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Dielectric Relaxation in Some Substituted Benzaldehydes in Benzene at Different Temperatures

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Measurements of the relative permittivity at 1 MHz and 9.27 GHz, and of the refractive index for the sodium-D line have been made for (A) *o*-nitrobenzaldehyde, (B) *m*-nitrobenzaldehyde, (C) *m*-chlorobenzaldehyde, and (D) *p*-chlorobenzaldehyde, at 15, 25, 35, and 45 °C in dilute solutions of benzene. The dielectric relaxation times $\tau_{(1)}$ and $\tau_{(2)}$ have been calculated using the Higasi, Koga, and Nakamura method. The results suggest that the relaxation time for the overall rotation decreases at a greater rate than the one for the internal rotation. The thermodynamic energy parameters have been calculated. The results show that the freedom of rotation of the –CHO group increases around the C_{alip}–C_{arom} bond as an electronegative substituent moves from the *o*- to *m*- to *p*- positions.

The present work is an extension of the study previously undertaken on the dielectric relaxation mechanism in some substituted benzaldehydes[1] to include temperature as another variable. Since our previous communication, we have come across the results reported by Mountain and Walker[2] on benzaldehyde, *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-nitro-benzaldehydes in dilute solutions of *p*-xylene at a single temperature and *p*-chlorobenzaldehyde at five temperatures. On the whole, our results and some of the inferences drawn agree with them, though we studied the materials only at a single frequency in the dispersion region. This provides a good test for the Higasi, Koga, and Nakamura method[3,4] of analysing the relative permittivity data. Our results[1] showed that benzaldehydes interact with the benzene molecule through the π-electrons from the benzene molecule. Mountain and Walker's results[2] of benzaldehydes in *p*-xylene show a similar interaction. They have postulated it to be a weak hyderogen bonding of the type $-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{H}\cdots\pi$. On the other hand, our results,[1] on the study of the benzaldehyde–dioxane systems, indicated that the hyderogen bonding of the type $-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{H}\cdots\mathrm{O}$, if at all, there is fairly weak. There is no confirmation to this fact as yet.

The temperature is introduced as another variable in making a comparative study of the benzaldehydes and their interactions with benzene.

Experimental and Results

The materials are of the same purity standard as previously discussed.[1] The relative permittivity and the refractive index measurements have been made by the same techniques. However, the dielectric cell used for the measurements at 1 MHz was a two terminal one with an air capacitance of 17.9 pF. The cell was calibrated

TABLE 1. VALUES OF a_0, a', a'', $a_{\infty1}$, $a_{\infty2}$, $\tau_{(1)}$, $\tau_{(2)}$, AND LIT. VALUES[2] OF τ_1 AND τ_2, AND $\mu_{\text{int., rot.}}$, FOR THE SUBSTANCES A—D AT DIFFERENT TEMPERATURES

T(K)	a_0	a'	a''	$a_{\infty1}$	$a_{\infty2}$	$\tau_{(1)}$ (ps)	$\tau_{(2)}$ (ps)	τ_1 (lit) (ps)	τ_2 (lit) (ps)	$\mu_{\text{int., rot.}}$ (D)
				o-Nitrobenzaldehyde						
288	15.70	6.75	5.54	0.297	3.32	14.7	27.7	—	—	1.99
298	14.75	7.21	5.40	0.315	3.35	13.5	24.0	—	—	2.04
308	14.10	7.33	5.18	0.312	3.36	12.7	22.4	—	—	2.10
318	13.05	7.45	4.88	0.303	3.20	11.7	19.7	—	—	2.10
				m-Nitrobenzaldehyde						
288	9.90	4.27	3.37	0.265	2.26	14.5	28.7	—	—	1.61
298	9.25	4.29	3.31	0.279	2.08	14.2	25.7	—	—	1.57
308	8.77	4.15	3.26	0.283	1.85	14.5	24.3	—	—	1.48
318	8.28	4.39	3.10	0.283	1.92	12.9	21.5	—	—	1.59
				m-Chlorobenzaldehyde						
288	6.43	3.65	2.46	0.254	1.47	12.4	19.4	—	—	1.21
298	6.12	3.72	2.37	0.241	1.38	11.4	17.4	—	—	1.21
308	5.81	3.65	2.26	0.254	1.29	11.4	16.4	—	—	1.19
318	5.33	3.60	2.17	0.260	0.88	11.1	13.7	—	—	0.95
				p-Chlorobenzaldehyde						
288	3.95	1.83	1.02	0.276	1.34	11.3	35.7	36.0	13.0	1.14
298	3.66	1.87	0.95	0.270	1.37	10.2	32.3	33.0	10.8	1.18
308	3.47	1.90	0.94	0.263	1.34	9.9	28.7	18.0 (40°C)	9.0 (40°C)	1.21
318	3.25	1.85	0.90	0.256	1.32	9.9	26.7	—	—	1.22

Table 2. Values of $\tau_{(2)}$, ΔF_ε, ΔF_ε (lit values[2]), ΔF_η, ΔH_ε, ΔH_η, ΔS_ε, ΔS_η, and $x(=\Delta H_\varepsilon/\Delta H_\eta)$ for the substances A—D at different temperatures

T(K)	$\tau_{(2)}$ (ps)	ΔF_ε	ΔF_ε (lit, values)	ΔF_η	ΔH_ε	ΔH_η	ΔS_ε	ΔS_η	$x=\Delta H_\varepsilon/\Delta H_\eta$
		kcal/mol					cal/deg mol		
				o-Nitrobenzaldehyde					
288	27.7	2.93	—	2.89	1.49	2.51	−5.00	−1.32	0.59
298	24.0	2.97	—	2.91			−4.97	−1.34	
308	22.4	3.05	—	2.93			−5.06	−1.36	
318	19.7	3.08	—	2.95			−5.00	−1.38	
				m-Nitrobepzaldehyde					
288	28.7	2.95	—	2.89	1.28	2.51	−5.80	−1.32	0.51
298	25.7	3.01	—	2.91			−5.81	−1.34	
308	24.3	3.10	—	2.93			−5.91	−1.36	
318	21.5	3.14	—	2.95			−5.85	−1.38	
				m-Chlorobenzaldehyde					
288	19.4	2.73	—	2.89	1.25	2.51	−5.14	−1.32	0.50
298	17.4	2.78	—	2.91			−5.13	−1.34	
308	16.4	2.85	—	2.93			−5.23	−1.36	
318	13.7	2.85	—	2.95			−4.94	−1.38	
				p-Chlorobenzaldehyde					
288	35.7	3.08	3.08	2.89	1.18	2.51	−6.60	−1.32	0.47
298	32.3	3.15	3.15	2.91			−6.61	−1.34	
308	28.7	3.20	2.97 (40°C)	2.93			−6.56	−1.36	
318	26.7	3.28	—	2.95			−6.60	−1.38	

Literature values of ΔF_ε for *p*-chlorobenzaldehyde are calculated from the values of the relaxation time for overall rotation (τ_1) reported by Mountain and Walker.[2]

for each temperature. The values of the slopes are calculated from the experimental plots of the data *versus* weight fraction. The dielectric relaxation times are calculated using the same techniques.[1]

Values of the parameters a_0, a', a'', $a_{\infty 1}$, $a_{\infty 2}$, $\tau_{(1)}$, and $\tau_{(2)}$ (defined already[1]), for all the four materials at each temperature, are given in Table 1. The table also includes the literatures values[2] of τ_1 and τ_2 for *p*-chlorobenzaldehyde in *p*-xylene as well as value of the dipole moment for internal rotation ($\mu_{\text{int., rot.}}$) which was calculated in the same way as described earlier[1] (Table 1).

The thermodynamic energy parameters are calculated using Eyring's equation[5,6] for the relaxation time $\tau_{(2)}$ since it has been shown[4] to be nearly equal to the relaxation time for overall rotation (τ_1). These values are given in Table 2.

Discussion

Comparing the present values of the dielectric realaxtion times $\tau_{(2)}$ with those of τ_1 given by Mountain and Walker,[2] for *p*-chlorobenzaldehyde in *p*-xylene, and also, keeping in view the accuracy of determination and a slight viscosity difference betweem the two solvents, we find that the agree is reasonably good. This establishes at least the fact that benzene and *p*-xylene have similar characteristics in so far as the interactions with benzaldehydes are concerned. Values of $\tau_{(1)}$ and $\tau_{(2)}$ for each material at a particular temperature are quite distinct from each other. This shows that these molecules possess more than one dielectric relaxation time.

A comparison of the enthalpy of activation (ΔH_ε) for the isomers shows an interesting aspect. The energy barrier for the dielectric relaxation mechanism decreases from *o*- to *m*- and from *m*- to *p*- isomers both for the chloro- and nitro-benzaldehydes.

Since the relaxation time involved is $\tau_{(2)}$, the energy barrier is a combination of barrier to the molecular and to the internal rotations. However, if one assumes, at the worst, that the barrier to the molecular rotation remains the same for the different isomers of a substituted benzaldehyde, the barrier to the internal rotation decreases in the order, *o*- to *m*- and from *m*- to *p*- substituents. This shows indirectly that the freedom of the –CHO group along the C_{alip}–C_{arom} bond increases when these substituents move from the *o*- to *p*- position through *m*- position. Mountain and Walker[2] have explained it in terms of inductive and mesomeric effects of the substituents on the electron density of the C_{alip}–C_{arom} bond. This concept successfully explain why the aldehyde group, when present alone, dose not rotate around the C_{alip}–C_{arom} bond.

Another interesting aspect of the results is that $\Delta H_\varepsilon < \Delta H_\eta$. The ratio $\Delta H_\varepsilon/\Delta H_\eta(=x)$ for the different materials is listed in Table 2. The values of this factor is 0.59 for *o*-nitrobenzaldehyde whereas it is $\approx$0.50 for the other materials. According to the classification of polar liquids, given by Krishnaji and Mansingh,[7] substances for which $x > 0.55$ do not show solid rotator phase and those for which $x < 0.45$ show such a phase. Since the values of x for the three materials B, C, and D are between the two limits, there is some possibility that these materials, particularly *p*-chlorobenzaldehyde, may show a solid rotator phase.

Values of $\mu_{\mathrm{int.,\,rot.}}$ for a particular material remain constant with temperature within experimental error. This indicates that the internal rotations of the -CHO group and the nature of its interactions with the benzene molecule are independent of temperature.

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References

1) B. Singh and J. K. Vij, *Bull. Chem. Soc. Jpn.*, **48**, 2551 (1975).

2) P. F. Mountain and S. Walker, *Can J. Chem.*, **52**, 3229 (1974).

3) K. Higasi, Y. Koga, and M. Nakamura, *Bull. Chem. Soc. Jpn.*, **44**, 988 (1971).

4) J. K. Vij, I. Krishan, and K. K. Srivastava, *Bull. Chem. Soc. Jpn.*, **46**, 17 (1973).

5) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

6) S. Glasstone, K. J. Laidler, and H. Eyring, "The Thory of Rate Process," McGraw-Hill, N. Y. (1941), pp. 544—551.

7) Krishnaji and Mansingh, *J. Chem. Phys.*, **44**, 1590 (1966).