



Study of volumetric and electromagnetic properties of binary and ternary mixtures of {2-Propanol (1) + 1, 3-Diaminopropane (2) + 2, 5- Dimethoxytetrahydrofuran (3)} at (298.15- 328.15) K at 81.5 kPa-Prediction with geometrical models

Farnoosh. Panahi, Mahdi. Jafarnejad*, Khaterreh. Khanlarzadeh, Hossein. Iloukhani

Department of Physical chemistry, Faculty of Chemistry, Bu-Ali Sina University, P.O. Box 65178-38695, Hamedan, Iran.

*Corresponding Author: Tel: +988138381601, Fax: +988138380663.

E-mail address: me.jafarnejad@gmail.com

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Abstract

The densities, ρ and refractive index, n_D of mixtures consisting of 2-Propanol, 1, 3-Diaminopropane, and 2, 5-Dimethoxytetrahydrofuran have been measured at different temperatures. V_m^E , $\bar{V}^E_{m,i}$, Δn_D , α^E and $(\partial H_m^E / \partial P)_{T,x}$ for binary and V_m^E and Δn_D for ternary mixtures were derived. V_m^E and Δn_D for binary mixtures were correlated with the Redlich-Kister equation and for ternary mixtures were correlated with several equations. Prediction geometrical solution models were used to predict $\bar{V}^E_{m,i}$, Δn_D of ternary mixtures and standard deviation for their fitting was reported. Positive deviation from ideal state were recorded for $\bar{V}^E_{m,i}$ in mixture of 1, 3-Diaminopropane + 2, 5-Dimethoxytetrahydrofuran and 2-Propanol + 2, 5-Dimethoxytetrahydrofuran mixtures. However, in mixture of 2-Propanol and 1, 3-Diaminopropane negative deviation in the high composition of 1, 3-Diaminopropane varies to positive in the dominated mole fraction of alcohol which was analyzed to interpret the molecular interactions.

Keywords: Ternary mixtures, Volumetric properties, Refractive index, Molecular interactions, Prediction models

Introduction

The main branch in the study of solutions is the investigating of the thermodynamic properties of the mixtures. Thermodynamics and thermodynamic properties have been of interest for researchers for many years in the various fields of science, technology and industry in particular, and have been widely studied. The properties of the solutions that are studied in this work are the most complex thermodynamic quantities due to various factors such as structural effects, interactions between similar and non-similar components, and are very useful in explaining and justifying interactions and renovating due to the mixing process. Due to the fact that most of the biological and industrial processes are in the liquid phase, the solubility phenomenon is very important and the solvent effect is very important on soluble properties. Among the issues that researchers and chemists investigate in this regard, is the importance of solubility of materials and changes in the thermo physical properties of compounds as a result of solubility in the processes of separation and purification. Interpretation and justification of the nature of molecular interactions are widely used in these processes, and the knowledge of these interactions is possible by measuring and computing the Physico-chemical characteristics and thermodynamic properties of these systems. These interactions are influenced by short-range repulsive forces and long-range molecular attraction with the effects of polarity and etc., that the correct understanding of the nature and intensity of these forces helps us to understand and interpret the interactions.

Thermodynamic properties of mixtures of amines, methoxy and hydroxyl groups are seemed to be interesting and would give great outcomes of molecular interactions in solutions. Meanwhile the studies of volumetric and electromagnetic properties of liquid mixtures provide valuable information on the structure and molecular interactions in solutions. In this sense, structural changes as a result of the molecular interaction can be provided by investigating the deviation of the refractive index deviations and volumetric properties from the ideal state due to compositions and temperatures. The deviations in the properties of solutions from the ideal state result from the breaking of the bonds of primary pure components and the formation of new bonds between non-similar molecules.

In fact, these deviations are affected by three factors: a physical, chemical, and molecular structure that includes breaking the dipole-dipole, ionic, and hydrogen bonds and causes positive deviation or forming solvent-soluble bonds, which can be even hydrogen and dipolar type with proper orientation in some of the molecules that lead to negative deviations. In addition to these factors, the steric effect result of some large groups, as well as diversity in size and shape of components in mixtures are effected deviations substantially [1, 2].

The aim of our research group is developing the thermodynamic data for analysis and identification of molecular interactions in non-electrolyte solutions at different temperatures [3-5]. In this regard, present paper reports the density, ρ , and excess molar volume, V_m^E , refractive index deviations Δn_D of 2-Propanol(1) + 1, 3-

Diaminopropane (2) + 2, 5-Dimethoxytetrahydrofuran (3) and its corresponding binary systems at different temperatures (298.15, 308.15, 318.15, and 308.15) K and at ambient pressure. Also, Partial excess molar volumes \overline{V}_m^E , excess thermal expansion coefficient α^E and isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ for binary mixtures were reported. Data for the binary systems was fitted to Redlich–Kister equation [6, 7] and for ternary mixtures were correlated with Cibulka [8], Singe [9], Jasinski and Malanowski [10], Calvo [10], Nagata [11] equations and parameters have also been calculated.

2. Experimental

2.1. Materials

The 2-Propanol (CAS No. 67-63-0), 1, 3-Diaminopropane (CAS No. 109-76-2), and 2, 5-Dimethoxytetrahydrofuran (CAS No. 696-59-3) were purchased from Merck, and used without any further purification. Information about the liquids employed in this work are given in Table 1. The experimental densities and refractive indices of pure materials with corresponding literature value are presented in Table 2. The pure components were stored in the dark glasses at constant humidity and temperature.

2.2. Apparatus and procedure

Mixtures were prepared based on sample weight, using electronic balance (Sartorius AG. GK 1203, Germany) with precision of ± 0.0001 g. Density of pure components and mixtures were measured using digital vibrating-tube densimeter

(Anton Paar DMA 4500), with an accuracy of ± 0.01 K in temperature. The measurement of refractive indices of pure components and mixtures were obtained by digital automatic refractometer (Anton Paar Abbemat 500) with the accuracy of ± 0.01 K in temperature. The details regarding density and refractive index measurement using Anton Paar DMA4500 and Anton Paar Abbemat 500 are described in our previous literature [3]. The estimated uncertainty for density and refractive index measurement, and mole fraction, are $\pm 1 \times 10^{-5}$ g · cm⁻³, $\pm 5 \times 10^{-5}$, and $\pm 4 \times 10^{-4}$.

Each system was immediately used after it was well-mixed by shaking. After measuring density and refractive index of mixtures over the temperature range $T = (298.15$ to $328.15)$ K with intervals of 10 K in ambient pressure, excess molar volume for all mixtures was calculated using density data by following equation:

$$(1) \quad V_m^E = \left(\frac{\sum_{i=0}^n x_i M_i}{\rho} \right) - \left(\sum_{i=0}^n \frac{x_i M_i}{\rho_i} \right)$$

where ρ , is the density of system, ρ_i and M_i are the density and molar mass of the pure component and x_i is the mole fraction and n is the number of components in mixture. The refractive index deviations Δn_D , for mixtures can be calculated as:

$$(2) \quad \Delta n_D = n_D - \sum_{i=1}^n x_i n_{Di}$$

Where n_D is the refractive index of the mixture and n_{Di} is the refractive index of pure components, i and n is the number of components in mixture.

3. Results and discussion

3.1 Binary mixtures

The excess molar volume for binary mixtures was calculated from density results according to equation (1) with uncertainty of $\pm 8 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$. Excess molar volumes for binary systems are appeared in Table 3 and are graphically represented in Figure 1. The experimental data of the binary systems were correlated with the following type of Redlich–Kister polynomial:

$$(3) Y_m = x(1-x) \sum_{i=0}^k \sum_{j=0}^2 B_{ij} T^j (1-2x)^i$$

where $Y_m = (V_m^E \text{ or } \Delta n_D)$; B_{ij} is adjustable temperature dependent parameters obtained by fitting algorithm.

The parameters B_{ij} for all the binary systems are listed in Table 4, along with standard deviation, σ , were obtained by this equation:

$$(4) \sigma(Y_m) = \left[\sum_{i=1}^n (Y_{m,exp,i} - Y_{m,calc,i})^2 / (n-p) \right]^{1/2}$$

where n is the number of experimental data and p is the degree of the polynomials.

As can be seen in Figures 1, V_m^E values for binary systems of 1, 3-Diaminopropane (1) + 2, 5-Dimethoxytetrahydrofuran (2), and 2-Propanol (1) + 2, 5-Dimethoxytetrahydrofuran (2) are positive over the whole composition range which indicates the expansion of mixing. As quantified by the Hammett equation, methoxy is an electron-donating group [12]. On the other hand, like ammonia,

amines are bases [13]. In fact, deviations are influenced by three physical, chemical and structural factors that include breaking or weakening bipolar-bipolar, ionic bonds, hydrogen bands, and London dispersion force, which divert the solution to positive deviations. In addition, the steric effect also has a noticeable effect on this positive deviation. These effects lead to expansion in volume of mixtures and therefore positive deviations are obtained as can be seen in Figure 1 (b) – 1(c), which clearly indicate that there is a kind of repulsive interactions in these binary mixtures. But for binary system of 2-Propanol (1) + 1, 3-Diaminopropane (2), deviation of V_m^E values in the high concentrations of 1, 3-Diaminopropane are negative which indicates attractive interactions and increasing the concentration of 2-Propanol leads to found repulsion forces which appears in Figure 1(a). In addition, interactions those cause formation of the structures result negative amounts of excess molar volume and interactions that cause structural destruction, leading to the positive amount of excess molar volume; the contribution of accumulation in the molar volume is negative.

Nevertheless, the positive deviation of V_m^E from the ideal state for the examined systems in this project shows that short-range repulsive forces are in the ruling system, which expresses the fact that due to mixing, soluble-solvent molecule interactions would weakened and relatively strong interactions between similar molecules are formed.

Correlations are complicated owing to the effects of solvation which are opposite the trends for inductive effects. According to the calculated refractive index deviation

values, the optical behavior of these systems is similar to volumetric behavior as the values specified in Table 3 and graphically presented in Figure 2. Studding effect of temperature released that as temperature of 2-Propanol + 2, 5-Dimethoxytetrahydrofuran mixture rises, V_m^E deviations are increase but it is contrary in 1, 3-Diaminopropane + 2, 5-Dimethoxytetrahydrofuran mixture. With increasing temperature, V_m^E deviations dedicate a negative value and with further increase in temperature, a value of V_m^E is much less.

The partial molar volume, \bar{V}_i , for binary systems were calculated over the whole concentration rang by using equation (5) and the excess partial molar volume values calculated by equation (6) are reported in Table 3.

$$(5) \bar{V}_i = V_m^E + V_i^o + (1 - x_i) \left(\frac{\partial V_m^E}{\partial x_i} \right)_{p,T}$$

$$(6) \bar{V}_i = \bar{V}_i^E + V_i^*,$$

The thermal expansion coefficient α , for pure components was calculated by analytical differentiation of density fitting equation:

$$(7) \alpha = -\rho^{-1} \left(\frac{\partial \rho}{\partial T} \right)_P$$

The excess thermal expansion coefficient α^E , was obtained by the following expression:

$$(8) \alpha^E = \alpha - \sum_{i=1}^2 x_i \alpha_i,$$

The isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ can be derived accurately from volumetric measurements by application of the following equation:

$$(9) \left(\frac{\partial H_m^E}{\partial P} \right)_{T,x} = V_m^E - T \left(\frac{\partial V_m^E}{\partial T} \right)_{P,x}$$

The computed values of α^E and $(\partial H_m^E / \partial P)_{T,x}$ for binary mixtures are listed in Tables 3 and at $T = 298.15$ K is graphically represented in Figure 3, 4.

The negative values of the excess thermal expansion coefficient α^E for the examined systems, that become more negative with increasing temperature, indicate that the mixture is more stable than the pure components, which is consistent with the data of the excess molar volume. The observed trend of isothermal coefficient of pressure excess molar enthalpy $(\partial H_m^E / \partial P)_{T,x}$ is the opposite of the observed trend for the excess thermal expansion coefficient α^E values. Positive values of $(\partial H_m^E / \partial P)_{T,x}$ indicate that by increasing the pressure, the molecular gravity of the system increases in the system under study. This trend is in accordance with equation (9), why so the sign of equation $(\partial H_m^E / \partial P)_{T,x}$ for a mixture, whose volume at constant temperature and constant composition decreases with increasing pressure, should be positive. In other words, the positive values of this quantity indicate that the increase in pressure increases the excess molar enthalpy and the relative instability of the binary system.

3.2 Ternary mixtures

Empirical studies of thermodynamic systems require a lot of time and cost, and with increasing number of components in the study system, these techniques are more difficult and require more time and cost. Therefore, the extraction of the

thermodynamic properties of multi-component systems seems to be very beneficial using the thermodynamic data of binary systems.

In this work, the excess molar volumes of ternary mixture of 2-Propanol (1) + 1, 3-Diaminopropane (2) + 2, 5-Dimethoxytetrahydrofuran(3) were calculated using equation (1) and refractive index deviations were calculated using equation (2) and the results were listed in Table 5 and graphically represented in Figure5. Ternary data were fitted to the Cibulka [8], Singh [9], Jasinski and Malanowski [10], Calvo [10], and Nagata [11] equations. These expressions include three terms corresponding to binary contributions evaluated by the Redlich-Kister [6, 7] equation adjusted to the binary data. The expression suggested by:

Cibulka equation:

$$(10) \quad Y_{123}^E = Y_{m,binary}^E + x_1 x_2 x_3 (B_0 + B_1 x_1 + B_2 x_2)$$

Singh et al. equation:

$$(11) \quad Y_{123}^E = Y_{m,binary}^E + x_1 x_2 x_3 (B_0 + B_1 x_1 (x_2 - x_3) + B_2 x_1^2 (x_2 - x_3)^2)$$

Jasinski and Malonowski equation:

$$(12) \quad Y_{123}^E = Y_{m,binary}^E + x_1 x_2 x_3 (B_0 + B_1 (2x_1 - 1) + B_2 (2x_1 - 1)^2)$$

Calvo et al. equation:

$$(13) \quad Y_{123}^E = Y_{m,binary}^E + x_1 x_2 x_3 (B_0 + B_1 (2x_1 + 2x_2 - 1) + B_2 (2x_1 + 2x_2 - 1)^2)$$

Nagata Equation:

$$(14) \quad Y_{123}^E = Y_{m,binary}^E + x_1 x_2 x_3 B$$

where $Y_{m,binary}^E$ are the contributions of binary mixture i, j .

$$(15) \quad Y_{m,binary}^E = Y_{12}^E + Y_{13}^E + Y_{23}^E$$

every B_i ternary parameter is a function of temperature as expressed in Eq. (10)–(14):

$$(16) \quad B_i = \sum_{j=0}^2 C_{iq} T^q,$$

The parameters C_{iq} for the ternary mixtures are listed in Table 6, along with the standard deviation σ .

3.3 Prediction of Excess Molar Volumes for the Ternary Mixture

Obviously, the thermodynamic properties of ternary systems are strongly dependent on intermolecular interactions of compounds, and it is not easy to predict the thermodynamic properties of these mixtures. In recent years, however, several empirical and semi-experimental equations have been presented in the form of symmetric models for predicting thermodynamic properties. Symmetric models are those geometric models that consider the interactions of ternary systems from the same combination of binary interactions. In order to use these equations, the relationship between the binary systems corresponding to the ternary system must be determined. The Redlich-Kister equation is the most well-known relation in this field. By having the coefficients in these equations and correlating with the empirical results obtained in the laboratory and using the relationship obtained from the Redlich-Kister equation, excess molar volume is predicted as one of the most widely used thermodynamic properties.

Accordingly, excess molar volumes and refractive index deviations for studied ternary mixtures were predicted using Radojkovic[14], Colinet [15], Jacob-Fitzner [16], Kohler [17], and Rastogi [18] geometrical solution models. These models also use binary contributions evaluated by Redlich-Kister equation and proposed an equation for ternary system of the form:

Radojkovic Model:

$$(17) \quad Y_{123}^E = Y_{12}^E + Y_{13}^E + Y_{23}^E$$

Colinet Model:

$$(18) \quad Y_{123}^E = 0.5(Y_{12}^E(x_2/1 - x_1) + Y_{12}^E(x_1/1 - x_2) + Y_{13}^E(x_3/1 - x_1) + Y_{13}^E(x_1/1 - x_3) + Y_{23}^E(x_3/1 - x_2) + Y_{23}^E(x_2/1 - x_3))$$

Jacob-Fitzner Model:

$$(19) \quad Y_{123}^E = \frac{Y_{12}^E x_1 x_2}{[(x_1 + x_3/2)(x_2 + x_3/2)]} + \frac{Y_{13}^E x_1 x_3}{[(x_1 + x_2/2)(x_3 + x_2/2)]} + \frac{Y_{23}^E x_1 x_3}{[(x_2 + x_1/2)(x_3 + x_1/2)]}$$

Kohler Model:

$$(20) \quad Y_{123}^E = Y_{12}^E(x_1 + x_2)^2 + Y_{13}^E(x_1 + x_3)^2 + Y_{23}^E(x_2 + x_3)^2$$

Rastogi Model:

$$(21) \quad Y_{123}^E = \left[\frac{Y_{12}^E(x_1 + x_2) + Y_{13}^E(x_1 + x_3)}{2} + Y_{23}^E(x_2 + x_3) \right] / 2$$

Standard deviation for the fitting of excess molar volumes and refractive index deviations prediction models for ternary mixture (2-ropanol (1) +1, 3-Diaminopropane (2) +2, 5-

Dimethoxytetrahydrofuran (3)) using prediction solution model equations (17) - (21) at $T = (298.15$ to $328.15)$ K are reported in Table 7. As can be seen in Table 7, in general the agreement between Colinet geometrical solution models is in better consistency with experimental results for both excess molar volumes and refractive index deviations.

4. Conclusion

Understanding of molecular interactions is essential in chemical processes and thermodynamic properties are one of the best means to interpret and justify these interactions. In this paper we obtain densities and refractive indices of binary and ternary mixtures including of 2, 5-Dimethoxytetrahydrofuran, 1, 3-Diaminopropane, and 2-Propanol and its derivatives were obtained from experimental results and fitted by Redlich-Kister type function to obtain the binary coefficients and estimate the standard deviations. V_m^E , Δn_D , α^E and $(\partial H_m^E / \partial P)_{T,x}$ were calculated. By using excess molar volume and refractive index deviations of binary systems from ideal state, molecular interactions are estimated. In general it can be concluded that chemical interactions consequences to negative deviations and the positive quantities are indicated the physical interactions in binary systems.

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