Dielectric Relaxation Processes in Some Substituted Amides in Dilute Solutions

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The dielectric measurements have been carried out in the microwave region (3.1 cm) over a range of temperatures on propionamide, *N*-methylpropionamide, *N*,*N*-dimethylpropionamide, and *N*-ethylacetamide. All the molecules except propionamide exhibit high value of distribution parameter. The dielectric dispersion, when resolved by Higasi, Koga, and Nakamura method gives two relaxation times $\tau(1)$ and $\tau(2)$ widely different from each other, suggesting the two separate processes occurring in the system. The enthalpies for different processes involved have been evaluated by the Eyring equations. The comparison with NMR data of enthalpy to $\Delta H_{\tau(1)}$, which is related to the process other than molecular, suggests that the rotation of $-NR_2$ group around the carbonyl carbon nitrogen bond is not feasible. The observed result indicates that this may be due to group inversion process. These results are in agreement with the earlier investigations of Saxena *et al.* on some substituted amides and of Phillips on *N*,*N*-dimethylamide using proton resonance spectra. The substituted amides in dilute solution of benzene exhibit some association with the benzene molecules.

Leader and Gromley[1] reported a remarkable variation in the dielectric constant in the amides and substituted amides. The high values of dielectric constant of monosubstituted amides were suggested to be due to their association as a chain polymerisation. Since his initial work, a series of investigations have been carried out by several workers.[2–10] Jordon *et al.*[11] recently confirmed Debye behaviour for formamide, Itoh *et al.*[12] for *N*-methylacetamide and Srivastava *et al.*[13] for dimethylformamide. Brown and Price[14] have ruled out the molecular flexibility in dimethylacetamide. Karamyan and Shakhparonov[15] confirmed a long frequency dispersion region for *N*-substituted amides with much smaller amplitude at mm wavelength. In order to study the possibility of molecular flexibility and to ascertain the thermodynamics of dipolar relaxation Misra *et al.*[16] recently made a study of *N*-methylformamide, *N*-methylacetamide, dimethylformamide, and dimethylacetamide in the dilute solution of benzene over a range of temperatures. The enthalpies of different relaxation processes observed suggest the possibility of molecular and group inversion processes in the above molecules. Due to interesting results observed in the case of *N*-substituted amides, a further study in this direction has been undertaken. The molecules chosen are propionamide, *N*-methylpropionamide, dimethylpropionamide, and *N*-ethylacetamide so that the effect of propionyl (CH_3CH_2-CO) group in different substituted amides could be studied. The possibility of molecular association as pointed out by other workers[8,10] has also been examined.

Experimental

The chemicals were of purest quality available and the physical properties were checked against literature values. The solvent used in the measurements was benzene (A. R. Grade) obtained from B. D. H., England and was distilled twice before use. The dielectric constant ε' and dielectric loss ε'' at X- band have been measured by the technique given by Dakin and Works.[17] The static dielectric constant ε_0 was measured by dipolmeter and dielectric constant at infinite frequencies ε_∞ was determined from the measured refractive indices of the system ($\varepsilon_\infty = n_D^2$). The slopes a_0, a', a'', and a_∞, the most probable relaxation time τ_{OH} and the distribution parameter 'α' have been evaluated using Higasi method.[18] The details of determining these parameters and the dipolemoments have been reported in our earlier paper.[19] The dielectric absorbtion has been further resolved by using Higasi *et al.* method[20] in terms of two seperate relaxation processes $\tau(1)$ and $\tau(2)$ where $\tau(2)$ stands for the molecular relaxation process and $\tau(1)$ is associated with the group process being an implicit function of τ_1, τ_2, and the weight factor C_2. The parameter $\tau(0)$ stands for the average relaxation time given by $[\tau(0) = \sqrt{\tau(1), \tau(2)}]$ and τ_0 is the average relaxation time (Cole-Cole method) as reported in the literature.[14] Eyring equations[21] have been utilised to evaluate the thermodynamical parameters. The enthalpies associated with different modes of relaxation have been evaluated by plotting the relaxation times against $1/T$. The dipolemoments calculated using Higasi method[18] have been compared with the literature values (Table 2).

Discussion

The distribution parameter 'α' has been found to be low in the case of propionamide but its value is sufficiently high in the case of other three *N*- substituted amides indicating the flexibility of all the three molecules under microwave field. The dielectric dispersion is further resolved by Higasi *et al.* method[20] in terms of molecular relaxation time $\tau(2)$ and the relaxation time associated with group relaxation time $\tau(1)$. The $\tau(1)$ (=23.7 ps) and $\tau(2)$ (=30.5 ps) are not widely different from one another in the case of propionamide. Thus a single Debye dispersion seems to occur for the above molecule. Further $\tau(2)$ and τ_{OH} calculated by Higasi method[18] are close to each other for propionamide, suggesting that the molecular process and the overlapped process are similar to one another in this molecule. The observed single Debye dispersion for this molecule is in agreement with the earlier results of Jordon *et al.*[11] on formamide.

The most probable relaxation time τ_{OH} at 297 K for *N*-methylpropionamide (=22.8 ps) and *N*-ethylacetamide (=26.2 ps) can be compared with our

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Table 1. Values of a_0, a', a'', a_∞ for the samples in benzene at different temperature using Higasi method[18]

Compound	T/K	a_0	a'	a''	a_∞
Propionamide	313	18.10	4.00	6.10	0.363
	321	21.00	6.15	8.00	0.606
	329	15.40	5.71	6.70	−0.289
N-Methylpropionamide	289	23.50	8.00	8.00	−1.18
	297	21.05	8.20	7.50	−0.53
	305	19.04	9.60	7.30	−0.33
	313	15.70	8.90	6.90	−0.31
N,*N*-Dimethylpropionamide	289	22.2	8.30	8.7	−1.00
	297	19.0	8.00	8.3	−0.68
	305	18.0	10.00	7.4	−0.18
	313	15.4	10.30	7.0	−0.25
N-Ethylacetamide	297	36.4	13.00	13.5	−0.72
	305	33.0	12.30	12.9	−0.71
	313	26.6	13.50	10.5	−0.43
	321	24.6	15.00	10.00	−0.25

Table 2. Relaxation times and dipolemoment using Higashi method[18] and corresponding activation parameters

Compound	T/K	α	τ_{OH}	μ / Debye	ΔF_ε / kJ mol^{-1}	ΔH_ε / kJ mol^{-1}	ΔS_ε / J mol^{-1} deg^{-1}	μ_{1it} / Debye
Propionamide	313	0.08	37.8	3.56	(13.6—14.2)	22.5	(25.2—27.0)	3.47
	321	0.07	30.0					
	329	0.00	21.4					
N-Methylpropionamide	289	0.24	26.4	3.72	(10.6—12.2)	18.2	(20.0—24.3)	3.59
	297	0.22	22.8					
	305	0.18	15.8					
	313	0.09	13.6					
N,*N*-Dimethylpropionamide	289	0.17	21.8	4.0	(11.2—11.7)	14.2	(8.1— 9.6)	—
	297	0.14	19.2					
	305	0.12	14.2					
	313	0.02	11.5					
N-Ethylacetamide	297	0.19	26.2	5.0	(11.7—12.7)	19.1	(21.3—23.1)	—
	305	0.15	23.1					
	313	0.16	15.6					
	321	0.10	12.0					

Table 3. Relaxation times $\tau(1)$, $\tau(2)$, and $\tau(0)$ and enthalpy of activation $\Delta H_{\tau(1)}$, $\Delta H_{\tau(2)}$, and $\Delta H_{\tau(0)}$ using Higasi, Koga, and Nakamura method[20]

Compound	T/K	$\tau(1)$ / ps	$\tau(2)$ / ps	$\tau(0)$ / ps	$\Delta H_{\tau(1)}$ / kJ mol^{-1}	$\Delta H_{\tau(2)}$ / kJ mol^{-1}	$\Delta H_{\tau(0)}$ / kJ mol^{-1}
Propionamide	313	27.6	38.0	32.4	16.6	22.5	21.3
	321	23.7	30.5	26.9			
	329	18.4	23.7	20.9			
N-Methylpropionamide	289	14.3	31.8	21.3	—	21.3	13.7
	297	14.1	27.7	19.8			
	305	12.0	21.3	16.0			
	313	12.3	16.2	14.1			
N,*N*-Dimethylpropionamide	289	15.4	26.3	20.1	8.1	15.9	12.8
	297	15.7	21.8	18.5			
	305	12.7	17.8	15.0			
	313	11.4	12.0	11.7			
N-Ethylacetamide	297	16.2	29.6	21.9	10.9	21.3	15.3
	305	16.3	26.4	20.7			
	313	12.4	20.5	15.9			
	321	10.8	15.8	13.1			

previous results[16] on *N*-methylformamide (=17.8 ps) and *N*-methylacetamide (=18.0 ps). The observed results are supported by the earlier observations of Dannhauser and Johari[9] establishing that the relaxation times show specific dependence on the shape and size of alkyl group attached to the carbonyl or amino group. The τ_{OH} for dimethylpropionamide (=21.8 ps) can be compared with our earlier work[16] on dimethylformamide (=18.1 ps) and dimethylacetamide (=25.6 ps). The value is comparatively high as regards to τ_0 (6.0—8.4 ps) reported for dimethylacetamide by Brown and Price[14] in benzene at 293 K. The longer value of relaxation time seems to result from the association of disubstituted amide. The association in amides has been observed by many earlier workers.[8,10] Further, $\tau(1)$ and $\tau(2)$ are widely different for all the three *N*-substituted amides showing the non rigid behaviour of these molecules in the microwave region.

The enthalpies corresponding to $\tau(1)$, $\tau(2)$, $\tau(0)$, and τ_{OH} processes have been evaluated. $\Delta H_{\tau(1)}$ and $\Delta H_{\tau(2)}$ are widely different from each other except in case of propionamide, showing again the flexible nature of the molecules in the microwave field. $\Delta H_{\tau_{OH}}$ for *N*-ethylacetamide (=19.1 kJ mol^{-1}), *N*-methylpropionamide (=18.2 kJ mol^{-1}) are comparable with those *N*-methyl acetamide (=14.9 kJ mol^{-1}) and *N*-methyl formamide (=14.2 kJ mol^{-1}) observed in our earlier study.[16] Further $\Delta H_{\tau_{OH}}$ for dimethylpropionamide (=14.2 kJ mol^{-1}) can be compared with the values for dimethylformamide (=13.7 kJ mol^{-1}) and dimethylacetamide (=12.8 kJ mol^{-1}) reported in our previous work.[16] The enthalpies for $\Delta H_{\tau_{OH}}$ and $\Delta H_{\tau(2)}$ are almost equal, showing the probability of the molecular process being predominant. The enthalpy $\Delta H_{\tau(1)}$ for *N*-methylpropionamide could not be evaluated due to irregular variation of $\tau(1)$. However, the observed value of $\Delta H_{\tau(1)}$ for *N*-ethylacetamide and for dimethylpropionamide which represent a process other than molecular has been found to be small when compared with the enthalpy of activation for internal rotation of $-NR_2$ group (>40 kJ mol^{-1}), reported using NMR data.[22,23] Therefore, this value can not be assigned to the internal rotation of –NXR (where R=CH_3, C_2H_5, and X=H, CH_3). This, however, could be assigned to the group inversion process of R and X substituents from their respective position within the –NXR group. This is in agreement with our earlier investigations on *N*-substituted amide[16] and with the studies of Phillips[24] using proton resonance spectra of *N*,*N*-dimethylamides.

The dipolemoments of all the four molecules have been evaluated by Higasi method[18] and they agree well with the literature values[25-27] wherever available. The slightly higher value of dipolemoments may be due to the association and the interaction of benzene with, *N*-subsituted amide. The observed association is in agreement with the earlier studies of many workers[8,10] and such interactions in the dilute solution of benzene have been prodicted by Ellision and Mayer.[28]

The free energy of activation has been found to be almost of the same order in all the molecules and the entropy values of them have been found to be positive. These have been reported in Table 2.

Conclusion

All the amides studied including propionamide follow Debye behaviour. The propionamide has been found to behave as a rigid molecule. This is in agreement with the earlier work of Jordon *et al.*[11] on formamide.

It is observed that *N*-substituted amides give rise to a high value of the distribution parameter, indicating that the three systems exhibit flexible behaviour which is supported by two discrete relaxation times $\tau(1)$ and $\tau(2)$. There appears to be a possibility of group inversion in amides, which is in agreement with our previous work[16] and also with the studies of Phillips,[24] using proton resonance spectra of *N*,*N*-dimethylamide.

Also a close study of the molecular process shows that in *N*-substituted amides the relaxation time varies according to the shape and size of the alkyl group attached to the carbonyl or the amino group. This agrees well with the studies made by Dannhauser and Johari.[9] In almost all the cases investigated, the relaxation times associated with the molecular process and with the overlapped process have been found to be longer than the values expected for such species. The dipolemoments have been calculated and found to be slightly higher than the literature values. This indicates the possibility of association of the amide molecules with the solvent benzene. The higher value of dipolemoment in dilute solution of benzene has been reported in an earlier study by Worsham and Hobbs[8] in *N*-substituted amide.

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References

1) G. R. Leader and J. F. Gromley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).
2) J. W. Vaughan and P. G. Sears, *J. Phys. Chem.*, **62**, 183 (1958).
3) A. E. Lutskie and S. A. Mikhailenko, *Zh. Straukt. Khim.*, **4**, 350 (1960).
4) L. R. Dawson, J. W. Vaughan, M. E. Pruitt, and H. C. Eckstrom, *J. Phys. Chem.*, **66**, 2684 (1962); **67**, 278, 281 (1963).
5) R. Y. Lin and W. Dannhauser, *J. Phys. Chem.*, **67**, 1805 (1963).
6) G. P. Johari and P. N. Tewari, *J. Phys. Chem.*, **69**, 3167 (1967); **70**, 197 (1966).
7) O. P. Donner, G. F. Gordon, and K. W. Bunzel, *J. Phys. Chem.*, **68**, 2450 (1964).
8) J. E. Worsham and M. E. Hobbs, *J. Am. Chem. Soc.*, **76**, 206 (1954).
9) W. Dannhauser and G. P. Johari, *Can. J. Chem.*, **46**, 3143 (1968).
10) S. J. Bass, W. I. Nathan, R. M. Meighan, and R. H. Cole, *J. Phys. Chem.*, **68**, 509 (1964).
11) B. P. Jordon, R. J. Sheppard, and S. Szwarnowski, *J. Phys. D*, **11**, 695 (1978).

12) K. Itoh, H. Sato, H. Takshashi, and K. Higasi, *Bull. Chem. Soc. Jpn.*, **49**, 329 (1976).
13) G. P. Srivastava, P. C. Mathur, and K. N. Tripathi, *Ind. J. Pure Appl. Phys.*, **6**, 113, 561 (1968).
14) V. L. Brownsell and A. H. Price, *J. Phys. Chem.*, **74** 4004 (1970).
15) G. G. Karamyan, M. I. Shakhparonov deposited Doc. VINITI, 1098—76, 15 (1976) Russ, Avail VINITI.
16) C. K. Misra, J. P. Shukla, and M. C. Saxena, *Adv. Mol. Relax. Procs*, **15**, 181—192 (1979).
17) T. W. Dakin and C. N. Works, *J. Abb. Phys.*, **18**, 789 (1947).
18) K. Higasi, *Bull. Chem. Soc. Jpn.*, **39**, 2157 (1966).
19) S. K. Saxena, J. P. Shukla, and M. C. Saxena, *Bull. Chem. Soc. Jpn.*, **53**, 1732 (1980).
20) K. Higasi, Y. Koga, and M. Nakamura, *Bull. Chem. Soc. Jpn.*, **44**, 988 (1971).
21) S. Glasstone, K. J. Leider, and H. Eyring "The Theory of Rate Process," McGraw-Hill Book Co., New York (1941), p. 548.
22) L. W. Reeves, R. C. Sheddick, and K. N. Shaw, *Can. J. Chem.*, **49**, 3683 (1971).
23) A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, 42, 3320 (1965).
24) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955).
25) M. E. Hobbs and W. B. Bates, *J. Am. Chem. Soc.*, **74**, 746 (1952).
26) R. M. Meighan and R. H. Cole, *J. Phys. Chem.*, **68**, 503 (1964).
27) M. J. Aroney, R. J. W. Le Fevere, and A. N. Singh, *J. Chem. Soc.*, **1965**, 3179.
28) H. R. Ellision and B. W. Meyer, *J. Phys. Chem.*, **74**, 3861 (1970).