Asian Journal of Chemistry Vol. 15, No. 2 (2003), 1187–1189

NOTE

Investigation of Dielectric Virial Coefficients of Methoxyacetic Acid

M.B.R. MURTHY*, B.S. DAYASAGAR and R.L. PATIL†
F.E.T. Multimedia University, Melaka-75450, Malaysia
E-mail: mandalaparty.ramamurthy@mmu.edu.my
Tel: 00606–2523331, Fax: 00606–2316552.

Dielectric virial coefficients throw light on short-range molecular interactions. This provides an insight into solute dimerization. An attempt is made to evaluate dielectric virial coefficients of methoxy acetic acid in three solvents. Using the first virial coefficient the apparent solution moment of methoxy acetic acid is calculated.

Key Words: Dielectric virial coefficients, dipole moment, Methoxyacetic acid.

Buckingham and Raab[1] described a method of finding *solution dielectric virial coefficients.* The *orientation polarization* is expressed as a power series of concentration of the solute.

$$\left[\left(\frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}\right)-\left(\frac{n_{12}^2-1}{n_{12}^2+2}\right)\right]\frac{1}{c_1} = A + Bc_1 + Cc_1^2 + \ldots \tag{1}$$

where ε_{12} = Dielectric constant of solution, n_{12} = Refractive index of solution, c_1 = Concentration of the solute = (W_2d_{12}/M_2), W_2 = Weight fraction of solute, d_{12} = Density of solution, M_2 = Molecular weight of solute and the coefficients A,B,C etc. are constants called as dielectric virial coefficients that are independent of concentration but depend on temperature.

If one assumes the solution to contain a number of monomers, dimers, trimers, etc., coefficient A represents contribution of the single polar molecules, coefficient B corresponds to that of dimers and so on. Based on Debye theory[2], using the equation

$$A = \left(\frac{4\pi N}{9KT}\right)\mu_s^2 \tag{2}$$

the solution dipole-moment determined gives dipole-moment of monomer even if the solute is an associated liquid. In a dimer assume that there exist only two

---

†Physics Department, Karnatak University, Dharwad, 580 003, India.

types of interactions within the spherical volume under consideration, namely, (i) short range forces due to interactions within the sphere and (ii) long range forces due to intra- and intermolecular interactions. Hence coefficient B may be written as

$$B = B_S + B_L. \tag{3}$$

The contribution of B_L to B is negative as polarization induced on the surface of elementary sphere is of opposite sign to that of dipole.

Buckingham and Raab[1] derived an expression for the dilute solutions as below:

$$\left(\frac{n_{12}^2 - 1}{n_{12}^2 + 2}\right) - \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right) = Xc_1 + Yc_1^2 + \ldots \tag{4}$$

where ε_1 = static permittivity of solvent and coefficients X and Y are functions of temperature but not of concentration.

The expressions for B_L and B_S are given by:

$$B_L = \frac{-4(\varepsilon_1^2 - 1)(\varepsilon_1 + 2)}{3\varepsilon_1(2\varepsilon_1 + 1)} A(A + X) \tag{5}$$

$$B_S = \frac{A}{k'}\left[\frac{\langle m_{12}^2\rangle}{m^2} - 2\right]. \tag{6}$$

To find B_S using eqn. (6) one must know the equilibrium constant for dissociation of dimers k′ and the mean square dipole moment of dimer inside the volume $\langle m_{12}^2\rangle$.

Alternatively, without measuring the values of k′ and $\langle m_{12}^2\rangle$ another method of finding *solution dielectric virial coefficients* is to find the dielectric constant ε_{12}, refractive index for sodium D line n_{12} of several graded dilute solutions of the sample. From these data, using equation (4) given above, formulating appropriate number of simultaneous equations (neglecting c_1^3 and higher order terms) the values of the coefficients A, B and X can be evaluated. Using eqn. (5) B_L can be found and B_S is estimated from the equation

$$B_S = B - B_L. \tag{7}$$

From the value of A the dipole moment of polar molecule in solution μ_S can be evaluated. This methodology is adopted in the present work.

The static dielectric constant ε_{12} of several graded dilute solutions of methoxy acetic acid in three different solvents namely benzene, dioxane and cyclohexane are measured at 1.00 MHz by measuring the capacitance of dielectric cell with and without sample using the author's simple technique[3]. The values of n_{12}, the refractive index for sodium-D line of the dilute solutions, are determined. The values of A, B, μ_S, X, Y, B_L and B_S are determined using the method described above. Using Higasi method[4] the r.f. μ is calculated. The results are presented in Table-1[5].

TABLE-1
EVALUTION OF DIELECTRIC VIRIAL COEFFICIENTS OF METHOXY ACETIC ACID AND COMPARISON OF STATIC DIPOLE MOMENT

Solvent	r.f. μ (debyes)	A (cm^3)	B (cm^6)	B_L (cm^6)	B_S (cm^6)	μ_s (debyes)
Benzene	2.16	170.9	–235369	–32234	–203135	2.89
1,4-Dioxane	2.59	190.6	32510	–708314	740824	3.06
Cyclohexane	1.95	32.2	191474	–3944	195418	1.30

Conclusion

Normally positive values for B_S in solution are to be expected as solvent reduces the possibility of closed pairs. This is the case with solvents 1,4-dioxane and cylohexane. However, with benzene B_S is negative and this may be due to anti-parallel arrangements being favoured in pair formation. In such case mean square dipole moment of pair will be greatly reduced leading to negative values for B_S. The magnitude of B_S depends on interaction potential energy when the two molecules are paired. Large negative values can be attributed to strong binding between the two interacting molecules in a closed dimer, which is the case with benzene. The dimerization is also solvent dependent. The interaction potential energy between two molecules in a closed dimer also varies from solvent to solvent. As such a particular solute may possess different values for B, B_S, B_L in different solvents, which is clear from the results in Table-1. Further the coefficient A varies from solvent to solvent, being smallest in cyclohexane and smaller in benzene than dioxane.

The solution dipole moments calculated using A are in satisfactory agreement with values found by other methods. The small differences observed in the values of μ for a solvent may be due to the approximations made in deriving the mathematical expressions for virial coefficients (namely, neglecting the difference between ε_1 and n_1^2 and neglecting the higher order terms of c_1 etc.).

REFERENCES

1. A.D. Buckingham and B.R. Raab, *Trans. Faraday Soc.*, **55**, 377 (1959).
2. P. Debye, Polar Molecules, The Chemical Catalog Company, New York (1929).
3. M.B.R. Murthy and R.L. Patil, *J. Instrument Society of India*, **19**, 297 (1989).
4. K. Higasi, *Bull. Chem. Soc. (Japan)*, **39**, 2168 (1966).
5. M.B.R. Murthy, Application of microwave techniques for the study of dielectric properties of some substances, Ph.D Thesis, Karnatak University, Dharwad (1989).

(*Received*: 25 November 2002; *Accepted*: 22 January 2003) AJC-3009