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Solvent Effect on the Dielectric Properties of Nitroalkanes

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Permittivity and dielectric loss of four nitroalkanes have been measured in solution in three solvents *viz.*, *n*-heptane, benzene and cyclohexane at 9.8 GHz and 30°C. The variation of the relaxation time calculated from the data, with the viscosity of the solutions has been discussed. It has been found that the results cannot be explained on the basis of known relations between relaxation time and viscosity. It is expected that some other interactions such as proton-proton interaction are responsible for the relaxation time in cyclohexane lower than in benzene. The loss tangents are found to vary linearly with the concentration of the solution. Dipole moments have also been evaluated in all the three solvents and are in good agreement with the values in literature within experimental error.

The measurement of dielectric relaxation time provides a means of studying the molecular interaction and intermolecular forces. Many papers have appeared in which the authors have given the relaxation time of polar molecules in non-polar solvents. They have tried to correlate the relaxation time with some molecular model but with only partial success. Most of the work has been done to prove or disprove the theory given by Debye.[1] The Debye theory considers the molecule as a sphere embedded in a continuous viscous fluid with inner friction coefficient ζ which is related to the relaxation time τ by

$$\tau = \zeta/2kT.$$

Using Stokes' law, Debye identifies the inner friction coefficient with the viscosity η of the fluid by

$$\zeta = 8\pi\eta a^3,$$

where a is the radius of the sphere. Thus the Debye equation becomes

$$\tau = \frac{4\pi\eta a^3}{kT}.$$

Several empirical and semi-empirical formulae have been suggested to modify the Debye equation. On the basis of the present theories, it is expected that the relation between ln τ and ln η will be linear. It has been found that this is not true for the case of nitroalkanes when τ is measured in solvents of different viscosity *viz.*, *n*-heptane, benzene and cyclohexane.

Experimental

Measurements have been made at 9.8 GHz and at 30°C. The permittivity and dielectric loss (ε' and ε'') have been determined using Smyth's method[2] and short wave technique. The relaxation time τ and the dipole moment μ were then determined by the Gopal

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TABLE 1. PERMITTIVITY AND DIELECTRIC LOSS OF NITRO ALKANES IN SOLUTIONS

a) Nitromethane

Concentration in mol/cc × 10^4	ε'	ε''	tan δ	X	Y
Solvent: *n*-Heptane			Viscosity=0.390 cp		
0.937	1.970	0.010	0.0050	0.2471	0.0018
1.945	2.046	0.013	0.0063	0.2585	0.0024
2.817	2.087	0.016	0.0076	0.2659	0.0028
3.864	2.114	0.017	0.0080	0.2708	0.0030
4.864	2.155	0.020	0.0092	0.2779	0.0034
Solvent: Benzene			Viscosity=0.564 cp		
0.857	2.388	0.023	0.0096	0.3174	0.0036
1.913	2.503	0.036	0.0143	0.3355	0.0053
2.905	2.621	0.048	0.0183	0.3530	0.0068
3.931	2.699	0.055	0.0203	0.3639	0.0074
4.896	2.813	0.063	0.0223	0.3794	0.0080
Solvent: Cyclohexane			Viscosity=0.808 cp		
0.988	2.100	0.010	0.0048	0.2683	0.0019
1.895	2.198	0.017	0.0077	0.2853	0.0030
2.764	2.248	0.022	0.0098	0.2938	0.0037
3.838	2.281	0.028	0.0122	0.2991	0.0046
4.966	2.313	0.030	0.0129	0.3045	0.0048

c) 1-Nitropropane

Concentration in mol/cc × 10^4	ε'	ε''	tan δ	X	Y
Solvent: *n*-Heptane			Viscosity=0.390 cp		
1.034	2.025	0.023	0.0113	0.2547	0.0042
1.921	2.114	0.041	0.0193	0.2709	0.0074
2.885	2.213	0.058	0.0262	0.2880	0.0098
3.809	2.313	0.073	0.0315	0.3046	0.0118
4.857	2.425	0.094	0.0387	0.3223	0.0144
Solvent: Benzene			Viscosity=0.564 cp		
0.854	2.394	0.041	0.0169	0.3172	0.0063
1.829	2.503	0.064	0.0255	0.3339	0.0094
2.825	2.621	0.099	0.0378	0.3511	0.0139
3.778	2.750	0.144	0.0526	0.3691	0.0192
4.763	2.808	0.164	0.0583	0.3767	0.0212
Solvent: Cyclohexane			Viscosity=0.808 cp		
0.393	2.100	0.024	0.0114	0.2683	0.0043
1.227	2.209	0.048	0.0217	0.2874	0.0081
2.510	2.313	0.069	0.0298	0.3046	0.0113
3.575	2.412	0.088	0.0364	0.3203	0.0136
4.410	2.530	0.114	0.0450	0.3382	0.0167

d) 2-Nitropropane

Concentration in mol/cc × 10^4	ε'	ε''	tan δ	X	Y
Solvent: *n*-Heptane			Viscosity=0.390 cp		
0.982	2.020	0.018	0.0089	0.2538	0.0034
1.910	2.129	0.032	0.0150	0.2734	0.0055
2.822	2.260	0.047	0.0207	0.2958	0.0078
3.586	2.370	0.073	0.0308	0.3136	0.0115
4.780	2.486	0.097	0.0390	0.3316	0.0145
Solvent: Benzene			Viscosity=0.564 cp		
0.948	2.429	0.031	0.0128	0.3276	0.0048
1.848	2.554	0.052	0.0205	0.3414	0.0076
2.875	2.728	0.091	0.0334	0.3657	0.0122
3.748	2.773	0.103	0.0372	0.3717	0.0136
4.679	3.006	0.163	0.0544	0.4014	0.0196
Solvent: Cyclohexane			Viscosity=0.808 cp		
0.981	2.057	0.023	0.0111	0.2605	0.0041
1.681	2.233	0.041	0.0183	0.2913	0.0068
2.800	2.347	0.065	0.0276	0.3101	0.0103
3.611	2.436	0.082	0.0336	0.3238	0.0124
4.482	2.571	0.111	0.0431	0.3440	0.0159

b) Nitroethane

Concentration in mol/cc × 10^4	ε'	ε''	tan δ	X	Y
Solvent: *n*-Heptane			Viscosity=0.390 cp		
0.770	1.982	0.011	0.0056	0.2466	0.0020
1.728	2.124	0.019	0.0089	0.2726	0.0033
3.013	2.223	0.043	0.0193	0.2897	0.0072
3.903	2.314	0.061	0.0263	0.3046	0.0099
5.043	2.418	0.073	0.0310	0.3210	0.0113
Solvent: Benzene			Viscosity=0.564 cp		
0.911	2.388	0.041	0.0173	0.3163	0.0064
2.839	2.706	0.091	0.0337	0.3627	0.0123
4.788	2.891	0.125	0.0434	0.3871	0.0157
6.813	2.993	0.149	0.0496	0.3997	0.0179
8.820	3.387	0.220	0.0650	0.4440	0.0227
Solvent: Cyclohexane			Viscosity=0.808 cp		
1.002	2.120	0.019	0.0089	0.2718	0.0034
1.886	2.217	0.029	0.0130	0.2886	0.0048
2.851	2.327	0.047	0.0201	0.3076	0.0075
3.988	2.445	0.068	0.0278	0.3252	0.0103
5.005	2.550	0.081	0.0317	0.3409	0.0117

TABLE 2. RELAXATION TIMES AND DIPOLE MOMENTS OF NITROALKANES IN SOLUTION

λ=3.1 cm Temperature, 30°C

Solvent	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
n-Heptane	$\tau=1.1\times10^{-12}$ sec	$\tau=1.8\times10^{-12}$ sec	$\tau=2.5\times10^{-12}$ sec	$\tau=2.2\times10^{-12}$ sec
η=0.390 cp	μ=2.06 D	μ=2.91 D	μ=2.97 D	μ=3.31 D
	Δ (tan δ)/c=0.0012	Δ (tan δ)/c=0.0060	Δ (tan δ)/c=0.0079	Δ (tan δ)/c=0.0074
Benzene	$\tau=1.3\times10^{-12}$ sec	$\tau=2.2\times10^{-12}$ sec	$\tau=4.7\times10^{-12}$ sec	$\tau=3.3\times10^{-12}$ sec
η=0.564 cp	μ=2.79 D	μ=2.75 D	μ=2.69 D	μ=3.22 D
	Δ (tan δ)/c=0.0039	Δ (tan δ)/c=0.0061	Δ (tan δ)/c=0.0114	Δ (tan δ)/c=0.0107
Cyclohexane	$\tau=1.3\times10^{-12}$ sec	$\tau=1.9\times10^{-12}$ sec	$\tau=2.7\times10^{-12}$ sec	$\tau=2.7\times10^{-12}$ sec
η=0.808 cp	μ=2.44 D	μ=2.95 D	μ=3.06 D	μ=3.11 D
	Δ (tan δ)/c=0.0028	Δ (tan δ)/c=0.0060	Δ (tan δ)/c=0.0107	Δ (tan δ)/c=0.0080

Krishna method.[3] Viscosities of the solutions were determined by an Ostwald viscometer. All the chemicals were distilled twice before use.

Results

The experimental data and results are presented in Tables 1 and 2 respectively.

Discussion

The relaxation times τ for nitroalkanes have been determined from the data obtained with dilute solution of these compounds in *n*-heptane, benzene and cyclohexane. The values of relaxation times obtained in solutions are lower than the values obtained in pure liquids. In *n*-heptane the lower values of relaxation time can be explained on the basis of the low viscosity value of the solvent because the viscosity of *n*-heptane at 30°C is 0.390 cp whereas the viscosities of the nitro compounds are 0.617, 0.644, 0.759 and 0.718 cp respectively. The viscosity of benzene is 0.564 cp which is again less than the viscosities of the solute molecules at the same temperature. The values of relaxation times in benzene are greater than the values obtained in *n*-heptane. This seems reasonable due to the difference in viscosities of the two solvents. The other reason is the hindrance of molecular rotation by dipole-dipole interaction which is present in the pure liquid and mostly absent in dilute solutions. Since the polar molecules used in the present investigation are not quite spherical, viscosity of the surrounding medium should have considerable effect on the dielectric relaxation time. Such results have already been reported by others.[4,5] However, in the case of cyclohexane the values of τ obtained are smaller than the values of relaxation time in benzene, although the viscosity of cyclohexane is about one and a half times that of benzene and three times that of *n*-heptane. This cannot be explained on the basis of the effect of viscosity. The relation between τ and η given recently by Krishnaji and Mansingh[6,7] requires that at constant temperature the plots of $\ln \tau$ *vs.* $\ln \eta$ should be linear. Such plots for four nitroalkanes have been made, but the curves are not linear, the values of relaxation time in cyclohexane being less than the values obtained in benzene. Data of other workers[8-11] give straight lines for $\ln \tau$ *vs.* $\ln \eta$ because they have used a single solvent and have changed the viscosity by varying the temperature. By varying the temperature the viscosity changes but the interactions of solute and the solvent molecules remain the same. They used the same concentration at a single frequency, but in the present investigation the concentration variation at a single frequency method has been used. The viscosity has been varied by using different solvents. The behaviour of $\ln \tau$ *vs.* $\ln \eta$ plots in this case cannot be explained in the light of existing theories. The dependence of $\ln \tau$ upon $\ln \eta$ cannot be explained on the basis of the viscoelastic relaxation time. Such results, however, giving smaller relaxation times in solvents of higher viscosity than in the solvent of lower viscosity have been reported by Higasi[12,13] and Walker *et al.*[14] Walker has also obtained lower values of relaxation time in benzene and carbon tetrachloride for chloroform and has suggested that this might be due to hydrogen bonding of the hydrogen atom in chloroform to the π-electrons. Higasi,[12] on the other hand, has explained the difference in relaxation times as due to the solvent effect. The relaxation time is a physical quantity which is easily affected by the surroundings. The relaxation times and the dipole moments in aromatic solvents are greater than those in aliphatic solvents. There is a possibility of complex formation due to hydrogen bonding or a large interaction energy due to proton-proton interactions. It is possible that the molecule goes into a different isomeric configuration because of these short range interactions. Such an effect has been observed by Higasi[13] in 1,2-dichloroethane.

The relaxation times in each solvent increase with the increase in the number of carbon atoms and molecular size. This is in accordance with the Debye relationship relating the relaxation time τ with the molecular radius, a. The dependence of relaxation time τ on the chain length can be explained on the basis of Fröhlich's equation[15]

$$\tau = AE^{nH/kT}$$

where H is the energy required to lift a link of the

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chain over the potential barrier. Experimental values of log τ have been plotted against the number of carbon atoms and they are found to be straight lines satisfying the above relationship.

From the plots of $\tan\delta$ *vs.* concentration it is seen that the loss tangent varies linearly with concentration for all the four liquids in all the three solvents. The rates of variation of the loss tangents, $\tan\delta$, with concentration, c, are given in Table 2 and it is found that the rate of variation of $\tan\delta$ with c in a particular solvent increases with increase in the number of carbon atoms.

The dipole moment values obtained are in agreement, within experimental error, with the solution values given in literature. The values are slightly lower than those reported, and this is in agreement with the apparent tendency to obtain slightly lower moments by the microwave method.

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