

## Measurements on polar liquids at a microwave frequency – evaluation of molecular parameters – a new method

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**Abstract.** A simple method of estimating the dipole moment ( $\mu$ ) and relaxation time ( $\tau$ ) of polar molecules in liquid state, from a single set of dielectric measurements at high frequency, is proposed by using the concept of dielectric virial coefficients and employing Onsager model. The proposed method is tested in a number of polar liquids and the results are discussed.

**Keywords.** Dipole moment; dielectric relaxation; dielectric virial coefficients.

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### 1. Introduction

There are methods available for the estimation of dipole moment of polar molecules from static dielectric measurements on pure polar liquids [1–4]. But there are no simple methods available to evaluate the dipole moment and relaxation time of polar molecules in the liquid state from a single set of measurements at high frequencies apart from a few empirical relations [5–8]. In the process of searching for a simpler technique, the authors have succeeded in arriving at a simpler method. The method is described below.

The concept of dielectric virial coefficients of dilute solutions is approximated suitably for the case of liquids. Buckingham and Raab [9] developed a comprehensive treatment of concentration variation of ellipsoidal molecules. The orientation polarisation is expressed as a power series of the concentration of the solute.

$$\left[ \left( \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \right) - \left( \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \right) \right] \frac{1}{c_1} = A + Bc_1 + Cc_1^2 + \dots, \quad (1)$$

where  $\epsilon_{12}$  is the dielectric constant of the solution,  $n_{12}$  the refractive index of the solution,  $c_1$  the concentration of the solute =  $(W_2 d_{12} / M_2)$ ,  $W_2$  the weight fraction of the solute,  $d_{12}$  the density of the solution and  $M_2$  the molecular weight of the solute.

$A, B, C$  etc. are constants called as dielectric virial coefficients which are independent of concentration but dependent on temperature.  $A$  represents contribution due to monomers,

$B$  due to dimers and  $C$  due to triplets. The above equation of Buckingham and Raab seems to be based on Debye's [10] model. For pure polar liquids the possible interactions are only of dipole–dipole in nature. Except in associative liquids the chances of formation of dimers, triplets etc. are very very remote in pure polar liquids. Hence the contribution of only monomers need be considered. Further, Onsager's [2] model gives a better representation of liquid molecules than Debye model. Using the Onsager model eq. (1) is rewritten for liquids as

$$\left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2\epsilon + n^2)(\epsilon + 2)}{3\epsilon(n^2 + 2)} \frac{M}{d} = A, \quad (2)$$

where  $M$  is the molecular weight of the liquid,  $d$  the density of the liquid,  $\epsilon$  the permittivity of the liquid and  $n$  the refractive index of the liquid.

At the high frequency region where dispersion occurs, the permittivity becomes a complex quantity  $\epsilon^* = \epsilon' - j\epsilon''$  and the magnitude of permittivity is  $\epsilon = |\epsilon^*| = (\epsilon'^2 + \epsilon''^2)^{1/2}$ . This value of  $\epsilon$  is used in the above equation.

Using the method of Murthy *et al* [11]  $\epsilon'$  and  $\epsilon''$  are determined for several liquids. In addition, the refractive index  $n$  of the liquids for sodium light is also measured. Using these data and eq. (2),  $A$  is evaluated. The dipole moment  $\mu$  of the polar molecule can be calculated from the relation

$$\mu^2 = \frac{9KT}{4\pi N} A, \quad (3)$$

or

$$\mu = 0.0128\sqrt{AT}, \quad (4)$$

where  $T$  is the temperature in Kelvin where measurements are carried out.

The relations of complex permittivity are [12]

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + \omega^2\tau^2}, \quad (5)$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + \omega^2\tau^2}. \quad (6)$$

By division we get

$$\frac{\epsilon''}{\epsilon' - \epsilon_\infty} = \omega\tau. \quad (7)$$

Assuming  $\epsilon_\infty = n^2$ , knowing  $\epsilon', \epsilon''$  using eq. (7)  $\tau$  can be calculated.

Thus as per the method proposed, to find  $\mu$  and  $\tau$  of a liquid molecule the data required are  $\epsilon', \epsilon''$  at a single frequency at room temperature and  $n^2$ . The molecular parameters of several polar liquids at 9.2 GHz are computed using the proposed method and eqs (4) and (7) taking relevant data from [13–17]. The results are given in table 1 along with the static values from literature.

**Table 1.** Molecular parameters of some polar liquids.

Polar liquid	Parameters at 9.2 GHz (present method)		Static parameters from literature	
	$\mu$ (Debye)	$\tau$ (pico-sec)	$\mu$ (Debye)	$\tau$ (pico-sec)
1-2 Dibromopropane	1.07	10.4	1.27	10.6
Bromobenzene	1.09	15.5	1.39	16.4
Chlorobenzene	1.29	10.3	1.47	10.3
Benzyl acetate	1.39	9.7	1.68	11.8
Fluorobenzene	1.39	5.5	1.46	5.7
Amyl butyrate	1.55	7.8	2.07	9.4
Butyl butyrate	1.61	8.1	1.97	8.6
Ethyl butyrate	1.68	7.9	1.97	7.8
Methyl acrylate	1.70	4.0	1.90	5.3
Butyl acrylate	1.75	6.8	2.03	7.9
Nitrobenzene	2.33	32	4.19	46

## 2. Conclusions

The agreement between  $\tau$  values is satisfactory (the present method also gives values of  $\tau$  of the same order of magnitude as in literature). The differences observed in some cases could be due to the approximation  $\epsilon_\infty = n^2$  or because the present method evaluates the data at 9.2 GHz. Regarding  $\mu$ , the values obtained by the present method are lower than the literature values. This is due to the reason that the present method gives values at 9.2 GHz whereas literature values are static values either in liquid or in gaseous state. Further, in formulating the method the contribution due to monomers only is considered.

The proposed method enables a quick determination of both molecular parameters of polar liquids at a microwave frequency from a single set of measurements.

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