures that include alcohols are not treated herein, since in previous papers, they were presented and analyzed in detail.<sup>11-23</sup> In addition, a review<sup>17</sup> was particularly devoted to molecular interactions of binary liquid mixtures containing alcohols, *i.e.*, *n*-alcohols, branched alcohols and alkanediols in mixtures with aromatics, nitroaromatics, halo-aromatics, amines, *n*-alkanes, ketones and esters.

With the aim of a deeper understanding of molecular liquid structures and intermolecular interactions that occur in diverse types of non-alcohol containing organic mixtures, in this manuscript, non-electrolyte systems containing amines, amides, ethers, esters and chloro-alkanes with different polar or non-polar compounds are treated. Bearing in mind that an analysis of non-ideal behaviour mainly focuses on excess molar volumes, it is desirable to mention the factors that produce positive or negative values of  $V^E$ .<sup>1-10</sup>

The magnitude and the positive sign of  $V^E$  can arise mainly from the following factors: *i*) absence of strong specific interactions between the components of a mixture; *ii*) the consequence of the rupture of H-bonds in self-associated

alcohol molecules and the physical dipole–dipole interactions between real species, as well as the breaking of chemical and/or non-chemical interactions among molecules in pure components during the mixing process; *iii*) predominant intermolecular H-bond stretching of associated alcohol molecules in the presence of other component; *iv*) steric hindrance of branched substances; *v*) improper interstitial accommodation due to similar molar volumes and free volumes between unlike molecules.

The negative contributions are consequence of the effects: *vi*) a more efficient packing in the mixture than in the pure liquids is considered to be the major contribution to negative  $V^E$  values. This could be the consequence of strong intermolecular interactions attributed to charge-transfer complex, dipole–dipole and dipole-induced dipole interactions and H-bonding between unlike molecules; *vii*) structural effects that arise from proper interstitial accommodation and orientation ordering leading to more compact structures and greater packing in mixtures; *viii*) the presence of electron donor–acceptor interactions between different molecules.

Complex behaviour and specific characteristics of different molecules determine the predominance of particular type of interactions in each mixture stipulating which contribution is dominant, as can be seen in the mixtures considered as follows.

The empirical and theoretical models used to correlate or predict corresponding thermodynamic and transport properties in the considered articles are also mentioned here.

#### INTERACTIONS IN DIFFERENT TYPES OF MIXTURES

##### *Systems containing amines*

*Aliphatic amines + n-alkanes.* Kašparek *et al.*<sup>24</sup> measured the  $V^E$  values of some aliphatic amines with members of a homologous series of *n*-alkanes. The  $V^E$  values were positive over the whole range of concentration for all mixtures and increase with increasing length of the *n*-alkane molecule for mixtures containing *n*-hexylamine and di-*n*-propylamine. Maximum values were obtained for *n*-alkane + diethylamine mixtures. These positive values of  $V^E$  are probably due to the dissociation of hydrogen-bonded aggregates of the amines. The similar situation exists in the case<sup>25</sup> of the  $V^E$  values of mixtures of *cyclo*-hexylamine with *n*-alkanes, benzene and substituted benzenes.

*Aliphatic amine + benzene or substituted benzene + n-alkane compounds.* Letcher<sup>26</sup> determined the  $V^E$  values of binary mixtures for primary amines (*n*-propylamine and *n*-butylamine), secondary amines (diethylamine, di-*n*-propylamine and di-*n*-butylamine) and tertiary amines (triethylamine, tri-*n*-propylamine and tri-*n*-butylamine) with benzene, chlorobenzene, nitrobenzene, toluene, hexane, heptane and cyclohexane at 25 °C.

For the mixtures of tertiary amines with cyclohexane, the  $V^E$  values were the result of the reduction of predominantly dipole–dipole interactions between the amine molecules. This effect was partly dipole–dipole in nature. The mixtures of tertiary amines with hexane and heptane showed small  $V^E$  values, which were more negative when the alkyl chains on the amine were longer. This trend could be attributed to the fitting of alkanes in the lattice of a long-chain amine, giving reductions in volume. However, the negative values of  $V^E$  showed that cross interactions dominated. Secondary amines show positive values of  $V^E$  in mixtures with cyclohexane due to the decrease in H-bonded self-association of the amines caused by dilution with cyclohexane. Negative changes of  $V^E$  increase in mixtures of secondary amines with alkanes with increasing size of the amine molecule. Namely, an alkane molecule fits better into the more open structure of longer chain amines than into shorter chain amines. The explanation for the negative values of  $V^E$  for secondary amines with benzene and substituted benzenes is similar to that for the case of mixtures of tertiary amines + aromatics. This is probably due to the size of the alkyl groups which diminish the effect of the amine–aromatic interaction. The  $V^E$  values of primary amines + cyclohexane are positive, as in the case of mixtures with secondary amines. The maximum  $V^E$  value for mixtures with primary amines is larger. This is probably due to the breakdown of the more compact H-bonded structure of the primary amines. The  $V^E$  values for primary amines with alkanes are much larger than their secondary or tertiary counterparts. This could be the consequence of two effects: *i*) the breakdown of the H-bonded structure of primary amines and *ii*) primary amines have more compact structures than secondary and tertiary amines. Namely, an alkane molecule cannot pack into the structure of primary amine as easily as into those of secondary and tertiary amines. In the mixtures of primary amines with benzene and substituted benzenes, it could be concluded that the substituted groups are responsible for the fact that these aromatics do not fit into the primary amine lattice as easily as benzene molecules. For this reason, the  $V^E$  values are more negative for the mixtures of primary amines with benzene.

*Trialkylamines + n-alkanes or alkylamines.* Oswal *et al.*<sup>27</sup> determined the isentropic compressibilities,  $\kappa_s$ , and changes of isentropic compressibility,  $\Delta\kappa_s$ , from measurements of speeds of sound,  $u$ , and densities,  $\rho$ , for 14 binary mixtures of triethylamine (TEA) and tri-*n*-butylamine (TBA) with *n*-hexane, *n*-octane, *n*-propylamine, *n*-pentylamine, *n*-hexylamine and *n*-octylamine. The values of  $\Delta\kappa_s$  for mixtures with alkanes are positive for systems containing TEA and negative for systems containing TBA. The positive values of  $\Delta\kappa_s$  are the consequence of the disruption of dipole–dipole association in TEA. On the other hand, the negative values of  $\Delta\kappa_s$  arise due to the following contributions: *i*) a positive effect due to the disruption of dipole–dipole association in the TBA molecule and *ii*) the negative effect due to the interstitial accommodation of alkane molecules into

the large free volume of the TBA structure. It is clear that the contribution  $ii$  is quite large and dominates over the contribution  $i$ .

In the cases of TEA + primary amines, the  $\Delta\kappa_s$  values are less positive and become negative as the chain length of the primary amine increases.

For the TBA + primary amine mixtures, the  $\Delta\kappa_s$  values first increase from *n*-propylene to *n*-butylamine and then decrease as the chain length of the alkyl amine increases to *n*-octylamine. Positive values of  $\Delta\kappa_s$  for TEA and TBA mixtures with primary amines are connected with destruction of H-bonds in these amines, for TEA + *n*-propylamine and *n*-pentylamine mixtures and for all mixtures with TBA. For the mixtures of TEA with *n*-hexylamine and *n*-octylamine, positive effect of  $\Delta\kappa_s$  associated with the destruction of H-bonds is masked by the negative effect due to interstitial accommodation. The experimental speed of sound,  $u$ , was analyzed in terms of the collision factor theory, free length theory and Prigogine–Flory–Patterson statistical theory of solutions.

*Diethylamine + ethyl acetate + n-heptane.* Lillo *et al.*<sup>28</sup> calculated excess molar volumes and viscosity deviations for the ternary system diethylamine + ethyl acetate + *n*-heptane at 25 °C and for the corresponding binary systems. The positive values of  $V^E$  for all binaries indicate that molecular interactions between different molecules are weaker than interactions between the same molecules in their pure liquid. In addition, repulsive forces were dominant in these mixtures, causing very small excess viscosities for all binary systems.

*Aniline + benzene + N,N-dimethylformamide.* In the work of Kharat and Nikam,<sup>29</sup> the excess molar volumes and viscosity deviations for the ternary system aniline + benzene + *N,N*-dimethylformamide at 298.15, 303.15, 308.15 and 313.15 K were determined. At all temperatures, the  $V^E$  and  $\Delta\eta$  values were negative. The main contribution to the negative values for  $V^E$  was the consequence of the interstitial accommodation of non-associated benzene molecules into aggregates of aniline. This also implies that no complex-forming interactions were present in system, leading to the negative values of  $\Delta\eta$ .

The McAllister three-body interaction model<sup>30</sup> was used to correlate the kinematic viscosities of the investigated systems. The  $V^E$  and  $\Delta\eta$  values were predicted by the polynomial equations of Radojković *et al.*,<sup>31</sup> Kohler<sup>32</sup> and Scatchard *et al.*<sup>33</sup>

#### *Systems containing esters*

*Methyl butanoate + n-heptane + (n-octane or cyclooctane or 1-chlorooctane).* Matos *et al.*<sup>34,35</sup> and Trenzado *et al.*<sup>36</sup> determined the  $V^E$  and  $\Delta\eta$  values for the ternary systems of (methyl butanoate + *n*-heptane) with *i*) *n*-octane, *ii*) cyclooctane or *iii*) 1-chlorooctane at 283.15, 293.15, 303.15 and 313.15 K at atmospheric pressure over the entire concentration range.

The mixing effects corresponding to each binary system were the consequence of the following specific interactions and net packing effects: *i*) systems of methyl butanoate with *n*-heptane and *n*-octane exhibited positive values of  $V^E$  because the net rupture of dipole–dipole interactions in methyl butanoate dominates over the molecular packing and heteromolecular dipole–dipole induced interactions; *ii*) in the system *n*-heptane + *n*-octane, molecular packing was the prevalent factor; *iii*) in the system *n*-heptane + cyclooctane, the negative values of  $V^E$  confirmed that the packing effect predominated over physical interactions; *iv*) the positive  $V^E$  values for the system methyl butanoate + cyclooctane indicated that the rupture of dipole–dipole interactions between the ester molecules predominated over the effect of molecular packing and volume contraction; *v*) the negative values of  $V^E$  at all the investigated temperatures for the system *n*-heptane + 1-chlorooctane showed that the molecular packing effect was the prevalent factor, exhibiting a slightly endothermic effect. Moreover, the effects of the breakage of dipole–dipole interactions in the 1-chlorooctane molecule predominated over those due to molecular packing and heteromolecular dipole–dipole induced interactions, *vi*) the positive values of  $V^E$  and endothermic effect for the system methyl butanoate + 1-chlorooctane suggested that net rupture of heteromolecular dipole–dipole interactions prevailed over dipole–dipole heteromolecular interactions. The negative values of  $\Delta\eta$  for both binary systems showed that the effect of dispersive forces prevailed.

The viscosity values were used to test the predictive capability of the UNIFAC-VISCO<sup>34–36</sup> and UNIVAC<sup>34,35</sup> group contributions models.

*n*-Butyl acetate + aromatic hydrocarbons. The dependences of  $V^E$  on temperature for the mixtures *n*-butyl acetate + aromatic hydrocarbons (toluene, ethylbenzene, *p*-xylene, mesitylene, *i*-propylbenzene, *n*-butylbenzene, *i*-butylbenzene and *t*-butylbenzene) were analyzed in the article by Resa *et al.*<sup>37</sup>

*n*-Butyl acetate is a weakly polar compound while the aromatic hydrocarbons are nearly non-polar. The aromatic hydrocarbon molecules intersperse among the *n*-butyl acetate molecules, affecting decreased interactions among the dipoles of butyl acetate and destruction of the dispersive interactions among the benzene rings. The obtained interaction between unlike molecules was weak, which caused expansion. It is clear that the influence of the intermolecular forces was higher than the packing effect caused by geometrical fitting for some chemicals (mesitylene, butylbenzene, *etc.*). For the mixtures that contained light solvents, the opposite effect would be detected, as aromatic hydrocarbon molecules with small molecules destroy neither  $\pi$  electron dispersive forces nor ester polar attraction.

The experimental data were used to test the Soave–Redlich–Kwong<sup>38</sup> and the Peng–Robinson<sup>39</sup> equations of state, which are of general interest in the calculation of thermodynamic properties of multicomponent complex mixtures.



*Methyl ethanoate + 1-chlorooctane + n-alkane.* Matos *et al.*<sup>40</sup> reported  $V^E$  values at 25 °C of four ternary mixtures of methyl ethanoate + 1-chlorooctane + (*n*-heptane, *n*-octane, *n*-nonane or *n*-decane). The values of  $V^E$  for 1-chlorooctane + *n*-alkane showed that the packing effect was significant in the mixture containing *n*-heptane (negative values of  $V^E$ ), which decreased with increasing number of carbon atoms in the *n*-alkane. As a result, positive values of  $V^E$  for the mixtures with *n*-nonane and *n*-decane were obtained. Moreover, the determination of the excess molar enthalpies<sup>41</sup> suggested that the breakage of dipole–dipole interactions in the chloro-alkanes predominates over the dispersive and induced heteromolecular dipole–dipole interactions in these binaries. For methyl ethanoate + *n*-alkane mixtures, the positive values of  $V^E$  imply that the effects due to heteromolecular interactions and degree of molecular packing efficiency decrease as the difference in molecule size of the compounds in the mixture increases.

Investigations of mixing enthalpies for these systems<sup>40</sup> confirmed that the dominant factor was breakage of dipole–dipole interactions in the methyl ester molecules. Finally, the small values of  $V^E$  of the system methyl ethanoate + 1-chlorooctane suggest that the effects due to the heteromolecular dipole–dipole interactions are more important than those related to the breakage of dipolar interactions among the 1-chlorooctane molecules.

The  $V^E$  values were utilized to test the Nitta–Chao group-contribution model.<sup>42</sup> In addition, several empirical and semi empirical models were used to predict the experimental results of the ternary mixtures.<sup>32,43–46</sup>

#### *Systems containing ethers*

*1,1-Dimethylethyl methylether with ethyl acrylate/butyl acrylate/methyl methacrylate/styrene.* Peralta *et al.*<sup>47</sup> calculated the  $V^E$  values of the binary systems of 1,1-dimethylethyl methylether (MTBE) with ethyl acrylate, butyl acrylate, methyl methacrylate and styrene at 298.15 K and atmospheric pressure. The interactions between MTBE as an almost non-polar component and esters as polar components could be considered as complex formation between two species by  $n$ – $\pi$  interaction. For all binary systems, negative values of  $V^E$  were obtained as a result of the effect of breaking the dipole–dipole association of the ether and the net packing effect contributed to by structural effects arising from interstitial accommodation. The largest negative values of  $V^E$  obtained for the system MTBE + styrene indicate that the disruption of dipolar associations of the MTBE as an ether is remarkably less than the additional specific interactions between its pair of electrons and the  $\pi$  electron of the aromatic ring. It is important to emphasize that the values of  $V^E$  increase as an ester chain increases from methyl to butyl, apparently due to pronounced contribution of interstitial accommodation.

The calculated  $V^E$  values were correlated with the Redlich–Kister Equation and with a series of Legendre polynomials.

*MTBE with allyl methacrylate, n-butyl methacrylate, methacrylic acid and vinyl acetate.* Wisniak *et al.*<sup>48</sup> calculated  $V^E$  of the binary systems 1,1-dimethylethyl methylether (MTBE) with allyl methacrylate, *n*-butyl methacrylate, methacrylic acid and vinyl acetate at 298.15 and 308.15 K and atmospheric pressure. The magnitude and sign of  $V^E$  are consequence of the type of interactions present in the mixtures. A double bond and an ester group are simultaneously present in acrylate solutes. In addition, methacrylic acid has a free –COOH group, which can lead to H-bonding. The  $V^E$  values are the result of the effect of breakage the dipole–dipole association in the ether; negative values of  $V^E$  indicate a net packing effect contributed by structural effects arising from interstitial accommodation. The maximum value of  $V^E$  for the system MTBE + methacrylic acid is considerably higher than that for the system MTBE + *n*-butyl methacrylate, reflecting a substantial additional packing by H-bonding between the different molecules. With increasing temperature, the  $V^E$  values are more negative, bearing in mind that the kinetic energy of the molecules of both components facilitates interaction of one specie into the other and both H-bonding and interaction between the tertiary ether group and the carbonyl group of the ester.

The calculated  $V^E$  values were correlated with the Redlich–Kister Equation and with a series of Legendre polynomials.

*MTBE + toluene + isooctane.* Morávková *et al.*<sup>49</sup> calculated the excess molar volumes,  $V^E$ , and adiabatic compressibility,  $\kappa_s$ , of the ternary system methyl tetrabutylether + toluene + isooctane (2,2,4-trimethylpentane) at temperatures from 298.15 to 328.15 K.

Molecular interactions for investigated binary systems are as follows: *i*) in the binary system toluene + trimethylpentane, small deviations are the consequence of a slightly different packing effect in the mixture compared to those in the pure substances; *ii*) this effect is much stronger in the binary mixture MTBE + trimethylpentane; *iii*) in the binary mixture MTBE + toluene, on the contrary, two effects are dominant, packing effects and specific  $n+\pi$  interactions. No special ternary interactions are present.

The  $V^E$  and  $\kappa_s$  values for the ternary mixtures and corresponding binaries were fitted to the Redlich–Kister Equation.

*Tetrahydrofuran + cyclic ether + hydrocarbon.* Pintos *et al.*<sup>50</sup> investigated the effect of alkane chain-length on the  $V^E$  values of binary mixtures containing a cyclic ether at 298.15 K and atmospheric pressure. The binary mixtures of tetrahydrofuran (THF) and tetrahydropyran (THP) with *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane were treated. In all cases the positive values of  $V^E$  increase with the length of the alkane chain for a given ether. However, the  $V^E$  values decrease with increasing length of the hydrocarbon chain of the ether. The positive values



of  $V^E$  could be explained by the breakage of interactions among molecules of pure species during the mixing process. Moreover, the spatial arrangement of the molecules of these ethers enables an easier accommodation of molecule of *n*-alkanes in the mixtures with THP than in those with THF.

The Nitta–Chao<sup>42</sup> Equation provides a reasonable correlation of the results.

*Ether + chloro-ethylenes.* Pal and Singh<sup>51</sup> calculated the  $V^E$  values of binary mixtures of trichloro-ethylene and tetrachloro-ethylene with 1,4-dioxane and some *n*-alkoxyethanol components at 298.15 K. The  $V^E$  values are positive for the mixture tetrachloro-ethylene + 1,4-dioxane, while an inversion in the sign of  $V^E$  values was obtained from positive to negative in the mixture with trichloro-ethylene. The  $V^E$  value are the result of several opposing effects: differences in the molecular size and shape of the components, and complex formation between the  $\pi$ -electrons of chloro-ethane and oxygen (–O–) in 1,4-dioxane.

These results were fitted to the Redlich–Kister Equation to estimate the binary coefficients.

*Anisole/MTBE + benzene or chlorobenzene or benzonitrile or nitrobenzene.* Viswanathan *et al.*<sup>52</sup> calculated  $V^E$  and  $\Delta\eta$  values for binary systems of anisole or MTBE with benzene, chlorobenzene, benzonitrile and nitrobenzene at 288.15, 293.15 and 298.15 K.

The  $V^E$  values of all anisole and MTBE systems were negative, except for the anisole + chlorobenzene system, which showed a change in sign. The deviations in viscosity  $\Delta\eta$  were negative for all the investigated temperatures. The MTBE systems gave greater  $V^E$  and  $\Delta\eta$  values than the anisole systems, showing that the former systems deviated more from ideal behaviour. This fact could also indicate that the attractive interactions of the unlike molecules were stronger in the MTBE systems. Namely, the existence of electron-pair donor–electron pair acceptor type of interactions in all investigated systems is evident, showing that MTBE is a better electron-pair donor than anisole.

All the results are fitted by the Redlich–Kister Equation.

*Anisole + 2-chloroethanol or 1,4-dioxane or tetrachloroethylene or tetrachloroethane or DMF or DMSO or diethyl oxalate.* Baragi *et al.*<sup>53</sup> calculated  $V^E$ ,  $\Delta\eta$ ,  $\Delta R$ ,  $\Delta u$  and  $\Delta\kappa_s$  values for the binary mixtures of anisole + 1,4-dioxane or tetrachloroethylene or tetrachloroethane or dimethylformamide (DMF) or dimethyl sulphoxide (DMSO) or diethyl oxalate at 298.15, 303.15 and 308.15 K. The  $V^E$  data for mixtures anisole + 1,4-dioxane and anisole + tetrachloroethylene are positive. Dispersion forces combined with a low molar volume of 1,4-dioxane led to the small positive values of  $V^E$  for the mixture anisole + 1,4-dioxane. Higher positive values of  $V^E$  for system anisole + tetrachloroethylene were the consequence of dispersion forces between the electronic charges on the O atom of the anisole molecules and the  $\pi$  electrons of the double bond of the tetrachloroethylene molecule, having a higher molar volume. Negative values of  $V^E$  were

obtained for the mixtures anisole + tetrachloroethane or dimethyl sulphoxide or diethyl oxalate or dimethylacetamide.

The computed quantities were fitted to the Redlich–Kister Equation to derive the coefficients and to estimate the standard error values.

#### *Systems containing amides*

*Xylene + N,N-dimethylformamide.* Chen and Liu<sup>54</sup> calculated the  $V^E$  values of binary mixtures of *o*-xylene, or *m*-xylene, or *p*-xylene with *N,N*-dimethylformamide (DMF) in the temperature range 293.15 to 353.15 K and at atmospheric pressure. In all cases, the  $V^E$  values were negative as result of chemical or specific interactions between DMF and xylene or a structural effect leading to the formation of molecular complexes. These interactions may be classified as electron (donor + acceptor)-type interactions involving the  $\pi$ -electrons of the xylene ring and the carbonyl group of DMF, or interactions through H-bond formation with xylene acting as the H donor and DMF as the acceptor.  $V^E$  data increase with rise in temperature for all analysed systems. The kinetic energy of molecules also increases leading to a decrease of interactions between molecules, so the contraction in volume decreases and as the result  $V^E$  increases.

The  $V^E$  results were correlated using the fourth-order Redlich–Kister polynomial equation with maximum likelihood principle being applied for the determination of the adjustable parameters.

*N,N-Dimethylformamide + aniline + benzonitrile.* Nikam and Kharat<sup>55</sup> calculated the  $V^E$  and  $\Delta\eta$  values for the binary systems *N,N*-dimethylformamide (DMF) with aniline and benzonitrile at 298.15, 303.15, 308.15 and 313.15 K. The negative values of  $V^E$  and  $\Delta\eta$  for the system DMF + aniline are caused by interstitial accommodation of the DMF molecules into the clusters of aniline. Namely, molar volumes of aniline and DMF differ considerably and no associated DMF molecules are geometrically fitted into aggregates of aniline. This shows that complex forming interactions are not present in the DMF + aniline system and therefore, the calculated  $\Delta\eta$  values are negative. The negative values of  $V^E$  and positive values of  $\Delta\eta$  for the DMF + benzonitrile system indicate strong specific interactions through dipolar association between the DMF and benzonitrile molecules.

The  $V^E$  and  $\Delta\eta$  values are fitted by the Redlich–Kister polynomial equation.

*DMF + benzene or toluene or ethylbenzene.* Peng *et al.*<sup>56</sup> calculated the  $V^E$  values for the binary systems DMF with benzene or toluene or ethylbenzene in the temperature range 293.15 to 353.15 K and at atmospheric pressure. The negative values of  $V^E$  for all binary mixtures are the consequence of molecular interaction between the polar molecules of DMF and the non-polar molecules of the aromatic hydrocarbons. Namely, these mixtures are formed by dipole–dipole interactions of DMF molecules and the interaction of dipole–induced dipole

between DMF and the aromatic hydrocarbon molecules. It is clear that interaction between unlike molecules is stronger than the intra-molecular interactions. In addition, the small size of the DMF molecules and its linear aliphatic configuration could be other factors giving rise to the contraction in the  $V^E$  of the mixtures.

The increase in the kinetic energy of molecules with increasing temperature leads to a decrease in the interactions of the molecules. The interaction between DMF molecules is smaller than between aromatic molecules, so the contraction in volume increases and the  $V^E$  values decrease.

The  $V^E$  were fitted by the fourth-order Redlich–Kister Equation.

*Cyclohexanone + N,N-dimethylacetamide.* Iloukhani and Rakhshi<sup>57</sup> calculated the  $V^E$ ,  $\Delta\eta$  and  $\Delta n_D$  values for the binary system cyclohexanone + *N,N*-dimethylacetamide at 298.15, 308.15 and 318.15 K as a part of the ternary system with *N,N*-diethylethanolamine as the third component. The positive  $V^E$  is due to chemical and structural effects with more positive values on increasing the temperature from 298.15 to 318.15 K. The negative values of  $\Delta\eta$  and  $\Delta n_D$  suggest that the forces between the pairs of unlike molecules are weaker than the forces between like molecules due to the difference in shape and size of the component molecules.

The binary results of  $V^E$ ,  $\Delta\eta$  and  $\Delta n_D$  were fitted by Redlich–Kister Equation, while the Cibulka,<sup>58</sup> Jasinski and Malanowski,<sup>59</sup> Singe *et al.*, Pintos *et al.* and Calvo *et al.* Equations were used to correlate the ternary properties.<sup>60</sup> The predictions were performed by the Kohler<sup>32</sup> and Jacob–Fitzner Equations.<sup>61</sup> The McAllister three-body interaction model and the Hind *et al.*<sup>62</sup> Equation were used for correlation of kinematic and dynamic viscosities, respectively.

#### *Systems containing chloro-alkanes*

Zhang<sup>63</sup> determined the  $V^E$  and  $\Delta\eta$  values for three binary mixtures of chlorinated alkanes: carbon tetrachloride + chloroform, carbon tetrachloride + dichloromethane and chloroform + dichloromethane, and one ternary mixture of chloroform + 1:1 carbon tetrachloride:dichloromethane at 303.15 K.

Both binary systems with carbon tetrachloride have positive values of  $V^E$ . The larger values of  $V^E$  for the system with chloroform are the consequence of two factors: *i*) carbon tetrachloride as non-polar component interacts weakly with polar dichloromethane and chloroform, where dichloromethane has a larger polarity than chloroform; *ii*) the present molecules show differences both in size and shape. The values of  $V^E$  for chloroform + dichloromethane are negative. The small magnitude is the consequence of very weak specific interactions, most probably due to dipole–dipole interactions between different molecules. The positive values of  $V^E$  could be explained from the fact that the most compact packing of spherical carbon tetrachloride is destroyed by mixing with spherical molecules of

the two other components. Negative  $\Delta\eta$  could be caused by differences in size, shape and polarity between carbon tetrachloride and dichloromethane or chloroform. In addition, molecular interactions between these species are weaker than those in their pure state.

### CONCLUSIONS

It is evident that thermodynamic and transport properties of mixtures could provide more and deeper information on molecular interactions. They show very complex behaviour expressed by three main effects: chemical, physical and geometrical. Which of the contributions is dominant depends on the nature of investigated mixture.

For the investigated mixtures, these contributions are balanced giving the corresponding values of thermodynamic and transport properties and the explained complex behaviour of the mixtures.

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### ИЗВОД

#### ФИЗИЧКИ, ХЕМИЈСКИ И СТРУКТУРНИ ЕФЕКТИ КАО ВАЖНИ ФАКТОРИ ЗА ОДРЕЂИВАЊЕ И МОДЕЛОВАЊЕ ТЕРМОДИНАМИЧКИХ И ТРАНСПОРТНИХ СВОЈСТАВА НЕЕЛЕКТРОЛИТНИХ РАСТВОРА

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

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У нашем прегледном раду учињен је покушај да се повежу волуметријски ефекти укључени у бинарне смеше нормалних и разгранатих алкохола. У овом раду су укратко изложене неке изабране истраживачке активности аутора повезаних са сложеним молекулским структурама које су објављене у водећим међународним часописима. Главни циљ је био боље разумевање комплексне структуре различитих смеша неелектролита, без алкохола, које су најчешће присутне у хемијској, петрохемијској и сродним индустријама. Анализиран је утицај основних физичких, хемијских и структурних ефеката више изабраних типова различитих бинарних и тернерних смеша. Оваква истраживања су од примарног значаја за одређивање и моделовање термодинамичких, транспортних и других особина.

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