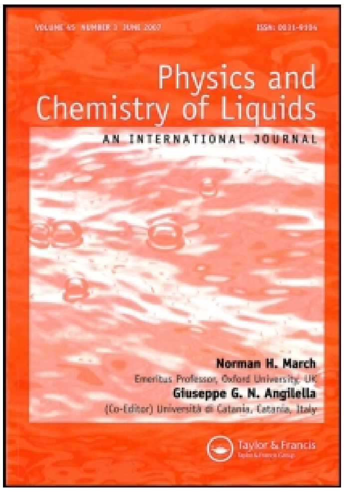

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Temperature Dependence of Dielectric Constant in Light and Heavy Water

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Letter

Temperature Dependence of Dielectric Constant in Light and Heavy Water

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It is shown that the two-state approach of water is quite successful in representing the correct temperature dependence of dielectric constant in case of light and heavy water.

The continuum theory of Onsagar[1] predicts a value of dielectric constant of water as 35 at 0°C whereas its true value is almost 88. But, the continuum theory is capable of describing accurately the behaviour of nonassociating polar liquids even with higher dipole moment than water. This may be due to the fact that the water molecules are associated by hydrogen-bond which in turn produces strong correlation between the individual molecules and thus may enhance the total polarization.

A number of theoretical calculations, based on molecular models, have been done regarding the temperature dependence of dielectric constant in water. Essentially, all these models assume that the hydrogen bonding enhances the orientation polarization while the distortion polarization is being expressed as n_D^2 where n_D is the refractive index of water corresponding to the sodium line.

Oster and Kirkwood[2] assumed a free rotation about hydrogen-bond and considered the interaction between the central molecule and the first shell of the nearest neighbours. Haggis *et al.*[3] modified this model and proposed water structure consisting of a statistical assembly where each water molecule is considered to be bonded to four-, three-, two-, one- and no other water molecule. The water molecules are allowed to pass from one form to another with the help of breaking and forming of hydrogen-bonds.

On the other hand, Lennard-Jones and Pople[4] assumed a considerable amount of bending in place of the breaking of hydrogen-bonds. This model was further extended by (i) Harris and Alder[5] who included the polarization resulting from the distortion of the molecules due to the electric field and (ii) Harris[6] who included the fluctuation effects on the molecular dipole moment. All the models discussed have a little success.

Thus, it is rather interesting to note that till today no theory of the dielectric constant in case of H_2O and D_2O is available which can predict correctly the temperature dependence of it.

The purpose of the present paper is to show that the two-state approach[7,8,9,10] is quite successful in representing the temperature dependence of dielectric constant in H_2O and D_2O. The other Physical properties of water like ultrasonic absorption,[11] NMR chemical shift[12] viscosity[13] and refractive index[14] have already been reported as successfully calculated on the basis of this approach.

From the two-state point of view, water is considered as a mixture of two-species, namely, an open-packed and a closed-packed structure, in equilibrium at all temperatures. Thus, the volume of water, V_w, in equilibrium on this approach is given as

$$V_w = X_0 V_0 + X_c V_c \tag{1}$$

where X_0, V_0 and X_c, V_c are mole fraction and molar volume corresponding to open-packed and closed-packed species, respectively. Moreover, X_0 and X_c are related by $X_0 + X_c = 1$.

Recently, Mitra *et al.*[14] have developed a relation for the refractive index of water, n_w, on the basis of two-state approach and is given as:

$$n_w = (X_0 V_0 n_0 + X_c V_c n_c)/V_w \tag{2}$$

where n_0 and n_c are the refractive index of open-packed and closed-packed species, respectively.

Equation (2) can be easily transformed to

$$(n_w - 1)V_w = X_0 K'_0 + X_c K'_c \tag{3}$$

on the basis that both n_0 and n_c follow Gladstone Dale[15] relation, that is,

$$n_0 - 1 = K'_0/V_0 \quad \text{and} \quad n_c - 1 = K'_c/V_c \tag{4}$$

In Eqs (3) and (4), K'_0 and K'_c are the temperature-independent constants.

To prove that Eq. (4) obeys the additive law of polarizibility, we rewrite Eq. (4) in term of polarizibility, α that is

$$n_0 - 1 = 4\pi N\alpha_0/V_0 \quad \text{and} \quad n_c - 1 = 4\pi N\alpha_c/V_c \tag{5}$$

Where N is the Avogadro's number. Now, substituting Eq. (5) into Eq. (2), we get the additive law, that is,

$$(n_w - 1)V_w = 4\pi N(X_0\alpha_0 + X_c\alpha_c) \tag{6}$$

Hence, Eqs (3) and (4) can be written in term of dielectric constant, ε, and are given as:

$$(\varepsilon_w^{1/2} - 1)V_w = X_0 K_0 + X_0 K_c \tag{7}$$

$$(\varepsilon_0^{1/2} - 1) = K_0/V_0 \tag{8}$$

and

$$(\varepsilon_c^{1/2} - 1) = K_c/V_c \tag{9}$$

where K_0 and K_c are new temperature-independent constants and are to be determined from the experimental data.

To calculate the temperature dependence of ε_w of H_2O and D_2O, we need the values of X_0, X_c, V_w and ε_w. The values of X_0 and X_c are taken from Davis and Litovitz[9] in case of H_2O and from Davis and Bradley[10] in case of D_2O. The values of V_w and ε_w for both the liquids are taken from Handbook of Physics and Chemistry.[16] The values of K_0 and K_c computed by least square fit are reported in Table I.

Once the values of K_0 and K_c become available then the values of ε_w can be easily calculated. The calculated values of ε_w so obtained in H_2O and D_2O are reported in Table I along with the experimental data. On comparison, it is found that the calculated values of ε_w are in very good agreement with the

TABLE I

Dielectric constant as a function of temperature in H_2O and D_2O

	H_2O				D_2O			
T°C	ε_0	ε_c	ε_w (calc.)	ε_w (exptl.)	ε_0	ε_c	ε_w (calc.)	ε_w (exptl.)
0	98.54	63.22	88.04	87.90	—	—	—	—
5	—	—	—	—	95.61	65.20	85.934	85.480
10	97.00	59.66	84.18	83.95	94.55	62.95	83.599	83.526
20	95.10	56.82	80.31	80.18	92.58	60.00	79.698	79.755
30	93.09	54.71	76.56	76.58	90.29	57.68	75.967	76.161
40	90.63	52.78	72.98	73.15	87.74	55.70	72.448	72.735
50	88.19	51.25	69.57	69.88	84.96	54.01	69.080	69.470
60	85.59	49.91	66.43	66.76	82.13	52.58	65.953	66.358
70	82.84	48.61	63.54	63.78	79.15	51.21	63.071	63.391
80	80.11	47.48	60.83	60.93	76.17	50.01	60.431	60.561
90	77.41	46.44	58.37	58.20	73.16	48.90	57.954	57.554
100	74.86	45.53	56.08	55.58	70.19	47.83	55.710	55.278
K_0			10.17				9.19	
K_c			5.25				4.85	

experimental data in case of both the liquids. The maximum discrepancy found is ±0.5% in H_2O and ±0.8% in D_2O. However, we have also reported the values of ε_0 and ε_c in these liquids by taking the values of V_0 and V_c from Refs 12 and 13.

Thus, we can conclude from the present study that the two-state approach is quite successful in representing the correct temperature dependence of the dielectric constant in the case of H_2O and D_2O.

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