BU-ALI SINA UNIVERSITY
FACULTY OF CHEMISTRY

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TITLE:

The Study of Physico-Chemical Properties of Binary and Ternary Non-electrolyte Liquid Mixtures

(excess molar volumes, viscosity deviations, refractive index deviations and isentropic compressibility deviations)

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In The Name of Allah

The Study of Physico-Chemical Properties of Binary and Ternary Non-electrolyte Liquid Mixtures

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (Ph.D) in Physical Chemistry

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Dedicated to

My dear parents

and

My dear wife

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Publications:

[1] Densities, Viscosities, Speeds of Sound, and Refractive Indices for Binary Mixtures of Diethylcarbonate, Acetophenone, and 1-Hexanol at (293.15, 303.15, 313.15, and 323.15) K for the Liquid Region and at Ambient Pressure, **Iloukhani, H.** and **Rostami, Z.**, *J. Chem. Eng. Data*, **2007**, Vol. 52, pp. 921–928.

[2] Densities and derived thermodynamic properties of binary mixtures of diethylcarbonate, acetophenone, and 1-hexanol at T = (293.15 to 323.15) K for the liquid region and at ambient pressure, **Iloukhani, H.** and **Rostami, Z.**, *J. Chem. Thermodyn.*, **2007**, Vol. 39, pp. 1231–1240.

[3] Densities, speeds of sound and refractive indices for binary and ternary mixtures of {diethylcarbonate (1) + *p*-chloroacetophenone (2) + 1-hexanol (3)} at 303 K for the liquid region and at ambient pressure, **Iloukhani, H., Rostami, Z.,** and **Afshari, N.**, *Phys. Chem. Liq.*, **2008**, (In press).

[4] Densities, viscosities, and derived thermodynamic properties of binary mixtures of diethylcarbonate with acetophenone, *p*-chloroacetophenone, 3-bromoacetophenone and propiophenone at (293.15, 303.15, 313.15, and 323.15) K for the liquid region and at ambient pressure, **Iloukhani, H., Rostami, Z.,** and **Basiri-Parsa**, J. , *J. Chem. Thermodyn.*, **2007**, (Accepted with revisions).

[5] Densities, excess molar volumes, and viscosities of the binary and ternary mixtures diethylcarbonate (1) + *p*-chloroacetophenone (2) + 1-hexanol (3) at 303 K for the liquid region and at ambient pressure, **Iloukhani, H.** and **Rostami, Z.**, *J. Mol. Liq.* **2007**, (submitted).

[6] Densities, speeds of sound and refractive indices of binary mixtures of diethylcarbonate with acetophenone, *p*-chloroacetophenone, 3-bromoacetophenone and propiophenone at (293.15, 303.15, 313.15, and 323.15) K for the liquid region and at ambient pressure, **Iloukhani, H.** and **Rostami, Z.**, *J. Can. Chem*, **2007**, (submitted).

[7] Russian International Conference on Chemical Thermodynamics, **Iloukhani, H.** and **Rostami, Z., 2005**, Moscow, Russia.

[8] International Conference Thermodynamics, **Iloukhani, H., Rostami, Z.,** and **Afshari, N., 2007**, Paris, France

[9] Thermodynamics of Solutions Conference, **Iloukhani, H.** and **Rostami, Z., 2007**, Bangkok, Thailand

Abstract

Three binary and two ternary non-electrolyte liquid mixtures were studied and their thermodynamic properties (excess molar volumes V_m^E, excess partial molar volumes $\overline{V}_{m,i}^E$, apparent molar volumes $V_{\phi,i}$, excess thermal expansion coefficient α^E and isothermal coefficient of pressure excess molar enthalpies $\left(\partial H_m^E/\partial P\right)_{T,x}$), acoustic properties (isentropic compressibility κ_s, isentropic compressibility deviations $\Delta\kappa_s$ and excess intermolecular free length L_f^E), transport properties (viscosity deviations $\Delta\eta$, excess Gibbs energies of activation of viscous flow ΔG^{*E}) and magnetic property (refractive index deviations Δn_D) were also calculated. The extended real of associated solutions (ERAS) model was applied for consistency of excess molar volume and enthalpy with literature values. A few models were applied to estimate the speeds of sound such as Collision Factor theory and Free Length theory and some semi-empirical equations were tested to correlate the viscosity. The following mixtures are considered in this project:

(1) Binary mixtures of (diethylcarbonate + acetophenone, + propiophenone, + *p*-chloroacetophenone and + 3-bromoacetophenone), (diethylcarbonate + 1-hexanol) and (1-hexanol + *p*-chloroacetophenone).

We have measured densities ρ, viscosities η, speeds of sound u and refractive indices n_D for the pure and binary for all mixtures at (293.15 to 323.15) K and for the binary mixture of (1-hexanol + *p*-chloroacetophenone) at 303.15 K. Excess molar volumes, excess thermal expansion coefficients, isothermal coefficient of pressure excess molar enthalpies, viscosity deviations, excess Gibbs energies of activation of viscous flow, speed of sound deviations, isentropic compressibilities, isentropic compressibility deviations and excess intermolecular free lengths were calculated. The experimental data of the constitute binaries are analyzed to discuss the nature and strength of intermolecular interactions in this mixtures. Excess and deviation properties were correlated by Redlich–Kister equation in terms of mole fraction of composition.

(2) Ternary mixtures of (diethylcarbonate + acetophenone + 1-hexanol) and (diethylcarbonate + *p*-chloroacetophenone + 1-hexanol)

We have measured densities, viscosities, speeds of sound and refractive indices for the pure and first ternary mixture at (293.15 to 323.15) K and for the second one at 303.15 K. Excess molar volumes, excess thermal expansion coefficients , isothermal coefficient of pressure excess molar enthalpies, viscosity deviations, excess Gibbs energies of activation of

viscous flow, speeds of sound deviation, isentropic compressibilities and isentropic compressibility deviations were calculated. Excess and deviation properties were correlated by Redlich–Kister, Cibulka and Nagata equations in the form of ternary mixtures.

For the first ternary mixture the best correlation method for viscosities was the equation of Iulan *et al.* as compared to the others at the temperatures of 303.15 K and 323.15 K and for speeds of sound of this ternary mixture the theory of Van Deal's ideal mixing relation (IMR) gives the best results, where as for the second ternary mixture our analyses show that the best correlation methods for viscosities are found Katti–Chaudhri, Nissan–Grunberg and Frenkel and for speeds of sound of this ternary mixture the theory of Nomoto's relation (NR) gives the best results.

(3) Application of extended real of associated solutions (ERAS) model

The ERAS model allows a reasonably good description of excess molar volume and excess molar enthalpy of the binary mixtures. As to be expected the model predicts the binary excess properties close to the experimental values. The results of the ERAS model calculations for the binary mixture of *N*-methyl-2-pyrrolidinone (NMP) + 2-propanol, + 1-butanol and + 2-butanol at 298.15 K in which both a self-association and cross-association of alcohol molecules occurs, have been reported and discussed in details in chapter 6.

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