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## A linear representation of permittivity *versus* temperature data for pure alcohols

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In previous works, permittivity of some pure aliphatic alcohols was measured as a function of temperature and, together with data from the literature, was fitted with an empirical modification of Onsager equation. This representation is complicated because one has to solve the Onsager quadratic equation and then fit the experimental values. Here a new set of data is used in a different representation, with the inverse of the temperature, and a straight line is obtained for each sample. The slopes of these lines are not coincident with those calculated with Onsager or Kirkwood–Fröhlich models, and one can evaluate the differences between the experimental and theoretical values. This is a very simple and clear representation and the good quality of the linear fits attained with the two sets of our measurements and data from several authors is encouraging. A qualitative explanation of the differences observed with the theoretical values is offered.

*Keywords:* Permittivity; Dielectric constant; Alcohols; Onsager; Kirkwood

### 1. Introduction

In several previous works we have presented measurements and interpretations of the behavior of permittivity of pure [1] and diluted alcohols as a function of temperature [2–4]. In all of them we proved that the theoretical models do not fit the experimental values, so an empirical modification was introduced to Onsager model [5,6].

The problem in the previous works is that the Onsager's expression [5,6] is quadratic in  $\epsilon_0$  and it has to be solved, the positive root should be chosen and only then the fit can be performed. The results of these calculations are the best set of values of  $\epsilon_\infty$  and the thermal correction parameters (for each alcohol) [1].

Following with that line of work, we look for another way of representing the data to show more easily and clearly the dependence of static permittivity with temperature, and to analyze the behavior of the Onsager and Kirkwood–Fröhlich models for alcohols.

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The data used in these works, and in the present one, were both our own values and some found in the literature to demonstrate that the problem in the fittings is not due to the experimental errors of only one set of measurements.

## 2. Experimental

The new measurements were done with a 4191 A Hewlett–Packard Impedance Analyzer at a fixed frequency of 10 MHz, using a TJ 228 coaxial cell, in the range of temperatures from 293 to 353 K. A water circulation thermostat (Colora, Germany) was used to control the temperature with an accuracy of a 10th of a degree. The differences between the new set of data with the previous one was  $<0.5\%$  for all the samples measured. The samples used were pure normal alcohols of chromatographic quality (supplied by Merck), and they were appropriately distilled and dried by the usual methods. The final water content was  $<0.3\%$ , determined using the Karl Fischer technique.

The permittivity was calculated from the values of admittance of the cell with and without the sample and the equivalent circuit, using a variation of the procedure described elsewhere [7].

The system, at all temperatures, was calibrated measuring reference liquids as benzene, carbon tetrachloride, and acetone and the values obtained were within the 1% of error.

The density of each alcohol was also measured in the range of temperatures involved in this work to obtain the density number variation due to thermal expansion.

## 3. Results and conclusions

According to the theoretical models of permittivity mentioned above, it can be seen that in all of them,  $\varepsilon_0$  is a function of a set of constants and properties of the sample divided by  $T$ .

E.g., in the case of the Onsager equation [5,6], one has:

$$\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} = \frac{4\pi\rho\mu^2}{9kT}. \quad (1)$$

The left-hand side is a combination of the static permittivity value ( $\varepsilon_0$ ) and a constant, the permittivity in the high-frequency limit ( $\varepsilon_\infty$ ), and this is equal to the constant factor  $4\pi\mu^2/9k$ , times the dipole numerical density ( $\rho$ ), divided by the temperature ( $T$ ).

In the equation of Kirkwood–Fröhlich, the only difference with the previous one is a new variable in the right term ( $g$ ), which depends on  $T$ ,  $\varepsilon_\infty$ , and geometrical considerations and is quite difficult to calculate.

The left-hand side of equation (1) (which we shall call from now on, Factor of Onsager, FO, for simplicity) can be plotted against  $1/T$ . We calculate this term from the measured value of  $\varepsilon_0$  and the previously fitted value of  $\varepsilon_\infty$  [1].

If we call  $A_{\text{theo}}: 4\pi\rho\mu^2/9k$ , the graph must be a straight line, of slope equal to this factor ( $A_{\text{theo}}$ ), because we have an equation of the form:

$$FO = \frac{A_{\text{theo}}}{T}. \tag{2}$$

As we can see in figures 1–3, all the plots, for some pure alcohols, are straight lines, but their slopes are very different to the calculated values ( $A_{\text{theo}}$ ).

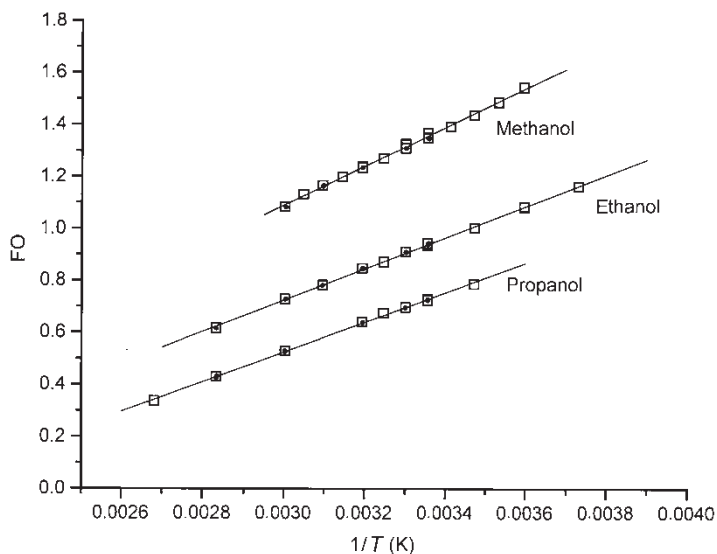


Figure 1. Factor of Onsager vs.  $1/T$  (K) for methanol, ethanol, and propanol: squares with central dot are data from our measurements, open squares are data from [9,10,12,13,16–18].

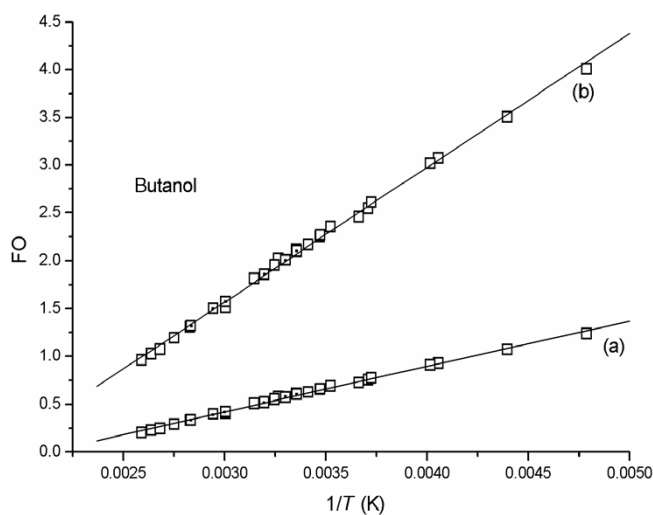


Figure 2. Factor of Onsager vs.  $1/T$  (K) for Butanol; (a) calculated with  $\epsilon_{\infty}$  (slope=475.78) and (b) calculated with  $n^2$  (slope=1405.16) (see text); symbols as for figure 1, and data from [9,10,13–16].

In the calculation we used, the tabulated values [8] of the constants present in the factor  $A_{\text{theo}}$ :  $\mu = 1.65 \text{ D}$ ;  $k = 1.38 \times 10^{-16} \text{ erg K}^{-1}$ ;  $\rho =$  numerical density of dipoles per  $\text{cm}^3$ . This value is calculated with the measured density, the Avogadro's number, and the molecular weight. Although the numerical density varies with the thermal expansion, in the measured range of temperatures this variation is  $< 1\%$ ; so it has no importance on the analyzed behavior.

In figure 2 there are two sets of data represented for butanol: in (a) we used, for calculating the Onsager's factor, the value of  $\epsilon_{\infty}$  obtained from the fittings [1], and in (b) we used the value of the square of the refraction index [8] in place of  $\epsilon_{\infty}$ . As we can see from this plot, the line (b) has a higher slope than (a); so the differences with the models are greater.

The experimental points were fitted with a line using a program of least squares, which allowed us to obtain the slope and the vertical axis intercept of the straight line.

Table 1 shows the values obtained for the factor A (slope), both experimental and theoretical.

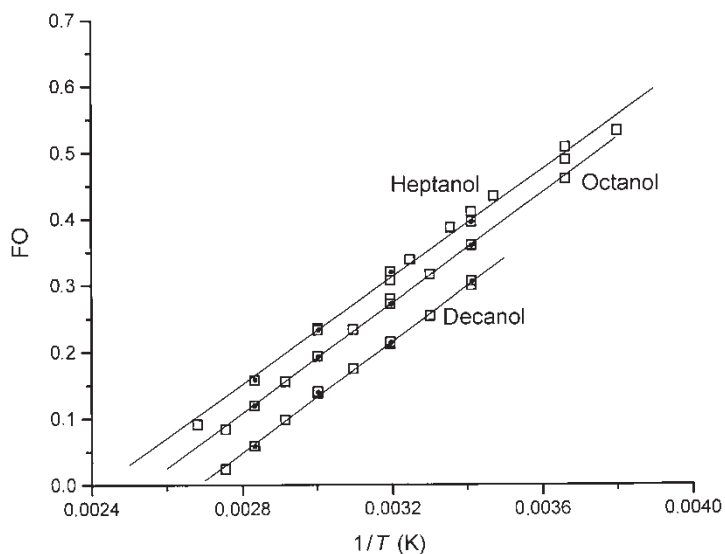


Figure 3. Factor of Onsager vs.  $1/T$  (K) for heptanol, octanol, and decanol; symbols as for figure 1, and data from [9–12].

Table 1. Theoretical and experimental slopes, and their ratio for each alcohol.

Alcohol	$A_{\text{theo}}$ (K)	$A_{\text{exp}}$ (K)	$A_{\text{exp}}/A_{\text{theo}}$
Methanol	409.88	748.13	1.83
Ethanol	284.27	603.82	2.12
Propanol	221.74	571.16	2.58
Butanol	181.25	475.98	2.63
Pentanol	153.15	455.97	2.98
Heptanol	117.34	403.37	3.44
Octanol	105.36	413.83	3.93
Decanol	86.96	416.49	4.79

The slopes obtained from the fittings increases with the number of molecules per unit volume, which means they are higher for the short alcohols than for the long ones.

This can be understood because the small molecules are more sensitive to the thermal agitation than the longer ones, and multimers are more easily broken.

Obviously these plots cannot be extended for all the temperatures, they are only reliable in the range were the alcohol remains liquid.

Neither is it sensible to analyze the values of the vertical axis intercept, because this should correspond to a practically infinite temperature.

It is important to note the quality of the plots, despite data of different works that are represented [1,9–18]. The experimental points agree with the fitted line with a very low dispersion and a correlation factor of 0.99 in all the represented cases. Also in this representation it is very easy to see if there are wrong measures because they are out of the general behavior.

In the last column of table 1 are the values of the ratio between the slopes, experimental and theoretical ( $A_{\text{exp}}/A_{\text{theo}}$ ). This ratio changes for different alcohols and increases its value with the chain length, that means, it is higher for decanol than for methanol.

The inclusion of the Kirkwood's  $g$  factor does not correct the values of the theoretical slopes, because this factor depends on temperature [6] and normally increases with the number of dipoles, and the behavior of the ratio, as seen in the table, is opposite.

For the correction we need a fixing parameter that depends only on the alcohol properties and this one must take into account the behavior of the increasing length of the alcohol tail. The influence of this tail is never considered in the derivation of the dielectric models.

Finally, this is a very clear representation that can be used to check the theoretical predictions of the different models, or the differences with them, and to evaluate the quality of the single measures.

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