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Static permittivity, density, speed of sound, and refractive index of 2-propoxyethanol mixtures with water in a wide temperature range

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ABSTRACT

The static permittivity, ε_r, density, ρ, speed of sound, u, and refractive index, n_D, of water + 2-propoxyethanol mixtures were measured over the entire range of mixture composition in a wide temperature range. The experimental values of density and speed of sound were used to determine the molar volume, V_m, adiabatic compressibility, β_S, and their excess values. Also the values of partial molar volumes $\overline{V}_1$ and $\overline{V}_2$ as well as the thermodynamic parameters namely the entropy derivative after pressure, $\partial S/\partial p$, enthalpy derivative after pressure, $\partial H/\partial p$ and molar heat derivative after pressure, $\partial C/\partial p$ of the mixtures were determined.

The experimental data of static permittivity were used to determine deviations from the additivity of permittivity, $\Delta\varepsilon_r$, excess of this value, ε_r^E, temperature coefficient of permittivity, $\partial \ln \varepsilon_r/\partial T$, and their excesses, $(\partial \ln \varepsilon_r/\partial T)^E$.

Using the results of refractometric analysis and static permittivity, the values of Kirkwood's correlation factor, g_K, and their excess values, g_K^E, were also determined.

The concentration and temperature dependent results of the mixtures were used in the analysis of hydrogen bond interactions occurring between the molecules of water and 2-propoxyethanol.

1. Introduction

Physicochemical and thermodynamic properties of liquid mixed solvents are a valuable information source concerning the system internal structure and intermolecular interactions occurring in them [1–5]. So, the investigations of density, sound speed, permittivity and refractive index, especially within a wide temperature range, are a valuable tool to recognize and understand the microscopic properties of liquids, or finally to design theoretical models describing experimental data [6]. Excess thermodynamic functions and excess and deviation from additivity of other properties of mixed solvents are of paramount importance for understanding the interactions between the mixture components.

Mixed solvents have a variety of uses, ranging from chemical, biological and pharmaceutical to industrial applications [7,8]. 2-Alkoxyethanols, including 2-prop- oxyethanol, constitute a very interesting group of compounds with a wide range of uses [6,7,9–11]. The properties of these compounds, being of interest to researchers, are connected with the structure of their molecules. The presence of ether oxygen and hydroxyl group determines their donor-acceptor properties and a possible formation of intra- and intermolecular associated molecules [9,11,12].

Literature data concerning the physicochemical properties of the mixtures of water and 2-propoxyethanol are exceptionally skimpy. The study of Douhéret et al. [13] concerns volumetric and acoustic investigations of this system but it has been exclusively limited to a temperature of 298.15 K. A paper by Shindo and Kusano [14] presents the values of density and refractive indices of the mixtures at a temperature of 298.15 K, only within the composition range of 0–0.55 mole fraction of 2-propoxyethanol.

In the present study, we determined the values of density, ρ, static permittivity, ε_r, sound speed, u, and refractive index, n_D, within the whole composition range of the water-2-propoxyethanol mixture and in a wide temperature range (288.15–318.15) K for ρ, n, u and (283.15–333.15) K for ε_r. Based on the physicochemical data obtained, the coefficients of volumetric expansion, α, isentropic coefficients of compressibility, β_S, and Kirkwood's correlation factors, g_K. were determined. The examinations within a wide

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temperature range made it possible to determine a number of thermodynamic functions, such as the derivative of molar heat after pressure, $\partial C/\partial p$, derivative of enthalpy after pressure, $\partial H/\partial p$, and derivative of entropy after pressure, $\partial S/\partial p$. It was also possible to determine the temperature coefficient of permittivity, $\partial \ln \varepsilon_r/\partial T$. A systematic study of so many physicochemical properties may be helpful in explaining the nature of interactions between the components of water–2-propoxyethanol mixtures. It is worth noting that such a detailed and comprehensive study of the mixtures of water and 2-propoxyethanol was carried out for the first time.

2. Experimental

2.1. Chemicals

2-Propoxyethanol from Aldrich (mass fraction 0.994) was stored in a dark bottle and used without further purification. Water content determined by Karl-Fisher's method amounted to 200 ppm. The water used for mixed solutions was distilled twice and then deionized on ionic exchangers. Electrolytic conductivity was equal to $1.2 \cdot 10^{-7}$ S·cm^{-1}. Information concerning the solvents used are contained in Table 1aS.

The mixtures of water and 2-propoxyethanol were prepared by the gravimetric method with the use of a Sartorius RC 210D electronic balance with an accuracy of $\pm 10^{-5}$ g. The liquids were outgassed in an ultrasonic washer directly before measurements.

The literature [13–31] and our own laboratory measured values of density, ρ, refractive index, n, sound velocity, u, and relative permittivity ε_r are collected in Table 1bS and presented graphically in Figs. 1S–8S. The comparison shows high compliance of the density values obtained in this work with the literature data. The study of Douhéret et al. [13] contains values of speed of sound in mixtures of water with 2-propoxyethanol at 298.15 K. Comparison of our data with the literature data [13] shows that in the region of the observed maximum, a deviation of about 6 m·s^{-1} is seen (Table 6Sb). Moreover, for the mixtures with compositions similar to that for which the speed of sound reaches a maximum, values given in [13] are a bit smaller than those reported by us. There may be some reasons of these observed facts. The authors of [13] were using 2-propoxyethanol with a lower purity than that used by us. Furthermore, the authors [13] were using 2-propoxyethanol without checking the water content. However, it should be emphasized that the maximum speed of sound in [13] occurs for mixtures of the same composition as in our work. Slightly worse compatibility show the values of the refractive index obtained by us with the values contained in [30]. Our values are about 0.15% higher and compatible with the available literature data of other authors at temperature 298.15 [14]. The authors of [30] do not compare their values n_D with the data of other authors and do not give the water content in the used propoxyethanol. It should be expected that with increasing water content decreases the value n_D (Fig. 4S). Fig. 4S contains comparison of the refractive indices of water(1)–2-propoxyethanol(2) mixtures measured at 298.15 K with literature data [14]. The values of n_D given by us and those contained in [14] are almost identical in the case of water and 2-propoxyethanol (Table 1bS). The exact analysis of the dependences shown in Fig. 4S demonstrates that in the case of the mixtures of water with propoxyethanol, differences between our data and given in [14] relate to only three mixtures containing more than 0.2 mole fraction of 2-propoxyethanol. Discrepancies are only about (0.10–0.13)%. In [14] for $x_2 \geqslant 0.2$ were tested only three mixtures. In our work there are 10 mixtures examined for $x_2 > 0.2$. We also want to underline that the refractometer used by Shindo et al. (Atago301 Abbe refractometer) can measure the refractive index with an accuracy of 0.0002. Digital refractometer used in our work (Kruss DR 5000) ensures the accuracy of an order of magnitude better. However, minor discrepancies seen in Fig. 4S, do not affect the shape and character of the relationship $n_D = f(x_2)$. We can also notice that the values of relative permittivity quoted in [20,28] are systematically higher than those obtained by us. In [20,28] is not specified water content in used 2-propoxyethanol. The increase in water content can cause an increase in the value of ε_r. It may also cause an increase in the density values [20]. It should also be noted that the value of ε_r for ethoxyethanol presented in [20,28] are much higher than those presented by other authors [32]. In the whole temperature range, the values of relative permittivity of water obtained by us are almost the same as the values contained in [33], generally regarded as reference values. Also the values of density and refractive index obtained by us is practically the same as those cited in [33].

2.2. Measurements

The density measurements were carried out by means of an Anton Paar DMA5000 apparatus with a measurement accuracy of $\pm 5 \cdot 10^{-6}$ g·cm^{-3} and repeatability of $\pm 10^{-6}$ g·cm^{-3}. The measurement of temperature was maintained with an accuracy of ±0.01 K and repeatability of ±0.001 K. The density meter was calibrated using pure water and dry air according with manufacturer's instruction. Taking into account the purity of 2-propoxyethanol should be assumed that the increase of its content in the mixtures increases the uncertainty of density. In the case of 2-propoxyethanol uncertainty of density reaches value of about 0.0006 g·cm^{-3}.

The speed of sound was measured by means of an OPCARD – 01/100 apparatus made by OPTEL (Wrocław, Poland) that made it possible to measure the sound speed with repeatability of ±0.05 m·s^{-1}. The measuring frequency was 5 MHz. A detailed description of the apparatus for measuring the sound speed is presented in our previous papers [34,35].

The measurements were carried out by the dilution method in a cell whose temperature was maintained by a HAAKE B5 thermostat with an accuracy of ±0.01 K.

Static relative permittivity measurements were made using the measuring capacitor constructed in the Department of Physical Chemistry at the University of Łódź. Its construction is very similar to that described by Barthel et al. [36] and Bešter-Rogač and Habe [37]. The capacitor has the form of a coaxial cylinder. The difference was only on the method of temperature control. The measuring capacitor used by us had its own thermostatic jacket supplied with transformer oil. To establish and maintain a desired temperature, a Julabo F32MH thermostat operating with an accuracy of ±0.01 K was used. The measurement of capacitor capacity was carried out with the use of a Precision Component Analyzer – 6430B (Wayne Kerr Electronics). The uncertainty of the relative permittivity was estimated to be approximately ±0.2. The measuring frequency was 100 kHz.

Refractive index for the sodium D line, n_D, was measured by means of a Kruss DR5000 refractometer with a measurement accuracy of $2 \cdot 10^{-5}$. The accuracy of thermostat operation was 0.10 K.

3. Results and discussion

The experimental values of density, ρ, sound speed, u, refractive index, n_D, and permittivity, ε_r, of the water–2-propoxyethanol mixtures are listed in Tables 2aS, 2bS, 2cS and 2dS, respectively (Supplementary Materials).

As is seen in Fig. 1, the values of density of the mixture of water and 2-propoxyethnol decrease with increasing the organic solvent content. At the beginning of adding 2-propoxyethanol, changes in