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Abstract

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THE TIME OF DIPOLE RELAXATION AND THE ACTIVATION ENERGY OF BROMIDES, OBTAINED FROM SPECTROSCOPIC MEASUREMENTS

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The time of orientational relaxation is one of the principal characteristics of a dipolar liquid, since it determines the position of the dispersion region of electromagnetic waves. At present, in many cases this quantity can be determined not only directly from dispersion curves, but also by certain other indirect methods.

In the present work we give the results of determining the time of dipole relaxation in bromides by means of one such indirect method—the method of light scattering from the broadening of the scattering line. We studied 9 normal bromides, from ethyl bromide to decyl bromide. The relaxation times were determined in exactly the same way as in previous work of our laboratory (1), on an ISP-51 spectrograph with a UF-84 camera, from the broadening of the anisotropic component of the Hg 4358 Å scattering line. The investigations were carried out with carefully purified liquids contained in sealed tubes. This made it possible to heat the liquids above the boiling point by several tens of degrees. The liquids were studied at several temperatures in the interval from 20 to 160°. Only for the first two substances did we restrict ourselves to a temperature of 100°.

The results we obtained fall well on straight lines if $\lg \tau$ is plotted as a function of $\frac{1}{T}$. This indicates that the dependence of the relaxation time on temperature is described fairly well by the formula

$$\tau = \tau_0 e^{U/RT} \tag{1}$$

where U is the activation energy for reorientation of the molecules.

In our experiments we measured the relaxation time of the anisotropy, τ, which is related to the dipole relaxation time τ_{dip} by the relation

$$3\tau = \tau_{\text{dip}}. \tag{2}$$

Table 1 gives the values determined from the graphs of $\lg \tau - \frac{1}{T}$ (the values of 3τ) for three temperatures (20; 100; 160°). The error of these numbers does not exceed 10%.

Let us compare our relaxation times with the dipole relaxation times obtained from radio-wave dispersion curves. The substances considered were studied by Smyth and co-workers (2,3) at temperatures of 1; 20–25 and 55°. In the first column of Table 1 their results at 20° are given. Comparison of the two columns of values τ_{dip} and 3τ shows that, for the first members of the series, the discrepancies are within 10%; toward the end of the series the numbers differ by up to 30%. Such agreement between two series of numbers obtained by completely different methods should be considered very good.

Thus, the present work shows that in many cases the position of the radio-wave dispersion region in a dielectric can be determined with sufficiently good accuracy by a spectroscopic method in the visible region of the spectrum. The use of a new method makes it possible to study more fully

properties of a dielectric. In particular, the spectroscopic method makes it possible without great difficulty to determine the relaxation time at high temperatures up to the critical temperature.

The small difference between the value 3τ and τ_{dip} is possibly connected with the fact that relation (2), strictly speaking, applies only to molecules with an axially symmetric polarizability tensor. In the present case, when the rotational mobility of the molecule is obtained as a result of averaging its mobility about three axes, the difference between the two relaxation times may be connected with the fact that the relative contributions of these three terms to the relaxation of the dipole polarization and to the relaxation of the anisotropy are not the same.

Table 1

Relaxation times and activation energy of *n*-bromides

n-Bromides	$\tau_{\text{dip}} \cdot 10^{12}$ sec., 20°	$3\tau \cdot 10^{12}$ sec., 20°	$3\tau \cdot 10^{12}$ sec., 100°	$3\tau \cdot 10^{12}$ sec., 160°	U, kcal/mol
Ethyl bromide	4.2	4.2	2.6	–	1.35
Propyl bromide	6.2	6.4	3.9	–	1.40
Butyl bromide	9.1	10.0	6.0	4.6	1.40
Amyl bromide	13.0	14.5	8.1	6.1	1.50
Hexyl bromide	17.0	19.5	10.5	7.8	1.65

n-Bromides	$\tau_{\text{dip}} \cdot 10^{12}$ sec., 20°	$3\tau \cdot 10^{12}$ sec., 20°	$3\tau \cdot 10^{12}$ sec., 100°	$3\tau \cdot 10^{12}$ sec., 160°	U, kcal/mol
Heptyl bromide	21	26	14.0	9.8	1.75
Octyl bromide	24	33	17	12	1.80
Nonyl bromide	31	39	20	14	1.85
Decyl bromide	37	45	22	15	1.90

Another reason for the difference between 3τ and τ_{dip} may be a certain nonrigidity of the bromide molecules. If, for example, the dipole group, which here is CH_2Br, has a certain freedom of rotation independently of the remaining part of the molecule, then this, of course, will lead to a decrease in the time of dipole relaxation in comparison with the time of anisotropy relaxation. In bromides these two quantities differ little from one another; therefore there is no reason here to ascribe to the dipole group CH_2Br, or to larger units, any considerable freedom of independent rotation, as is done in work (4).

Table 1 also gives the values of the activation energy of reorientation obtained by us, from which it is seen that the activation energy in the homologous series of normal bromides gradually increases from 1.35 kcal/mol for ethyl bromide to 1.90 kcal/mol for decyl bromide. These energy values are appreciably smaller than the activation energy of dipole relaxation obtained from the temperature dependence of the dipole relaxation time (2). It is possible that such a discrepancy is explained by the fact that the study of dipole relaxation was carried out in a lower temperature interval (1-55°) than above (20-160°).

It is also of interest to compare the activation energy of reorientation U with the activation energy of viscous flow U_η. In a large number of cases, as was noted earlier (5), $U = U_\eta$. The viscosities of the bromides at temperatures 1-55° are given in work (2). We also measured the viscosities up to a temperature of 90°. The activation energies obtained from these data prove to be somewhat greater than the activation energies of reorientation, which may be connected with a certain nonrigidity of the molecules. At the same time, the data obtained by us definitely show that the mobility of individual units in the molecules of bromides is not very great. This is also confirmed by the fact that the contour of the scattering line differs little from a dispersion form.

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