56. savetovanje
Srpskog hemijskog društva

KNJIGA
RADOVA

56th Meeting of
the Serbian Chemical Society

PROCEEDINGS

Srpsko hemijsko društvo

The International
Year of the
Periodic Table
2019
IYPT

СХД

'N 'C
101 Md
'O 'H

1897

Serbian Chemical Society

56. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA

KNJIGA RADOVA

56th MEETING OF THE SERBIAN CHEMICAL SOCIETY

Proceedings

Niš 7. i 8. juni 2019.
Niš, Serbia, June 7-8, 2019

56. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA
Niš, 7. i 8. juni 2019.
KNJIGA RADOVA

56th MEETING OF THE SERBIAN CHEMICAL SOCIETY
Niši Sad, Serbia, June 7-8, 2019
PROCEEDINGS

Naučni Odbor
Scientific Committee

Dušan Sladić, predsednik/chair
Vesna Mišković-Stanković
Niko Radulović
Gordana Stojanović
Snežana Tošić
Aleksandra Pavlović
Aleksandra Zarubica
Tatjana Anđelković
Miloš Đuran
Ljiljana Jovanović
Marija Sakač
Janoš Čanadi
Velimir Popsavin
Mirjana Popsavin
Katarina Anđelković
Dragica Trivić
Maja Gruden Pavlović
Tanja Ćirković Veličković
Maja Radetić

Organizacioni Odbor
Organising Committee
Niko Radulović, predsednik/chair
Aleksandar Dekanski
Danijela Kostić
Dragan Đorđević
Emilija Pecev Marinković
Marija Genčić
Ana Miltojević
Milan Stojković
Milan Nešić
Milica Nikolić
Marko Mladenović
Dragan Zlatković
Miljana Đorđević
Milena Živković
Sonja Filipović
Milica Stevanović
Jelena Aksi

*Ova knjiga sadrži **20 radova***
(obima od najmanje četiri stranice)
pojedinih saopštenja prezentovanih na
56. savetovanju Srpskog hemijskog društva.

*This book contains **20 Proceedings***
of some of the contributions presented at
the 56th Meeting of the Serbian Chemical Society.

Experimental measurements and theoretical simulations of alcohol and hydrocarbon binary systems

Milana M. Zarić, Petra Imhof*, Ivona R. Radović**, Mirjana Lj. Kijevčanin**

ICTM – Scientific Institution Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia

*Department of Physics, Freie Universität Berlin, Germany, present address: Department of Chemistry, Biochemistry and Environmental Engineering, University of Stavanger, Norway

**Department of Chemical Engineering/Faculty of Technology and Metallurgy, University of Belgrade, Serbia

Abstract

Experimental and theoretical methods were used to study two mixtures, 1-hexanol with n-hexane and cis-3-hexen-1-ol with n-hexane. The experimental technics were used to determine excess molar volume and viscosity deviations in the temperature range from 288.15K to 318.15K. The data of excess molar volume indicate similar behavior of the two alcohols, 1-hexanol and cis-3-hexen-1-ol in mixtures with n-hexane. The experimental data are in accordance with molecular dynamics simulation of these mixtures, showing similar number of hydrogen bonds in the two mixtures. The experimental data of viscosity deviations show difference of the two mixtures, where the deviation is significantly larger for cis-3-hexen-1-ol and n-hexane mixture, indicating stronger interactions within cis-3-hexen-1-ol and n-hexane binary mixture. These experimental data are in accordance with quantum chemical calculations on interactions energies. Namely, calculated interaction energies show that interaction between single and double bonds are stronger, than interactions between two single bonds.

Introduction

Insight in different types of mixtures' properties has a great importance in understanding and predicting the behavior of mixtures. The properties of liquid mixtures, such as volumetric and transport properties depend on the geometry and steric effects and intermolecular interactions between molecules. Many papers were published on describing and explaining how to analyze the experimentally measured properties. Intense research in last decades increased the amount of available data and the models describing the behavior are in constant improvement. Depending on the availability and usage of substances and their mixtures, and practical interest in certain mixtures, the models for describing the liquid mixtures can be more or less accurate[1-4].

Another aspect of investigating the properties of mixtures is a theoretical aspect, which can be used for analyzing the non-covalent interactions. The theoretical aspect can quantitatively and accurately model these interactions using the quantum mechanical methods. These methods can be used to find the interaction energies and the geometries of interactions in the investigated systems. For quantum mechanical calculations, a benchmark study for finding the best level of theory is an essential step[5]. The benchmark study assures that the level of theory gives reasonably accurate data. The very accurate CCSD(T)/CBS level is used as a reference, because it has been recognizes as a gold standard in the quantum mechanical world. The use of CCSD(T)/CBS level is very time

consuming and that is the reason to find other, less demanding level of theory that have at the same time a reasonable accuracy. So far, we have studied the interactions of double and single bonds and interactions between two double or two single bonds on a model system of 2-butene and butane molecules[6].

From the theoretical aspect, besides the quantum mechanical calculations and analyses, the molecular dynamic simulations have been used for analysis. The molecular dynamic (MD) simulations can be used for analyzing structural and dynamic properties, connecting the microscopic and macroscopic world, as well as making a connection between the experimental results and theoretical predictions[7]. The MD is based on the solving step-by-step the equation of motion, predicting the dynamics of the system. The system is represented by a simulation box represented like in Figure 1 using Visual Molecular Dynamic (VMD)[8]. The essential for an accurate MD is right set of force fields, which in this study was generated by Amber Force Field[9].
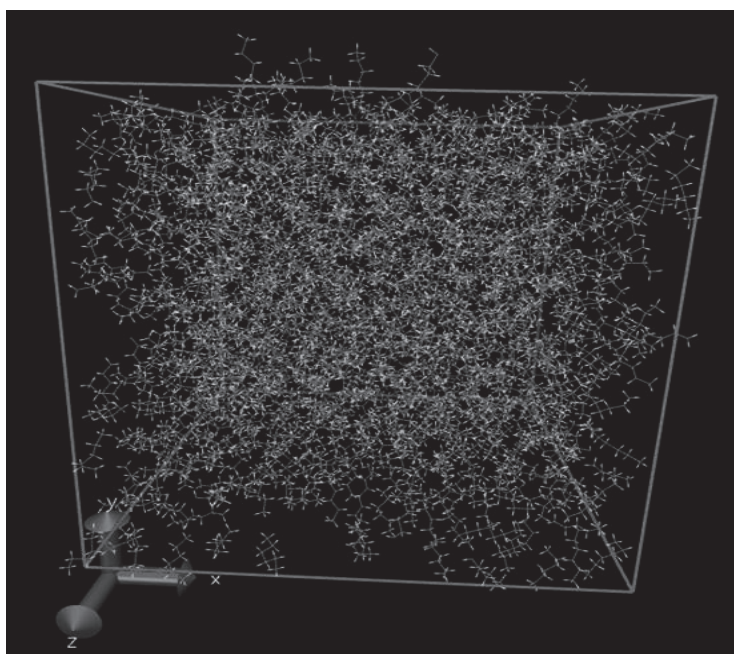

Figure 1. A visual representation of a "box" for the MD simulation in VMD

The results provide the insights of interactions at molecular level, offering an understanding of experimental measured properties of substances and mixtures with double bonds.

The aim of this work is to combine the two aspects of analyzing the liquid mixtures. First, the experimental measured properties and their deviations from ideal mixtures and second, use the computational modeling for analyzing the same effects of deviations at molecular level. The mixtures containing alcohols and hydrocarbons have been studied in this research. The combination of experimental measurement and computational modeling is the future in predicting chemical processes in systems and mixtures, providing better and more complete information on properties and chemical processes.

Experimental and methodology section

For experimental measurement, the mixtures of 1-hexanol or cis-3-hexen-1-ol with n-hex-ane have been studied. Substances *cis*-3-hexen-1-ol (>98 mas %) and 1-hexanol (98 mas %)

were provided by Sigma Aldrich and n-hexane (>99 mas %) was provided by Merck. All compounds were dried over Sigma (type 0.3nm) molecular sieves and degassed by ultrasonic before each experimental measurement. The measured properties of pure substances for 1-hexanol and n-hexane shown good agreement with literature data on temperate of 288.15K.

The densities of pure substances and their mixtures were measured with an Anton Paar DSA 5000 M density and sound velocity meter with a stated accuracy ±5×10^{-3} kgm^{-3} for density. The viscosity of pure substances and their mixtures were measured on an Anton Paar Stabinger SVM 3000/G2 viscometer with accuracy of ± 0.1 %.

Theoretical quantum mechanical calculations were preformed on Gaussian 09 (version D.01)[10]. The benchmark study was performed using various DFT and MP2 methods with basis sets of various sizes[5]. The interaction energy at the CCSD(T)/CBS level, which was used as reference level, was calculated using the extrapolation scheme proposed by Mackie and Dilabio[11]. The single point energies were calculated creating a potential curve and for each of the investigated system and at minima of each potential curve the optimized geometries and energy of interaction are analyzed.

From the input molecular coordinates of the molecules obtained by quantum chemical calculations, the topology and parameters for amber force field were generated by ANTECHAMBER and the xleap ABMER tools[12]. The set up of system was structured as mixtures of 1000 molecules in a cubic simulation box of 6x6x6 nm side length (Figure 1) with different sets of concentrations and at different temperature. The force field was used with a cutoff of 1.2 nm for van der Waals and for the short ranged electrostatic interactions, together with Particle-Mesh-Ewald treatment (on a 0.16 grid). After 500 steps of steepest descent minimization, short equilibration runs of 100 ps length were performed at the target temperature, employing the V-rescale thermostat. Subsequently, production runs of 1 ns length were performed, in an NPT ensemble at the respective target temperature and target pressure. For temperature control the V-rescale thermostat was employed, pressure control was achieved with the Parrinello-Rahman barostat. All bonds hydrogen atoms were constrained by LINCS. Trajectories were saved every 2fs. Molecular dynamic simulations were performed in GROMACS[13-15]. Visualization and analysis of the MD trajectories was done with Visual Molecular Dynamic (VMD)[8].

Results and discussion

In this paper, the results of measured density and viscosity data are shown in combination of the quantum mechanical calculation and dynamic modeling simulations. The experimental measurements were done for the binary mixtures of 1-hexanol + n-hexane and cis-3-hexen-1-ol + n-hexane in the whole range of concentration at seven temperatures from 288.15K to 318.15K with a step of 5K at atmospheric pressure.

The excess molar volume was calculated by the next equation

$$V^E = \sum_{i=1}^{N} x_i M_i \left[\left(1/\rho \right) - \left(1/\rho_i \right) \right]$$ (1)

where N is the number of components, x_i is the mole fraction and M_i is the molecular mass of component i, while ρ and ρ_i are the measured densities of a mixture and the pure component i, respectively.

The viscosity deviations, $\Delta\eta$, were calculated from the equation:

$$\Delta\eta = \eta - \sum_{i=1}^{N} x_i\eta_i \tag{2}$$

where η and η_i are the measured viscosities of a mixture and the pure component i, respectively.

Redlich-Kister (RK) polynomial equation[16] was used for correlating the calculated experimental values of excess molar volume V^E and viscosity deviations $\Delta\eta$.

$$Y^E(\Delta Y) = x_i x_j \sum_{p=0}^{k} A_p \left(2x_i - 1\right)^p \tag{3}$$

where $Y^E(\Delta Y)$ represents V^E or $\Delta\eta$, and A_p represents the adjustable parameters of the property, and the degree of adjustable parameters ($k + 1$) determined applying the F-test.

a   b

Figure 2. Experimental data of (a) excess molar (V^E) and (b) viscosity deviations ($\Delta\eta$) for the two binary mixtures: 1-hexanol (1) + n-hexane (2) and cis-3-hexen-1-ol (1) + n-hexane (2) at 288.15 K (■, ●) and 323.15 K (■, ●) and at atmospheric pressure. Symbols refer to experimental data points while lines represent the values calculated by RK equation (Eq. 3.).

In Figure 2 excess molar volume (V^E) and viscosity deviations ($\Delta\eta$) are shown at two temperatures, 288.15K and 318.15K. The results of excess molar volumes show a „S"-shaped curve, characteristic for mixtures of alcohols and hydrocarbons. The values are negative for the molar content of an alcohol larger than 0.2. This behavior is expected in mixtures richer in an alcohol due to the alcohol self-association interaction. Namely, alkanol molecules are polar and can form homo-associates trough hydrogen bonding between –OH groups[17].

Figure 3 represents three sets of simulations: pure 1-hexanol and pure cis-3-hexen-1-ol, mixtures alcohol + n-hexane containing 60 % of an alcohol, and mixtures containing 20 % of an alcohol, at the temperature 318.15K.

As data represented in Figure 3 show, simulation of pure 1-hexanol has an average of about 480 hydrogen bonds, while for the mixture 60 % (1-hexanol) + 40 % (n-hexane) there are 284 and for mixture 20 % (1-hexanol) + 80 % (n-hexane) there are about 90 hydrogen bonds. For pure cis-3-hexen-1-ol there are 395, and for 60 % (cis-3-hexen-1-ol) +40 % (n-hexane) and 20 % (cis-3-hexen-1-ol) + 80 % (n-hexane) there are in average 228

and 65 number of hydrogen bonds, respectively. This is in agreement with experimental data that show small differences in values of two mixtures, as represented in Figure 1(a).

a   b

Figure 3. Number of hydrogen bonds analyzed by VMD after the MD simulations for mixtures (a)1 –hexanol + n-hexane and (b) cis-3-hexen-1-o l+ n-hexane at 318.15 K

As for the values of deviation of viscosity (Figure 2b), the values are negative in the whole range of composition. The differences between the two mixtures are much larger. This provides information that the energy of interactions in mixture of cis-3-hexen-1-ol and n-hexane are larger than in the mixture of 1-hexanol and n-hexane. This indicates different energy interactions between the double bonds in cis-3-hexen-1-ol and the single bonds in 1-hexanol within the mixtures with n-hexane. This observation about the interactions have been confirmed by analyzing the difference in interactions of double and single bonds on molecular level. In our previous paper, we confirmed that the highest energy interactions are in mixture of double/single bond[5]. Interaction energies of systems with double and single bonds using model system: 2-butene/2butene (for double bond/double bond system), 2-butene/butane (for double bond/single bond system), and butane/butane (for single bond/single bond)[5] has been calculated. The results of quantum mechanical calculations, obtained at very accurate CCSD(T)/CBS level are presented in Table 1, showing that interaction energies are the strongest in systems with interaction of double and single bonds, than in systems with two single bonds, and the weakest in systems with two double bonds.

Tabel 1. Energy interaction (ΔE) of model systems for double and single bonds interaction

Model systems	ΔE (CCSD(T)/CBS), kcal/mol
Double bond/double bond	(-1.95) ÷ (-2.53)
Double bond/single bond	(-2.50) ÷ (-2.82)
Single bond/single bond	(-2.44) ÷ (-2.58)

Conclusions

In this work we applied methodology that combines two theoretical methods, quantum chemical and molecular dynamics with experimental measurements on properties of two liquid mixtures, 1-hexanol with n-hexane and cis-3-hexen-1-ol with n-hexane. The

experimental data on excess molar volume of the two mixtures show high similarity, while viscosity deviations of the two mixtures show significant difference of the two mixtures. The similar behavior considering excess molar volume indicates similar number of hydrogen bonds between molecules of alcohols in the mixtures. It is in accordance with MD simulation of these mixtures, showing similar number of hydrogen bonds in the two mixtures. Difference of the two mixtures considering viscosity deviations, indicates difference in the interaction energies between 1-hexanol and n-hexane and cis-3-hexen-1-ol and n-hexane. It is in accordance with calculated interaction energies showing that interactions between single and double bods are stronger, than interactions between two single bonds. The results presented in this work show that our methodology combining two theoretical methods, quantum chemical and molecular dynamics with experimental measurements gives opportunity to obtain, understand and predict data on liquid mixtures.

References

1. B. D. Djordjević, I. R. Radović, M. Lj. Kijevčanin, A. Ž. Tasić, S. P. Šerbanović, *J. Serb. Chem. Soc*. **74** (2009) 477-491.
2. B. D. Djordjević, M. Lj. Kijevčanin, I. R. Radović, S. P. Šerbanović, A. Ž. Tasić, *J. Serb. Chem. Soc.* **78** (2013) 2201-2214.
3. M. A. Aissa, I. R. Radović, M.Lj. Kijevčanin, *Fluid Phase Equilib.* **473** (2018) 1-16
4. D. M. Majstorović, E. M. Zivković, M. Lj. Kijevčanin, *J. Chem. Eng Data* **62** (2017) 275-291.
5. M. M. Zarić, B. Bugarski, M. Lj. Kijevčanin, *Comput. Theor. Chem.* **1117** (2017) 150-161.
6. M. M. Zarić, B. Bugarski, M. Lj. Kijevčanin, *ChemPhysChem*, **17** (2016) 317-324.
7. M. P. Allen, *Introduction to Molecular Dynamics Simulation*, *Computational Soft Matter: From Synthetic Polymers to Proteins*, Lecture Notes, Norbert Attig, Kurt Binder, Helmut Grubmüller , Kurt Kremer (Eds.), John von Neumann Institute for Computing, Jülich, Germany, NIC Series, **23** (2004) 1-28.
8. W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graph.* **14** (1996) 33–38.
9. J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, *J Comput Chem*. **25** (2004) 1157-1174.
10. 10. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A: Petersson, H. Nakatsuji, M. Caricat, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J.Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09 (Revision D.01), Gaussian, Inc. (2013) Wallingford, CT
11. I. D. Mackie, G. A. DiLabio, J*. Chem. Phys.* **135** (2011) 134318.
12. D. van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, *et al. J Comput Chem* **26** (2005) 1701–1718.
13. J. Wang, W. Wang, P. A. Kollman, D. A. Case, *J Mol Graphics Model*. **25** (2006) 247-60.
14. G. Bussi, D. Donadio, M. Parrinello, *J Chem Phys* **126** (2007) 014101.

15.   B. Hess, *J. Chem. Theory Comput*. **4** (2008) 116-122.
16.   H. J. C. Berendsen, D. van der Spoel, R. van Drunen, *Comp. Phys. Comm.* **91** (1995) 43 -56.
17.   O. Redlich, A. T. Kister, *Ind. Eng. Chem*. **40** (1948) 345.
18.   Y. Marcus, *Introduction to Liquid State Chemistry*, Wiley-Interscience, NewYork, 1977.

Eksperimentalna merenja i teorijske simulacije binarnih sistema alkohola i ugljovodonika

Eksperimentalne i teorijske metode korišćene su za proučavanje dve smeše, 1-heksanola sa n-heksanom i cis-3-heksen-1-ola sa n-heksanom. Eksperimentalne tehnike su korišćene za određivanje dopunskih zapremina i promene viskoznosti za temperaturni opseg od 288.15K do 318.15K. Podaci o dopunskoj molarnoj zapremini ukazuje na slično ponašanje dva alkohola, 1-heksanola i cis-3-heksen-1-ola u smešama sa n-heksanom. Eksperimentalni podaci su u skladu sa simulacijom molekularne dinamike ovih smeša, pokazujući sličan broj vodoničnih veza u dve smeše. Eksperimentalni podaci o promeni viskoznosti pokazuju značajnu razliku između dve smeše, odstupanje je značajno veće za smešu cis-3-heksen-1-ol i n-heksan, što ukazuje na jaču interakciju u binarnoj smeši cis-3-heksen-1-ola i nheksana. Ovi eksperimentalni podaci su u skladu sa kvantno-hemijskim proračunima energija interakcija na molekulskom nivou. Naime, izračunate energije interakcije pokazuju da je interakcija između jednostrukih i dvostrukih veza jača, nego interakcija između dve jednostruke veze.