TEMPERATURE DEPENDENCE OF PERMITTIVITY
OF POLAR LIQUIDS

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By means of the Eyring significant structure theory an equation was derived for calculating the temperature coefficients of permittivity of polar liquids. The calculated values of temperature coefficients agree well with experimental values. The equation derived represents, for the present best, the changes of permittivity with temperature on the basis of molecular properties of liquids.

THEORETICAL

The changes of permittivity with temperature are usually described by means of empirical and semi-empirical equations[1,2] which correspond well to the experimentally found values but have no relation to molecular properties of liquids. Dannhauser[3] analyzed the temperature dependence of permittivity by means of the Kirkwood equation

$$(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)/3\varepsilon = 4\pi N_A \mu^2 (\varepsilon_\infty + 2)^2 \, g/27VkT, \qquad (1)$$

where ε is the static permittivity of a liquid, ε_∞ is the permittivity measured at optical frequencies, N_A is Avogadro's number, V is the molar volume of liquid at a temperature T, k is Boltzmann's constant and μ is the dipole moment of the isolated molecule. Dannhauser drew a conclusion that the temperature dependence of permittivity is a resultant of several partial dependences. The main effect of temperature on permittivity is expressed by the term T^{-1} in the Debye equation, as well as in the Onsager and Kirkwood ones but the change in temperature can cause in addition to it: *a)* a change of dipole moment – especially if the molecule contains several polar groups, *b)* a change of the concentration of dipoles (change of density), *c)* a change of $\varepsilon_\infty \approx n^2$ (change of refractive index), *d)* a change of the correlation factor g. This last dependence causes that the Kirkwood equation is not suitable for calculating the temperature coefficients of permittivity.

On the basis of the significant structure theory of water Eyring and coworkers[4] proposed a new equation describing the dielectric behaviour of hydrogen-bonded liquids. According to this theory a part of molecules in liquid is bonded into some domains and only a part of molecules is mutually isolated.

TABLE I

Temperature Coefficients of Permittivity of Water and Lower Aliphatic Alcohols at 20°C

Substance	n	μ, D	ε	$-d\rho/dT \cdot 10^3$ g cm^{-3} K^{-1}	$-d\varepsilon/dT$, K^{-1} calc.	$-d\varepsilon/dT$, K^{-1} exp.	Ref.[a]
Water	1·3330	1·84	80·10	0·2100	0·306	0·364	5
Methanol	1·3286	1·69	32·35	0·9250	0·188	0·174	6
Ethanol	1·3616	1·69	25·00	0·8460	0·140	0·152	6
n-Propanol	1·3856	1·66	20·81	0·8180	0·115	0·140	6
Isopropyl alcohol	1·3771	1·63	18·62	0·8090	0·102	0·133	6
n-Butanol	1·3994	1·65	17·50	0·6990	0·090	0·104	our
Isobutyl alcohol	1·3960	1·63	17·68	0·7510	0·094	0·110	measurement

TABLE II

Temperature Coefficients of Permittivity of Some Polar Liquids at 20°C

Substance	n	ε	ρ g cm^{-3}	μ, D	$-d\rho/dT \cdot 10^3$ g cm^{-3} K^{-1}	$-d\varepsilon/dT$, K^{-1} calc.	$-d\varepsilon/dT$, K^{-1} exp.	Ref.[a]
Acetone	1·3588	21·26	0·7908	2·85	1·0000	0·118	0·100	7, 8
Cyclohexanone	1·4502	15·74	0·9495	2·90	0·8540	0·074	0·058	8, 9
Nitromethane	1·3935	38·57	1·1380	3·54	1·3400	0·200	0·160–0·180	7, 8, 9
Nitrobenzene	1·5524	35·72	1·2032	4·21	0·9870	0·172	0·174–0·185	7, 8, 9
Aniline	1·5863	7·06	1·0220	1·53	0·8650	0·030	0·020–0·030	7, 8
Acetonitrile	1·3443	37·45	0·7830	3·94	1·0600	0·190	0·160–0·180	7, 8, 9
Benzonitrile	1·5289	25·58	1·0051	4·39	0·8760	0·113	0·090–0·100	7, 8
Chlorobenzene	1·5241	5·60	1·1058	1·70	1·0600	0·022	0·017–0·020	7, 8, 9
Bromobenzene	1·5597	5·39	1·4950	1·77	1·3450	0·020	0·014–0·017	7, 8
Methyl acetate	1·3614	6·91	0·9342	1·67	1·2700	0·033	0·030	8
Ethyl acetate	1·3724	6·00	0·9006	1·76	1·1700	0·028	0·021	8
Chloroform	1·4457	4·78	1·4890	1·86	1·8600	0·016	0·017–0·019	7, 8, 9
Diethyl ether	1·3527	4·32	0·7135	1·15	1·1044	0·022	0·020	7, 8
Pyridine	1·5090	13·23	0·9820	2·20	1·0000	0·065	0·060	8

[a] It refers to the permittivity and its temperature coefficient only; references for the other quantities are given in the text.

In the Debye derivation, the mean dipole moment is obtained by space averaging the value of $\mu \cos \Theta$ over all possible values of the angle Θ and the contribution of permanent dipoles to the resulting polarization is then $\mu^2/3kT$. This holds, according to the significant structure theory, only for that part of molecules which can orient freely in the external electric field (gaslike). The mean dipole moment for solidlike parts of molecules, i.e. the molecules which form the domains is derived on the assumption that the domains can orient in the external field only in the parallel or antiparallel way. The contribution of these molecules to the resulting polarization is then $\mu^2 \cos^2 \Theta/kT$, where $\cos^2 \Theta \approx 1$.

According to the significant structure theory of liquids, the part of molecules having the solidlike character is V_s/V, where V_s is the molar volume of the solidlike structure in the liquid and V is the molar volume of the liquid at the temperature of observation. The remaining part of molecules $(V - V_s)/V$ is gaslike.

According to the theory described, the permittivity of water or other hydrogen-bonded liquid is given by the equation

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon} = \frac{4\pi N_A}{V} \left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \left[\frac{V_s}{V} \cdot \frac{\mu^2 \cos^2 \Theta}{kT} + \frac{V - V_s}{V} \cdot \frac{\mu^2}{3kT}\right]. \quad (2)$$

From this equation, the temperature coefficient of permittivity $d\varepsilon/dT$ can be already calculated. On rearranging we get

$$\frac{d\varepsilon}{dT} = \left[\frac{1}{6}K - \frac{2\pi N_A \mu^2}{kTV}\left(\frac{n^2 + 2}{3}\right)^2 + (2\varepsilon - n^2)\left(1 + \frac{K}{3(n^2 + 2)}\right)\right].$$

$$\cdot \frac{1}{\varrho}\frac{d\varrho}{dT} - \left(\varepsilon - \frac{n^2}{2}\right)\frac{1}{T}, \quad (3)$$

where $K = (n_0^2 - 1)(n_0^2 + 2)$, n_0 is the value of refractive index at 20°C, ε, n, V, and ϱ are the permittivity, refractive index, molar volume and density, respectively, at a temperature T. When deriving Eq. (3), the assumption $\varepsilon_\infty = n^2$ was used and for the temperature dependence of the refractive index, the validity of the Clausius–Mosotti equation was assumed.

RESULTS

The temperature coefficients of permittivity of water and some lower aliphatic alcohols at 20°C were calculated using Eq. (3). The calculated values are compared in Table I with the values obtained experimentally. The calculated values of the temperature coefficients of permittivity of some additional polar liquids are summarized in Table II. These liquids were chosen considering that their experimentally found

temperature coefficients were known from the literature[6-9]. The values of dipole moments were obtained from ref.[10] and the equations expressing the temperature dependence of density were taken over from International Critical Tables.

With respect to experimental errors that occur on measuring permittivity by different authors, the calculated and measured values agree very well. On the basis of this agreement it is to be assumed that all polar liquids probably form the domain structure. Eq. (3) represents, for the present best, the changes of permittivity with temperature on the basis of molecular properties of liquids.

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