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Evaluation of Molecular Parameters: Viscosity Variation Method

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A new method of evaluating dipole moment of a polar molecule in a non-polar solvent by viscosity variation is proposed. This method needs dilute solution of only one concentration and will be quite useful to evaluate molecular parameters of newly synthesized compounds.

Key Words: Electrical dipole moment, Dielectric relaxation time, Viscosity.

INTRODUCTION

Various methods are available in literature for finding molecular parameters, dipole moment μ and dielectric relaxation time τ from dilute solution measurements can be classified into two methods involving (i) frequency variation at single concentration[1–3] and (ii) concentration variation at single frequency[4–10].

For dilute solutions well-tested Debye theory is available dealing with dielectric dispersion and absorption[11, 12]. The Debye relations are

$$\varepsilon' = \varepsilon_\infty + \frac{4\pi w_2 N d\mu^2(\varepsilon_0 + 2)(\varepsilon_\infty + 2)}{27KTM(1 + \omega^2\tau^2)} \quad (1)$$

$$\varepsilon'' = \frac{4\pi w_2 N d\mu^2(\varepsilon_0 + 2)(\varepsilon_\infty + 2)\omega\tau}{27KTM(1 + \omega^2\tau^2)} \quad (2)$$

where ε_0 = static permittivity, ε_∞ = optical permittivity, τ = dielectric relaxation time, μ = dipole moment, K = Boltzman constant, N = Avogadro's number, T = absolute temparature, d = density, w_2 = concentration of solute molecule, M = molecular weight of solute molecule and ω = angular frequency.

$$\text{Loss tangent } \tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

For dilute solutions Smyth[13] suggested that the difference between ε_0, ε_∞ and ε' is not much and therefore the equation for loss tangent can be written as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon' + 2)^2 4\pi w_2 N d_{12}\mu^2\omega\tau}{\varepsilon' 27KTM(1 + \omega^2\tau^2)} \quad (4)$$

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or low concentrations, for which Debye theory is valid, the density of solution d_{12} can be taken as equal to the density of solvent d_1. Further, when viscosity of the solution is varied by adding paraffin, ε' does not change much at a given temperature and hence the equation for loss factor can be written as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{A\omega\tau}{1+\omega^2\tau^2} \tag{5}$$

where $$A = \frac{(\varepsilon'+2)^2 4\pi w_2 N d_1 \mu^2}{\varepsilon' 27\, KTM} \text{ is a constant.} \tag{6}$$

According to Debye relation, $$\tau = \frac{4\pi\eta a^3}{KT} \tag{7}$$

This relation indicates that as viscosity η increases, τ will increase. The loss factor tan δ exhibits a maximum when $\omega\tau = 1$ and $\tan \delta_{max} = A/2$. Thus, measurement of the maximum loss factor enables evaluation of A. Hence μ can be calculated using equation (6).

Using a set up similar to that of Heston *et al.*[14], the waveguide dielectric cell is filled with a single concentration dilute solution of a polar solute in a non-polar solvent. The inverse standing ratio ρ_n at n different minima along the dielectric cell is measured. From the distance between different adjacent minima positions in dielectric cell, wavelength in dielectric sample λ_d is calculated. A plot of ρ_n *vs.* n is made and its slope is evaluated. From the slope of this linear plot ε' and ε'' are determined using the relations[14]

$$\varepsilon'' = [\text{Slope of } \rho_n \textit{ vs. } n\lambda_d/2](1/\pi)(\lambda_0^2/\lambda_g) \tag{8}$$

$$\varepsilon' = [\lambda_0/\lambda_c]^2 + [\lambda_0/\lambda_d]^2 \tag{9}$$

where λ_0 = free space wavelength, λ_c = cutoff wavelength of waveguide, λ_g = guide wavelength.

This procedure is repeated by varying the viscosity of the medium, by adding paraffin, till tan δ reaches a maximum. From this maximum value of tan δ, A is found and μ is calculated using equation (6).

From the same experimental data, the relaxation time τ also can be calculated using method of Patil *et al.*[15]. According to this method the ratio of tan δ with no paraffin and tan δ_{max} is

$$\frac{\tan \delta}{\tan \delta_{max}} = \frac{2\omega\tau}{1+\omega^2\tau^2}. \tag{10}$$

This equation is solved and appropriate root gives the value of τ.

To test the validity of the proposed method, the molecular parameters μ and τ of some polar molecules are computed using the method and nonpolar solvents of spectral grade. The results are given in Table-1. The molecular parameters are also evaluated using Gopalakrishan's concentration variation method[6] and are given for comparison. Some of the data are taken from literature[16–18].

TABLE-1
LOSS FACTOR, DIPOLE MOMENT AND DIELECTRIC RELAXATION TIME

Compound	% paraffin	tan δ	I		II	
			μ Debyes	τ picosec	μ Debyes	τ picosec
Ethyl benzoate	0	0.0167	1.73	10.4	1.82	10.4
	10	0.0189				
	20	0.0174				
Amyl benzoate	0	0.0135	1.94	12.3	1.86	13.4
	10	0.0189				
	20	0.0174				
Amyl salicylate	0	0.0171	2.26	13.9	2.09	14.5
	10	0.0175				
	20	0.0162				
Dimethyl phthalate	0	0.0145	2.23	8.5	2.5	6.6
	10	0.0175				
	20	0.0183				
	30	0.0174				
Diacetyl adipate	0	0.0141	2.31	6.3	2.47	5.0
	10	0.0163				
	20	0.0169				
	30	0.0218				
	40	0.0172				
Diethyl phthalate	0	0.0170	2.52	9.5	2.65	9.5
	20	0.0198				
	30	0.0201				
	40	0.0181				
Indole	0	0.0126	2.00	10.1	2.25	13.0
	5	0.0144				
	10	0.0124				
Methyl benzoate	0	0.0167	1.84	8.6	1.92	6.3
	10	0.0182				
	20	0.0216				
	30	0.0200				
o-Nitrophenyl acetic acid	0	0.0203	2.91	9.5	3.03	12.7
	7	0.0247				
	15	0.0232				
o-Tolyl acetic acid	0	0.0108	2.50	4.5	2.22	4.4
	5	0.0188				
	20	0.0221				
	30	0.0207				

Conclusions

The variation of loss tangent with viscosity indicates that tan δ increases with increasing viscosity, reaches a maximum and then decreases. The present method gives values of molecular parameters comparing well with that of the method of Gopalakrishna[6].

The proposed method will be quite useful to evaluate molecular parameters of newly synthesized compounds. In such cases quantity available may not be sufficient enough to make different concentration dilute solutions as required in some other methods. The proposed method needs dilute solution of only one concentration. Accuracy can be improved by taking readings at closer intervals of % paraffin.

However, this method is useful in finding molecular parameters of molecules which have a relaxation time τ such that $\omega\tau < 1$ at a given frequency.

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