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Microwave Absorption and Molecular Structure in Liquids. LXXV. The Relaxation Processes of Several Long-Chain Aliphatic Molecules in *n*-Heptane Solutions[1]

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Abstract: The dielectric constants and losses of di-*n*-butyl ether, *n*-dodecyl methyl ether, *n*-octylaldehyde, *n*-octylamine, *n*-octyl bromide, and *n*-octanone-2 have been measured at 0.2, 1.2, 3.2, 9.9, 24.8, and 49.8 cm wavelengths at several concentrations in *n*-heptane solution at 25°. Asymmetric plots for dielectric loss against dielectric constant are found for di-*n*-butyl ether, *n*-dodecyl methyl ether, *n*-octylaldehyde, and *n*-octylamine. *n*-Octyl bromide and *n*-octanone-2 show symmetrical depressed center arcs. Analyses in terms of two relaxation times for the first four compounds yield consistent parameters for molecular and intramolecular rotation. *n*-Octyl bromide and *n*-octanone-2 are more reasonably described in terms of a distribution of relaxation times.

The dielectric absorption in most aromatic compounds having a rotatable polar group is characterized by two discrete relaxation processes: an intramolecular, having a small relaxation time, and a molecular, with a relatively large relaxation time.[3] In contrast to this, many aliphatic compounds have been found to show a symmetrical distribution of relaxation times. The *n*-alkyl bromides have been systematically investigated as pure liquids[4,5] and in solutions[6] at microwave frequencies. A large distribution increasing with increasing chain length was reported and interpreted, first, in terms of a possible distribution around a single most probable relaxation time[4–6] and, later, as possibly arising from a distribution of relaxation times between two extreme values corresponding to $-CH_2Br$ and molecular end-over-end rotation.[7,8] One would expect most long-chain molecules to exhibit such behavior However, measurements in this laboratory on severa long-chain ethers and sulfides in dilute solution showed different behavior in that they gave Cole–Cole plots exhibiting quite clearly two dispersion regions.[9] Actually, the behavior found in ethers and sulfides may be consistent with rather than in contradiction to the mechanism proposed by Higasi, Bergman, and Smyth for relaxation in long-chain molecules at microwave frequencies.[7] In alkyl bromides, and in other compounds, where the polar group and the segmental reorientation both occur about C–C bonds, which have similar potential energy barriers to internal rotation, it is possible to define a distribution by eq 1 between limits as in ref 7, but when the polar group reorientation occurs about a bond different from that of segmental reorientation, the difference in the barrier heights to rotation may be expected to give rise to a distribution of energies different from that defined in ref 7. One would then anticipate the existence of two relaxation processes in long-chain

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[1] This research was supported in part by the U. S. Army Research Office (Durham). Reproduction in whole or in part by or for the U. S. Government is permitted.

[2] Author to whom correspondence should be addressed.

[3] C. P. Smyth, *Advan. Mol. Relaxation Processes*, **1**, 1 (1967–68).

[4] W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4093 (1948).

[5] F. H. Branin, Jr., and C. P. Smyth, *J. Chem. Phys.*, **20**, 1121 (1952).

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

[7] K. Higasi, K. Bergman, and C. P. Smyth, *J. Phys. Chem.*, **64**, 880 (1960).

[8] W. E. Vaughan, W. S. Lovell, and C. P. Smyth, *J. Chem. Phys.*, **36**, 753 (1962).

[9] S. Dasgupta, K. N. Abd-El-Nour, and C. P. Smyth, *ibid.*, **50**, 4810 (1969).

Table I. Dielectric Constant and Loss Data for Some Aliphatic Compounds (Mole Fraction, f_2) in *n*-Heptane Solutions at 25°

λ_0, cm	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
			Di-*n*-butyl Ether					
	f_2 = 0.081		f_2 = 0.140		f_2 = 0.204		f_2 = 0.249	
0.205	1.931	0.014	1.946	0.026	1.962	0.038	1.973	0.047
1.199	1.977	0.023	2.012	0.041	2.052	0.058	2.085	0.074
3.226	1.988	0.018	2.040	0.034	2.096	0.048	2.133	0.060
9.856	1.999	0.007	2.060	0.013	2.128	0.019	2.177	0.025
24.75	2.000	0.004	2.063	0.005	2.134	0.008	2.183	0.010
49.82	2.003	0.001	2.067	0.003	2.137	0.004	2.186	0.005
3×10^6	2.003		2.069		2.141		2.190	
			n-Dodecyl Methyl Ether					
	f_2 = 0.091		f_2 = 0.202					
0.204	1.956	0.017	2.001	0.035				
1.203	1.995	0.036	2.076	0.074				
3.226	2.018	0.031	2.113	0.070				
9.990	2.036	0.019	2.175	0.044				
24.77	2.044	0.011	2.197	0.025				
49.88	2.047	0.007	2.201	0.014				
3×10^6	2.048		2.202					
			n-Octanone-2					
	f_2 = 0.008		f_2 = 0.016		f_2 = 0.033			
0.205	1.926	0.010	1.935	0.022	1.947	0.040		
1.199	1.949	0.011	1.978	0.027	2.037	0.050		
3.226	1.955	0.007	1.999	0.018	2.066	0.035		
9.856	1.956	0.004	2.003	0.007	2.085	0.015		
24.75	1.957	0.001	2.004	0.004	2.086	0.006		
49.82	1.957	0.001	2.004	0.001	2.087	0.002		
3×10^6	1.958		2.004		2.087			
			n-Octylaldehyde					
	f_2 = 0.017		f_2 = 0.029		f_2 = 0.036		f_2 = 0.048	
0.205	1.941	0.018	1.956	0.033	1.967	0.041	1.980	0.054
1.199	1.960	0.020	2.003	0.034	2.029	0.047	2.069	0.057
3.226	1.974	0.015	2.023	0.025	2.055	0.034	2.095	0.044
9.856	1.985	0.008	2.043	0.015	2.081	0.018	2.129	0.024
24.75	1.990	0.003	2.051	0.007	2.086	0.009	2.138	0.011
49.82	1.990	0.002	2.051	0.004	2.086	0.009	2.139	0.006
3×10^6	1.990		2.053		2.087		2.140	
			n-Octylamine					
	f_2 = 0.072		f_2 = 0.124		f_2 = 0.164		f_2 = 0.198	
0.202	1.981	0.024	2.021	0.047	2.047	0.106	2.094	0.103
1.199	2.013	0.017	2.083	0.038	2.158	0.057	2.245	0.052
3.226	2.020	0.013	2.112	0.026	2.203	0.040	2.285	0.051
9.856	2.025	0.005	2.124	0.010	2.219	0.015	2.311	0.021
24.75	2.027	0.002	2.126	0.003	2.223	0.007	2.317	0.009
49.82	2.028	0.001	2.126	0.003	2.223	0.005	2.317	0.006
3×10^6	2.028		2.126		2.223		2.318	
			n-Octyl Bromide					
	f_2 = 0.032		f_2 = 0.053		f_2 = 0.076		f_2 = 0.113	
0.204	1.928	0.012	1.938	0.020	1.945	0.026	1.962	0.039
1.203	1.955	0.036	1.985	0.050	2.015	0.075	2.060	0.109
3.226	1.973	0.029	2.007	0.047	2.057	0.068	2.123	0.100
9.856	2.000	0.023	2.056	0.037	2.119	0.052	2.213	0.075
24.75	2.014	0.013	2.078	0.020	2.153	0.030	2.274	0.047
49.82	2.014	0.006	2.082	0.015	2.154	0.015	2.277	0.024
3×10^6	2.014		2.085		2.156		2.280	

molecules having a polar group rotating about a bond other than the C–C bond, as in ethers, amines, alcohols, etc. In order to examine this possible behavior in long-chain molecules having polar groups capable of rotating around bonds other than the C–C bond, this paper reports on a study of several octyl compounds in dilute *n*-heptane solutions.

Experimental Methods

Apparatus. Dielectric constants and losses were measured at 0.2, 1.2, 3.2, 10, 25, and 50 cm wavelengths by methods which have been described previously.[4–6,10,11]

Purification of Materials. All chemicals were obtained from Aldrich Chemical Co. *n*-Dodecyl methyl ether was dried over sodium and fractionally distilled, while *n*-octyl bromide was dried over calcium chloride and distilled. *n*-Octanone, *n*-octylaldehyde, and di-*n*-butyl ether were refluxed over calcium hydride and fractionally distilled under reduced pressure. *n*-Octylamine was dried over calcium chloride and fractionally distilled under reduced pressure. *n*-Heptane (Matheson Coleman and Bell) was stored over sodium wire and used as such.

Results

The experimental values of the dielectric constant, ϵ', and dielectric loss, ϵ'', are given in Table I. Figures 1–6 show typical plots for each system. For *n*-octanone-2 (Figure 3) and *n*-octyl bromide (Figure 6) it was possible to draw smooth depressed-center, semi-

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(10) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(11) S. K. Garg, H. Kilp, and C. P. Smyth, *J. Chem. Phys.*, **43**, 2341 (1965).

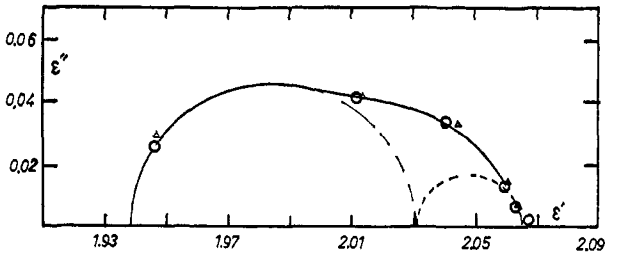

Figure 1. Cole-Cole plot for di-*n*-butyl ether in *n*-heptane solution at f_2 = 0.140. Triangles are the points calculated with the parameters in Table II.

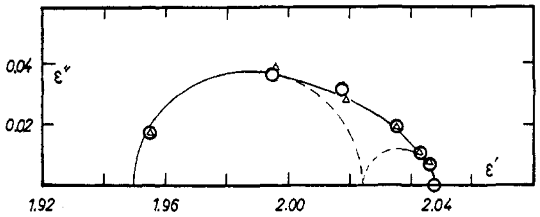

Figure 2. Cole-Cole plot for *n*-dodecyl methyl ether in *n*-heptane solution at f_2 = 0.091. Triangles are the points calculated with the parameters in Table II.

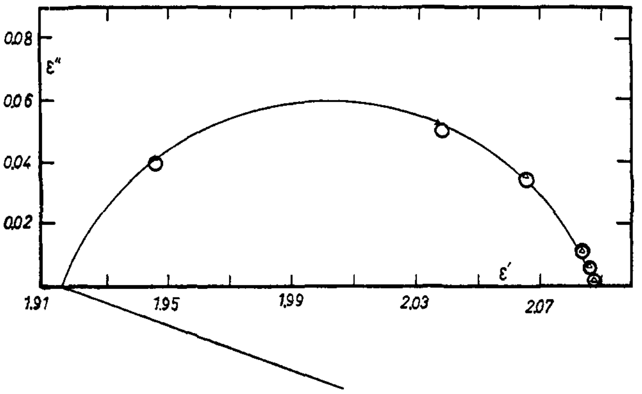

Figure 3. Cole-Cole plot for *n*-octanone-2 in *n*-heptane solution at f_2 = 0.032. Triangles are the points calculated with the parameters in Table II.

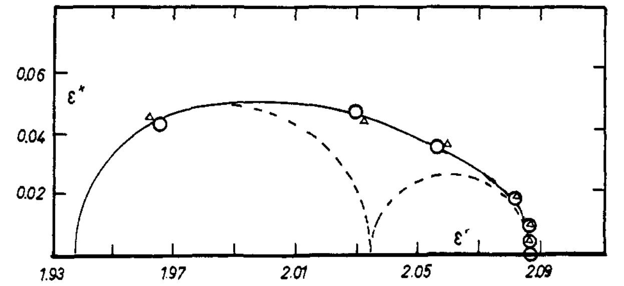

Figure 4. Cole-Cole plot for *n*-octylaldehyde in *n*-heptane solution at f_2 = 0.036. Triangles are the points calculated with the parameters in Table II.

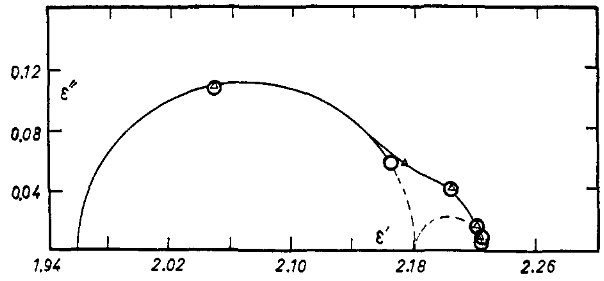

Figure 5. Cole-Cole plot for *n*-octylamine in *n*-heptane solution at f_2 = 0.165. Triangles are the points calculated with the parameters in Table II.

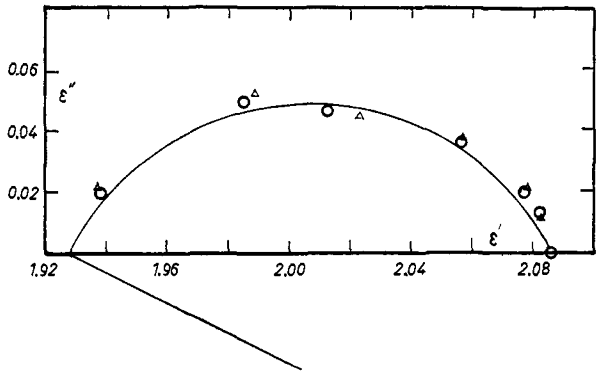

Figure 6. Cole-Cole plot for *n*-octyl bromide in *n*-heptane solution at f_2 = 0.053. Triangles are the points calculated with the parameters in Table II.

circular arcs through the points. These data were analyzed by an IBM 7094 computer programmed to solve the Cole-Cole equation for the most probable relaxation time, τ_0, distribution parameter, α, and very high-frequency or optical dielectric constant ϵ_∞. The plots for the other systems were asymmetric. In all cases an attempt was made to analyze the data in terms of a superposition of two Debye-type dispersion regions by a previously described computer-based method.[12] The values of ϵ' and ϵ'' calculated from the computer analysis are compared with the experimental points in Figures 1-6. Apparent dipole moments (μ) were calculated using the equation

$$\mu = 0.01281[3T(\epsilon_0 - \epsilon_\infty)]/(\epsilon_0 + 2)(\epsilon_\infty + 2)c$$

where c is the concentration in moles/ml. The values of ϵ_∞, α, τ_0, τ_1, τ_2, C_2, and μ obtained by the above procedure are listed in Table II.

Discussion

The Cole-Cole plots for di-*n*-butyl ether, *n*-dodecyl methyl ether, *n*-octylaldehyde, and *n*-octylamine (Figures 1, 2, 4, and 5) at all concentrations are asymmetric and indicate the presence of more than one dispersion region. The *n*-octanone-2 and *n*-octyl bromide data fit smooth, depressed-center, semicircular arcs (Figures 3 and 6). These molecules are of two types, in which more or less analogous dipole orientations and dielectric dispersions would be anticipated. The two apparently different types of absorption behavior in these solutions are intriguing. Because of the different dispersions obtained, it is more convenient to discuss each system separately.

Di-*n*-butyl Ether. Although the Cole-Cole plot for this compound can be drawn as a smooth depressed-center arc with a large distribution parameter, the data are best represented in terms of two dispersion regions, the parameters in Table II giving a fairly good fit at all

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[12] S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, **46**, 373 (1967).

Table II. Optical Dielectric Constants, Distribution Parameter, Relaxation Times, Relative Contribution, and Dipole Moment in *n*-Heptane Solutions at 25°

f_2	ϵ_∞	α	τ_0, psec	τ_1, psec	τ_2, psec	c_2	μ, D
Di-*n*-butyl Ether							
0.081	1.922			18.5	3.4	0.77	1.21
0.140	1.926			14.3	3.4	0.75	1.18
0.204	1.934			15.6	3.4	0.77	1.20
0.249	1.935			15.4	3.5	0.75	1.18
n-Dodecyl Methyl Ether							
0.091	1.950			(50.4)	4.9	0.74	1.24
0.202	1.984			34.5	4.2	0.62	1.25
0.152[a]				36.1	3.7	0.71	1.28
n-Octanone-2							
0.008	1.914	0.23	4.0				2.56
0.016	1.917	0.27	4.1				2.68
0.033	1.917	0.23	4.0				2.63
n-Octylaldehyde							
0.017	1.925			17.9	1.8	0.55	2.31
0.029	1.937			18.6	1.9	0.65	2.31
0.036	1.937			17.5	1.9	0.65	2.33
0.048	1.943			17.5	1.9	0.65	2.34
n-Octylamine							
0.072	1.968			15.4	1.9	0.83	1.17
0.124	1.970			15.4	1.9	0.83	1.17
0.164	1.998			16.4	1.3	0.83	1.45
0.198	2.025			15.4	1.8	0.75	1.30
n-Octyl Bromide							
0.032	1.920	0.16	11.2				1.98
0.053	1.934	0.28	12.7				1.98
0.076	1.935	0.19	12.7				1.98
0.112	1.948	0.19	12.7				1.95

[a] Results from ref 9 given for comparison.

concentrations. The τ_2 value of 3.4×10^{-12} sec is smaller than would be expected for $-OC_4H_9$ reorientation by rotation about the O–C bond, being even smaller than found for the $-OCH_3$ group in *n*-dodecyl methyl ether in the present investigation. As has been discussed earlier,[9] in symmetrical ethers, the dipole orientation may occur by twisting around the C–O bond, which will give rise to a much shorter relaxation time for an intramolecular process. The τ_1 value of $\sim 16 \times 10^{-12}$ sec is consistent with those of the other molecules having the same number of carbon atoms. As indicated by the values of c_2, the relative contribution of the intramolecular process, in Table II, the absorption region is dominated by the intramolecular process.

***n*-Dodecyl Methyl Ether.** The asymmetric plots of dielectric constant against dielectric loss for this compound were analyzed in terms of two relaxation times (Table II). As seen in Figure 2 there is good agreement between the calculated and measured values. It is difficult to estimate the effect of resonance on the potential barrier for group rotation, but, in view of the values of 6.2×10^{-12} sec for *p*-dimethoxybenzene and 6.5×10^{-12} sec for anisole in benzene at 20°,[13] the τ_2 value seems reasonable for $-OCH_3$ rotation in this ether. The τ_1 value of 34.5×10^{-12} sec for the 0.202 solution agrees satisfactorily with the value previously found for the 0.152 solution, but the value 50.4 for the 0.091 solution suggests an unusually large error.

***n*-Octanone-2.** The data are well represented by the arc in Figure 3. It is interesting to note that the distribution parameter value is much larger than that found for acetone, *n*-heptanone-2, and *n*-heptanone-4 as pure liquids.[14] The data can also be analyzed in terms of two relaxation processes, but the values thus obtained for the various parameters are unrealistic. The most probable relaxation time, $\tau_0 = 4 \times 10^{-12}$ sec, is, as might be expected, lower than that of pure *n*-heptanone-2, $\tau_0 = 13 \times 10^{-12}$ sec, and is also smaller than the value $\sim 7 \times 10^{-12}$ sec which has been found for the acetyl group rotation in aromatic molecules studied in solutions at similar temperatures.[15,16] However, in benzene solution at 25°, the acetone molecule, which rotates about axes perpendicular to the C=O bond sweeping out a volume similar to that swept out by the acetyl group in *n*-octanone-2, has a relaxation time of 3.2×10^{-12} sec.[17,18] The small value of τ_0 suggests that there is little contribution from the rotation of larger segments in the molecule, the acetyl group rotation being the dominating process.

***n*-Octylaldehyde.** Examination of the asymmetric Cole–Cole plots for this compound (Figure 4) reveals, in contrast to the ketone, fairly well defined contributions from species other than the relatively small end groups. The data were analyzed for two relaxation times, which give a reasonable fit to the experimental values (Figure 4). The short τ_2 values in Table II can be accounted for by –CHO group rotation though they are shorter than anticipated by analogy with –OH relaxation times in alcohols (3×10^{-12} sec).

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(13) E. Forest and C. P. Smyth, *J. Am. Chem. Soc.*, **86**, 3473 (1964).

(14) J. H. Calderwood and C. P. Smyth, *ibid.*, 78, 1295 (1956).

(15) D. Farmer and S. Walker, *Tetrahedron*, 22, 111 (1966).

(16) F. K. Fong and C. P. Smyth, *J. Am. Chem. Soc.*, **85**, 548 (1963).

(17) D. H. Whiffin and H. W. Thompson, *Trans. Faraday Soc.*, **41A**, 114 (1946).

(18) F. J. Cripwell and B. B. M. Sutherland, *ibid.*, **42A**, 149 (1946).

n-**Octylamine.** The separation into two absorption regions is even more apparent for this molecule (Figure 5) and the analyses, presented in Table II, yield ϵ' and ϵ'' values in good agreement with the experimental results. In this case, the assignment of τ_2 is complicated by the possibility of inversion of the nitrogen atom as a relaxation mechanism. The values $\sim 2 \times 10^{-12}$ sec are slightly longer than those obtained for aniline and N,N-dimethylaniline, which gave evidence of inversion, and almost identical with the τ_2 values for *n*-octylaldehyde. The τ_1 values are of the same order as those for *n*-octylaldehyde.

n-**Octyl Bromide.** This compound has been previously measured as the pure liquid[4,5,8] and in solution.[6] The latter measurement did not include millimeter points, but, as with the pure liquid, for which 2- and 4-mm data were obtained, the Cole–Cole plot showed a broad dispersion (Figure 6). An attempt was made to analyze the data in terms of two discrete relaxation processes. The τ_2 values obtained from this analysis were similar to the shorter limit obtained by Vaughan, Lovell, and Smyth[8] for isobutyl bromide and amyl bromide ($\sim 6 \times 10^{-12}$ sec), but the τ_1 values were much longer than those for *n*-octylamine, *n*-octylaldehyde, and di-*n*-butyl ether and even longer than in *n*-dodecyl methyl ether which shows that absorption in *n*-octyl bromide cannot be satisfactorily described in terms of two relaxation processes. It has been mentioned that the dielectric absorption in *n*-alkyl bromides can more plausibly be represented by a distribution function between limits corresponding to $-CH_2Br$ group and molecular rotation.[7,8] The most probable relaxation time of 12×10^{-12} sec and distribution parameter, $\alpha = 0.19$ (Table II), are very close to those obtained earlier in this laboratory in *n*-heptane solution at 20° ($\tau_0 = 11 \times 10^{-12}$ sec, $\alpha = 0.24$) at wavelengths down to 1.2 cm only.[6] It seems that the behavior of *n*-octyl bromide is best described by a distribution of relaxation times, rather than two discrete processes.

The dipole moments calculated for the molecules in Table II are in good agreement with values obtained by conventional methods,[19] it being borne in mind that the use of ϵ_∞ in these calculations, instead of the square of the refractive index, should give slightly lower and more nearly correct values.

Conclusions

In the absence of more exact analyses, due to an insufficient number of data points, the relaxation times presented in Table II and discussed above may be an over-simplification in some cases. However, several results which seem common to all these molecules, obtained from the foregoing analyses, are worth pointing out. The relaxation times τ_2 for end-group reorientation in molecules where separation into two dispersion regions is clearly seen are generally lower than those found in aromatic molecules having the same polar group at comparable solvent viscosity and temperature. This would not seem unreasonable since the potential barrier to rotation for a polar group in an aromatic molecule may be considerably increased by resonance with the aromatic ring. The Cole–Cole plots, the c_2 values, and also the τ_0 values, in cases where a distribution of relaxation time seems more plausible, show that contribution due to the faster relaxation process is dominant.

It appears from this study that aliphatic molecules in which the polar group rotation occurs about a bond other than the C–C bond, as well as around the C–C bond, tend to show two relaxation processes, while those in which the polar group reorients only about C–C bonds tend to show a distribution of relaxation times. It is interesting to note that, in dilute solutions, long-chain alcohols,[20,21] sulfides, and ethers[9] show two discrete relaxation processes, while alkyl cyanides,[22] halides,[4–8] and ketones[14] show a distribution of relaxation times consistent with the mechanism proposed earlier. It must be pointed out, however, that the foregoing observation is based on a highly simplified picture of a complicated process, but appears at least qualitatively valid. The increased number of possible modes of dipolar reorientation with increasing chain length tend to complicate this further.

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[19] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[20] F. F. Hanna and G. Klages, *Z. Electrochem.*, **65**, 620 (1961).

[21] G. P. Johari and C. P. Smyth, *J. Am. Chem. Soc.*, in press.

[22] Krishnaji and A. M. Singh, *J. Chem. Phys.*, **41**, 827 (1964).