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A new representation of permittivity *versus* temperature for alkanols of the same chain length

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The alkanols of three carbon length have been studied by dielectric methods during many years and they do not obey any theoretical model. These substances have the same chain length and have one, two or three dipoles per molecule, so their ability to form hydrogen bridges changes from one substance to other, and one can obtain information by comparative studies. In previous works, we have measured the thermal dependence of permittivity of these substances and analysed the results with an empirical modification of the Onsager equation. Now we shall analyse and compare the results using a different representation. In this representation, the data shows straight lines, whose slopes depend on the quantity of dipoles of each molecule encouraging the high quality of the fittings obtained with the three substances, and also that they behave in the same dielectric way with the rise of temperature.

Keywords: permittivity; dielectric constant; alkanols; Onsager model

1. Introduction

In the past, these three substances have been extensively studied by dielectric spectroscopy, in pure state [1–11], in mixtures with non-polar solvents [12–19], in aqueous solutions [20–24] or in mixtures with other polar liquids [25–28], in all the range of liquids temperatures, and also in the super-cooled state [29–31].

In these systems, the hydrogen bonding between molecules and the dielectric behaviour is present and is governed by this association. At the present time there is still a controversy in the detailed explanation of how these clusters form and evolve [32–38]. Despite this lack of an explicit model, one can obtain valuable information by doing comparative studies of the dielectric behaviour of these substances.

Static permittivity brings information about the molecular associations, and its variations with temperature gives knowledge on the dynamics of the structures made by the hydrogen bonding.

In previous works, we have measured the static permittivity as a function of temperature in pure and diluted alcohols, and also in this family of alkanols, and analysed the results obtained with an empirical modification of the Onsager equation [39–43].

Now the objective is to compare the results obtained with a new representation [44] that put in evidence the differences in the dielectric behaviour of liquids that have the same chain length and an increasing number of dipoles per molecule.

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2. Experimental

The measurements were made with a Hewlett-Packard Impedance Analyser 4191A at a frequency of 10 MHz. We used a coaxial cell, which has a very small empty capacity. The permittivity was calculated from the admittance values of the cell with and without the sample, and the correspondent equivalent circuit, using a variation of the method described in [45].

All the systems were calibrated using reference liquids, such as benzene, carbon tetrachloride and acetone, and the values of permittivity obtained have a difference of less than 1% with that of the tabulated values. The samples used were of chromatographic quality and were distilled and dehydrated with the usual methods.

A continuous flow of water provided by a Colora Thermostat allows the control of temperature with a precision to the tenth of degree.

The error was calculated with a variational method and results in less than 1% for all the samples and temperatures measured.

3. Results and discussion

We search for a different way to represent the data that will more clearly show the dependence of permittivity with temperature than the usual representation. If one checks the theoretical models in all of them, then ε_0 is a function of several constants and values belonging to the sample, and is always divided by the absolute temperature.

In the Onsager equation [33,38]:

$$(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)/[\varepsilon_0(\varepsilon_\infty + 2)^2] = 4\pi\rho\mu^2/[9kT], \quad (1)$$

it is easy to see that the left term is a combination of the value of static permittivity (ε_0), with a constant, which is the permittivity in the limit of high frequency (ε_∞), and this is equal to other constants ($4\pi\mu^2/[9k]$), the numerical density of dipoles (ρ) that is a property of the sample, and that the right term is divided by the temperature (T).

The only difference between the Onsager equation (1) and the Kirkwood–Fröhlich equation [34–38] is the presence of a new factor, (g), in the right term; the calculation of this factor in an analytical way is impossible, and also, g depends on temperature.

Analysing Equation (1), the left term can be calculated if one has the measured values of ε_0 and the fitted values of ε_∞ [46]. We shall call it the Factor of Onsager (FO), for reasons of simplicity.

In the right term we can define A_{teo} as the factor $4\pi\rho\mu^2/[9k]$, so Equation (1) is reduced to:

$$\text{FO} = A_{\text{teo}}/T. \quad (2)$$

If one represents FO *versus* $1/T$, a straight line must be obtained, whose slope is A_{teo} .

As we can see in Figure 1, the graph for FO *versus* $1/T$ for the three alkanols gives straight lines, but the slopes of these lines are very different of those calculated with the correspondent values in the factor A_{teo} .

In the calculations we used, the tabulated values [47] of the different constants included in the factor A_{teo} were $\mu = 1.65 \text{ D}$ for propanol; 2.25 D for propanediol and 2.6 D for propanetriol [15]; $k = 1.38 \times 10^{-16} \text{ erg K}^{-1}$; ρ = molecular number per centimeter cube of alkanol. This value (ρ) is calculated with the density of the liquid, the Avogadro's number

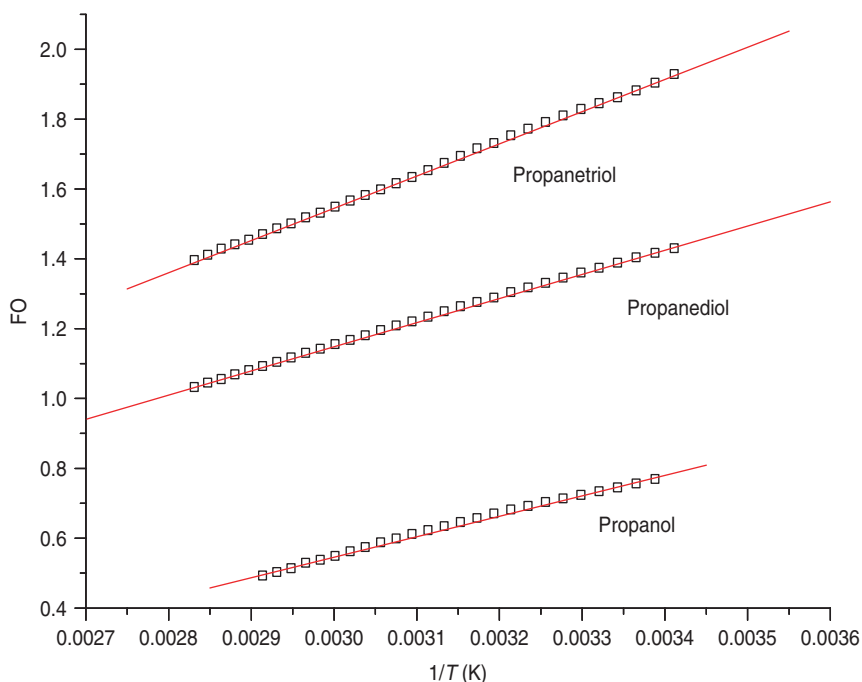


Figure 1. Factor of Onsager, FO, defined in text, vs. $1/T(K)$ for propanol, propanediol and propanetriol.

Table 1. Experimental and theoretical slopes, their ratio for each sample, and the correlation factor of the linear fittings.

Sample	A_{exp} (K)	A_{teo} (K)	$A_{\text{exp}}/A_{\text{teo}}$	Correlation factor
1-Propanol	585	222	2.63	0.9998
1,2-Propanediol	691	420	1.64	0.9997
1,2,3-Propanetriol	922	564	1.63	0.9998

and the molecular weight. We did not make corrections for the thermal expansion of the liquids with temperature because it has a variation that is less than 1% of the decrease in the density (in the range of temperatures in our measurements), and this has little importance in the behaviour analysed.

In Figure 1 we show a linear fitting of the values by means of a least-squares program. Table 1 presents the results obtained for the experimental slopes of the three samples, the theoretical slopes, their quotient and the correlation factor of the fittings.

The values obtained for the slopes, experimental and theoretical, grow with the dipole number per molecule, which means that it is higher for propanetriol than for propanol.

This can be understood because there is more hydrogen bonding in the propanetriol than in the propanol, so, in consequence, the number of broken bonding is greater with the increment of temperature.

Obviously, these graphs cannot be extended for all the temperatures; they are only true in the range where the samples are liquids. There is no sense in analysing the values of the vertical axis intercept, because this would correspond to a practically infinite temperature.

The quality obtained in the graphs is remarkable, because the experimental points define a very good straight line with a very small dispersion and a very high-correlation factor (Table 1) in the three samples. Besides, it is very easy to note if there are incorrect measurements because they will be out of the common line.

In the third column of Table 1 shows the values of the quotient between the slopes of the experimental and theoretical ($A_{\text{exp}}/A_{\text{teo}}$), where we can see how this value changes for different alkanols. This quotient is larger for the propanol and almost has the same value for the other two liquids.

The use of the Kirkwood model, with the geometrical factor g , does not decrease the differences between the experimental and theoretical slopes. Besides, this factor g depends on temperature and in the present case we need something that depends only on the number of dipoles of the molecule. Also, g is incremented with the number of dipoles per unit of volume [38] and decreases with temperature, and this is not our situation.

The only possibility of increment in A_{teo} is to consider that the values of the dipole moments, used in the calculation, are too low. These values are from the table, and they are determined at infinite dilution of the alkanols in different solvents, so we can say that in the pure liquids these values of dipole moments must be higher.

If we calculate the values of the dipole moments needed to obtain the experimental slopes, the results are: 2.67 D for propanol; 2.88 D for propanediol and 3.32 D for propanetriol.

If one compares the values of the slopes, it can be seen that it is lower for propanol than for the polyalcohols, and the values of permittivities are lower at all the temperatures (Figure 1). The behaviour of propanediol is in the middle and propanetriol has the higher values in permittivity and also in the slope.

In other words, because of the thermal agitation, less hydrogen bridges are broken in the alcohols than in the other liquids, and in these the variation is higher in the propanetriol than in the propanediol.

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