Activation energies and times of relaxation for binary mixtures in dilute solution

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The dielectric relaxation times have been evaluated for six binary mixtures of anilines and xylenes in dilute solutions of benzene in the 3 cm microwave region. The relaxation times of each of the mixtures have been found to be nearly the average of the relaxation times of its two components. The various energy parameters have also been evaluated and discussed.

1. Introduction

The dipole orientation in polar liquids in dilute solutions cannot be treated as an isolated molecular motion (Bauer & Magat 1938). The dielectric relaxation in liquids is a cooperative process involving the relaxation of a number of molecules around any particular individual. In his study of binary mixtures of polar liquids, Schallamach (1946) found that the curve of the dielectric constant as a function of temperature showed a single maximum. The two polar media appear to have merged to provide a single local environment in the liquid. Kabada (1958), Forest & Smyth (1965) observed that for some mixtures two relaxation times were obtained. This was interpreted by Schallamach as a result of the mixtures being not microscopically homogeneous, such as a mixture of an associated and a nonassociated liquid.

Keeping in view the involvement of a single relaxation time for a microscopically homogeneous mixture, the authors have investigated the relaxation times of several binary mixtures of substituted aniline and xylene molecules in dilute solutions in benzene. These values are then compared with those of the components of the mixtures reported earlier by Srivastava (1960), Mehrotra & Saxena (1966). The energy parameters for the dielectric relaxation and for the viscous flow of the solvent have also been obtained for the dipolar mixtures.

2. Experimental Procedure

A 3 cm microwave bench has been used for the measurement of the dielectric constant ϵ' and the loss factor ϵ'', utilising the technique of Roberts & Von Hippel (1946), described by Mehrotra *et al* (1967). The varying concentration method

of Gopala Krishna (1957) has been used for the determination of the relaxation time τ using the following relations

$$x = \frac{\epsilon'^2 + \epsilon''^2 + \epsilon' - 2}{(\epsilon' + 2)^2 + \epsilon''^2}, \qquad y = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2}$$

and

$$\tau = \frac{\lambda}{2\pi c} \cdot \frac{dy}{dx}.$$

The thermodynamical parameters were evaluated using the Eyring's theory of rate process (Glasstone et al 1941).

The chemicals used were of the purest available quality, obtained from Aldrich Chemicals. The AR grade benzene was obtained from B.D.H. Ltd., England and was distilled before use.

3. Results and Discussions

The relaxation times of six binary mixtures and their thermodynamical parameters at varying temperatures have been reported in table 1. The relaxation times of the component molecules in solutions are also stated for comparison. The relaxation times of all mixtures are found to decrease with an increase in temperature as in the case of individual molecules. The relaxation times of investigated mixtures and those of their component liquids, on comparison reveal that the former are nearly the average of the latter values. This has been interpreted by the fact that the relaxation of liquid mixtures is a cooperative process, involving the relaxation of the structure around any particular molecule. Similar results have been obtained by Dhar & Saxena (1972).

The relaxation time for the mixture : 3-nitro-o-xylene+N-N'-dimethyl-4-methyl aniline in mixture, and is slightly greater than the average relaxation times of its component molecules, showing that the relaxation process of mixtures is influenced more by the molecule having a higher relaxation time. This is in agreement with the investigations of Ritson (1946).

The free energy of activation (ΔF_ϵ) is maximum for that set of mixture which has got the highest relaxation time and it increases with increasing temperature. The free energy of activation due to viscous flow of the solvent (ΔF_ϵ), is always greater than that due to dielectric relaxation (ΔF_ϵ) indicating greater interference by neighbours to the viscous flow than to the dielectric relaxation. The enthalpy of activation (ΔH_ϵ) is found to be less than that for viscous flow (ΔH_η), because the latter involves both the rotational and translational motion (Petro & Smyth 1957). The negative value of the entropy of activation indicates

Table 1. Relaxation times and energy parameters for binary mixtures at $\lambda = 3.10$ cm.

Mixture	$T°K$	$\tau \times 10^{12}$ Sec	ΔF_ϵ Kcal/mol	ΔF_η Kcal/mol	ΔH_ϵ Kcal/mol	ΔH_η Kcal/mol	ΔS_ϵ Cal/mol	ΔS_η Cal/mol
2-nitro-*m*-xylene[a]	298	15.55	2.71	4.27	1.68	2.52	−3.46	−5.88
+	304	14.63	2.74	4.31	1.68	2.52	−3.49	−5.90
m-chloroaniline[b]	310	13.54	2.76	4.36	1.68	2.52	−3.48	−5.92
2-nitro-*m*-xylene[a]	298	16.96	2.76	4.27	1.83	2.52	−3.12	−5.88
+	304	15.82	2.78	4.31	1.83	2.52	−3.13	−5.90
N-N′-dimethyl-4-[c] methylaniline	310	14.36	2.79	4.36	1.83	2.52	−3.10	−5.92
2-nitro-*m*-xylene[a]	298	14.03	2.65	4.27	0.71	2.52	−6.51	−5.88
+	304	13.59	2.69	4.31	0.71	2.52	−6.51	−5.90
N-N′-diethyl-4-[d] aminoaniline	310	13.05	2.73	4.36	0.71	2.52	−6.52	−5.92
3-nitro-*o*-xylene[e]	298	20.39	2.87	4.27	1.95	2.52	−3.09	−5.88
+	304	19.74	2.91	4.31	1.95	2.52	−3.16	−5.90
N-N′-dimethyl-4-[c] methylaniline	310	17.61	2.92	4.36	1.95	2.52	−3.13	−5.92
3-nitro-*o*-xylene[e]	298	18.26	2.80	4.27	2.06	2.52	−2.48	−5.88
+	304	16.31	2.81	4.31	2.06	2.52	−2.47	−5.90
m-chloroaniline[b]	310	14.84	2.82	4.36	2.06	2.52	−2.45	−5.92
m-chloroaniline[b]	298	11.41	2.53	4.27	0.51	2.52	−6.78	−5.88
+	304	11.15	2.57	4.31	0.51	2.52	−6.78	−5.90
N-N′-dimethyl-4-[c] methylaniline	310	10.76	2.62	4.36	0.51	2.52	−6.81	−5.92

[a]295 18.26 from the data of Mehrotra & Saxena (1966)
[b]303 9.10 from the data of Srivastava (1960)
[c]303 13.59
[d]303 10.20 from author's unpublished data
[e]298 21.90

the possibility of fewer configurations in the activated state and for these configurations the activated state is more ordered than the normal state. Similar results were obtained for single molecules by Shukla *et al* (1969).

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