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1. Introduction

Mixing effects for thousands of compounds and their mixtures used in the process industry are rather difficult to be known, hence knowledge of thermodynamic properties such as densities, as well as excess molar volumes, $V_E$, of organic mixtures at various temperatures is of great importance. Selection of systems for analysis should be based on molecular structure of the individual components, as well as their industrial and ecological significance. Mixing of the compounds with different and complex molecular structure leads to various intermolecular interactions, resulting in non-ideal behaviour of mixtures. Therefore, knowledge of volumetric properties of individual components and their mixtures helps in understanding the complex structure of liquids.

In order to have good insight in molecular interactions present in mixtures of alcohols and organic solvents, this chapter presents the extension of our earlier studies (Djordjević et al., 2007, 2009; Kijevčanin et al., 2007a, 2007b, 2007c, 2009, 2010; Radović et al., 2008, 2009, 2010a, 2010b, 2011; Smiljanić et al., 2008a, 2008b; Šerbanović et al., 2006) of the thermodynamic properties and mixing effects present in following type of mixtures: alcohols + hydrocarbons (benzene and alkane), + chlorobenzene, + amine, + chloroform, + 2-butanone. Also, with the intention to present more general conclusion, systems of organic solvents with alkanediols have been included in the analysis.

Concerning the aforementioned tasks, our previous results have been extended with the experimental measurement and modelling of the density of the binary mixtures of acetone with the 1-propanol, 1,2-propanediol and 1,3-propanediol at atmospheric pressure over the whole composition range and at temperatures from 288.15 up to 323.15 K.

The reason of this additional selection was diverse industrial application of the proposed organic compounds.
Acetone is used for various applications in the pharmaceutical, cosmetic and food industries. For example, acetone is one of the agents used in the process of skin rejuvenation by chemical peeling. It is also listed as a component in food additives and food packaging. In chemical industry acetone is used as a solvent for most plastics and synthetic fibers (polystyrene, polycarbonate and some types of polypropylene), as a volatile component of some paints and varnishes and in production processes of solvents such as methyl isobutyl alcohol and methyl isobutyl ketone.

In laboratory, acetone has a wide range of practical applications; as a polar solvent in organic chemical reactions, in acetone/dry ice baths used to conduct reactions at low temperatures but also as a solvent for rinsing laboratory glassware and instruments. Acetone is fluorescent under ultraviolet light, and its vapor may be used as a tracer in fluid flow experiments.

Alcohols, including 1-propanol, alone or in combination with other solvents, are widely used in the pharmaceutical and chemical industry (Kiječanin et al., 2007a; Riddick et al., 1988; Swarbrik & Boyland, 1993; Šerbanović et al., 2006), for production of pesticides, fats, oils, rubber, paints, varnishes, waxes, plastics, explosives, drugs, detergents, perfumes and cosmetics. Some alcohols (especially ethanol and 1-buthanol) are used as biofuel derived from biomass sources (Radović et al., 2010a).

Alkanediols such as 1,2-propanediol or 1,3-propanediol are basic structural units for polyhydroxy compounds. These compounds have a variety of industrial applications such as solvents, coolants, antifreezes, plasticizers, chemical intermediates, food additives, heat transfer fluids. Both 1,2-propanediol and 1,3-propanediol are of very low toxicity, biodegradable and can be obtained as a by-product of biodiesel production.

At the moment, 1,2-propanediol or propylene glycol is more widely used than its isomer 1,3-propanediol. Among other applications due to the similarity of its properties to those of ethylene glycol, 1,2-propanediol is recommended as a substitute for ethylene glycol when safer properties are desired. In the food industry 1,2-propanediol is used as a solvent for food colors and flavorings and as a food additive, labeled E1520. Some of its applications in the cosmetic industry are as a moisturizer in toothpaste, shampoo, mouth wash and hair care products, as the main ingredient in deodorant sticks, as a carrier in fragrance oils and as an ingredient in massage oils. 1,2-Propanediol is also used as a solvent in many pharmaceuticals, including oral, injectable and topical formulations.

1,3-Propanediol finds application in the chemical industry mainly in the production of polymers, composites, adhesives, laminates, coatings and moldings. It is also a solvent and used as an antifreeze and wood paint.

Additional insight in volumetric behaviour is performed by excess volume modeling, including correlation by the Redlich-Kister (Redlich & Kister, 1948) equation, partial volumetric properties determinations, and in addition, modeling of $V^E$ performed by cubic CEOS and CEOS/$G^E$.

Using the measured density data, and results obtained by modelling of volumetric properties, the excess molar volumes were evaluated in terms of molecular interactions...
between different molecules of the investigated mixtures. Finally, detailed explanation of the molecular interactions typical for each of the investigated mixture was given.

2. Research methods

2.1 Experimental study

Densities $\rho$ of the binary mixtures, and corresponding pure substances were measured with an Anton Paar DMA 5000 digital vibrating U-tube densimeter with a stated accuracy $\pm 5 \times 10^{-3}$ kg m$^{-3}$. The temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers with the stability better than $\pm 0.002$ K; temperature was regulated to $\pm 0.001$ K with a built-in solid-state thermostat.

In order to minimize evaporation of the volatile solvents and to avoid the errors in composition, all mixtures presented in this paper were prepared using the cell and the procedure described previously (Radojković et al., 1976; Tasić et al., 1995). The mixtures were prepared by mass using a Mettler AG 204 balance, with a precision of $1 \times 10^{-4}$ g. The experimental uncertainty in the density was about $\pm 1 \times 10^{-2}$ kg m$^{-3}$, and the uncertainty in excess molar volume has been estimated at $\pm 3 \times 10^{-9}$ m$^3$ mol$^{-1}$.

2.2 Modeling of volumetric properties

The non-ideal binary mixtures behavior, presented by excess molar volumes $V_E$, were analysed from the experimentally determined density data using following equation:

$$V_E = \left( x_1 M_1 + x_2 M_2 \right) / \rho - \left( x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2 \right)$$

(1)

where $x_i$ is the mole fraction of component $i$ ($i = 1, 2$) in the mixture; $M_i$ is its molar mass; $\rho$ and $\rho_i$ are the measured densities of the mixture and the pure component $i$, respectively.

The values of $V_E$ were correlated with the Redlich-Kister (RK) equation (Redlich & Kister, 1948):

$$V_E = x_i x_j \sum_{p=0}^{k} A_p (2x_i - 1)^p$$

(2)

where $A_p$ are the adjustable parameters, and the number of adjustable parameters ($k + 1$) has been determined using the F-test.

The $V_E$ data for all systems, grouped by specific system of alcohol + organic solvents, are presented in Figure 1.

2.2.1 Derived volumetric properties

Partial molar properties are very important for the extensive properties analysis, particularly their changes with composition at constant pressure and temperature conditions demonstrating the volume contraction or expansion. Effect at infinite dilution appears to be of particular interest since at the limit of infinite dilution, solute-solute interactions disappear. Hence, the partial molar volume values at infinite dilution region provide insight into solute-solvent interactions (Iloukhani & Ghorbani, 1998).
Fig. 1. Continued

(a) methanol (1) + chlorobenzene (2)
ethanol (1) + chlorobenzene (2)
1-propanol (1) + chlorobenzene (2)
1-butanol (1) + chlorobenzene (2)
2-butanol (1) + chlorobenzene (2)
2-methyl-2-propanol (1) + chlorobenzene (2)
1-pentanol (1) + chlorobenzene (2)

(b) 1-propanol (1) + cyclohexylamine (2)
1-butanol (1) + cyclohexylamine (2)
1-pentanol (1) + cyclohexylamine (2)
2-butanol (1) + cyclohexylamine (2)
2-methyl-2-propanol (1) + cyclohexylamine (2)
1-butanol (1) + hexylamine (2)

(c) methanol (1) + benzene (2)
ethanol (1) + benzene (2)
1-propanol (1) + benzene (2)
1-butanol (1) + benzene (2)
2-butanol (1) + benzene (2)

(d) methanol (1) + chloroform (2)
ethanol (1) + chloroform (2)
1-propanol (1) + chloroform (2)
1-butanol (1) + chloroform (2)
2-butanol (1) + chloroform (2)

\[ V = \frac{x_1}{10^6} m \text{ mol}^{-1} \]
Partial molar volumes of component 1, $\bar{V}_1$, and component 2, $\bar{V}_2$, are calculated from the following relations:

$$\bar{V}_1 = V^E + V_1 + (1 - x_1) \left( \partial V^E / \partial x_1 \right)_{p,T}$$  \hspace{1cm} (3)$$

$$\bar{V}_2 = V^E + V_2 + x_1 \left( \partial V^E / \partial x_1 \right)_{p,T}$$  \hspace{1cm} (4)

where $V_1$ and $V_2$ denote molar volumes of pure compounds 1 and 2. The derivative term of equations (3) and (4) is obtained by differentiation of equation (2) which leads to the following equations for $\bar{V}_1$ and $\bar{V}_2$:

$$\bar{V}_1 = V_1 + (1 - x_1) \left[ \sum_{p=0}^{k} A_{p}(2x_1 - 1)^p + x_1 \sum_{p=1}^{k} 2pA_{p}(2x_1 - 1)^{p-1} \right]$$  \hspace{1cm} (5)$$

$$\bar{V}_2 = V_2 + x_1 \left[ \sum_{p=0}^{k} A_{p}(2x_1 - 1)^p + x_2 \sum_{p=1}^{k} (-2p)A_{p}(2x_1 - 1)^{p-1} \right]$$  \hspace{1cm} (6)
Excess partial molar volumes $\bar{V}^E_1$ and $\bar{V}^E_2$ are then calculated by using the following relations:

$$\bar{V}^E_1 = \bar{V}_1 - V_1 = V^E + (1 - x_1)(\partial V^E / \partial x_1)_{p,T}$$  \hspace{1cm} (7)$$

$$\bar{V}^E_2 = \bar{V}_2 - V_2 = V^E + x_1(\partial V^E / \partial x_1)_{p,T}$$  \hspace{1cm} (8)$$

### 2.2.2 Excess molar volume correlation by CEOS and CEOS/\text{G}^E models

For the excess molar volume calculation the two-parameter cubic equation of state (CEOS) was used. General form of the two parameter CEOS is given by the following equation:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+ub)(V+wb)}$$  \hspace{1cm} (9)$$

where $P$, $T$, $V$, and $R$ denote pressure, temperature, molar volume and gas constant, respectively; the CEOS dependent constants $u$ and $w$ for the Peng-Robinson-Stryjek-Vera (PRSV) equation (Stryjek & Vera, 1986) applied here are: $u = 1 - \sqrt{2}$ and $w = 1 + \sqrt{2}$.

Parameters for the pure substance, the energy $a_i$ and covolume $b_i$ parameters are determined as:

$$a_i(T) = 0.457235 \frac{(RT^2_{ci})^2}{P_{ci}} \left[1 + m_i \left(1 - T_{ci}^{1/2}\right)^2\right]$$  \hspace{1cm} (10)$$

$$b_i = 0.077796 \frac{RT^2_{ci}}{P_{ci}}$$  \hspace{1cm} (11)$$

$$m_i = k_{0i} + k_{1i} \left(1 + T_{ci}^{1/2}\right) \left(0.7 - T_{ci}\right)$$  \hspace{1cm} (12)$$

$$k_{0i} = 0.378893 + 1.4897153o_i - 0.1713848o_i^2 + 0.0196554o_i^3$$  \hspace{1cm} (13)$$

where $T_{ci}$ and $P_{ci}$ are the critical temperature and critical pressure of component $i$, respectively, $T_{ni}$ stands for the reduced temperature $(T/T_{ci})$, $o_i$ is the acentric factor, and $k_{1i}$ represents the pure substance adjustable parameter (Stryjek & Vera, 1986).

For the determination of $a$ and $b$ parameters of a mixture, two different types of mixing rules were used: CEOS (vdW1) and CEOS/\text{G}^E (TCBT) models.

i. The vdW1 mixing rule (Adachi & Sugie, 1986) is given by the following equations:

$$a = \sum_i \sum_j x_iz_j \left[a_ia_j\right]^{1/2} \left[1 - k_{ij} + l_{ij} \left(x_i - x_j\right)\right]$$  \hspace{1cm} (14)$$
where \( k_{ij}, l_{ij} \) and \( m_{ij} \) are the binary interaction parameters.

ii. Typical presentation of CEOS/\( G^E \) models could be given as:

\[
\frac{a}{bRT} = f \left( a_i, b_i, x_i, G^E \text{ or } A^E \right)
\]  

(16)

The TCBT mixing rule (Twu et al., 1999) is developed from equation (16) for no reference pressure conditions and based on the van der Waals reference fluid (vdW). TCBT model is given as follows:

\[
\frac{G^E}{RT} = \frac{G_{vdW}^E}{RT} + (Z - Z_{vdW}) = \ln \left[ \left( \frac{V_{vdW}^* - 1}{V^* - 1} \right) \left( \frac{b_{vdW}}{b} \right) \right] - \frac{1}{w-u} \left[ \frac{a^*_i}{p} \ln \left( \frac{V^* + w}{V^*} \right) - \frac{a^*_i}{p} \ln \left( \frac{V_{vdW}^* + w}{V_{vdW}^* + u} \right) \right]
\]

(17)

where \( G_{vdW}^E \) is calculated for the PRSV CEOS and \( V^* = V / b = Z / b^* \) denotes the reduced liquid volume at \( P \) and \( T \) of the mixture. The compressibility factors \( Z \) and \( Z_{vdW} \) are calculated from Eq. (9) expressed in the \( Z \) form.

Parameters \( a_{vdW} \) and \( b_{vdW} \) are determined by using equations (14) and (15). NRTL equation (Renon & Prausnitz, 1968) proposed by Renon & Prausnitz was used as the \( G^E \) model:

\[
\frac{G^E}{RT} = \sum_i x_i G_{ji}\tau_{ji}
\]

(18)

where:

\[
G_{12} = \exp(\alpha_{12}\tau_{12}) \quad G_{21} = \exp(\alpha_{12}\tau_{21}) \quad \tau_{12} = \frac{\Delta g_{12}}{RT} \quad \tau_{21} = \frac{\Delta g_{21}}{RT} = \frac{\Delta g_{21}}{RT}
\]

(19)

The results for whole investigated temperature range were obtained by the CEOS and CEOS/\( G^E \) models with incorporated temperature dependent parameters as follows:

\[
Y = Y_1 + Y_2T
\]

(20)

where \( Y = k_{ij}, l_{ij}, m_{ij}, \Delta g_{12} \) and \( \Delta g_{21} \).
mixing rules were treated as temperature independent or temperature dependent (only for whole temperature range correlation).

Modeling by CEOS and CEOS/$G^E$ models was conducted by two and three parameter mixing rules. Models were established based on the following equations:

- equations (9) – (15), with optimized parameters $k_{ij}$ and $m_{ij}$, while parameter $l_{ij}$ was set to 0 - two parameters vdW1-2 model,
- equations (9) – (15), with optimized parameters $k_{ij}$, $m_{ij}$ and $l_{ij}$ - three parameters vdW1-3 model,
- equations (9) – (19), with optimized parameters $\tau_{ij}$ and $\tau_{ji}$, while parameters $k_{ij}$, $m_{ij}$, $l_{ij}$ were set to 0; $\alpha_{ij}$ was set to 0.3 - two parameters TCBT-2 model,
- equations (9) – (19), with optimized parameters $\tau_{ij}$, $\tau_{ji}$ and $k_{ij}$ while parameters $m_{ij}$, $l_{ij}$ were set to 0; $\alpha_{ij}$ was set to 0.3 - three parameter TCBT-3 model.

Generally, considering the number of optimization parameters, the models with three parameters (vdW1-3 and TCBT-3) show better results than two parameter models (vdW1-2 and TCBT-2). But difference in quality of the obtained results strongly depends on type of the systems, present molecular interactions, deviation from ideal mixtures, shape of $V^E$ - $x$ curves (symmetric, asymmetric, S-shape) etc. Usually, very poor results of $V^E$ correlation were obtained in the case of systems with very small $V^E$ values. For example, in the case of methanol + benzene, or methanol + chlorobenzene mixtures (with S-shaped $V^E$ curve) and acetone + 1-propanol system (with negative $V^E$ values), only results obtained by TCBT-3 models could be assessed as acceptable.

Symmetrical systems, with positive $V^E$ values, such as 2-butanol + benzene, presented at Figure 1c, usually show very good agreement between experimental and correlated data obtained by the temperature independent two parameters models (in this case errors were up to 1%). Therefore, two parameter models could be recommended for the excess volume modeling.

As a consequence of very specific interactions present in the systems of alcohols with benzene or chlorobenzene, as well as the systems alcohols + chloroform, almost all of them show S-shape $V^E$ - $x$ curves (except of the 2-methyl-2-propanol + chlorobenzene system). Consequently, only results obtained by three parameter models could be considered as more than acceptable. For methanol + benzene system, only TCBT-3 model is recommended. Also, as it can be seen in our previous paper (Radović et al., 2008), the results obtained for both models reproduce the tendencies of error of excess molar volume calculation increase as temperature rises (from 2 up to 5%). The vdW1-2 and TCBT-2 models, for the same systems gave very high deviations (vdW1-2 for low alcohols had errors close to 30%). Inadequate modeling of $V^E$ by these models is a consequence of the fact that the two parameter model was not suitable for modeling of this type of $V^E$ data.

Finally, it can be concluded that two parameter CEOS and CEOS/$G^E$ models are not suitable to describe systems with S-shape of $V^E$ - $x$ curves.

Typical results of $V^E$ calculation by the CEOS models for S-shaped $V^E$ - $x$ curve are presented graphically in Figure 2.
Results of modeling of $V^E$ in the case of negative symmetric, or slightly asymmetric $V^E$ - $x$ data, system 1-butanol+hexylamine (errors up to 1% for all models, except of 1.5% for vdW1-2) and alcohols + cyclohexylamine show that quality of correlation is very similar to those obtained for systems with symmetric positive values, and all investigated models could be recommended. However, in spite of the fact that 1,3-propanediol + acetone system shows quite symmetrical negative values of $V^E$, the TCBT-2 model, with error higher than 10%, could not be recommended for modelling of experimental values.

For the asymmetric 1-butanol + n-heptane system, with positive $V^E$ - $x$ values, the best results were obtained by the three parameter TCBT-3 model (errors up to 3%), especially comparing to two-parameter vdW1-2 and TCBT-2 models. The other three parameter model, vdW1-3 gave acceptable results for this system at lower temperature but errors increase with temperature rising (up to 2%).

In addition, the correlation of $V^E$ data for all investigated systems was tested with linear temperature dependent CEOS and CEOS/$G^E$ parameters, equation (20), but no significant improvement was obtained related to the quality of the fitting of each isotherm separately, therefore simpler models, with lower number of parameters, can be recommended.

For the correlation of $V^E$ in whole temperature interval, the results achieved by the vdW1-3 and TCBT-3 (three parameters models) were superior comparing to the results obtained with two parameter models, but in some cases (for the S-shape curves) inclusion of temperature dependent parameters is mandatory. For example using temperature
dependent parameters in the TCBT-3 model of correlation for 1-butanol + chloroform, error drops to 2.9%, while without temperature dependence it was 6.5%, or in the case of 1-butanol + heptane system, using temperature dependent parameters in vdwI-3 model, error drops from 6.6 to 2.15%.

3. Molecular interaction study

As can be seen from the number of studies, the experimental $V^E$ values are treated in the following effects: a) physical, b) chemical and c) structural - geometrical contributions.

The magnitude and the positive sign of $V^E$ can arise mainly from the factors: (i) Positive contribution indicates that there are no strong specific interactions between components of a mixture. It is a consequence of the rupture of the H bonds in the self-associated alcohol and the physical dipole-dipole interactions monomer and multimer of the substance. In addition it might be a result of breaking of chemical and/or nonchemical interactions among molecules in the pure components during the mixing process; (ii) Predominant intermolecular H bond stretching of the associated alcohol molecules in the presence of other substances; (iii) The steric hindrance as unsuitable interstitial accommodation due to different molar volumes and free volumes of unlike molecules.

The negative contributions are a consequence of the effects: (i) Strong intermolecular interactions attributed to the charge-transfer complex, dipole-dipole and dipole-induced dipole interactions and H-bonding between unlike molecules finally leading to the more efficient packing in the mixture than in the pure liquids; (ii) structural effects which arise from unsuitable interstitial accommodation giving more compact structure of mixtures. The nature and specific characteristics of different molecules in considered mixtures of ketone, alcohol and multifunctional alcohols determine the predominance of a particular type of interactions in the mixture.

For example, alcohol molecules are polar and self - associated through hydrogen bonding of their OH groups, however, multifunctional molecules are self - associated through inter and intra - hydrogen bonding.

Molecule of 1-propanol exists in 5 different conformations, or rotamers as a result of rotation about the central C-C and C-OH bonds. Information on the structures and relative energies of the separate rotational isomers and the potential barriers between them has been obtained by different experimental techniques including infrared, Raman, nuclear magnetic resonance and microwave spectroscopy, gas electron diffraction etc. In addition, this molecule has been studied by ab initio methods like molecular orbital theory (Radom et al., 1973). A microwave study (Abdurahmanov et al., 1970) of 1-propanol has shown the existence of two rotational isomers corresponding to gauche (G) and trans (T) arrangements about the C-C bond. Ab initio studies (Radom et al., 1973) have indicated that the two most stable rotamers have the Gt and Tt forms while the remaining three isomers are probably destabilized by steric effect.

It is a well known fact confirmed by experimental methods like infrared spectroscopy and ab initio studies that the alcohols and polyols have a tendency to form intermolecular hydrogen bonds. One of the main questions concerning the structural characteristics of polyols such as 1,2-propanediol or 1,3-propanediol is the question of the intramolecular hydrogen bonds
existence. One of the most studied vicinal diols is ethylene glycol. There have been many experimental studies on ethylene glycol including infrared spectroscopy (Buckley and Giguere, 1967), gas phase electron diffraction (GED) (Kazercouni et al., 1997) and microwave spectroscopy (Christen et al., 2001). At the same time numerous ab initio studies have been conducted on ethylene glycol based on density functional theory (DFT) with BP, B3P, BLYP and B3LYP functionals, Hartree-Fock (HF) or Moeller–Plesset (MP2 and MP4) levels of theory (Csonka & Csizmadia, 1995; Nagy et al., 1991, 1992). Most of the authors agree that the two lowest energy conformers (g-Gt and g-Gg, where upper/lower case letters refer to rotations about C-C/C-O bonds and a positive sign designates counterclockwise motion of the forward group along the chain away from the gauche conformation) contain a weak intramolecular hydrogen bond configuration. However, there have also been different opinions. Theoretical studies by Klein (Klein, 2002, 2003, 2006) have concluded that an intramolecular hydrogen bond is not present in EG based on the hydrogen bonding criteria. Based on ab initio calculations using DFT methods Klein (Klein, 2002, 2003) suggested that 1,2-diols are not able to form an intramolecular hydrogen bond. The interaction observed in 1,2-diols is interpreted as a mixture of weak polarization and electrostatic effects. For all vicinal diols the most stable turns out to be the gauche configuration with the O-C-C-O dihedral close to ±60°. Diols in which the hydroxyl groups are spaced further apart, i.e., (n, n+2) or greater, are showing evidence of intramolecular hydrogen bonding with optimal ring structures achieved in (n, n+3) diols.

Only a few studies have investigated 1,3-propanediol molecule. Ab initio studies (Bultinck et al., 1995; Vazquez et al., 1988) based on the HF and MP2 calculations have shown that the lowest energy conformers have gauche heavy-atom torsions, and that they are stabilized by intramolecular hydrogen bonding. The existence of intramolecular hydrogen bonds was also confirmed by gas-phase electron diffraction (GED) (Kinneging et al., 1982; Traetteberg & Hedberg, 1994). The results have shown that the molecule of 1,3-propanediol exists exclusively in G+G- conformation with OH groups in 1,3 parallel positions nearly ideally placed to form an intramolecular hydrogen bond.

**Alcohol + Chlorobenzene**

The dependence of $V^E$ on both composition and temperature, for the systems of alcohol and chlorobenzene, can be explained qualitatively as a balance between opposite effects (Letcher & Nevines, 1994; Saleh et al., 2005; Šerbanović et al., 2006): (i) positive contributions are predominantly attributed to hydrogen bond rupture and stretching of self-associated molecules of alcohol (in the alcohol lower region), (ii) negative contributions are considered to be a consequence of dipolar complexes involving alcohols and chlorobenzene (due to unlike intermolecular dipolar interactions), (iii) changes of free volume in real mixtures comprising alcohol monomers and multimers and chlorobenzene molecules and the geometrical fitting between components making this effect negative to $V^E$. The magnitude and sign of $V^E$ are explained on the basis of some of above factors being predominant in certain mole fraction regions. The obtained results can be discussed in terms of the chain length of alcohols, degree of branching in the chain and relative position of the alkyl and OH group in the alcohol.

As can be seen from Figure 1a, the mixtures of chlorobenzene with 1-alcohols show sigmoidal curves v.s. mole fractions. The mixture of chlorobenzene with 1-alcohols as
alcohol molecules were added to the large amount of chlorobenzene, would induce depolymerization of 1-alcohols resulting in positive values of $V^E$. The positive $V^E$ values for these mixtures show that the effects due to the factor (i) are dominating over corresponding negative contributions.

Negative factors (ii) and (iii) are dominant over the larger parts of composition ranges of these mixtures. Namely, there is a formation of OH-Cl atom hydrogen bonded complexes between OH group of alcohols and a chlorine atom of chlorobenzene (Garabadu et al., 1997; Letcher & Nevines, 1994; Roy & Swain, 1988; Swain, 1984). The attraction between the unshielded proton of a hydrogen and an electronegative chlorine atom is relatively strong. In addition, the π-electronic cloud of the aromatic ring and OH group interactions take place influencing in relatively weak extent on contraction in volume (Lampreia et al., 2004). Structural effects also can lead to closer geometrical packing of unlike molecules although structure contribution is less characteristic with an increase in the chain length of 1-alcohols.

It is evident from plots of 1-alcohols with chlorobenzene that maxima of dissociation of the polymeric aggregates of alcohols differ slightly, since ordinary aliphatic alcohols are relatively poor proton donors. But, as mole fraction of higher 1-alcohol rises, the rupture of hydrogen bonds of alcohol increases from 1-propanol to 1-pentanol and positive volume changes appears at higher mole fraction of 1-pentanol.

The decrease in negative values of $V^E$ with increase in chain length of 1-alcohols, could suggest that dipole-dipole interactions are weaker in higher 1-alcohols as a consequence of the decrease of their polarizability with rising chain length. Bearing in mind that complexation (Garabadu et al., 1997) is predominantly due to polarization interaction, trend of complex formation has the following order ethanol > 1-propanol > 1-butanol > 1-pentanol causing the rise of $V^E$ from lower to higher 1-alcohols. Then relatively high electron donor capacity of chlorobenzene, as a consequence of introducing Cl atom into the benzene, interacts more strongly with ethanol than with other higher alcohols. Also, only smaller fraction of hydrogen bonds are ruptured in higher alcohols, while a steric hindrance of 1-pentanol is higher than that of ethanol, giving less negative values of $V^E$.

A possible explanation for an unexpected behaviour occurring with the system with methanol, bearing in mind the dominant assumption (iii), is that the molecules of chlorobenzene are accommodated interstitially in a network of bonded alcohol molecules leading to more dense packing of unlike molecules of methanol (van der Waals volume $V_{al}=21.71 \text{ cm}^3\text{mol}^{-1}$) (Daubert & Danner, 1989) and chlorobenzene ($V_{cb}=57.84\text{ cm}^3\text{mol}^{-1}$) (Daubert & Danner, 1989). There are more methanol molecules in close contact, than larger alcohols leading to relatively weak interactions and decreasing the number of cross-associated OH-Cl bonds, that is the amount of possible formed complexes. As result, the contribution in volume decreases, having less negative values with respect to that of the ethanol + chlorobenzene mixture (Figure 1a).

Explanation for mixtures of chlorobenzene with branched alcohols (2-butanol, 2-methyl-2-propanol) compared to 1-butanol could be more difficult. The trend in positive values of $V^E$ in the order: 1-butanol < 2-butanol < 2-methyl-2-propanol suggests that steric hindrance mainly due to branching, predominates over that of specific interaction of unlike molecules since complexes for three butanols (Roy & Swain, 1988) are of intensity in the order 1-
butanol > 2-butanol > 2-methyl-2-propanol. This degree of association could be in connection with a decrease in charge redistribution tendency within branched molecules. As a consequence, $V^E$ values become increasing positive as the branching in the alcohol molecules increase in the order: 2-methyl-2-propanol > 2-butanol > 1-butanol. Therefore, the strength of interaction (H···Cl bonding) between chlorobenzene and these alcohols should follow the order 1-butanol > 2-butanol > 2-methyl-2-propanol.

When OH group is introduced at 2° carbon atom, the branching of the alkyl group in 2-butanol will create more steric hindrance for the proper orientation of chlorobenzene molecules to fit in associated network of alcohol. As a result $V^E$ is more positive than for the system with 1-butanol.

The globular shape and relative position of OH group on the 2-methyl-2-propanol suggest that the effect of intermolecular interactive reduction and the structural effects of the close packing hindrance are predominant.

It is clear that the presence of one propyl group at 1° carbon atom in 1-butanol, one methyl and one ethyl group at 2° carbon atom in 2-butanol and three methyl groups at 3° carbon atom in 2-methyl-2-propanol create steric hindrance near OH group in the order 1-butanol < 2-butanol < 2-methyl-2-propanol. The increase of $V^E$ for these systems is in accordance with this phenomenon. Finally, it could be indicated that plane structure of the chlorobenzene effects a smaller breaking of association in 1-alcohols than the steric arrangement of branched alcohols changing $V^E$ towards higher values, as can be seen from Figure 1a.

**Alcohol + Amines (cyclohexylamine or hexylamine)**

The magnitude and the sign of $V^E$ for the systems of alcohols and cyclohexylamine or hexylamine (Figure 1b) can arise from two opposing factors (Djordjević et al., 2009) (i) the positive contribution is a consequence of the disruption of the hydrogen bonds in the self-associated alcohol and the dipole–dipole interactions between alcohol monomer and multimer. The self-association of the amine molecules is rather small; (ii) negative contributions arise from strong intermolecular interactions attributed to charge-transfer, dipole–dipole interactions and hydrogen bonding between unlike molecules. Hence, the negative $V^E$ values of the investigated systems assume that heteroassociates forming cross complexes in the alcohol + amine mixtures have stronger O–H···N bonds than O–H···O and N–H···N bonds. This can be explained qualitatively by the fact that the free electron pair around the N atoms with less $s$ and more $p$ character has a higher polarizability and acts as a good proton acceptor for the donor –OH groups of the alcohols, which are more efficient than the –OH group itself.

The negative sign of $V^E$ indicates a net packing effect contributed to the structural changes arising from interstitial accommodation. As can be seen from Figure 1b, the negative $V^E$ values, are larger in the mixture with 1-propanol and decrease as the chain length of the 1-alkanol increases. This trend indicates that the strength of the intermolecular hydrogen bonding of cyclohexylamine with 1-propanol is much stronger than that with the other higher 1-alcohols in the following order: 1-propanol > 1-butanol > 1-pentanol. These strengths of the interaction OH···NH$_2$ bonds suggest that the proton donating ability of 1-alcohols is of the same order. Namely, longer 1-alcohols would increase the basicity of the oxygen and make the hydroxyl proton less available for H bonding. In addition, it means
that the most efficient packing can be attributed to the lower alcohol, which decreases with increasing chain length of 1-alcohol, where the packing effects are the result of their lower self-association (higher breaking of their H bonds) and the fact that the crowded molecules of amine, as a consequence of steric hindrance, are better packed in the more open structure of the longer alcohols. Also, the effect of increasing chain length of the 1-alcohol for a given amine can be considered using the effective dipole moment. Bearing in mind the discussion given in previous works referring to 1-alcohols and various amines, it can be concluded that in the present systems the following behavior could be expected. In the systems of 1-alcohols with cyclohexylamine, the absolute value of the $V^E$ decreases with decreasing effective dipole moment of the alcohol. The trend in the negative values of $V^E$ for mixtures of cyclohexylamine with branched alcohols (2-butanol, 2-methyl-2-propanol) compared to 1-butanol is in the order: 1-butanol > 2-methyl-2-propanol > 2-butanol, suggesting that the interactions between tertiary alcohol and cyclohexylamine are stronger than between the secondary alcohol with cyclohexylamine, which in turn are stronger than the interactions between the primary alcohol and the amine (Dharmaraju et al., 1981). The results shown in Figure 1b indicate that $V^E$ of the mixture of cyclohexylamine with 2-methyl-2-propanol are more negative than those with 2-butanol.

Qualitatively, this could be explained by the fact that the oxygen atom of 2-methyl-2-propanol should be regarded as a better acceptor towards the NH proton of the amine than the oxygen atoms of the 2-butanol. Also, the system with 2-methyl-2-propanol suggests that the steric hindrance of the tert-butyl group tends to hamper the complex less than with 2-butanol. This is a consequence of a predominating electrometric effect (+I effect) over steric effect in 2-methyl-2-propanol (Dharmaraju et al., 1981; Pikkarainen, 1982).

**Alcohol + hydrocarbons (benzene, heptane, 2-butanol)**

For the mixtures of alcohols and benzene the experimental data presented in Figure 1c can be explained qualitatively on the basis of the following resulting, opposite effects, predominated in a certain mole fraction region (Letcher & Nevines, 1994; Rodriguez et al., 1999; Tanaka & Toyama, 1997): (i) positive values (in the alcohol lower region) are attributed to rupture or stretch of the hydrogen bonding of self-associated molecules of alcohol, (ii) negative values are thought to be due to unlike specific interactions and (iii) the geometric fitting of benzene into remaining alcohol structure making this effect negative to $V^E$.

The magnitude and sign of $V^E$ are a consequence of contributions taking place in the mixture. Thus, the positive values of $V^E$ for the mixtures with benzene point out that there are no strong specific interactions between the components of mixtures, but this situation is a result of breaking down of the alcohol structure as alcohol molecules were added to the large amount of benzene. The negative volume changes in mixtures rich in alcohol could be result of predominant interaction between the -OH group of an alcohol and π electrons of aromatic ring of benzene.

Non-associating molecule n-heptane acts as an inert component, in the mixture with 1-butanol as associating components. For the binary system of 1-butanol + n-heptane (Kijevčanin et al., 2009) $V^E$ values are positive in the entire composition range with asymmetric $V^E - x_1$ curves, shifted towards the lower 1-butanol mole fractions. Also, the $V^E$ values increase with temperature rising from 288.15 to 323.15 K. As it was discussed previously (Treszczanowicz et al., 1981), the positive excess volumes in mixtures of n-
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Alcohols and n-alkanes are the result of (i) the disruption of alcohol multimers due to breaking of hydrogen bonds (chemical contribution) and (ii) non-specific physical interactions between the real species in a mixture (physical contribution). Negative $V^E$ values are mostly caused by interstitial accommodation and changes of free volumes (structural contribution). Since the chemical contribution of hydrogen bond breaking to $V^E$ is negligible, except for small mole fractions, it is assumed that physical contribution comprises the major part of positive $V^E$ values (Treszczanowicz et al., 1981) in this system. The sharp increases of the $V^E$ in the dilute 1-butanol region suggest the dominance of the disruption of the H-bonds of alcohol multimers by unlike n-heptane molecules. The effect of volume contractions obtained in the mixture of ethanol and 2-butanol (Grgurić et al., 2004) can be attributed to the association between the keto group of ketone and proton of the hydroxy group of an alkanol predominating the effect of dissociation of the alcohol molecules.

**Alcohol + chloroform**

As can be seen from Figure 1d, the systems alcohol (1) + chloroform (2) exhibit S-shape of the $V^E-x_1$ curves (maximum with positive and minimum with negative values of $V^E$). The shape of the $V^E-x_1$ curves might be influenced by three types of the interactions occurring in the mixture: (i) H-bondings between hydrogen atom of chloroform and OH group of an alcohol, (ii) intermolecular interactions between OH group and electronegative chlorine atom of chloroform and (iii) steric hindrance between alkyl group and chlorine atoms. The magnitude and sign of $V^E$ are a consequence of some of above factors being predominant in certain mole fraction regions.

**Acetone + 1-propanol, 1,2-propanediol and 1,3-propanediol systems**

The negative values of excess partial molar volumes for both acetone + 1,2-propanediol and acetone + 1,3-propanediol systems suggest that the molar volumes of each component in the mixture are less than their respective molar volumes in the pure state that results in the contraction of volume over the entire composition range. Very small excess partial molar volumes obtained for the acetone + 1-propanol system support the trend observed in the $V^E$ values shown in Figure 1e.

The thermodynamic behavior of solutions influenced by polyhydroxy compounds shows a noticeable non-ideality owing to the formation of hydrogen bonds. One of the most sensitive thermodynamic indicators of complex structure is probably the excess molar volume $V^E$. Measurements of this property could be very useful to determine a structural effect appearing in 1,2- and 1,3-diols.

**Polyhydroxy compounds.** Alkanediols are important structural units of polyhydroxy compounds. Great varieties of different approaches were employed to investigate these structures. Binary organic mixtures which include polyhydroxy compounds such as 1,2- and 1,3-propanediol are an important class of solutions. Unfortunately, the behavior of some of their thermodynamic properties is still not clear, particularly for highly associated systems. Interpretation of complex structure is extremely difficult because of various possible effects occurring in the process of mixing. Also, it should be emphasized that lack of experimental values of volumetric and other thermodynamic data may lead to an over-simplified explanation of molecular structure of this type of systems.
Despite of most of the conformational studies of diols, accepting the importance of the intramolecular hydrogen bonding, it is very difficult to distinguish a particular conformer, namely those able to form an intramolecular H bond, bearing in mind that this bond plays main role in the conformational behavior of each molecule. Namely, spectral signatures of the conformers of a similar type are very comparable, and the number of possible conformers is large.

In a number of different theoretical and experimental studies, there is no definitive criterion which could be established for the characterizing the presence, nature and strength of intramolecular H bonds. As already mentioned, many factors have been employed as an evidence of existence of an intramolecular H bond such as frequency shifts observed in infrared (IR) and NMR studies, change in intensity ratio (low frequency/high frequency), abnormal OH bond lengths and interatomic distances or stabilization of gauche conformers. However, some of these parameters could be also quoted as the consequence of diverse nonbonding interactions.

More recently Fourier-transform near-infrared spectroscopic study (Haufa & Czarnecki, 2009) has confirmed conclusion of Klein (Klein, 2002, 2003) that 1,2-propanediol does not possess an intramolecular H bond.

Two hydroxyl groups substituted in 1,3 parallel ended positions of 1,3-propanediol are nearly ideally situated to form an intramolecular H bond. GED study of 1,3-propanediol (Kinneging et al., 1982) shows that the molecules exist in +gauche-gauche conformation (G+G-) with 1,3 parallel OH groups.
Acetone + 1-propanediol or + 1,3-propanediol. Values of $V^E$ for the mixtures of acetone with 1,2-propanediol and 1,3-propanediol are large and negative (Figure 1e). The curve for the mixture with 1,2-propanediol is skewed towards low 1,2-diol mole fraction with the minimum occurring near $x_1=0.7$, whereas a similar phenomenon was not observed for the curve with 1,3-diol where the minimum is near $x_1=0.5$. It is clear that $V^E$ of acetone in the mixture with 1-propanol differs considerably from those of mixtures with diols.

Mixing of acetone with 1,2-propanediol would induce dissociation of H bonded structure present in the pure 1,2-diol and formation of H bonds (C=O···H-O) between proton-acceptor O atom (with two lone pair of electrons) of acetone C=O group and H atom of OH group of 1,2-diol, leading to a contraction in volume as can be seen from Figure 1e.

Large displacement of minimum value of $V^E$ is probably a consequence of the following factors: (i) presence of alkyl group of kind -CH$_3$ at a side chain of molecule, (ii) at low concentration of 1,2-diol, the OH groups are predominantly non-bonded and free for interaction with C=O group of acetone and (iii) when one of the OH groups is not located at the end of molecule as in the case of 1,2-propanediol the interstitial contribution, due to a possible cavity occupation by methyl group, results in larger volume loss with the minimum around $x_1=0.7$.

The negative values of $V^E$ for the mixture of acetone with 1,3-propanediol (Figure 1e) indicate that interaction by hydrogen bonding between C=O group of acetone and OH groups of 1,3-propanediol that are present at extreme ends of molecule are more available to form hydrogen bonding. Namely, in the most stable structures of OH and C=O complex the intramolecular hydrogen bonding (G+G-) is broken into two almost linear intermolecular H bonds with the acetone molecule as proton acceptor. It is clear that the formation of such symmetrical structures under precipitation of both OH groups is excluded for the acetone + 1,2-propanediol complex from steric points of view because of the vicinal hydroxyl group.

The weak temperature effect on the $V^E$ values of all investigated systems of acetone with 1-propanol, 1,2-propanediol and 1,3-propanediol, is most likely due to the fact that the
increase in kinetic energy of molecules is not sufficient to change in an appreciable manner, the interaction of the H-bond type and other effects which occur in the mixtures.

4. Conclusion

Determination of excess volume, $V^E$, represents a very reliable method for better understanding and explanation of complex structures of numerous binary mixtures having decisive influence on many processes in chemical and related industries.

A survey of our articles, appearing in leading international journals, confirmed a great importance of thermodynamic method in explanation of molecular interactions present in mixtures of monohydroxy alcohols with various organic substances very frequently encountered in industrial practice.

Intention of the inclusion of complex alcohols (alkanediols) in the analysis, as well as the extension of applicability of the thermodynamic method to strongly nonideal binary systems, was to show that this method of the volumetric data determination, can contribute to the spectroscopic, computational and to the other theoretical methods in interpretation of the inter- and -intra molecular interactions, positions and shapes of conformers, as well as their mutual influence on system behavior.

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6. References


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In a classical approach materials science is mainly dealing with interatomic interactions within molecules, without paying much interest on weak intermolecular interactions. However, the variety of structures actually is the result of weak ordering because of noncovalent interactions. Indeed, for self-assembly to be possible in soft materials, it is evident that forces between molecules must be much weaker than covalent bonds between the atoms of a molecule. The weak intermolecular interactions responsible for molecular ordering in soft materials include hydrogen bonds, coordination bonds in ligands and complexes, ionic and dipolar interactions, van der Waals forces, and hydrophobic interactions. Recent evolutions in nanosciences and nanotechnologies provide strong arguments to support the opportunity and importance of the topics approached in this book, the fundamental and applicative aspects related to molecular interactions being of large interest in both research and innovative environments. We expect this book to have a strong impact at various education and research training levels, for young and experienced researchers from both academia and industry.

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