BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2805—2807 (1970)

Dielectric Relaxation of Esters in Benzene Solutions

KRISHNAJI, S. C. SRIVASTAVA and DINA NATH

Physics Department, Allahabad University, Allahabad-2, India

(Received January 5, 1970)

Dielectric relaxation times and distribution parameters of three esters in benzene solutions have been evaluated using three methods, *viz.*, Cole-Cole arc plot method, Higasi's single frequency method and the Gopal Krishna method. Three microwave frequencies have been used to determine a' and a'' apart from the static and optical frequencies for a_0 and a_∞. The distribution parameters obtained from Cole-Cole arc plot and Higasi's method are in good agreement showing that the sploes a' and a'' have been determined accurately. In these esters the values of the distribution parameter are high. Since the dipole-dipole interactions are negligible in dilute solutions, the higher values of the distribution parameter suggests the existence of multiple relaxation processes.

Earlier[1] measurements on a few esters have been carried out in the pure liquid. In order to reduce the effect of dipolar fields we have studied the esters in solutions. In this paper three esters *viz.*, ethyl capronate, ethyl α-bromobutyrate and ethyl α-bromoisobutyrate have been studied in benzene solutions at three microwave frequencies apart from the static and optical frequencies. Because of the interesting results obtained by other workers on different esters it seemed desirable to determine their dielectric relaxation.

Method of Measurement and Analysis of Data. Static permittivity was measured at the frequency 1 MHz by means of a dipolemeter based on the principle of heterodyne beat method. The cell used for the purpose was calibrated with standard liquids. Refractive indices of all the solutions were measured with the help of an Abbe's refractometer and the square of the refractive index gave the values of optical permittivity ($\varepsilon_\infty = n_D^2$).

The permittivity and dielectric loss at microwave frequencies were determined using Smyth's method[2] and the shorted standing wave technique.

The compounds were obtained from M/s Fluka AG, Switzerland. Benzene, Analar Grade (B.D.H.), was used for making the solutions and was distilled twice before use.

It has been observed by earlier workers[3] that permittivity and dielectric loss in solutions are linear functions of the concentration. Thus one can represent the permittivity and dielectric loss by the equations,

$$\begin{aligned} \varepsilon_0 &= \varepsilon_{10} + a_0 c_2 \\ \varepsilon' &= \varepsilon_1 + a' c_2 \\ \varepsilon'' &= a'' c_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty c_2 \end{aligned} \qquad (1)$$

where ε_0 is static permittivity and $\varepsilon_\infty = n_D^2$ is optical permittivity. Subscript 1 refers to the pure solvent, c_2 is the molar concentration of polar solute and a's are the slopes of the straight lines obtained by plotting the dielectric quantity against concentration. These graphs have been plotted and the slopes determined from these plots are given in Table 1.

Cole-Cole[4] semi-empirical relation for the complex permittivity, $\varepsilon^* = \varepsilon' - j\varepsilon''$ is given by

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

TABLE 1. SLOPES OF THE PLOTS OF CONCENTRATION *vs.* PERMITTIVITY AT DIFFERENT FREQUENCIES

Substance	Frequency	a'	a''
Ethylcapronate	1.0 MHz	$a_0=2.41$	—
	3.4 GHz	2.40	0.07
	9.9 GHz	1.70	0.73
	27.2 GHz	1.16	0.90
	Optical	$a_\infty=-0.27$	—
Ethyl α-bromo-butyrate	1.0 MHz	$a_0=3.46$	—
	3.4 GHz	3.28	0.14
	9.9 GHz	2.25	0.90
	27.2 GHz	0.83	0.84
	Optical	$a_\infty=-0.12$	—
Ethyl α-bromoiso-butyrate	1.0 MHz	$a_0=3.29$	—
	3.4 GHz	3.20	0.15
	9.9 GHz	2.46	0.85
	27.2 GHz	1.14	0.98
	Optical	$a_\infty=-0.11$	—

1) P. L. McGeer, A. J. Curtis, G. B. Rathmann and C. P. Smyth, *J. Amer. Chem. Soc.*, **74**, 3541 (1952).
2) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).
3) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3447 (1950).

where τ and α are the relaxation time and the distribution parameter respectively and ω is the angular frequency. Substituting equations (1) into (2) we obtain

$$a^* = a' - ja'' = a_\infty + \frac{a_0 - a_\infty}{1 + (j\omega\tau)^{1-\alpha}} \tag{3}$$

The plot of a' *vs.* a'' is an arc of a circle with its centre below the abscissa. The angle which the line joining the centre with the a_∞ point makes with the abscissa is equal to $\alpha\pi/2$. The values of τ and α can thus be determined from the Cole-Cole are plot of a' *vs.* a''.

Higasi[5] has proposed that the values of relaxation time and the distribution parameter may be determined from a measurement of a' and a'' at a single frequency in the dispersion region. The equations for τ and α are

$$\tau = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{1/2(1-\alpha)} \tag{4}$$

$$1 - \alpha = (2/\pi)\tan^{-1}(A/B) \tag{5}$$

where

$$\begin{aligned} A &= a''(a_0 - a_\infty) \\ B &= (a_0 - a')(a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2 \end{aligned} \tag{6}$$

For the three esters studied here, we have calculated τ and α from Eqs. (4) and (5) using the data at 9.9 GHz.

Relaxation times have also been determined by the Gopal Krishna method.[6] In this method ε' and ε'' of a solution are determined at a single frequency at many concentrations. A graph is then plotted between X and Y. The parameters X and Y are related to the observed quantities as follows:

$$X = \frac{\varepsilon' + \varepsilon''^2 + \varepsilon'' - 2}{\varepsilon''^2 + (\varepsilon'+2)^2} \tag{7}$$

$$Y = \frac{3\varepsilon''}{\varepsilon''^2 + (\varepsilon'+2)^2} \tag{8}$$

and $$X = P + \frac{1}{\omega\tau}Y, \quad \text{where } P = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}.$$

The slope of the straight line plot is equal to $(1/\omega\tau)$ and thus the relaxation time τ can be determined. The distribution parameter α cannot be determined by this method.

The values of τ and α determined by the above three methods are compared in Table 2.

Discussion

The values of the distribution parameter α obtained from Cole-Cole and Higasi's method are in good agreement. In the Cole-Cole method α is evaluated from the semi-circular plot of a' *vs.* a'' (Figs. 1, 2 and 3) at different frequencies and then the most probable value of the relaxation time is calculated over the whole frequency region used, while in the Higasi method α is calculated from the slopes a', a'', a_0 and a_∞ and the value of the relaxation time is calculated at the single frequency of measurement. Since the values of the distribution parameter α calculated from both the methods are in good agreement, we can say that the values of the slopes obtained at the single frequency of observation in Higasi's method are quite accurate and hence the value of τ will also be accurate.

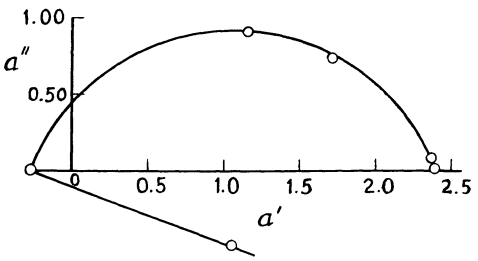

Fig. 1. Plot of a' *versus* a'' for ethyl capronate in benzene solutions.

TABLE 2. VALUES OF RELAXATION TIME AND THE DISTRIBUTION PARAMETER AT 30°C

Substance	τ and α from Cole-Cole arc plot	τ and α from Higasi method at 9.9 GHz	τ from Gopal Krishna method at 9.9 GHz
Ethyl capronate	$\tau = 7.42\times10^{-12}$ sec	$\tau = 5.98\times10^{-12}$ sec	$\tau = 6.1\times10^{-12}$ sec
$CH_3(CH_2)_4COOC_2H_5$	$\alpha = 0.23$	$\alpha = 0.27$	——
Ethyl α-bromobutyrate	$\tau = 9.69\times10^{-12}$ sec	$\tau = 7.14\times10^{-12}$ sec	$\tau = 6.5\times10^{-12}$ sec
$CH_3CH_2CHBrCOOC_2H_5$	$\alpha = 0.34$	$\alpha = 0.36$	——
Ethyl α-bromoisobutyrate	$\tau = 8.46\times10^{-12}$ sec	$\tau = 5.07\times10^{-12}$ sec	$\tau = 4.5\times10^{-12}$ sec
$(CH_3)_2CBrCOOC_2H_5$	$\alpha = 0.27$	$\alpha = 0.29$	——

4) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
5) K. Higasi, This Bulletin, **39**, 2157 (1966).
6) K. V. Gopal Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).
7) A. J. Curtis, P. L. McGeer, G. B. Rathmann and C. P. Smyth, *J. Amer. Chem. Soc.*, **74**, 644 (1952).

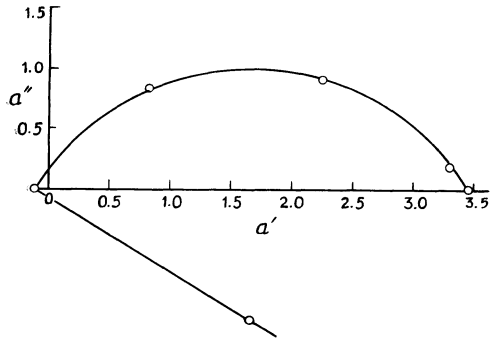

Fig. 2. Plot of a' *versus* a'' for ethyl α-bromo butyrate in benzene solutions.

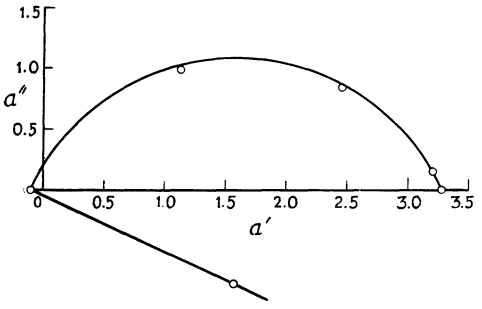

Fig. 3. Plot of a' *versus* a'' for ethyl α-isobromo butyrate in benzene solutions.

We have obtained, invariably, low values of relaxation time from the Gopal Krishna method. In this method, it has been assumed that the Debye equation of a single relaxation time holds good and the value of α is nearly zero. It means that this method is not applicable to the systems showing large distribution of relaxation times. It will give correct values of τ only in the case where α is zero or nearly zero, and smaller values of τ where α is large. The Gopal Krishna method does not give correct values also because the parameter P is not a constant as the concentration is changed.

The distribution of relaxation times obtained for these esters is large. It has been observed by some workers[8,9] that the distribution parameter in solution are larger than in pure liquid. In any liquid the distribution in the relaxation time is due to two basic causes. One factor is the variation in the local field about the individual molecule due to random field fluctuations; and the other is due to possible multiple relaxation processes in the molecule. The latter phenomenon depends on how the internal energy is distributed in the various possible ways of the motion of the molecule. In an actual case both these factors are significant in determining the value of the distribution parameter. In dilute solutions the distribution due to field fluctuations is small, and so if the distribution parameter in solution is large it indicates the existence of multiple relaxation processes.

The values of relaxation times are, however, not very high presumably due to the fact that the dipole-dipole interactions are reduced to a greater extent in dilute solutions. The value of the relaxation time of ethyl α-bromoisobutyrate is less than that of ethyl α-bromobutyrate, though both the compounds have nearly the same molar volume. Ethyl α-bromobutyrate has larger free volume of rotation than ethyl α-bromoisobutyrate, hence the volume swept away by ethyl α-bromobutyrate in the dipole rotation will be larger than the volume swept away by ethyl α-bromoisobutyrate. This explains the larger value of τ in ethyl α-bromobutyrate than in ethyl α-bromoisobutyrate.

One of us (Dina Nath) is thankful to the Atomic Energy Commission for financial support in the form of a Senior Research Fellowship.

8) E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *ibid.*, **70**, 4102 (1948).

9) V. K. Agarwal and P. Kumar, *Indian J. Pure Appl. Phys.*, **7**, 702 (1969).