BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1900 (1973)

Dielectric Relaxation in α,ω-Dichloroalkanes in Benzene Solution

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(Received June 16, 1972)

We have recently reported the asymmetric dielectric behaviour for α,ω-dichloroalkanes in pure liquid.[1] In order to confirm the behaviour, dielectric studies have been made in dilute solutions since the result would give an idea of the molecular structure in quasi-isolated state. Dielectric constants and loss of five α,ω-dichloroalkanes (1,2-dichloroethane; 1,4-dichlorobutane; 1,6-dichlorohexane; 1,8-dichlorooctane; and 1,10-dichlorodecane) have been measured at frequencies 450 KHz, 1.8 GHz, 4.0 GHz, and 23.7 GHz in dilute benzene solution at 35°C. The experimental arrangement and procedure are the same as described earlier.[2,3] An asymmetric distribution of relaxation time has been obtained for all cases giving skewed arcs when the dielectric loss slope is plotted against the dielectric constant slope (Fig. 1).

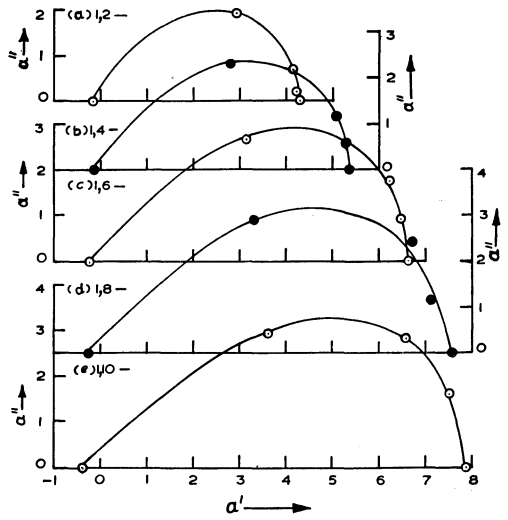

Fig. 1. Complex plot between a'' and a' for some α,ω-Dichloroalkanes in benzene solution.

The results have been analysed in terms of the Davidson-Cole plot.[4] They indicate the presence of some cooperative phenomenon in case of associated liquids[7,8] with a few exceptions.[1,5,6] Skewed arc behaviour in α,ω-dichloroalkanes can be understood in terms of intramolecular cooperative relaxation mechanism, *viz*; the intramolecular group rotations are such that the rotating electric moments interact sufficiently with one another and the reorientation of one segment triggers many other reorientations. Thus this intramolecular cooperative phenomenon has similar effect to that of intermolecular cooperative phenomena known to give skewed arc dielectric behaviour.

TABLE 1. DIELECTRIC RELAXATION PARAMETERS OF α,ω-DICHLOROALKANES IN BENZENE SOLUTION AT 35°C ASSUMING A DAVIDSON-COLE TYPE DISTRIBUTION

Parameters	1,2-DCE	1,4-DCB	1,6-DCH	1,8-DCO	1,10-DED
$\tau_{cs} \times 10^{12}$ (s)	7.3	11.6	16.5	23.6	31.6
β_{sol}	0.67	0.64	0.61	0.59	0.57

The characteristic relaxation time (τ_{cs}) and asymmetric distribution parameter (β_{sol}) in solution are presented in Table 1. We see that the value of τ_{cs} increases with increasing chain-length. The value of β_{sol} increases with decreasing chain-length suggesting more rigid structure with decreasing chain-length.

The authors are thankful to Prof. D. Sharma for his interest in the work.

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