MICROWAVE ABSORPTION IN AMYL ACETATE SOLUTIONS

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The dielectric absorption of dilute solutions of amyl acetate in cyclohexane, benzene, tetrachloroethylene and carbon tetrachloride has been examined in the microwave region at temperatures between 20 and 40°C. The relaxational properties of the system can be described in terms of dipole reorientation by molecular and intermolecular rotation. The thermodynamic parameters of the system are also studied.

1. Introduction

Recently, series of studies were done on the dielectric absorption of some aliphatic liquids at microwave frequencies and at different temperatures[1-3]. Dilute solutions of some aliphatic esters, namely methyl and ethyl esters, in heptane, cyclohexane and benzene were also studied[4]. In this work, more informations about the behaviour of esters is given by studying the dielectric relaxation of amyl acetate in four different non-polar solvents.

2. Experimental

The apparatus and procedure employed to determine the dielectric loss, ε'', at the frequency range from 4.2 GHz to 23 GHz have been described previously[5,6].

The accuracy of the measurements at frequencies 9.3 and 23 GHz amounts to 2% while at frequency 4.2 GHz amounts to 5%. Refractive index measurements, n_D, at the sodium D-line were made with an Abbé refractometer to an accuracy of 1.10^{-4}. Static dielectric constants, ε_0, were measured at 70 KHz using WTW decameter, schering bridge type to an accuracy of 1%.

The dispersion step $S/x = (\Delta\varepsilon_0 - \Delta n_D^2)/x$ (where x is the concentration in mole fraction, Δ means the difference between solution and solvent and n_D^2 is substituted for the dielectric constant at infinite frequency ε_∞) is obtained and used to calculate the reduced absorption $\eta'' = \Delta\varepsilon''/S$.

All the measurements were taken at diferent temperatures ranging from 20 to 40°C using an ultrathermostat. Pure grade materials from B. D. H. England were used. Three different concentrations with mole fraction not exceeding 0.02 were prepared from amyl acetate in the different non-polar solvents.

3. Results and discusion

The results obtained for amyl acetate in the different non-polar solvents are given in Table 1. The reduced absorption η'' is plotted versus log λ, a Fröhlich distribution[7] of relaxation times between two limiting values τ_1 and τ_2 is noticed and can be represented by:

$$\eta''_{(\omega)} = -\frac{1}{P} \arctan\left(\frac{\sinh P/2}{\cosh \ln \omega \, \bar{\tau}}\right)$$

where $P = \ln(\tau_1/\tau_2)$ and $\bar{\tau} = \sqrt{\tau_1 \tau_2}$ is the mean relaxation time. P is a measure of the breadth of distribution of the relaxation times. The results of $\bar{\tau}$ and P obtai-

TABLE 1

Solvent	t °C	$\dfrac{\Delta\varepsilon_0}{x}$	$\dfrac{S}{x}$	η'' at $\lambda =$		
				1.29 cm	3.24 cm	7.08 cm
Cyclohexane	20	3.01	3.42	0.364	0.283	0.192
	30	2.96	3.23	0.361	0.259	0.163
	40	2.88	3.13	0.359	0.243	0.132
Benzene	20	4.27	4.77	0.380	0.342	0.241
	30	3.98	4.50	0.408	0.335	0.210
	40	3.91	4.42	0.418	0.310	0.176
Tetrachloroethylene	20	3.65	4.13	0.348	0.340	0.274
	30	3.57	4.04	0.355	0.317	0.236
	40	3.23	3.68	0.360	0.310	0.218
Carbon tetrachloride	20	4.26	4.58	0.326	0.344	0.310
	30	4.01	4.29	0.359	0.330	0.260
	40	3.77	4.00	0.390	0.327	0.216

Measured values for the dilute solutions of amyl acetate in non-polar solvents. $\Delta\varepsilon_0/x$ is the difference between the static dielectric constant of the solutions and solvent, $S/x = \dfrac{\Delta\varepsilon_0 - \Delta n_D^2}{x}$ is the dispersion step, x is the concentration in mole fraction and $\eta'' = \Delta\varepsilon''/S$.

TABLE 2

Solvent	t °C	τ ps	P	$\mu_{xp.} \times 10^{30}$ Coul. m.	$\mu_{Lit.} \times 10^{30}$ Coul. m.	ΔH eV	$\Delta S \times 10^3$ eV/K
Cyclohexane	20	5.3	3.3	5.99		0.12	0.11
	30	4.3	3.3	5.99			0.11
	40	3.7	3.0	6.03			0.12
Benzene	20	7.9	3.0	6.09	6.36 at 25 °C[12]	0.11	0.05
	30	6.7	2.5	6.09			0.05
	40	5.7	2.2	6.16			0.05
Tetrachloroethylene	20	10.1	3.5	6.03		0.18	0.24
	30	7.7	3.5	6.13			0.25
	40	6.2	3.4	5.99			0.25
Carbon tetrachloride	20	13.0	3.5	6.23		0.24	0.44
	30	8.9	3.4	6.19			0.44
	40	6.7	2.9	6.13			0.44

Results of analysis of amyl acetate in the different non-polar solvents.

ned at the different temperatures for the different solvents are given in Table 2. From this table, it is clear that $\bar\tau$ and P decrease with increasing temperature as found before by Kreuter[8] and Hanna[9] for the rigid molecules. An example of the analysis is shown graphically in Fig. 1 for amyl acetate in carbon tetrachloride at the investigated temperatures. The values of the relaxation times of amyl acetate in the different solvents seems to be much shorter than those for corresponding molecules which relax predominantly by whole molecule rotation. Anyhow, this trend is found in the case of methyl and ethyl acetates where the relaxation times in benzene solutions at 30°C are 2.1 and 3.7 Ps, respectively[4], compared with 12 and 18 ps for methyl and ethyl trichloroacetates, respectively, in benzene[10]. Those values suggest that the reorientation of the whole molecule is not a dominant factor influencing the absorption of the aliphatic esters considered in the present
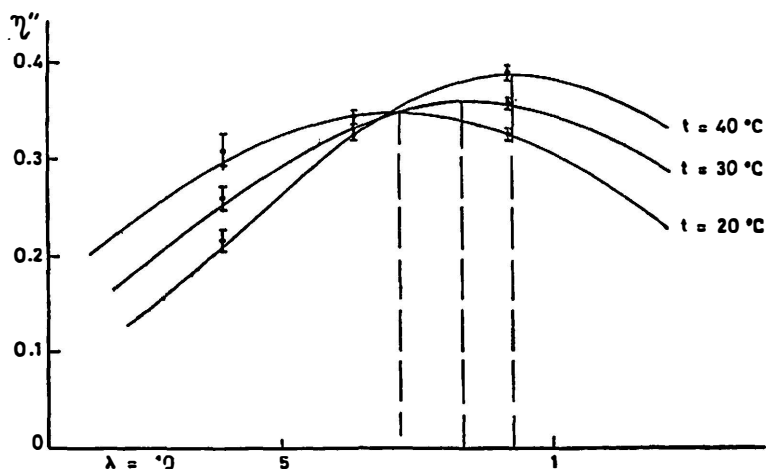

Fig. 1 Fröhlich analysis of amyl acetate in carbon tetrachloride at different temperatures.

investigation. The intramolecular relaxation process appears to make significant contribution to the relaxation behaviour which may be attributed here to the rotation of pentoxy group around C-O bond.
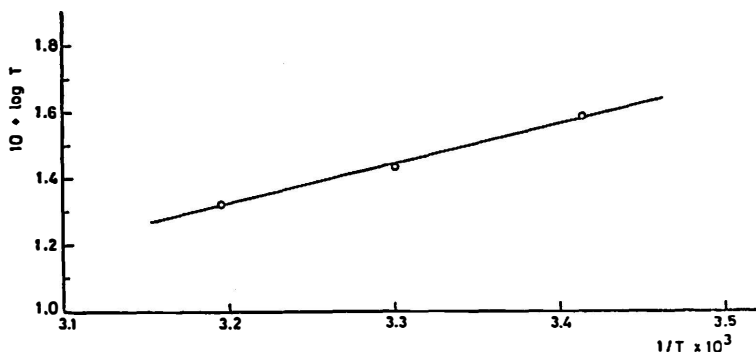

Fig. 2 Temperature-dependence of the mean relaxation time for amyl acetate in carbon tetrachloride.

The values of $\bar{\tau}$ in the different solvents as given in Table 2 show an increase in the order cyclohexane < benzene < tetrachloroethylene < carbon tetrachloride indicating no direct proportionality to the solvent viscosity suggesting the influence of other factors, such as size and shape of molecules and also the solute-solvent interaction giving rise to a variety of local environments and a range of energy barriers opposing reorientation. The molecular interaction of the solute with the solvent appears to be quite appreciable in benzene solutions.

The dipole moment of amyl acetate in the four different solvents is calculated[11] and found to be solvent and temperature independent. This value agrees well that in literature in benzene at $25°C$[12].

According to Eyring's chemical rate theory[13], the molar activation parameters, the heat of activation for dipole relaxation per mole ΔH and also the entropy of activation for dipole relaxation per mole ΔS are determined from:

$$\bar{\tau} = \frac{h}{kT} \, e^{\Delta H/RT - \Delta S/RT}$$

where h is Planck's constant, k is Boltzmann's constant, R is the gas constant and T is the absolute temperature. An example for determining ΔH is shown in Fig. 2 for amyl acetate in carbon tetrachloride. ΔH and ΔS in the different solvents as given in Table 2 show an increase in the order benzene < cyclohexane < tetrachloroethylene < carbon tetrachloride i. e. it follows the viscosity of the solvent as usual.

Acknowledgments

References

1) M. P. Madan, Can. J. Phys. **53** (1975) 23;
2) M. P. Madan, Can. J. Phys. **54** (1976) 794;
3) M. P. Madan, Can. J. Phys. **55** (1977) 297;
4) M. P. Madan, Can. J. Phys. **57** (1979) 1035;
5) F. F. Hanna and K. N. Abd-El-Nour, Proc. Math. Phys. Soc. A. R. Egypt **32** (1968) 7;
6) A. M. Bishai, Ph. D. Thesis, Cairo University (1971);
7) H. Fröhlich, *Theory of Dielectrics,* Clarendon Press, Oxford 1958;
8) K. Kreuter, Z. Naturforsch. **23** *a* (1968) 1728;
9) F. F. Hanna and K. N. Abd-El-Nour, Z. Phys. Chem., Leipzig **246** (1971) 168;
10) H. D. Purohit, H. S. Sharma and A. D. Vyas, Can. J. Phys. **55** (1977) 1902;
11) F. F. Hanna and K. N. Abd-El-Nour, Proc. Math. Phys. Soc. A. R. Egypt **32** (1968) 1;
12) Landolt and Börnstein, *Tabellenwerk,* 1,3 Berlin 1951, p. 423;
13) S. Glastone, K. J. Laidler and H. Eyring, *Theory of Rate Processing,* McGraw-Hill, New York 1941.

MIKROVALNA APSORPCIJA U OTOPINAMA AMIL ACETATA

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Ispitana je dielektrična apsorpcija u mikrovalnom području razrijeđenih otopina amil acetata u cikloheksanu, benzenu, tetraklor etilenu i ugljičnom tetrakloridu na temperaturama između 20 i 40°C. Relaksaciona svojstva sistema mogu se opisati pomoću dipolne preorijentacije molekularnom i intramolekularnom rotacijom. Također su proučeni i termodinamički parametri sistema.