SHORT COMMUNICATIONS

DIELECTRIC RELAXATION AT 9.2 GHz IN SOME ALDEHYDES

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THE high frequency dielectric constant ε', the loss factor ε'' at a frequency of 9.2 GHz, the static dielectric constant ε_0 at 1 MHz and at a temperature of 26°C and the refractive index n_D in the case of some organic molecules containing rotating polar groups, namely, propionaldehyde, acrolein, cinnamaldehyde, vanillin, furfural p-tolualdehyde in dilute solution in benzene and crotonaldehyde in dilute solution in CCl_4 are determined by carrying out dielectric measurements using standard methods described in literature[1-3]. The results are discussed in the light of Higasi's[4] method of analysing dielectric data at a single frequency.

Following Higasi[5] Debye equations for dilute solutions which can be used to determine the relaxation time (τ) of a polar solute in a non-polar solvent may be conveniently expressed by two independent equations, namely,

$$\tau = \frac{1}{w} \frac{a''}{a' - a_\infty}, \qquad (1)$$

and

$$\tau = \frac{1}{w} \frac{a_0 - a}{a''}, \qquad (2)$$

where the quantities $a_0, a_\infty (a_D) a'$ and a'' are the slopes of the linear plots in each case between the parameters $\varepsilon_0, n_D^2, \varepsilon'$ and ε'' versus W_2, the weight fraction of the solute and w is the angular frequency of measurement. It may be emphasised that if a system under consideration is characterised by a single relaxation time equations (1) and (2) lead to the same value of relaxation time. On the other hand if the system is characterised by more than one Debye type dispersion leading to two descrete relaxation times, one due to the overall rotation of the molecule (τ_1) and the other due to the intramolecular rotations (τ_2) then the relaxation time calculated by (1) and (2) may differ and these equations may be expressed as

$$\tau(1) = A\tau_2;$$

$$A = \frac{[m - (m-1)C_2] + mx^2[1 + (m-1)C_2]}{1 + [1 + (m^2-1)C_2]x^2},$$

$$\tau(2) = B\tau_2;$$

$$B = \frac{m^2 - (m^2-1)C_2 + m^2 x^2}{m - (m-1)C_2 + mx^2[1 + (m-1)C_2]},$$

where $m = \tau_1/\tau_2$ and $x = w\tau_2$ and $C_1 = 1 - C_2$ are the weight factors involved in the two Debye processes.

Thus $\tau(1)$ and $\tau(2)$ are not the actual relaxation times but are functions of τ_1, τ_2 and C_1 or C_2. However, $\tau(1) = \tau(2) = \tau_1$ for overall rotation only and $\tau(1) = \tau(2) = \tau_2$ for internal rotation only, of the molecule. Further, it is shown that[6] the relaxation time (τ_{GK}) determined by Gopalakrishna's procedure, yet another method of computing this quantity, corresponds, particularly, when applied to non-rigid molecules, to the quantity $\tau(2)$ rather than to $\tau(1)$. This is because this method is also based on the principle of linearity between the various dielectric parameters and the weight fraction of the solute and also that it uses equation for $\tau(2)$ to determine τ_{GK}. In the light of these considerations an attempt is made to analyse the observed relaxation times of the polar solute molecules, with a view to understanding whether the systems under consideration are characterised by a single or two discrete relaxation times. Further, the relaxation time of these molecules is also calculated using a procedure due to Ghosh and Ghosh[7] and all these results are presented in table 1. Also included in this table are the calculated values of $(a_\infty)_{cal}$ by equating $\tau(1) = \tau(2)$ as suggested by Grant[8].

It is seen from table 1 that (i) in all the cases $\tau(2) > \tau(1)$, (ii) there is a good agreement between τ_{GK} and τ_{GG} values (within the experimental errors of about 10% in the τ values in the present investigation) and (iii) either τ_{GK} or τ_{GG} value is nearer to the corresponding $\tau(1)$ value. The observed fact τ_{GK} or $\tau_{GG} \simeq \tau(1)$ may not mean that the former corresponds to $\tau(1)$ since $\tau(1)$ is not the actual relaxation time but a function of τ_1, τ_2 and C_1 or C_2. The nearness may be accidental as τ_{GK} value corresponds to $\tau(2)$. According to Higasi if the system under consideration is characterised by a single relaxation time it would result in $\tau(1) = \tau(2)$ which would imply that any random difference between $\tau(1)$ and $\tau(2)$ may be used as a criterion to indicate the possibility of another dispersion region. On the other hand, similar random difference between a_D and $(a_\infty)_{cal}$ may also suggest this possibility. It is clear from table 1 that the $\tau(1)$ and $\tau(2)$ values and a_D and a_∞ values differ much; the difference being well outside the experimental errors seems to suggest that the systems

Table 1 *Dielectric data for different solute molecules in dilute solution in benzene.*

Molecule	Dielectric parameters				Relaxation time in p. seconds				Dipole moments in Debye units			
	a_0	a'	a''	a_∞	$\tau(1)$	$\tau(2)$	τ_{GK}	τ_{GG}	μ_H	μ_{GK}	μ_{GG}	μ_{GU}
Propionaldehyde	11.62	11.11	1.90	0.37 (4.03)†	3.1	4.7	2.6	2.2	3.02	2.23	3.00	2.14
Acrolein	14.80	12.50	2.78	0.40 —	4.0	14.3	8.2	3.9	3.42	2.67	2.70	2.54
Crotonaldehyde (in CCl_4)	13.16	10.59	5.00	0.21 (0.86)	8.3	10.4	7.8	7.2	3.24	2.77	3.15	2.70
Furfural	15.00	10.00	5.31	0.09 (4.36)	9.3	16.3	12.0	8.7	3.48	3.36	3.59	3.68
Cinnamaldehyde	12.00	4.71	2.96	0.34 (3.51)	11.7	42.5	13.0	12.1	3.08	2.71	2.96	3.58
Vanillin	6.91	2.93	2.00	0.44 (1.93)	13.9	34.5	5.9	21.6	2.29	2.25	2.49	2.63
P-Tolualdehyde	6.25	4.00	3.25	0.12 —	14.47	11.96	12.5	13.8	2.23	2.78	2.84	3.06

† The values in the paranthesis in this column correspond to the values of $(a_\infty)_{cal}$ as calculated by equating $\tau(1) = \tau(2)$.

under consideration are characterised by more than one Debye type dispersion. Similar conclusions are arrived at in some other substituted anilines in dilute solution systems[9]. However, it may be mentioned that in the case of dilute solution systems it is hard to visualise the multiple relaxation processes but actual measurements at another higher frequency may be a more useful guide to decide this factor than the random difference criterion only.

Further details regarding the behaviour of τ values and electric dipole moments of these molecules may be found in literature[10,11].

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1. Dakin, T. W. and Works, C. N., *J. Appl. Phys.*, 1947, **18**, 789.
2. Gopalakrishna, K. V., *Trans. Far. Soc.*, 1957, **53**, 767.
3. Guggenheium, E. A., *Trans. Far. Soc.*, 1949, **45**, 714; 1951, **47**, 573.
4. Keniti Higasi, Yoshinori Koga and Masatiko Nakamura, *Bull. Chem. Soc., Jpn*, 1971, **44**, 988.
5. Keniti Higasi, *Bull. Chem. Soc., Jpn*, 1966, **39**, 2157.
6. Vij, J. J. and Srivastava, T. K., *Trans. Far. Soc.*, 1970, **66**, 1087.
7. Ghosh, A. K. and Ghosh, S. K., *Indian J. Pure Appl. Phys.*, 1982, **20**, 743.
8. Kazuo Chitoku and Keniti Higasi, *Bull. Chem. Soc., Jpn*, 1971, **44**, 993.
9. Amarsingh, Saxena, S. K. and Saxena, M. C., *Indian J. Pure Appl. Phys.*, 1982, **20**, 276.
10. Deshpande, D. K. and Suryanarayana Rao, K. Dr Bhagavantam's Commemoration Volume, 1969, 33.
11. Deshpande, D. K. and Suryanarayana Rao, K., *Curr. Sci.*, 1966, **35**, 360.

A NEW TANNIN FROM *ACACIA LEUCOPHLOEA* STEM BARK

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THE highly astringent bark of *Acacia leucophloea* has been reported to contain varying amounts of tannins. In the present communication we report the isolation and characterisation of isookanin, cyanin, leucodel-