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Multiple Relaxation Processes in Long Chain Molecules at Microwave Frequencies

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The permittivity ε' and dielectric loss ε'' of octanoyl, undecanoyl, and lauroyl chlorides have been measured in benzene for five different concentrations varying from 0.02 to 0.10 wt fraction at three different microwave frequencies, *viz.* 3.31, 9.83, and 26.90 GHz at 35 °C. The static permittivity ε_0 at 100 kHz and the high frequency limiting permittivity ε_∞ have also been measured at the same temperature. The permittivity and dielectric loss at different frequencies have been plotted against concentration and their slopes have been used to draw normalised complex plane plots between $(a'-a_\infty)/(a_0-a_\infty)$ and $a''/(a_0-a_\infty)$ for these compounds. Such plots show a skewed arc dielectric behaviour. The values of distribution parameter β, characteristic relaxation time τ_0, average relaxation time τ_{av}, and dipole moment μ have been reported for the first time. The relaxation mechanism in these three molecules has been explained on the basis of multiple relaxation processes.

Complex plane plots for most of the normal unassociated molecules are semicircular arcs represented by the Debye equation[1] or symmetric Cole-Cole arcs represented by the Cole-Cole equation.[2] However, there are a few exceptions. It has been observed that in case of long chain molecules[3,4] the complex plane plot is a skewed arc and can be represented by the Davidson-Cole equation.[5] Such a behaviour is also exhibited by higher thiols[6] and benzylidyne trifluoride.[7] The present studies have been carried out with three long chain molecules namely octanoyl chloride $CH_3(CH_2)_6COCl$, undecanoyl chloride $CH_3(CH_2)_9COCl$, and lauroyl chloride $CH_3(CH_2)_{10}COCl$ in dilute solutions of benzene.[8] These compounds are highly reactive and when exposed to the atmosphere react with moisture present to form hydrochloric acid. Further in pure liquids the internal field effects[9–11] are pronounced because of large dipolar field. The dielectric behaviour has, therefore, been studied in dilute solutions of benzene so that the solute molecules are in a quasi-isolated state practically unaffected by the dipolar field and solute-solute co-operative phenomenon. These molecules have been chosen because of the likelihood of multiple relaxation mechanism being present in them.

Experimental

Materials. *(a) Solute*: Octanoyl chloride of purum grade (of 98% purity), undecanoyl chloride of purum grade (of 98% purity) and lauroyl chloride of puriss grade (of 99% purity) were obtained from Messrs Fluka, A. G., Switzerland. They were used as such for experimental work.

(b) Solvent: Benzene of A. R. grade was purchased from Messrs British Drug House (India) Ltd. and was dried over sodium and fractionally distilled before use.

Experimental Details. The measurements of permittivity ε' and dielectric loss ε'' for each of the solutes in five dilute solutions of different concentrations (0.02 to 0.10 wt fraction) in benzene were made using the method suggested by Heston *et al.*[12] for low loss liquids and adapted for short circuited termination at three different microwave frequencies *viz.* 3.31, 9.83, and 26.90 GHz. The heterodyne beat method was used for determining the static permittivity ε_0 at 100 kHz. High frequency limiting permittivity ε_∞ was taken as square of the refractive index which was measured by an Abbe's refractometer. All measurements were made at 35 °C and the temperature was maintained within ±0.5 °C by circulating water from a temperature controlled bath. The values of ε', ε'', ε_0, and ε_∞ thus obtained were plotted against concentration in wt fraction. The slopes a', a'', a_0, and a_∞ are given in Table 1. The accuracy of measurement of a' is ±1 percent and of a'' is ±5 percent.

Table 1. Values of the slopes of plots of ε' and ε'' *versus* concentration

Frequency	a'	a''
(a) Octanoyl chloride		
100 kHz	$a_0=4.58$	—
3.31 GHz	4.00	1.30
9.83 GHz	2.88	2.13
26.90 GHz	0.63	1.19
Optical	$a_\infty=-0.23$	—
(b) Undecanoyl chloride		
100 kHz	$a_0=4.03$	—
3.31 GHz	3.60	1.25
9.83 GHz	2.30	1.81
26.90 GHz	0.65	1.09
Optical	$a_\infty=-0.18$	—
(c) Lauroyl chloride		
100 kHz	$a_0=3.78$	—
3.31 GHz	3.25	1.23
9.83 GHz	2.00	1.70
26.90 GHz	0.40	0.78
Optical	$a_\infty=-0.21$	—

Theory

A system having an asymmetric distribution of relaxation time can be represented by Davidson-Cole type relation.[5] This equation can be modified by substituting a', a'' *etc.* in place of ε', ε'' *etc.* The Davidson-Cole equation can be written for dilute solution as

$$\frac{a^*-a_\infty}{a_0-a_\infty}=\frac{1}{(1+i\omega\tau_0)^\beta}, \tag{1}$$

where β is a distribution parameter having values between 0 and 1, and τ_0 is the characteristic relaxation time. The average relaxation time τ_{av} is equal to $\beta\tau_0$. Putting the value of $a^*=a'-ia''$ and separating real and imaginary parts, one gets

$$a'-a_\infty = (a_0-a_\infty)(\cos\phi)^\beta \cos\beta\phi, \qquad (2)$$

$$a'' = (a_0-a_\infty)(\cos\phi)^\beta \sin\beta\phi, \qquad (3)$$

where $$\tan\phi = \omega\tau_0, \qquad (4)$$

hence $$\omega\tau_0 = \tan\left[\frac{1}{\beta}\tan^{-1}\frac{a''}{(a'-a_\infty)}\right]. \qquad (5)$$

An approximate value of β can be obtained from the skewed arc in which high frequency side approaches asymptotically a line making an angle $\beta\pi/2$ with real axis of a'. τ_0 can be calculated from Eq. 5 by substituting the measured values of $a''/(a'-a_\infty)$ at a given frequency. The value of β is then adjusted within the experimental range for getting constant value of τ_0 from different frequency data.

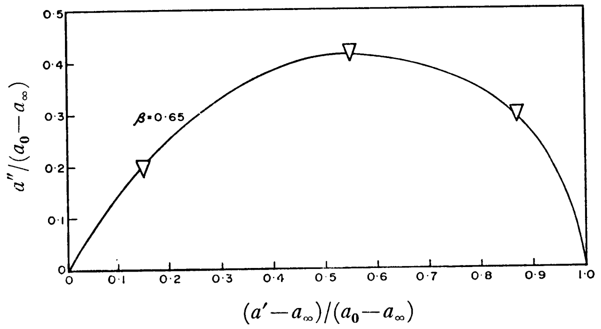

Fig. 1. Normalised plot of $(a'-a_\infty)/(a_0-a_\infty)$ *versus* $a''/(a_0-a_\infty)$ for lauroyl chloride in benzene.

A better method would be to draw curve between $(a'-a_\infty)/(a_0-a_\infty)$ and $a''/(a_0-a_\infty)$ (normalised plots) for different known values of β by varying ϕ by fixed amounts. The values of these quantities obtained experimentally are also plotted on the same graph. The value of β can be found out from the curve which fits the experimental values best. Knowing β, τ_0 can be calculated from Eq. 5 by substituting the measured values of $a''/(a'-a_\infty)$ at a given frequency. A representative normalised plot in case of lauroyl chloride is given in Fig. 1. The normalised maximum loss $a''_m/(a_0-a_\infty)$ which indicates the width of the distribution of relaxation time has also been calculated and reported in Table 2.

TABLE 2. VALUES OF β, $a''_m/(a_0-a_\infty)$, τ_0, τ_{av}, AND μ FOR OCTANOYL, UNDECANOYL AND LAUROYL CHLORIDES

Compound	β	$a''_m/(a_0-a_\infty)$	τ_0 (ps)	τ_{av} (ps)	μ (D)
Octanoyl chloride	0.75	0.430	18.6	13.6	2.74
Undecanoyl chloride	0.70	0.425	22.3	15.6	2.88
Lauroyl chloride	0.65	0.415	27.3	17.7	2.89

The dipole moments μ of these solute molecules have been calculated by the following equation proposed by Higasi:[13]

$$\mu = A(a_0-a_D)^{1/2} \qquad (6)$$

where A is a constant and is given by

$$A = \left[\frac{27kT}{4\pi N}\frac{M_2}{(\varepsilon_1+2)^2 d_1}\right]^{1/2}$$

Here d_1 is the density of the solvent and M_2 is the molecular weight of the solute. The values of μ for all the three solute molecules are reported for the first time and are given in Table 2.

Results and Discussion

The normalised arc plots for all the three solute molecules are skewed arcs which show that there is an asymmetric type of distribution of relaxation time. The value of β increases with the decrease of chain length which means that the distribution of relaxation time decreases with the decrease in chain length. In other words the distribution of relaxation time tends towards a symmetric distribution with decrease in chain length. The width of distribution of relaxation time which is indicated by the normalised maximum loss also increases with the decrease of chain length.

The skewed arc behaviour in liquids has been reported by many workers[14–17] and has been explained in terms of co-operative phenomenon and multiple relaxation processes. In dilute solutions the former possibility is ruled out. The only possible machanism which can explain the asymmetric distribution is due to multiple relaxation processes. This is borne out by the fact that the skewed behaviour increases with the increase in chain length. The molecule becomes less rigid and can relax in more than one way. A particular group or segment of the molecule may rotate, as well as the molecule may rotate as a whole. The former process has a smaller relaxation time as compared to the latter process. These are the limits between which the other relaxation times lie. The orientation of one segment may trigger many other orientations and consequently the rotating group does not relax independently. This intramolecular process has similar effects as intermolecular co-operative phenomenon which has been used to explain the skewed arc behaviour in pure liquids. The decrease in value of β with increase in chain length suggests that the segmental reorientations become increasingly possible with the increase in the number of C–C bonds, whereas with the decrease in chain length or decrease in the number of C–C bonds the segmental reorientation processes are reduced and the distribution becomes symmetric tending towards Cole-Cole behaviour. In the study of such molecules the possibility of solute-solvent interactions can not be ruled out.

The value of dipole moment increases with the increase in chain length. The characteristic relaxation time τ_0 of these compounds in solution increases with the increase in chain length, which is due to the increase in the molecular size. The average relaxation time τ_{av} also increases in the same manner as τ_0.

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References

1) P. Debye, "Polar Molecules," Dover Publication, Inc., New York (1945).

2) R. H. Cole and K. S. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

3) W. E. Vaughan, W. S. Lovell, and C. P. Smyth, *J. Chem. Phys.*, **30**, 753 (1962).

4) F. I. Mopslk and R. H. Cole, *J. Chem. Phys.*, **44**, 1015 (1966).

5) D. Davidson and R. H. Cole, *J. Chem. Phys.*, **19**, 1484 (1951).

6) Krishnaji, V. K. Agarwal, and P. Kumar, *J. Chem. Phys.*, **56**, 5304 (1972).

7) H. S. Sharma, "Dielectric Dispersion and Relaxation Mechanism in Some Trifluoro-compounds," D. Phil. Thesis, Jodhpur University, Jodhpur (1971).

8) H. D. Purohit, "Microwave Absorption and Dielectric Relaxation in Organic Molecules," D. Phil. Thesis, Jodhpur University, Jodhpur (1970).

9) C. P. Smyth, "Dielectric Behaviour and Structure," McGraw Hill Co., New York (1955), Chap. 2.

10) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdam (1952), Chap. 6.

11) R. H. Cole, *J. Chem. Phys.*, **43**, 637 (1965).

12) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3443 (1950).

13) K. Higasi, *Bull. Inst. Phys. Chem. Res.*, **22**, 865 (1943).

14) S. W. Tucker and S. Walker, *J. Chem. Phys.*, **45**, 1302 (1966).

15) S. H. Glarum, *J. Chem. Phys.*, **33**, 639 (1960).

16) D. W. Davidson, *Can. J. Chem.*, **39**, 571 (1961).

17) G. E. McDuffie, Jr. and T. A. Litovitz, *J. Chem. Phys.*, **37**, 1699 (1962).