# Excess Properties of Alcohol - Water Systems at 298.15 K

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## Abstract

Dielectric constants $\varepsilon$, viscosities $\eta$, refractive indices n and densities d have been measured over the entire mole fraction range for the water - methyl, ethyl, n-propyl alcohol binary systems at 298.15 K. From the experimental data excess dielectric constants $\varepsilon^E$, excess viscosities $\eta^E$ and Kirkwood correlation factors $g_k$ have been calculated and studied. Their behaviour suggests the existence of intermolecular interactions and plotted curves show that excess dielectric constant and $g_k$ values decrease with the increasing of carbon atom number, while excess viscosity increases.

**Key Words:** Dielectric constant, viscosity, excess properties, Kirkwood correlation factor

## 1. Introduction

It is well known that the thermophysical properties, of liquid systems such as density, viscosity, dielectric constant, refractive index among others, are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of these properties with composition gives us important data about intermolecular interactions and the structure.

There is a wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole-induced dipole interactions [1,2]. As a consequence of these interactions, deviations occur from ideal behavior of dielectric constant and viscosity. These deviations can be defined by excess dielectric constants and viscosities.

Experimental data on excess dielectric constant, excess viscosities and the Kirkwood correlation factor $g_k$ are known for a number of binary and ternary liquid mixture and can be found in several articles [3-6]; their study may lead to conclusions concerning the deviation of systems from an ideal mixture behaviour.

In a previous paper we have been concerned with excess properties of the water - methanol binary system within the temperature range of $15 - 45°C$ [1].

Mixtures of water with aliphatic alcohols are of considerable interest from the viewpoint of the existence of some interaction, such as hydrogen bonding between water-which contains an -OH group and can act as a $\pi$-type donor- and alcohol molecules, which have one acidic H atom on the -OH group and can act as $\sigma$-acceptors. The aim of the present work is to determine excess dielectric constants $\varepsilon^E$, excess viscosities $\eta^E$ and Kirkwood correlation factors $g_k$ for the water - methanol, ethanol and n-propanol systems at 298.15K and correlate these values with carbon chain length and intermolecular interactions.

## 2. Experimental section

The alcohol-water solutions were prepared from analytical grade alcohols without further purification and from deionized bidistilled water.

The equipment for dielectric constants, viscosities, refractive indices and densities measurements and the experimental procedures for $\varepsilon^E$, $\eta^E$, $g_k$calculations have been described else where [1,7]. The pure species are all polar molecules [$\mu$(methanol) = 1.70 D, $\mu$(ethanol) = 1.69 D, $\mu$(n-propanol) = 1.68 D and $\mu$(water)= 1.85 D].

## 3. Results and Discussion

The results for the dielectric constant are presented in Fig. 1. For all the studied systems the dielectric constant values decrease by increasing alcohol concentration or carbon atoms number, meaning that polarization is directly correlated to these facts.

Plots of the excess dielectric constants vs. mole fraction of alcohol for binary alcohol-water systems at 25°C show a minimum at about 0.5 mole fraction, as can be seen in Fig. 2. When the number of carbon atoms increases these minimum slightly shifts toward low concentrations, varying from 0.5 to 0.3 mole fraction.
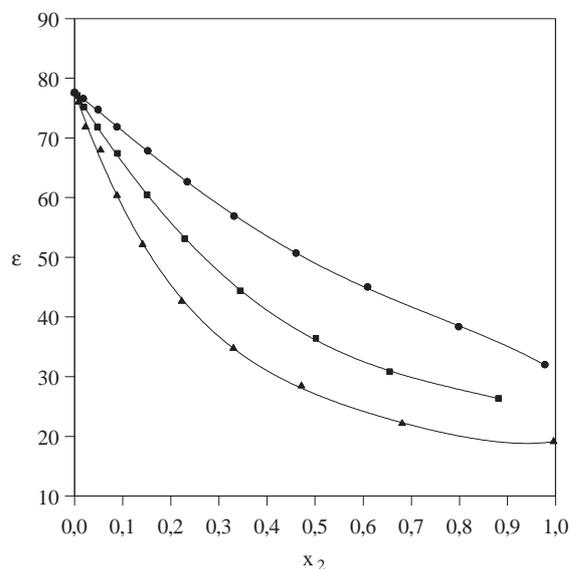


**Figure 1.** Variation of dielectric constant with mole fraction of alcohols (● methanol, ■ ethanol, ▲ n-propanol).
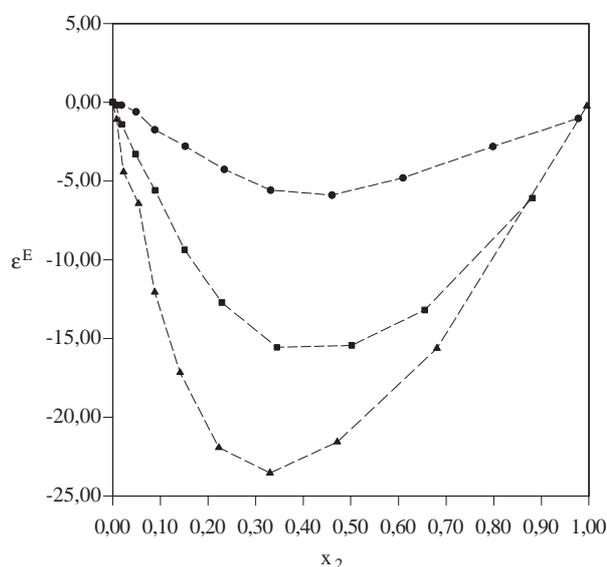
**Figure 2.** Variation of excess dielectric constant with mole fraction of alcohols (● methanol, ■ ethanol, ▲ n-propanol).

Binary mixtures can also be investigated by observing the shapes of the excess mixing property isotherms [1]. Shapes usually deviate from ideal theoretical behaviour ($\varepsilon^E \approx 0$) since the dielectric constants of both components are additive and any significant intermolecular interaction is effectively absent ($\varepsilon^E \neq 0$) [6] . Generally, polar intermolecular interactions cause more pronounced deviations from the above-mentioned additivity rule and are responsible either from maxima or minima in the plots of $\varepsilon^E$ vs. mole fraction of one component. It has been hypothesized that for $\varepsilon^E \leqslant 5$ weak dipolar association between unlike molecules, or an increase in the dipolar association by one component to form molecular aggregates of lower or higher dipole moment, could be invoked to justify the experimental evidence. The first hypothesis is more likely than the second. [8,9].

For our systems, all the three curves exhibit a pronounced minimum and they remain negative for the whole concentration range. These negative deviations from ideal may be attributed to a certain interaction between unlike molecules and, in particular, to hydrogen bonding. For a strong hydrogen bond donor mixing cosolvents-specific donor-acceptor interactions may probably produce stable stoichiometric complexes which are formed in competition with the simultaneous disruption of the structures of both the pure solvents [6].

At molecular level, negative values of $\varepsilon^E$ for various systems are a consequence of the formation of polar associates of lower dipol moment. In pure alcohol the formed linear n-mers present a higher dipol moment [10]. This behavior has been attributed to the fact that the O-H bond moment of these aggregates is increased through mutual induction. On the other hand, the H-bonded complexes of water present a dipole moment. Consequently, taking into account all these assumptions, we could attribute the observed negative deviations from dielectric ideality to all these effects.

All the plots of viscosity vs. mole fraction of alcohol show a maximum at around 0.3 mole fraction in Fig. 3. Alcohols in polar solvents associate by means of hydrogen bonds into a series of n-mers, and at the same time there is an intermolecular association between alcohol and water molecules. In very dilute solutions, the predominant species is the monomeric form, while in more concentrated solutions both linear and n-mers coexit. Finally, in pure alcohol or in high concentrated solutions of these substances only n-mers can be considered. Also, in solvents such as water, which can take part in hydrogen bond formation, the self-association of alcohols may be reduced in favor of hydrogen - bonded forms between solute and solvent. In our previous paper [1] the variation of the viscosity with concentration has been discussed, taking into account the association between two unlike polar molecules. In this paper the viscosities of three samples increase as carbon atoms number of alcohols increases. The data of Rived, Roses and Bosch (1995) at 303.2 K are in very good agreement with our results.

The excess viscosities are shown in Fig. 4. All the systems show positive deviations of excess viscosities $\eta^E$ from ideal over the entire mole fraction range. Maxima correspond to the near of 0.25 mole fraction. As the concentration decreases, the maxima position also decrease. As the molecular size increases, the magnitude of the excess viscosity increases, i.e., becomes more positive, showing a tendency to the ideal behavior [7].
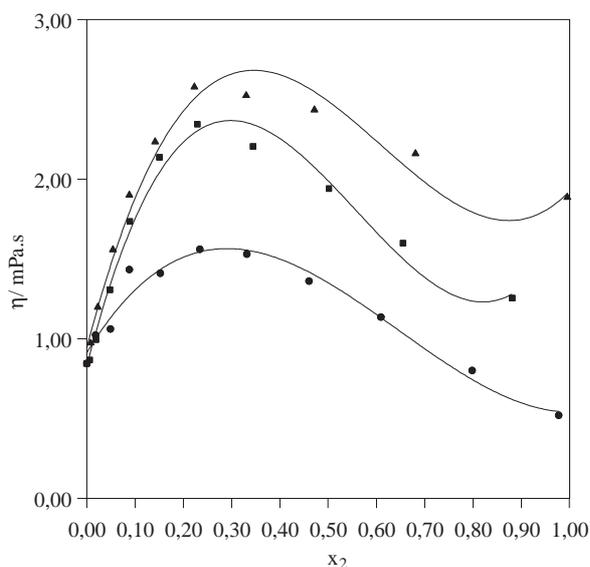


**Figure 3.** Variation of viscosity with mole fraction of alcohols (● methanol, ■ ethanol, ▲ n-propanol).
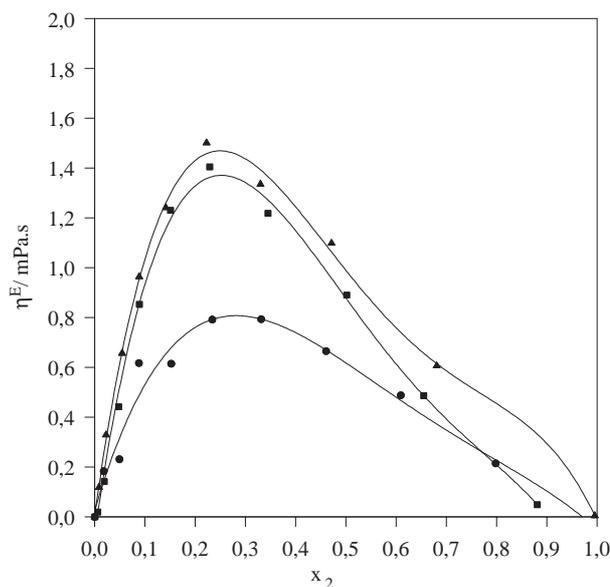
**Figure 4.** Variation of excess viscosity with mole fraction of alcohols (● methanol, ■ ethanol, ▲ n-propanol).

Another important parameter, which has also been taken into account in this work is the Kirkwood correlation factor, $g_k$ (Fig. 5). It is well known that water is a polar solvent with a structure which is determined to a great extent by hydrogen bonding between molecules. On the other hand, alcohols are well known protic solvents, which posses one acidic hydrogen atom on the -OH group. Values of $g_k$ for protic solvents are generally significantly higher than those for aprotic systems. The value of $g_k$ for water (2.87) is very close to that estimated on the basis of the Kirkwood model (2.65) [11]. The deviation of $g_k$ from unity is a measure of the short-range intermolecular interactions and associations. The values of $g_k$ for the short chain length are higher than that for longer.
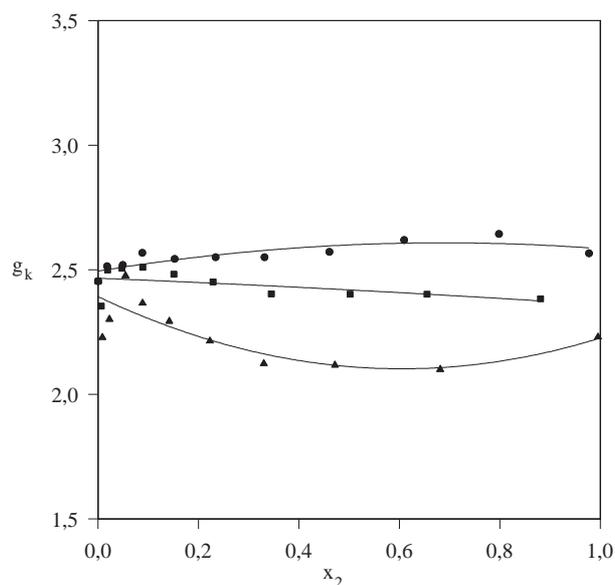
**Figure 5.** Variation of Kirkwood correlation factor with mole fraction of alcohols (● methanol, ■ ethanol, ▲ n-propanol).

# 4. Conclusion

As can be understood from the above results, the excess properties of the studied mixtures indicate some molecular interactions. Because of alcohols are associate liquids, they can interact with each other and with water molecules. Dielectric constant and viscosity were the most affected parameters from these interactions. The excess values of these components exhibited a minima or maxima which means a deviation from ideal behaviour. The variations in Kirkwood correlation factor with respect to solvent composition can be attributed to the short-range dipolar interactions which lead to structural changes in respective solvent mixtures.

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