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The dielectric properties of some α-w dibromo alkanes

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An investigation of the dielectric properties of some α — ω dibromo alkanes, as the pure liquids, has been made in the frequency range of 1 to 8.5 Gc/s. in order to study the behaviour of molecules with a large number of possible modes of internal rotation. Spectroscopic evidence [1] shows that the internal dipole rotation in the lower members of the α — ω dibromo alkane series is a hindered process, and the measured dipole moments of these compounds [2] are lower than the moments calculated assuming free rotation [2 *a*].

EXPERIMENTAL.

Dielectric measurements were made using a Central Research Laboratory Dielectrometer already described in previous communications from this laboratory [3]. Viscosities and refractive indices were measured using an Ostwald viscometer and an Abbe refractometer.

MATERIALS.

All materials were obtained commercially and purified before use. Their physical properties were then checked against the literature values.

EXPERIMENTAL RESULTS.

The experimental results obtained are tabulated in table 1.

In this table the viscosities (η) are given in centi poise (c. p.) units, n_D represents the refractive index, and ε' and ε'' the permittivity and loss factor respectively.

TABLE 1.

Refractive index, viscosity and dielectric data.

Compound	Temperature ° C	Frequency Gc/s	ε'	ε''	η c.p.	n_D
1:4 dibromo butane	0	1	8.74	1.31		
		3	7.27	2.89		
		8.5	4.38	2.27		
	18.5	1	8.69	0.96	2.88	1.5196
		3	7.86	2.31		
		8.5	5.08	2.39		
	34.5	1	8.50	0.70	2.13	1.5122
		3	8.05	1.90		
		8.5	5.61	2.65		
1:6 dibromo hexane	0	1	7.98	1.69		
		3	5.91	2.74		
		8.5	3.81	1.95		
	19	1	7.98	1.12	4.13	1.5061
		3	6.72	2.34		
		8.5	4.09	2.15		
	41.8	1	7.99	0.74	2.52	1.4962
		3	7.17	1.94		
		8.5	4.94	2.21		
1:8	20	1	6.80	1.20	6.01	1.4978
		3	5.29	2.07		
		8.5	3.54	1.58		
	31.5	1	6.84	0.96	4.25	1.4928
		3	5.64	1.94		
		8.5	3.79	1.70		
	44	1	6.90	0.90	3.23	1.4876
		3	6.05	1.72		
		8.5	4.16	1.74		

In cases where the system may be described by a single relaxation time (τ) the Debye equation

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty) \frac{\omega\tau}{1 + \omega^2 \tau^2} \qquad (1)$$

(where ε_0 and ε_∞ are the permittivities at very low and very high frequency respectively, and $\omega = 2\pi f$ (f = frequency in c/s)), is used to analyse the data. If ε''/f is plotted against $\varepsilon'' \times f$ then a straight line of gradient $- 4\pi^2\tau^2$ and intercept $(\varepsilon_0 - \varepsilon_\infty)\, 2\pi\tau$ should be obtained. If, however, the resulting points lie on a curve convex to the origin then there probably exists a distribution of relaxation times in the system [4]. In this case the variation of the dielectric loss factor with frequency may be analysed according to the Fuoss Krikwood equation [5]

$$\cosh^{-1} x = \cosh^{-1} \left[\left(\frac{\varepsilon''_m}{\varepsilon''} \right) \frac{2 + (1/\varepsilon'_m)^2}{2 + (1/\varepsilon')^2} \right] = 2.30\ \beta \log_{10} \frac{f_m}{f} \qquad (2)$$

where ε', ε'' are the permittivity and loss factor at frequency f, β is the distribution parameter and the subscript m refers to the properties at maximum absorption. Thus, a plot of $\cosh^{-1} x$ against $\log_{10} f$ should yield a straight line of gradient $- 2.30\ \beta$ and intercept $\log_{10} f_m$ when $\cosh^{-1} x = 0$. The values of ε''_m and ε'_m are found, by trial and error, as those values giving the best straight line for the above plot. The dielectric parameters so deduced are shown in table 2, and it is also found that these parameters agree with those obtained from a Cole-Cole arc plot.

TABLE 2.

The dielectric parameters.

Compound	Temp. °C	$\tau \times 10^{-12}$ sec.	ε''_m	β	$(\varepsilon_0 - \varepsilon_\infty)$	ε_0 (b)	ε_∞	n^2_D
1:4	0	38 ± 3	2.97	1.0	5.94	9.32	3.38	
dibromo	18.5	30 ± 2	2.73	1.0	5.46	9.00	3.54	2.31
butane	34.5	22 ± 2	2.69	1.0	5.37	8.44	3.07	2.28
1:6	0	48 ± 3	2.73	0.89	6.13 (*a*)	8.90	2.77	
dibromo	19.0	34 ± 2	2.59	0.96	5.40 (*a*)	8.43	3.03	2.27
hexane	41.8	27 ± 2	2.37	1.0	4.74	7.87	3.13	2.24
1:8	20.0	45 ± 3	2.12	0.89	4.65 (*a*)	7.55	2.90	2.24
dibromo	31.5	37 ± 3	2.05	0.92	4.46 (*a*)	7.30	2.84	2.23
octane	44.0	32 ± 2	2.00	0.94	4.26 (*a*)	7.04	2.78	2.21

(*a*) The values of $(\varepsilon_0 - \varepsilon_\infty)$ are calculated from the equation $(\varepsilon_0 - \varepsilon_\infty)\,\beta = 2\,\varepsilon''_m$ (see reference 6).

(*b*) ε_0 values are obtained from reference 2B.

At any one temperature both the relaxation time and viscosity increase with increasing chain length. However, according to the simple Debye theory

$$\frac{\tau}{\eta} = \frac{3\,V}{k\,T} \tag{3}$$

where V is the molecular volume, τ and η the relation time and liquid viscosity respectively. Thus the ratio of the relaxation time to viscosity should be a linear function of the molecular volume i.e. the number of carbon atoms in the chain. For the $\alpha - \omega$ dibromoalkanes the ratio of τ/η reaches a maximum at about 6 carbon atoms in the chain. Smyth [7] showed that the *n*-alkyl bromides also give an apparent maximum molecular volume at a chain length of six carbon atoms. This decrease in the ratio of the relaxation time to viscosity above a certain chain length indicates an increase in the ease of orientation of the molecule, and this could occur with a change in molecular shape from that of a rod towards a sphere. This effect is clearly observed in the series *n*-butyl, iso-butyl and *t*-butyl bromides. The ratio of the relaxation time to viscosity for these bromides decreases as the molecule becomes more spherical, but the viscosity increases on going from the *n*-butyl to the *t*-butyl bromide, thus showing that the ease of dipole rotation increases as the molecule becomes more spherical.

If the Onsager equation [8]

$$\mu^2 = \frac{9\,k\,T}{4\,\pi\,N_1}\;\frac{(\varepsilon_0 - \varepsilon_\infty)\,(2\,\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0\,(\varepsilon_\infty + 2)^2} \tag{4}$$

(where N_1 is the number of particles per unit volume, k is the Boltzmann constant, and T the absolute temperature) is used (taking the ε_∞ values from table 2) to determine the dipole moment of the rotating molecule then the dipole moment so deduced are very much smaller than the values calculated using refractive index data. Thus the dipole moment deduced for 1: 4 dibromo butane is 1.6 D (literature value (2 *a*) is 2.10 D); for the 1: 6 dibromo hexane is 1.9 D (literature values (2 *a*) is 2.37 D); and for the 1: 8 dibromo octane is 2.1 D (literature value (extrapolated from the data in reference 2 *a*) is 2.5 D). This difference between the ε_∞ values obtained in this work and the square of the refractive index may indicate the presence of a second absorption at much higher frequencies or it may be that the values of ε_∞ deduced here are too high. Further measurements at higher frequencies are needed to clarify this problem.

Both viscosity and dielectric relaxation may be treated as a rate process according to the well known Eyring equations [9], and the activation energies (ΔH) deduced are given in table 4.

TABLE 4.

Activation energies for viscous flow (ΔH_η) *and dielectric relaxation* (ΔH_τ).

Compound	ΔH_η k. cals./ gm. mole	ΔH_τ (k. cals./ gm. mole)
1 : 4 dibromo butane	3.62	2.5 ± 1.0
1 : 6 dibromo hexane	3.89	1.8 ± 1.0
1 : 8 dibromo octane	4.55	1.8 ± 1.0

It is seen that the activation energy for viscous flow is greater than that for the dielectric relaxation. This is not surprising as dielectric relaxation involves only rotation of the molecule, while viscous flow involves both rotation and translation of the molecule.

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DISCUSSION

M. J. Marchal. — Il est intéressant de rappeler, dans la discussion de la communication de M. Price et à la suite notamment de l'intervention de M. Piekara, les résultats obtenus dans notre laboratoire par N. Hamaide (*J. Chim. Phys.*, 1958, *55*, 9) qui a étudié, en solution benzénique, le moment électrique et la viscosité intrinsèque de divers ω-dibromoalcanes $Br\text{-}(CH_2)_n\text{-}Br$ en fonction de la valeur de n: $2 \leqslant n \leqslant 22$.

1) Les valeurs expérimentales des moments électriques se placent sur deux courbes distinctes suivant la parité de n, courbes qui se rejoignent si $n \geqslant 9$ lorsque μ a atteint la valeur limite 2,54 D. Ce fait a été interprété en tenant compte des limitations de rotation des atomes sur les cônes de valence dans le calcul de la statistique des configurations des molécules.

2) La valeur apparente 1,80 D de $\mu_{C\text{-}Br}$, calculée d'après la relation $\mu^2 = 2\mu^2_{C\text{-}Br}$ qui devrait être valable lorsque la valeur limite de μ est atteinte, est nettement inférieure à la valeur apparente 1,96 D fournie par l'étude des monobromures ($n \geqslant 4$) dans le même solvant. Cette anomalie, absente pour d'autres dérivés disubstitués analogues tels que les ω-glycols $HO\text{-}(CH_2)_n\text{-}OH$ et les ω-diméthoxyalcanes $CH_3\text{-}O\text{-}(CH_2)_n\text{-}O\text{-}CH_3$, caractérise de fortes interactions dipolaires qui doivent aussi modifier le comportement hydrodynamique des dibromoalcanes. On trouve effectivement que leur viscosité intrinsèque, malgré l'encombrement des atomes de brome, devient plus faible que celle des ω-glycols et des ω-diméthoxyalcanes si $n > 20$ et même probablement plus faible que celle des paraffines si $n > 25$ à 30. Il semble donc que les interactions dipolaires mises en évidence par l'étude de μ constituent principalement un couplage entre les deux extrémités des molécules favorisant les positions antiparallèles des dipoles terminaux. Cette conclusion qualitative permet d'expliquer à la fois la contraction des molécules mise en évidence par viscosimétrie et la faible valeur limite de μ. Elle mériterait d'être confirmée par une étude plus approfondie en fonction, par exemple, du solvant et de la nature des halogènes terminaux.