Study of dipole moment of 18-crown-6 in CCl\textsubscript{4} solutions at 298.15 K

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Dielectric constant (ε), density (d) and refractive index (n) measurements at 298.15 K for solutions of 18-crown-6 in CCl\textsubscript{4} (0.5 to 25 × 10\textsuperscript{-3} weight fraction of solute) have been reported. The data, along with partial molar volume data for solute are subjected to analysis using various equations to obtain solute polarization and dipole moment values at finite and infinitely dilute concentrations. The dipole moment value of 3.5 D has been compared with gas-phase value and the values in solutions of benzene and cyclohexane, reported earlier. The unexpected large value of dipole moment obtained has been discussed in terms of conformation adopted by the cyclic polyether in a solvent environment. It is further explained that, in solution phase if 18C6 molecules exist in $C_1$ symmetry conformation (this cannot have dipole moment), the atomic polarization via $-\text{CH}_2-$ chains must be making large contribution to account for the observed solute polarization.

1 Introduction

Macro cyclic polyethers have been the subject of much attention since these cyclic compounds and their derivatives exhibit remarkably high specificity in binding to several cationic species\textsuperscript{1}\textsuperscript{–}8. Crown ether 18-crown-6 (1,4,7,10,13,16 hexaoxaacyclo octadecane) (18C6) is the archetype of the great family of crown ethers. The most prominent feature of 18C6 is, its capability to complex alkali metal ions in a polar cage of oxygen by un-directed coulomb forces (spherical recognition) and to transport them eventually into lipophilic phases. The crown is able as well to bind neutral polar guest molecules by H-bonds and directed dipolar forces (molecular recognition)\textsuperscript{9}. Thus, many theoreticians in their simulation and molecular dynamic studies have considered 18C6 as the most simple model system for understanding the fundamental enzyme properties.

In recent years, the research work from this laboratory was concerned with the volumetric, viscosity, NIR spectral, self-diffusion coefficient and NMR relaxation properties of 18C6 in water and in non-aqueous solutions\textsuperscript{10}\textsuperscript{–}11. It has been shown from X-ray diffraction and Raman spectroscopic studies\textsuperscript{12}\textsuperscript{–}13 that, 18C6 molecules attain $D_{ad}$ conformation in the presence of certain guest or solvent molecules in solid state as well as in liquid phase\textsuperscript{12}\textsuperscript{–}13. In contrast, pure 18C6 exists in $C_1$ conformation, in the gas and solid phases along with little proportion of $C_1$, while, Ha & Chakraborty\textsuperscript{14} have interpreted their Monte-Carlo simulation results in liquid CCl\textsubscript{4}, in terms of $C_1$ conformation for 18C6. Kowall & Geiger\textsuperscript{15} from simulation studies, and the authors of present paper from experimental NIR spectral data have shown that, in aqueous 18C6 solutions, at least four water molecules are H-bonded with the oxygen atoms of 18C6 (two bridging and two singly H-bonded). These water molecules along with hydrophobic interaction with solvent stabilize the $D_{ad}$ conformation. The D\textsubscript{2}O relaxation studies of aqueous 18C6 and KBr solutions further indicated that, the electrostatic interaction of K\textsuperscript{+} dominates and replaces water molecule during complexation. Viscosity studies indicated that, in CCl\textsubscript{4} solutions, the B coefficient of Jones-Dole equation remain constant as a function of temperature, while in water, the B coefficient values are high and have $-dB/dT$ behaviour. This indicated that, in CCl\textsubscript{4} solutions, 18C6 might be in $C_1$ conformation while, it is in $D_{ad}$ in aqueous solutions.

Dipole moment is a molecular property and depends upon the charge distribution and shape of molecule. Similarly, the dielectric properties are to some extent structure-sensitive, that is, they depend upon the correlation or interaction between the electric dipoles, both permanent and induced. In order to gain additional information about $C_1$ conformation, a literature survey of dipole moment properties of 18C6 is made and found that, the dipole moment value is 2.6 D in gas phase while, it is 2.76 D in cyclohexane and the temperature
variation has been interpreted in terms of the presence of mixtures of conformers\textsuperscript{16,17}. The molecular dynamics simulation studies in cyclohexane have indicated shifts in the spectrum of conformations, and the value of average root-mean square dipole moment of 18C6 is in agreement with the experiment, on the basis of two potential models. However, this was achieved by studying modified charge-density distribution for 18C6 molecules\textsuperscript{16}. Since the potential assumed or derived should take into account the environmental effects as well, there is a need to have similar studies in variety of solvents. Therefore, it was thought interesting to measure dipole moment property which can be related to conformations of 18C6 in solutions. In this paper, the measurements of dielectric constant, refractive index and density parameters in solutions of 18C6 in CCl\textsubscript{4} have been reported. The derived dipole moment value is discussed on the basis of conformation and the properties of 18C6.

2 Experimental Details

18C6 (99% pure) procured from Merck-Schuchardt was used without further purification. The contact with atmospheric moisture was avoided by handling 18C6 in a dry box, fabricated in our laboratory. CCl\textsubscript{4} (HPLC grade, Merck) was used after distillation. All the solutions in CCl\textsubscript{4} were prepared on molality basis in glass-stoppered bottles using Mettler Toledo (AB204-S model), weighing balance having ±0.1mg readability. The concentrations were converted into molarity, weight-fraction (0.5 to 25 \times 10\textsuperscript{-3} range) and molar-fraction scales using density data and usual expressions.

The refractive index (n) measurements were carried out, using a Russian thermostat refractometer, at 298.15 ± 0.02 K. The values of (n) were obtained in daylight and have the accuracy of ±5 \times 10\textsuperscript{-4}. It was observed that, in the studied concentration range, n did not vary much and remained more or less constant within the limits of experimental uncertainty.

The density measurements were carried out by using Anton Paar oscillating tube digital densitometer (model DMA 60/602), at 298.15 ± 0.02 K. The reproducibility in the density values was of the order of ±1 \times 10\textsuperscript{-3} Kg m\textsuperscript{-3}. The details about the calculations of the partial molar volumes using the density data, at finite concentrations and at infinite dilution are described elsewhere\textsuperscript{19}.

The relative permittivity (ε) measurements were made at 298.15 ± 0.02 K and at a frequency of 1.8 MHz using Toshiba (Type No RL 09, Sr No 5243) dipole-meter. The cell was a two terminal body having electrodes made up of brass and then plated with gold (to avoid corrosion) and having capacity for air, equal to 19.1 pF. The cell was thermostated through the outer jacket, by circulating water from a constant temperature cryostat (Julabo-F25) having the accuracy in maintaining temperature constancy of ±0.02 °C. The cell was initially calibrated using the purified liquids like, benzene, toluene and CCl\textsubscript{4}, as well as mixtures of CHCl\textsubscript{3}-C\textsubscript{6}H\textsubscript{6} and p-nitrotoluene-CCl\textsubscript{4}. The dipole moment values for chloroform and p-nitrotoluene were found to be 1.15 and 3.9 D at 298.15 K which agreed very well with the best literature data available\textsuperscript{20,21}. The instrument is old but with careful experimentation, one could determine the dipole

<table>
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<th>m (Kg mol\textsuperscript{-1})</th>
<th>1000\textsuperscript{1}</th>
<th>d (Kg m\textsuperscript{-3})</th>
<th>10\textsuperscript{3} \times V\textsubscript{m} (mm\textsuperscript{3} mol\textsuperscript{-1})</th>
<th>ε</th>
<th>N</th>
<th>10\textsuperscript{3} \times P\textsubscript{2} (mm\textsuperscript{3} mol\textsuperscript{-1})</th>
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<th>μ/D</th>
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<td>97.09</td>
<td>2.2279*</td>
<td>1.4590*</td>
<td>332.3*</td>
<td>0.0170*</td>
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*Values at zero concentration
moment values in non-aqueous solvents with sufficient precision and accuracy. The data of relative permittivity, density and refractive index for various concentrations at 298.15 K are given in Table 1.

![Graph of polarization vs. weight fraction of 18C6 at 298.15 K]

3 Results and Discussion

The calculations of the average dipole moment (\( \mu \)) were made by applying three different equations as given below. It is assumed that, 18C6 is accommodated in a spherical cavity of a continuum of liquid CCl\(_4\), although in final calculations of \( \mu \), a shape factor correction, as carried out by Buckingham\(^{36}\), can be made. However, the authors deferred with such a correction, as it was difficult to visualize the exact conformation and shape of 18C6 in solutions. In the first method, the apparent dipole moment value (\( P_2 \)) for 18C6 was calculated by using mixture law and Eq. (1):

\[
P_2 = M_2P_2 = M_2\left(P + \frac{(P - P_1)}{w}\right)
\]  

where \( P_1 \) and \( P \) are the specific polarization of solvent and solution, respectively, while \( w \) and \( M_2 \), respectively represent weight fraction and the molecular weight of 18C6. \( P_1 \) and \( P \) were estimated using the Eqs (2) and (3), respectively as:

\[
P_1 = \frac{(\varepsilon_1 - 1)\nu_1}{(\varepsilon_1 + 2)}
\]  

\[
P = \frac{(\varepsilon - 1)\nu}{(\varepsilon + 2)}
\]

where \( \varepsilon_1 \) and \( \varepsilon \) are the dielectric constants of solvent and solution, respectively, while \( \nu_1 \) and \( \nu \) represent the corresponding specific volumes. In these equations, small errors in \( \varepsilon \) and \( \nu \) cause disproportionately large error in \( P_2 \), in dilute solutions. To avoid the consequent distortion of the \( P_2 \)-\( w \) plot in the region of dilute solutions, smoothed values of \( \varepsilon \) and \( \nu \) were calculated, using Eqs (4) and (5) and were substituted in Eq. (3) for solutions containing only monomers\(^{35}\).

\[
\varepsilon = \varepsilon_1 + \alpha w
\]

\[
\nu = \nu_1 + \beta w
\]

The resulting \( P_2 \)-\( w \) plot shown in Fig. 1 has the same form as that of experimentally determined \( \varepsilon \)-\( w \) plot (Fig. 2), and is thought to justify this approach. The values of coefficients \( \alpha \) and \( \beta \) are 9.4296 and 0.2588, respectively. In reality, a non-linear behaviour was observed due to some stacking type interaction, in the studied concentration region (weak solute-solute interactions). Such stacking type of interactions are also revealed from osmotic and activity coefficient study of 18C6 in CCl\(_4\), solutions\(^{38}\). The \( P_2 \) value was obtained by extrapolating \( P_2 \) values to infinite dilution. The same can be obtained by use of Halverstadt-Kumler equation\(^{31}\):

\[
P_{2w} = 3M_2\nu_1\alpha\left(\varepsilon_1 + 2\right) + M_2\nu_1 + \beta (\varepsilon_1 - 1)\left(\varepsilon_1 + 2\right)
\]  

where \( \alpha \) and \( \beta \) defined as \((\partial\varepsilon_1/\partial w)_{\nu=m}\) and \((\partial\nu/\partial w)_{\nu=m}\), respectively, were calculated from the equations \( \alpha = \Sigma(\varepsilon_1 - \varepsilon) / \Sigma w \) and \( \beta = \Sigma(\nu - \nu_1) / \Sigma w \). The \( P_{2w} \) value obtained is ~344, while the extrapolated value is 332.34 cm\(^3\) mole\(^{-1}\). The same also can be obtained by using mole fraction statistics. Electron polarization, \( P_e \) were obtained from refractive index values and allowing 10 % of \( \varepsilon P_2 \) for the atom polarization, the molar orientation polarization of 18C6, \( P_2 \), was calculated from Eq. (7).
\[ oP_2 = P_{2^\infty} - 1.1 \epsilon P_2 \]
and the dipole moment:
\[ \mu = 0.01281 (oP_2T)^{1/2} \]

The dipole moment value of 3.51 D has been calculated.

In the second method, the authors applied Guggenheim\textsuperscript{25} for Eq. (9).
\[ D = D_1 + (\alpha P_2 - \epsilon P_2 + \mu_2)C \]
where
\[ D = \frac{\epsilon - 1}{\epsilon + 2} \frac{n^2 - 1}{n^2 + 2} = \frac{3(\epsilon - n^2)}{(\epsilon + 2)(n^2 + 2)} \]
and \( C \) is the concentration of 18C6 in moles per unit volume. Hence, if \( D \) is plotted against \( C \), the intercept yields the value of \( D_1 \), while the initial slope gives the value of \( (\alpha P_2 - \epsilon P_2 + \mu_2) \) or \( [(\alpha P_2 - \epsilon P_2 + (4\pi N\mu^2/9kT)]. \) The variation of \( D \) parameter as a function of \( C \) of 18C6, is shown in Fig. 3. Using the slope value and Eq. (11), the dipole moment value of 3.49 D for 18C6 has been calculated, assuming that \( \alpha P_2 = \mu P_2 \).

\[ \mu = \sqrt{\frac{\text{slope} \times 9kT}{4\pi N}} \]

Of the various modern developments of the Onsagar & Kirkwood treatment in the field of dielectrics, that of Fröhlich\textsuperscript{26} is most generally accepted and used successfully by Stokes & Marsh\textsuperscript{27} for calculation of dipole moment of ethanol dissolved in non-polar solvents. Eq. (12) is used in the present work as a third method to obtain \( \mu \) for 18C6. The Eq. (12) is:
\[ V_m (\epsilon - 1) = \frac{1}{3\epsilon} \left[ (1-x)V_1 (\epsilon_1 - 1) + xV_2 (\epsilon_2 - 1) \right] + \frac{xV_2 (\epsilon_2 - 1)}{\epsilon_2 + 2\epsilon} \]
\[ + \frac{4\pi N \times g \mu^2 (\epsilon_2 + 2\epsilon)^2 (2\epsilon_2 + 1)}{27kT(\epsilon_2 + 2\epsilon)^2} \]

where \( V_m, x, V_1, V_2, \epsilon_1, \epsilon_2, g \) represent molar volume of solution, mole fraction of 18C6, molar volume of solvent, molar volume of solute and square of refractive index of solute by adding 10 \% to the molar refraction to take account of vibrational modes, not excited by visible radiation and Kirkwood correlation factor, respectively. The data used for the application of Eq. (12) are summarized in Table 1. In the last column of Table 1, the individual values of the parameter \( \mu \) are collected at various concentrations of 18C6. If \( g \) is assumed to be unity and the lowest concentration value is
neglected (it may involve large error), the average value of the dipole moment for 18C6 is found to be 3.54 D. It is estimated that, the error involved in the \( \mu \) value is of the order of ± 0.05.

The \( \mu \) values for 18C6 obtained using three methods, outlined above, are in excellent agreement with each other and assigning the average value of \( \mu = 3.51 \text{ D} \). On comparison with the values obtained in the gas-phase (3.02 D), in the cyclohexane (2.94 D) by simulation technique and experimentally determined value in cyclohexane (2.76D), it has been found that, value in CCl\(_4\) is quite high. A much better compound which can serve as a model for interpretation of these results is, 1,4-dioxane (6-crown-2) which has a small \( \mu \) value of 0.45 D. The arguments based on symmetry considerations point out that, for 18C6 in \( D_{6h} \) or in \( C_{1} \) conformation should have \( \mu = 0 \). But, the high value of the dipole moment probably can be attributed to the presence of flexibility of the crown ring, which leads to the existence of conformational dynamic equilibria. Other interpretation of high value of dipole moment is the existence of 18C6 in \( C_{1} \) (i.e. having a mean plane of reflection) symmetry point group (or of \( C_{1} \) type), which leads to a finite value of \( \mu \). The dynamic behavior of pure 18C6 has been studied by NMR relaxation, neutron-scattering technique\(^{28,29}\) and shows that, the interactions in the liquid state are governed by fast conformational dynamics of \(-\text{CH}_2-\) groups. The \( C_{1} \) conformation does not have a cavity and two \(-\text{CH}_2-\) groups occupy the interstitial space (structure A) having a rotational motion controlled by the rigidity of C-O-C linkage and have the potential barrier.

However, the high value of \( \mu \) can be attributed to the presence of unequal distribution of conformers and high polarizability of \(-\text{CH}_2-\) chains affecting the overall charge distribution. Caswell & Suvannunt\(^{7}\) have calculated dipole moment values with the assistance of a computer program and using bond angles, bond length, dihedral angles (from crystallography data) and Pauling electro-negativity values for various conformers of 18C6. They have calculated the dipole moment value of 3.38 D for the conformer (as shown in structure B) which agrees well with \( \mu \) values in CCl\(_4\), in which all the six dipoles in the molecule are pointing towards the same side of molecule and are having a larger angle. Alternatively, the results of \( \mu \) may indicate the importance of atomic polarization effects in \(-\text{CH}_2-\) chains, which effect cannot be neglected or appropriately subtracted in obtaining the orientation polarization value and hence the \( \mu \) value.

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References

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