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DIELECTRIC STUDY OF THE EFFECT OF DEUTERATION ON SELF-ASSOCIATION IN t-BUTANOL*

By J. Małecki and J. Nowak

Institute of Molecular Physics, Polish Academy of Sciences, Poznań**

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Results on linear and nonlinear dielectric polarization in solutions of t-BuOH and t-BuOD in n-hexane are reported, pointing to no influence of hydroxyl group polarization on the evolution of self-association of t-butanol. The change in hydrogen bond energy on deuteration is less than 5%, whereas the ratio of the bond energies of cyclic and linear multimers is affected by less than 1%.

1. Introduction

The isotopic effect on hydrogen bond properties has been studied repeatedly by IR spectroscopy [1, 2], thermodynamical [3–5] and dielectric methods [6, 7]. A fundamental problem is that of the influence of deuteration on the hydrogen bond energy and on the possibility and kinetics of proton and deuteron transfer in the bond.

Thermodynamical studies suggest that, on deuteration, the enthalpy of complex formation increases slightly by 0.2—0.5 kcal/mole. Most papers, however, fail to report any detectable isotopic effect on the energy of the bond. Rao [5], writing on the influence of deuteration on association in t–C_4H_9OH and t–C_4H_9OD, reports that the equilibrium constants and dimerisation enthalpies measured by him for the hydrogen and deuteron bonds are equal. This is in agreement with conclusions drawn from the spectroscopical results of Liddel and Becker [8]. Significantly, from IR studies, the force constants as well do not vary perceptibly on deuteration.

Nor have dielectric studies revealed any well defined isotopic effect, as shown by studies on H_2O and D_2O [6] and on solutions of normal and deuterized ethanol in benzene [7].

Here, we report dielectric results for solutions of t–BuOH and t–BuOD in n-hexane. In addition to classical dielectric polarization, we studied nonlinear dielectric effects (NDE).

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** Address: Instytut Fizyki Molekularnej PAN, Smoluchowskiego 17/19, 60-179 Poznań, Poland.

In the latter case, one measures the changes in dielectric permittivity ($\Delta\varepsilon$) under the influence of a strong electric field E. NDE is expressed in units of the material coefficient $\Delta\varepsilon/E^2$.

Solutions of alcohols exhibit large positive $\Delta\varepsilon/E^2$ values [9], a first interpretation of which is due to Piekara [10] on the basis of an electric field-induced jump of the proton in the hydrogen bond. At present it is assumed that the effects observed in alcohols are due to a field-induced shift in the association equilibria essentially between open and cyclic multimers. The idea has been suggested by Böttcher [11], Rivail and Thiebaut [12], as well as Brown and Jones [7]; the appropriate theory in general forms is due to one of us (J. M.) [13].

2. *Results of measurements*

Measurements were made for solutions of t–BuOH and t–BuOD in n-hexane. Deuteration of the alcohol was performed by mixing purified t-butanol and heavy water in the ratio 1 : 3. The solution was then distilled and dried with molecular sieves. The degree of deuteration was checked by the method of IR spectra using a 577 Perkin-Elmer spectrometer. The alcohol used in the measurements was deuterated to about 87 per cent.

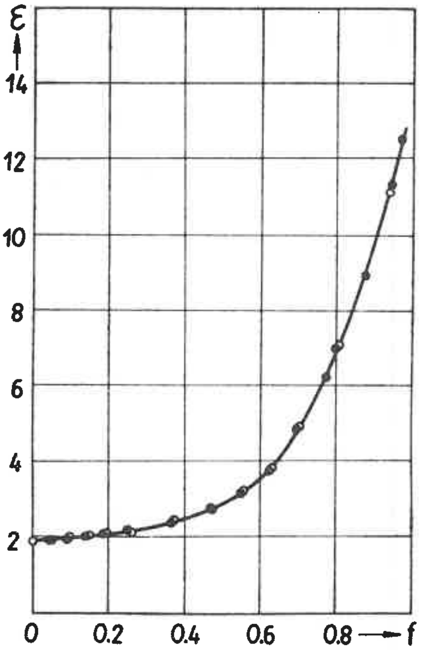

Fig. 1. Electric permittivity ε vs the concentration f of t-BuOH (●) and t-BuOD (○) in n-hexane. T = 20°C

The electric permittivity of the solutions ε was measured versus the concentration f (in molar fractions) with an accuracy of 0.1% with a DMO1 Dipolmeter, at the frequency 2 MHz, whereas $\Delta\varepsilon/E^2$ was measured with an accuracy of 3% applying the automatically

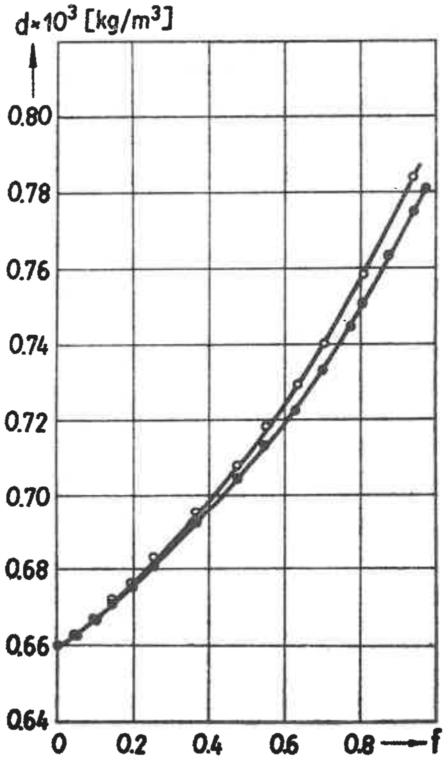

Fig. 2. Density *d* vs concentration *f*. Notations as in Fig. 1

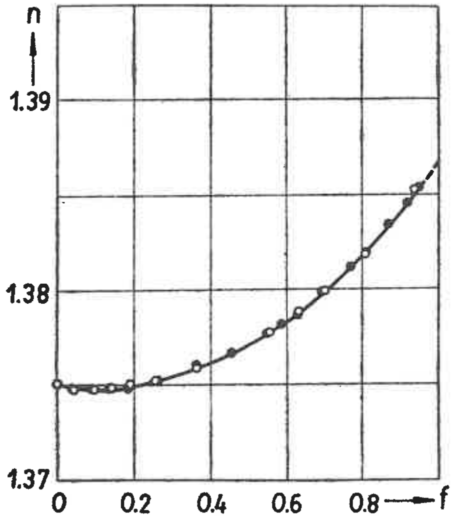

Fig. 3. Light refractive index *n* vs *f*. Notations as in Fig. 1

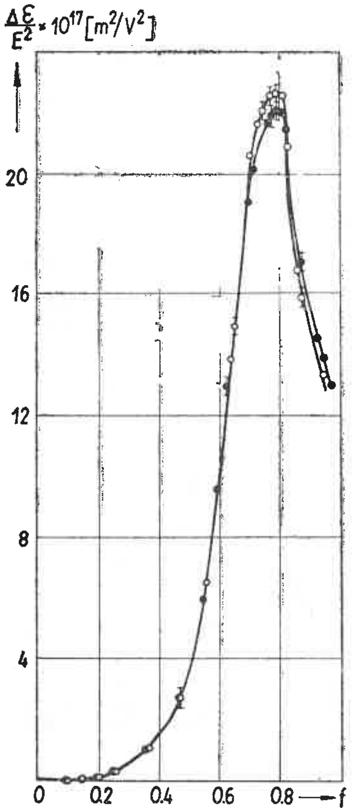

Fig. 4. $\Delta\varepsilon/E^2$ vs f. Notations as in Fig. 1

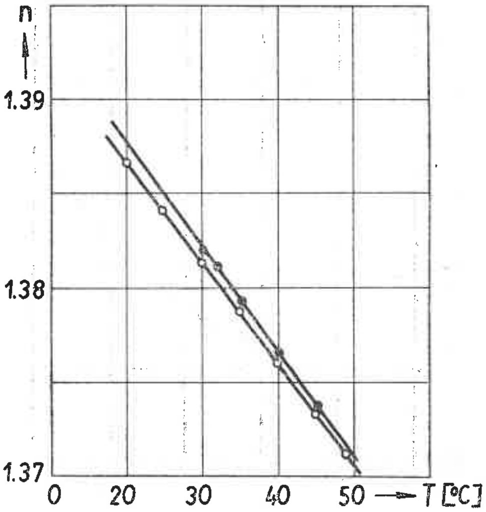

Fig. 5. Light refractive index n vs T. Notations as in Fig. 1

recording pulse device described in Refs [9, 14]. Experimental error did not exceed 0.01% when determining the density *d* and refractive index *n* of the solutions.

The measurements, at 20°C, extended throughout the entire range of concentrations. Figs 1–4 show the results for $\varepsilon(f)$, $d(f)$, $n(f)$ and $\Delta\varepsilon/E^2(f)$, respectively. The results for t–BuOH and t–BuOD do not differ essentially. The slightly higher density of t–BuOD is primarily due to the larger molecular mass. In order to calculate the molar quantities it is necessary to know *n* and *d* for the pure alcohol which, at 20°C, is a solid. We derived the necessary values by extrapolation of the temperature-dependent measurements shown in Figs 5 and 6. In the case of t–BuOD, are moreover measured *n* directly in the alcohol, over-cooled down to 20°C.

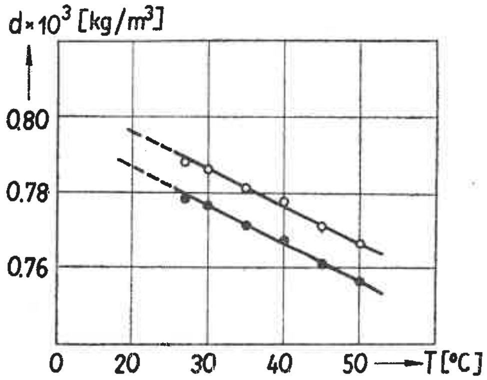

Fig. 6. Density *d* of t-BuOH (●) and t-BuOD (○) as a function of temperature *T*

3. *Discussion of the results, and conclusions*

The results are more conveniently discussed on introducing, in place of the experimental properties ε, n, d and $\Delta\varepsilon/E^2$, the molar dipole polarizability R_p and molar nonlinear polarizability R_s. We calculated R_p and R_s from previously derived formulae [15] and expressed them in dimensionless units of the linear and nonlinear molar polarizabilities of the monomer, thus obtaining the graphs of $R_p(f)$ and $R_s(f)$, plotted in Figs 7 and 8.

R_p and R_s depend on the concentrations x_i of the multimers and their dipole moments μ_i [13]:

$$R_p = \frac{1}{\mu_1^2}\sum_i \frac{x_i}{i}\,\mu_i^2, \tag{1}$$

$$R_s = \frac{1}{\mu_1^4}\sum_i \frac{x_i}{i}\,\mu_i^2\left(\mu_i^2 - \tfrac{5}{2}\,y_i\right), \tag{2}$$

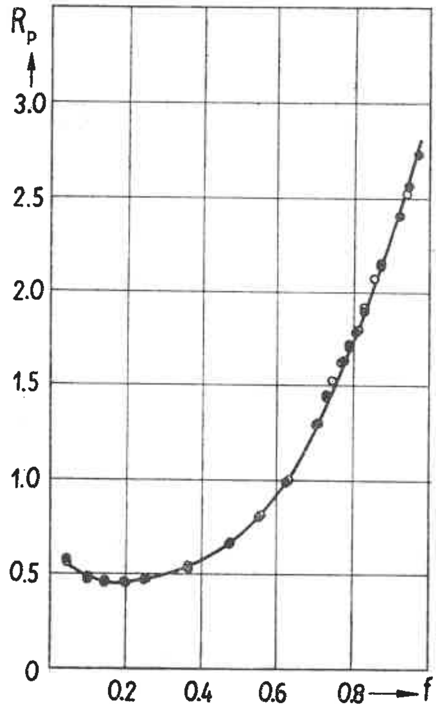

Fig. 7. R_p vs f. Notations as in Fig. 1

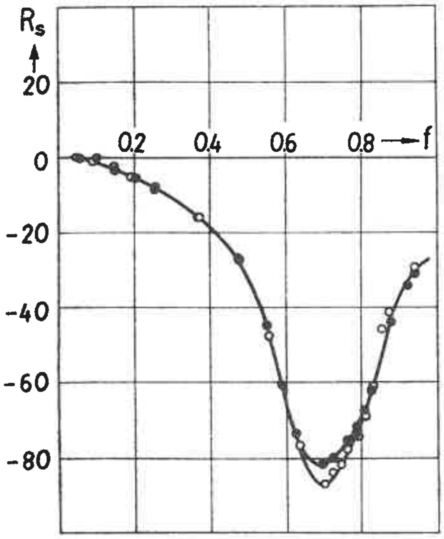

Fig. 8. R_s vs f. Notations as in Fig. 1

where the quantities y_i are proportional to the derivatives of the multimer concentrations with respect to the square of the external field $(\partial x_i/\partial(F^2))$ and can be calculated in each case provided the chemical equilibria governing the association process are known [13]. The dependence of R_p and R_s on the multimer concentrations x_i can be practically expressed by the dependence on the energies of interaction between the molecules. As shown in Ref. [13], already slight variations in interaction energy suffice to affect the values, and even the sign, of R_s. In the case of the self-association process decisive for the dielectric properties of the t-butanol solutions, the role of essential parameter is played (beside the free enthalpy of the hydrogen bonds) by the ratio of the free enthalpies of cyclic and linear bonds. A change in the latter ratio by 1 per cent causes changes in R_s markedly in excess of experimental error.

Within this framework, the results shown in Figs 7 and 8 have to be interpreted as direct proof that deuteration of the hydroxylic group has no effect on the free enthalpy of the hydrogen bonds. This conclusion is easily extended to the energy of the hydrogen bond since the changes in entropy caused by deuteration are negligible. Our evaluations show that the change in energy of the hydrogen bonds due to deuteration of t-butanol amounts to less than 5 per cent, whereas the energy ratio of cyclic and linear bonds varies by less than 1 per cent. The present results confirm with enhanced accuracy those obtained previously by various methods [1–8].

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