

Evaluation of electric dipole moment from dielectric studies of liquids

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Abstract: Dipole moments of 2-methyl-2-propanol (tert-butyl alcohol) and 2-methyl-2-propanethiol (tert-butyl mercaptan) have been determined using the Onsager equation with different feedback parameters the Debye equation under different approximations of the lattice structure formed by the solvent molecules and the simplified equations of Guggenheim and Halverstadt Kumler in the dilute solution limit of the non-polar solvents. For tert-butyl alcohol (TBA) the calculations have also been extended in the higher concentration range.

1. Introduction

Although the correct estimation of the electric dipole moment of an isolated molecule is possible only from the measurement of the stark splitting of the microwave spectral lines and by the molecular beam electric resonance (MBER) method at extremely low pressures, yet from the dielectric studies of the solutions the dipole moment of the solute molecule may be estimated. All such methods have been employing simple Debye equation in one or the other form or the Onsager equation, which has been used mainly for the determination of the dipole moment of the pure solution and the Kirkwood correlation parameter (g). Van-Vleck (1972) pointed out that the dielectric constants of even a very dilute solution of polar molecules in non-polar solvent depend upon the geometry of the non-polar and the polar molecules.

In the present communication the dipole moments of tert-butyl alcohol (TBA) and tert-butyl mercaptan (TBM) have been estimated using the Debye equation (Debye 1928), its simplified versions given by Guggenheim and Halverstadt Kumler and the Onsager equation. The modifications of Van-Vleck (1972) into the Debye and Onsager equations have also been considered. For TBA, taking the dielectric data of system TBA-benzene and TBA-cyclohexane (Dwivedi 1978), the calculations have been carried out in all the concentration range of solute at 31°C, while for TBM taking the dielectric data of TBM-benzene system at 25°C (Kumar 1970) calculations are confined in the dilute solution limit only.

According to Onsager (Onsager 1936) the dipole moment of a polar molecule may be obtained from the following equation

$$\frac{4\pi N_2}{3kT} \cdot \frac{\mu^2}{3} = \frac{(\epsilon_{02} - \epsilon_{\infty 2})(2\epsilon_{02} + \epsilon_{\infty 2})}{\epsilon_{02}(\epsilon_{\infty 2} + 2)^2} \quad (1)$$

where N_2 is equal to $\frac{N}{V_2}$, N being the Avagadro's number and V_2 the molar volume of the solute, μ is the electric dipole moment of the solute. This equation has been used by Crossley (1971), Eyring (1969) and many others for the solutions by substituting the solution data in RHS of equation (1). Van Vleck (1972) rederived the Onsager equation for solutions in the following form

$$\frac{(\epsilon_0 - 1)(2\epsilon_0 + 1)}{12\pi\epsilon_0} = N_1\gamma_1\alpha_1 + N_2\gamma_2\alpha_2 + \frac{N_2\gamma_2^3}{3kT} \mu^2 \quad (2)$$

where γ_1 and γ_2 are the feed-back or the amplification factor of the reaction field given by

$$\left. \begin{aligned} \gamma_1 &= \frac{1}{1 - \frac{8\pi}{3} \frac{\alpha_1}{v_1} \left(\frac{\epsilon_{01} - 1}{2\epsilon_{01} + 1} \right)} \\ \gamma_2 &= \frac{1}{1 - \frac{8\pi}{3} \frac{\alpha_2}{v_2} \left(\frac{\epsilon_{02} - 1}{2\epsilon_{02} + 1} \right)} \end{aligned} \right\} \quad (3)$$

here v_1 and v_2 represent the cavity volumes of the solvent and solute respectively and has been taken by Van Vleck as the mean molecular volume in the following form

$$v_1 = v_2 = \frac{1}{N_1 + N_2} = \frac{V}{N} \quad (4)$$

Tables 1 to 6 list the dipole moments of tert-butyl alcohol in benzene and cyclohexane at different concentrations, and of tert-butyl mercaptan in benzene. The dipole moments listed in tables 1, 2 and 3 have been calculated from the Debye equation (Van Vleck 1972) for $Q = 0, 16.8$ and 35.1 ; Guggenheim equation and Halverstadt Kumler equation (Guggenheim 1949, Kumler 1942) for the three systems. The dipole moments listed in tables 4, 5 and 6 have been calculated from the Onsager equation (1936), equation (1), Onsager equation (2) under the reaction field concept of Onsager and the Onsager equation under the reaction field concept of Van-Vleck (equations 3 and 4). From tables 1, 2 and 3 we find that for all the three systems the dipole moment for $Q = 16.8$ and 35.1 is almost the same as that of $Q = 0.0$ in the dilute solution limit as well as for

Table 1. Dipole moment in Debye with MF Concentration of TBA in TBA-benzene system determined from Debye equation with different Q values, Guggenheim equation and Halverstadt Kumler (HK) equation at 31°C

MF	Debye equation			Guggenheim equation	H.K. equation
	$Q = 0$	$Q = 16.8$	$Q = 35.1$		
0.0886	1.66	1.67	1.68	1.70	1.68
0.2164	1.60	1.61	1.61	1.73	1.68
0.2948	1.58	1.59	1.60	1.77	1.71
0.3883	1.57	1.58	1.58	1.82	1.74
0.4736	1.55	1.56	1.56	1.86	1.76
0.5976	1.58	1.58	1.59	2.03	1.88
0.7104	1.58	1.58	1.58	2.17	1.97
0.8104	1.57	1.57	1.57	2.28	2.06
0.8920	1.58	1.58	1.58	2.44	2.17
1.0000	1.57	1.57	1.58	2.66	2.33

Table 2. Dipole moment in Debye with MF concentration of TBA in TBA-cyclohexane system determined from Debye equation with different Q values, Guggenheim equation and Halverstadt Kumler (HK) equation at 31°C

MF	Debye equation			Guggenheim equation	H.K. equation
	$Q = 0$	$Q = 16.8$	$Q = 35.1$		
0.0778	1.17	1.18	1.19	1.21	1.26
0.1635	1.19	1.20	1.21	1.26	1.28
0.2470	1.22	1.22	1.23	1.31	1.31
0.3412	1.25	1.26	1.27	1.37	1.36
0.4328	1.32	1.33	1.33	1.49	1.43
0.5369	1.41	1.42	1.42	1.68	1.55
0.6907	1.53	1.53	1.53	2.02	1.78
0.7606	1.57	1.57	1.57	2.22	1.92
0.8831	1.60	1.60	1.60	2.59	2.18
1.0000	1.57	1.57	1.57	2.81	2.35

higher concentrations, which shows that it is immaterial to account for the lattice structure presented by the solvent molecules according Van-Vleck correction term $[2N_1^2 Q \alpha_1 (\alpha_2 - \alpha_1)]$. We also find that in all the systems for a particular

Table 3. Dipole moment in Debye with MF concentration of TBM in TBM-benzene system determined from Debye equation with different Q values, Guggenheim equation and Helverstadt Kumler (H K) equation at 25°C

MF	Debye Equation			Guggenheim equation	H K equation
	$Q = 0$	$Q = 16.8$	$Q = 35.1$		
0.0123	1.83	1.82	1.80	1.84	1.81
0.0246	1.74	1.72	1.71	1.75	1.76
0.0370	1.64	1.62	1.61	1.66	1.68
0.0494	1.60	1.59	1.58	1.64	1.66
0.0607	1.60	1.59	1.57	1.64	1.66
1.0000	1.36	1.36	1.36	1.74	1.70

Table 4. Dipole moment in Debye with MF concentration of TBA in TBA-benzene system determined from Onsager's Original equation, Onsager equation with his own concept of reaction field and Onsager equation with Van-Vleck concept of the reaction field at 31°C

MF	Onsager equation	Onsager Equation		
		Onsager Reaction Field	Van-Vleck Reaction Field	
			Solute data	Solution data
0.0886	1.67	1.65	1.67	1.65
0.2164	1.68	1.66	1.67	1.66
0.2948	1.71	1.68	1.70	1.69
0.3883	1.74	1.72	1.74	1.73
0.4736	1.77	1.75	1.78	1.77
0.5976	1.91	1.91	1.93	1.93
0.7104	2.03	2.03	2.06	2.05
0.8104	2.12	2.13	2.16	2.16
0.8920	2.26	2.25	2.28	2.28
1.0000	2.46	2.47	2.51	2.51

value of Q the concentration dependence of the dipole moment is irregular showing the inadequacy of the Debye equation for calculating the dipole moment. The Guggenheim equation yields the highest value of the dipole moment than obtained from Debye or H.K. equation, and may be because of the assumption that the factor $(\epsilon_0 + 2)(\epsilon_\infty + 2)$ is equal for both the solvent and the solutions, which does not hold at any concentration for the systems studied here. The

Table 5. Dipole moment in Debye with MF concentration of TBA in RBA-Cyclohexane system determined from Onsager's Original equation, Onsager equation with his own concept of reaction field and Onsager equation with Van-Vleck concept of the reaction field at 31°C

MF	Onsager Equation	Onsager Equation		
		Onsager Reaction Field	Van-Vleck Reaction field	
			Solute data	Solution data
0.0778	1.21	1.09	1.11	1.15
0.1635	1.24	1.13	1.14	1.18
0.2470	1.28	1.17	1.18	1.22
0.3412	1.33	1.24	1.24	1.28
0.4328	1.43	1.33	1.35	1.38
0.5369	1.57	1.49	1.51	1.54
0.6907	1.84	1.79	1.82	1.84
0.7606	2.00	1.97	1.99	2.01
0.8831	2.29	2.28	2.31	2.33
1.0000	2.46	2.47	2.51	2.51

Table 6. Dipole moment in Debye with MF concentration of TBM in TBM-benzene system determined from Onsager's Original equation, Onsager equation with his own concept of the reaction field and the Onsager equation with Van-Vleck concept of reaction field at 25°C

MF	Onsager equation	Onsager Equation		
		Onsager reaction field	Van-Vleck Reaction Field	
			Solute data	Solution data
0.0123	1.82	1.80	1.84	1.72
0.0246	1.74	1.72	1.75	1.65
0.0370	1.65	1.62	1.65	1.55
0.0494	1.62	1.59	1.62	1.50
0.0607	1.62	1.60	1.63	1.50
1.0000	1.63	1.67	1.70	1.70

departure from the basic Guggenheim assumption increases with the static dielectric constant of the solute. The differences in the values of the dipole moments, evaluated from Guggenheim and H.K. equation, are more in TBA

than in TBM for higher concentration. This may be because of the associated and non-associated nature of the solutes.

From tables 4, 5 and 6 we find that the dipole moment, as calculated according to the different forms of Onsager equation, increases with concentration in the systems TBA-benzene and TBA-cyclohexane, but with a larger difference in the values of dipole moment at extreme concentrations for the later. In TBM-benzene, which is a non-associated system, the dipole moment at first decreases with concentration and then starts increasing after about 0.05 M.F.

Debye equation, giving almost concentration independent dipole moment for TBA, does not seem to explain the association from the dielectric studies, whereas Onsager equation does. Guggenheim and H. K. equation, being the extensions of Debye equation, suffer the same approximation as the Debye equations. Onsager equation (1) is valid for pure liquid only, and therefore its extension as such for solutions is questionable. Thus the Onsager equation (2) with γ_2 given by equation (3) seems to be more plausible equations for estimating the values of dipole moments. Smaller values of the dipole moment of TBA in TBA-cyclohex system at low concentrations is due to the inductive mesomeric effects exhibited by the cyclohexane, showing that the cyclohexane is not an inert system.

Calculations of the dipole moment according to equation (2) under the Van-Vleck or the Onsager relation field concept does not require the refractive index (ϵ_∞) of the solution, needing ϵ_∞ of the pure solute only.

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