J. Chem. Thermodynamics 91 (2015) 384–395

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Study of intermolecular interactions through dielectric properties of the mixtures consisting of 1,4-butanediol, primary amyl alcohols and 1,4-dioxane at various temperatures

A. Ghanadzadeh Gilani [a,*], M. Moghadam [b], S.E. Hosseini [a]

[a] Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran
[b] Department of Engineering, East of Guilan, University of Guilan, Rudsar, Iran

ARTICLE INFO

Article history:
Received 23 May 2015
Received in revised form 6 August 2015
Accepted 16 August 2015
Available online 24 August 2015

Keywords:
Relative permittivity
Effective dipole moment
Molecular interaction
Kirkwood factor
Binary mixtures
Excess parameter

ABSTRACT

This paper presents relative permittivities, excess permittivities, effective dipole moments, and excess Kirkwood correlation factors of binary mixtures of 1,4-butanediol with two primary pentanol isomers [1-pentanol (amyl alcohol) + 3-methyl-1-butanol (isoamyl alcohol)] from $T = (298.15$ to $318.15)$ K at $p = 101.3$ kPa over the entire composition range. Experimental permittivity values for polar–non-polar binary systems of (1,4-dioxane + amyl alcohol or isoamyl alcohol) were also obtained as a function of composition at the same range of temperatures. The experimental permittivity data were fitted using Redlich–Kister equation to evaluate the adjustable parameters and the standard errors. From the experimental data, the excess parameters were calculated. In this work, variations of effective dipole moment and correlation factor were investigated using Kirkwood–Frohlich equation. The experimental data of measurements were used in the analysis of the homo- and hetero interactions occurring in these binary solutions.

1. Introduction

Relative permittivity or static dielectric constant is a macroscopic and intrinsic property that provides important information about molecular associations and geometrical structure of molecules [1–5]. The permittivity data of binary systems (polar–polar and polar–non-polar) over a range of mole fractions and temperatures are crucial for understanding of the nature and strength of intermolecular interactions and the consequential structural rearrangement of molecules [6–9]. Generally, type of solvent, concentration and temperature are very important factors that influence dielectric behavior of a liquid mixture [10].

Up to now, substantial dielectric studies have been carried out on many alcohol mixtures with various compositions and temperatures [11–14]. Due to the presence of the –OH group in these molecules, the dielectric behavior of alcohols depend mainly on the dipole–dipole interactions, hydrogen bonding and local structure of the alcohol. However, in the case of diols, due to the presence of two –OH groups in the molecule, the dielectric properties and the dipole moments of the diols strongly influenced by the location of –OH groups (the separation of the two –OH groups along the carbon skeleton), molecular conformations and molecular flexibility. Moreover, formation of network structure in diols, due to the molecular association, is a well-known phenomenon [15]. In general, the permittivity of the diols depends on the distance between the hydroxyl groups along the chains of these molecules as well.

The diol used in this study was 1,4-butanediol (1,4BD) with two primary hydroxyl groups. In this molecule, the existence of two non-adjacent hydroxyl groups at positions 1 and 4 leads to the formation of a network structure [16]. Up to now, several authors have reported dielectric data and electric dipole moments for pure or various systems consisting of 1,4BD [17–28].

The mono-alcohols studied are two primary pentanol isomers, namely 1-pentanol (amyl alcohol, AA) and 3-metyl-1-butanol (isoamyl alcohol, IAA). These isomeric pentanols were chosen in order to a comparative study of the influence of the chain branching on the dielectric properties of the alcohol/diol mixtures. Moreover, it is well known that heavy alcohols are useful chemical for the separation of diols from aqueous solutions. Thus, due to the structure characteristics of these isomers, they may be considered as good solvents for extraction of the diol. Consequently, the obtained dielectric results can be industrially and scientifically important.

* Corresponding author at: Department of Chemistry, University of Guilan, 41335 Rasht, Iran. Tel./fax: +98 131 3233262.
E-mail address: aggilani@guilan.ac.ir (A. Ghanadzadeh Gilani).

http://dx.doi.org/10.1016/j.jct.2015.08.021
0021-9614/

Experimental permittivity and excess permittivity data for mixtures consisting of 1,4BD at different temperatures were reported in our previous publications [29–31]. As a continuation of the previous works, we present and discuss the results of a systematic study of the temperature and concentration dependence of the permittivity, excess permittivity, and effective dipole moment of the binary mixtures of 1,4BD with two primary pentanol isomers (amyl and isoamyl alcohol) over the temperature range of (298.15 to 318.15) K. In this work, a comparative dielectric study of intermolecular interactions was carried out in these binary systems over the entire composition range. In addition, in order to obtain additional information about the homo interaction between alcohol molecules, the dielectric measurements were obtained for the (amyl or amyl alcohols + 1,4DX) binary mixtures for the investigated temperature range.

2. Experimental

2.1. Chemicals

1,4-butanediol (mass fraction purity > 0.98), amyl alcohol (mass fraction purity > 0.99), and isoamyl alcohol (mass fraction purity > 0.99) were obtained from Merck. 1,4-dioxane (mass fraction purity > 0.995) was supplied from AppliChem. HPLC grade cyclohexane (mass fraction purity > 0.999) was obtained from Merck and was used for the calibration of the dielectric cell. All chemicals were stored in dark bottles over molecular sieves (Merck 0.4 nm) to reduce water content. The chemical structures of the liquids are illustrated in figure 1. The stated purity of the alcohols was checked using density and refractive index measurements at 298.15 K. The measured refractive index and density data of the chemicals used in this study along with the literature values [31–33] are given in table 1.

2.2. Apparatus and procedure

Refractive indices and densities of the liquids were measured using an Abbe Refractometer (Model CETI) and a DA210 (Kyoto Electronic) density meter, respectively. The instruments were initially calibrated using HPLC grade water at $T = 298.15$ K ($n = 1.3325$ and $d = 0.99704$) before being used. The uncertainties in the refractive index and density measurements were ±0.0005 and ±0.00003 g · cm^{-3} respectively. The temperature of the instruments was maintained with an accuracy of within ±0.01 K, which was checked with a digital thermometer (Lutron TM-917). The samples were prepared by mass using an AND electronic balance (model HR-200) with an accuracy of ±0.0001 g. The uncertainty in the mole fraction was estimated to be better than ±0.001.

A three-terminal cylindrical cell with 27 pF of empty capacitance was used for the capacitance measurements. The electrical capacitance of the dielectric cell was measured using a Wayne Kerr model 6425B Digibridge. The samples were primarily checked for any ionic conditions. For the permittivity measurements, 100 kHz alternating current field frequency was used to avoid the contribution of ionic conduction and electrode polarization effects [34]. The cell was calibrated with air and a liquid with well-known dielectric permittivity at each working temperature.

The permittivity of the solutions was determined by electrical capacitance measurements. The capacitance of the dielectric cell was measured when empty, when filled with the standard liquid and when filled with solution of the interest. The relative uncertainty in the value of relative permittivity was about ±0.006, which was estimated by the calibration of the cell with standard liquids.

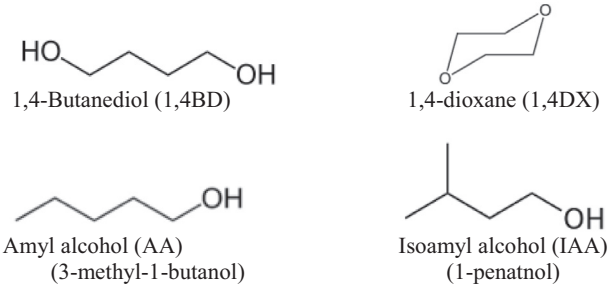

FIGURE 1. The molecular structures of the compounds used in this study.

2.3. Determination of molecular dipole moment

The molecular dipole moment (μ) of the liquids were determined using the Guggenheim–Debye equation [35].

$$\mu^2 = \frac{27kT}{4\pi N_A(\varepsilon_1 + 2)(n_1^2 + 2)}\left(\frac{\Delta}{C}\right)_{C\to 0}, \quad (1)$$

where ε_1 and n_1 are the permittivity and the refractive index of pure non-polar solvent, respectively. The subscript 12 denotes a property of the solution, C is the molar concentration (mol/cm^3), $\Delta = (\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^2)$, and $(\Delta/C)_o$ is the limiting gradient of the plot versus concentration. The uncertainty in the measured dipole moments is 0.03D.

3. Result and discussion

3.1. Relative permittivity data

Relative permittivity and refractive index data were measured for the four binary systems of (1,4DX + AA), (1,4DX + IAA), (AA + 1,4BD), and (IAA + 1,4BD) over the complete mole fraction range ($0 \leqslant x_2 \leqslant 1$).

In this research, the experimental permittivity data for the pure compounds were compared graphically with the literature data. Typically, figures 2(a–d) and 3(a–d) compare the experimental relative permittivity (ε_r) and refractive index (n_D) data obtained for the pure liquids at different temperatures with the literature data reported in previous publications [36–43]. As can be seen, there are

TABLE 1
Liquids used in this study; name, abbreviation, source, mass fraction purity and experimental values of refractive index, n, and density, d, of the liquids at $T = 298.15$ K and $P = 101.3$ kPa.[a]

Liquid	Source	Mass fraction purity	n		d/(g · cm^{-3})	
			Exp.	Lit.	Exp.	Lit.
1,4-Butanediol (1,4BD)	Merck	>0.98	1.4445	1.4447 [31]	1.01340	1.01345 [31]
Amyl alcohol (AA)	Merck	>0.99	1.4082	1.4082 [32]	0.81110	0.81106 [32]
Isoamyl alcohol (IAA)	Merck	>0.99	1.4048	1.4050 [33]	0.80716	0.80720 [33]
1,4-Dioxane (1,4DX)	AppliChem	>0.995	1.4202	1.4202 [31]	1.02786	1.02791 [31]

[a] Standard uncertainties u are u(n_D) = 0.0005, and u(d) = 0.00003 g · cm^{-3}.