Studies of Osmotic and Activity Coefficients in Aqueous and CCl_4 Solutions of 18-Crown-6 at 25 °C

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Received: March 29, 2002

The osmotic coefficients and densities of aqueous and CCl_4 solutions involving 18-crown-6 (18C6) as solute in the concentration range 0.1 to 2.0 m at 25 °C were measured. The data obtained is used to calculate activities of solvent and activity coefficient of solute and solvent at 25 °C as a function of concentration. It has been observed that activity coefficient of 18C6 increases with increase in concentration of 18C6 while the reverse is true for CCl_4 solutions. Using the partial molar volume of the solute at infinite dilution, the solute−solvent cluster integral values were evaluated which yielded information on solute−solvent interaction. Application of McMillan-Mayer theory enabled us to obtain second and third virial coefficients for solute, which have been decomposed into attractive and repulsive contributions to solute−solute interactions. These are compared with other solutes such as sucrose, glucose, urea, etc. On the basis of attractive and repulsive contributions to solute−solvent and solute−solute interactions in aqueous solutions, the results are interpreted in terms of hydrogen-bonding of water molecules in the crown cavity and hydrophobic stacking interactions mediated through water molecules. The results of CCl_4 solutions are further examined from the point of view of effect of conformational characteristics of 18C6 on the properties in a nonaqueous solvent.

1. Introduction

In recent years, the studies of crown ethers and cryptands have yielded valuable information about selective binding of alkali metal cations. It is well-known that the 18-crown-6 (18C6) forms stable complexes with several neutral molecules, such as water, acetonitrile, methanol, etc., through H-bonds and dipolar forces (“molecular recognition”). The interactions of crown ethers with such neutral molecules are important from the point of view of understanding the mechanism of biological transport, molecular recognition, and enzyme specific binding activities as well as extraction abilities of crown ethers.[1−3]

The most prominent feature of 18C6 is its capability to complex alkali metal ions in the polar cage of oxygen atoms through undirectional Coulombic forces (“spherical recognition”) and to transport them eventually into lipophilic phases.[3] It has been found that the stability of $18C6{:}K^+$ is higher in methanol than in water, meaning thereby that $18C6-H_2O$ interactions are comparatively stronger.[4] X-ray diffraction[5] and Raman spectroscopic[6] studies have revealed that 18C6 forms various hydrates (1:4, 1:8, and 1:12) in solid state which exists in D_{3d} conformation. The conformation of 18C6 in pure solid state is C_i (along with a small amount of C_s); thus, some energy is expended in conformational change from C_i to D_{3d} during complexation. The NMR relaxation, diffusion coefficient, NIR, FTIR, and partial molar volume studies in water have proved that the macrocyclic effect associated with such a neutral molecule requires the presence of bridged water molecules to have a cyclic structure.[7−11] It was shown that at least four water molecules are H-bonded with the oxygen atoms of 18C6.[9−11] This most probable hydration structure of 18C6 is composed of two bridging water molecules (doubly H-bonded), which forms H-bonds simultaneously with two oxygen atoms of 18C6 and, the two other water molecules that are singly H-bonded to the ring. The molecular dynamics study of Kowall and Gieger[12] shows that the hydrophobic hydration of 18C6 plays an important role in governing the conformational dynamics of 18C6 in aqueous solutions, while the ab initio[13] studies indicate that the cooperative electrostatic interactions governs the hydration pattern of 18C6 in aqueous solutions.

To understand the thermodynamic behavior of aqueous 18C6 solutions, from which the solute−solute as well as solute−solvent interactions can be investigated, precise and accurate activity coefficient data, along with partial molar volume data, are required. In this context, we are reporting the osmotic and activity coefficient study of aqueous 18C6 solutions. Also some measurements were made in CCl_4 medium since 18C6 exists in C_i conformation in CCl_4. The data are subjected to the analysis using the McMillan−Mayer theory[14] and approach evolved by Kozak et al.[15] Using activity coefficients, calculated from osmotic coefficient data, the minimum attractive and repulsive contributions to the second and third osmotic virial coefficients are estimated. The information about pairwise and triplet interactions is derived. Also the hydration number of 18C6 in aqueous solutions is determined using activity data following the method described by Robinson and Stokes.[16] The results are compared with other hydrogen bonding nonelectrolytes and discussed in terms of solute−solute and solute−solvent interactions.

2. Experimental Section

18C6 (99% pure) procured from Merk-Schuchardt was used without further purification. The contact with atmospheric moisture was avoided by handling 18C6 in a drybox fabricated in our laboratory. The salt NaCl of AR grade (BDH) was dried under vacuum for 24 h before use. All the solutions, either in water (doubly glass distilled) or CCl_4 (HPLC grade, Merck), were prepared on molality basis and converted to molarity scale using the density data at 25 °C.

10.1021/jp020839w CCC: $22.00

TABLE 1: Water Activity, Osmotic Coefficient, and Activity Coefficient Data for aqueous 18C6 Solutions at 25 °C

m/mol kg^{-1}	d/kg m^{-3}	ϕ	a_w	γ_1	γ_2	ΔG^E/ J mol^{-1}
0.09803	1001.082	1.0073	0.99822	0.99999	1.01497	0.037
0.23004	1006.319	1.0218	0.99577	0.99990	1.04155	0.214
0.39135	1012.422	1.044	0.99267	0.99966	1.08412	0.692
0.50768	1016.628	1.0630	0.99032	0.99938	1.12188	1.258
0.59459	1019.666	1.0784	0.98851	0.99910	1.15406	1.822
1.00633	1032.923	1.1611	0.97917	0.99692	1.35634	6.569
1.19382	1038.375	1.2012	0.97450	0.99545	1.47842	10.126
1.42104	1044.530	1.2490	0.96853	0.99333	1.65480	15.883
1.58257	1048.620	1.2810	0.96413	0.99162	1.80083	21.074
1.80021	1053.779	1.3198	0.95810	0.98917	2.02711	29.705
1.99733	1058.124	1.3487	0.95263	0.98690	2.26345	39.340

TABLE 2: CCl$_4$ Activity, Osmotic Coefficient, and Activity Coefficient Data for 18C6−CCl$_4$ Solutions at 25 °C

m/mol kg^{-1}	d/kg m^{-3}	ϕ	a_{CCl_4}	γ_1	γ_2	$-\Delta G^E$/ J mol^{-1}
0.06554	1573.398	0.9582	0.99039	1.00037	0.91983	1.08
0.13621	1562.166	0.9204	0.98090	1.00145	0.84738	4.64
0.29839	1538.401	0.8425	0.96207	1.00623	0.71697	20.06
0.56214	1504.670	0.7416	0.93789	1.01899	0.56910	59.72
0.80361	1477.860	0.6772	0.91970	1.03338	0.48091	104.65
1.03557	1454.853	0.6406	0.90299	1.04683	0.42512	149.39

The density measurement of 18C6−CCl$_4$ solutions were made using Anton Paar digital densitometer (model DMA 60/602) at 25 ± 0.02 °C. The reproducibility of the values was found to be better than $\pm 1 \times 10^{-2}$ kg m^{-3}. The details about the density data and the calculations of partial molar volumes of 18C6 in aqueous solutions are described elsewhere.[11]

The osmotic coefficients Φ of 18C6 solutions were determined using KNAUER K-7000 vapor pressure osmometer at 25 ± 0.001 °C. The instrument was kept in specially fabricated refrigerated thermostat working between 0 and 40 °C. The osmometer was calibrated using aqueous NaCl solutions for the measurement of aqueous 18C6 solutions while it was calibrated with benzil solutions prepared in CCl$_4$ for the measurement of 18C6−CCl$_4$ solutions. The osmotic coefficient data for NaCl solutions in water were obtained from the tabulation given by Robinson and Stokes.[17] These data was used to obtain instrumental constant and the osmotic coefficients of aqueous solutions of 18C6 were measured with water as reference. The utility of the adopted procedure was verified by doing measurements for aqueous KCl and aqueous sucrose solutions of which osmotic coefficient agree excellently with the reported data.[17] Similarly we used pure CCl$_4$ as reference for 18C6−CCl$_4$ solutions after obtaining the instrumental constant using benzil solutions. The accuracy in Φ measurements was found to be better than $\pm 1 \times 10^{-3}$ at the lowest concentration studied.

3. Results

The osmotic coefficients (Φ) of aqueous 18C6 solutions were determined over the range 0.1 to 2.0 mol kg^{-1} at 25 °C. The data are well represented by the equation

$$\Phi = 1 + 0.066m + 0.1356m^2 - 0.030m^3 + 0.0012m^4 \quad (1)$$

The solvent activity coefficients were calculated from the experimental osmotic coefficient data using the expression

$$\Phi = -\{\ln a_1/(x_2/x_1)\} \quad (2)$$

where χ_1 and χ_2 are the mole fractions of solvent and solute, respectively, and a_1 is solvent activity. Thus the solvent activity coefficient γ_1 can be expressed as a power series in the mole fraction of solute by the equation[15]

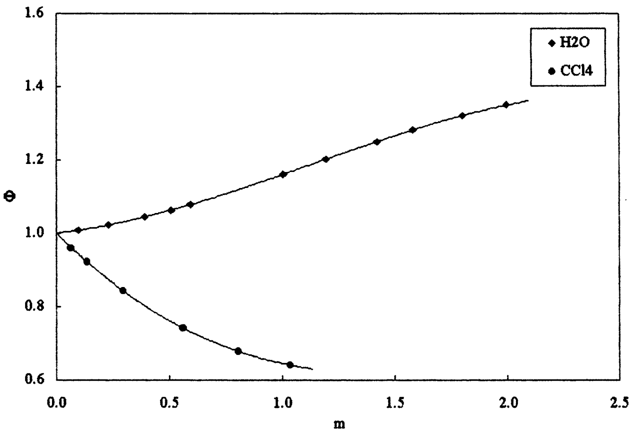

Figure 1. Variation of osmotic coefficient of 18C6 in aqueous and CCl$_4$ medium as a function of molality of 18C6 at 25 °C.

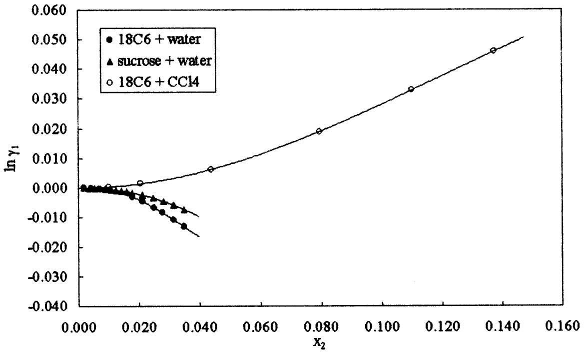

Figure 2. Variation of solvent activity coefficient of aqueous 18C6 and sucrose solutions and of solutions of 18C6 in CCl$_4$ as a function of mole fraction of solute (18C6/sucrose) at 25 °C.

$$\ln \gamma_1 = Bx_2^{\,2} + Cx_2^{\,3} + ... \quad (3)$$

The B and C coefficients appearing in this equation with its sign and magnitude are of special importance in understanding the thermodynamic behavior since they may be related to solute−solvent association, solute−solute interactions, and solute size.

The osmotic coefficients of 18C6−CCl$_4$ solutions were determined over the range 0.1 to 1.0 mol kg^{-1} at 25 °C. The data are represented by the expression

$$\Phi = 1 - 0.6198m + 0.3069m^2 - 0.0423m^3 \quad (4)$$

The data for the osmotic and activity coefficient for aqueous 18C6 solutions are collected in Table 1, while those for 18C6−CCl$_4$ solutions are given in Table 2 at 25 °C. The variation of osmotic coefficient of 18C6 in aqueous and CCl$_4$ medium as a function of molality of 18C6 at 25 °C are shown in Figure 1. It is observed that the osmotic coefficient of 18C6 in aqueous medium increases while that in CCl$_4$ medium decreases as the solute concentration is increased. Figure 2 represents the effect of increasing the mole fraction of solute on the solvent activity coefficient γ_1 in aqueous and CCl$_4$ medium. For the comparison purpose, the curve for aqueous sucrose solutions (data, ref 17) is also given in Figure 2. The solvent activity coefficient in aqueous 18C6 solutions decreases while that in 18C6−CCl$_4$ solutions increases as a function of solute mole fraction. In

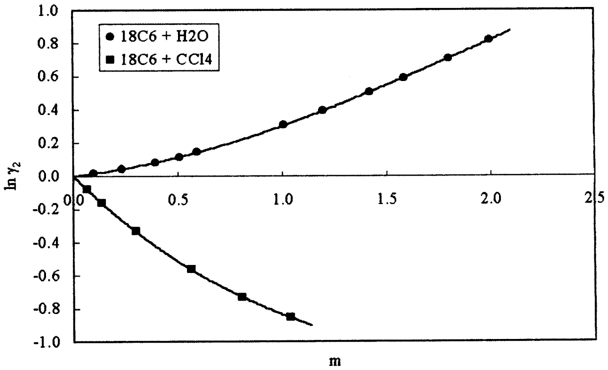

Figure 3. Variation of activity coefficient of 18C6 in aqueous and CCl_4 solutions as a function of molality of 18C6 at 25 °C.

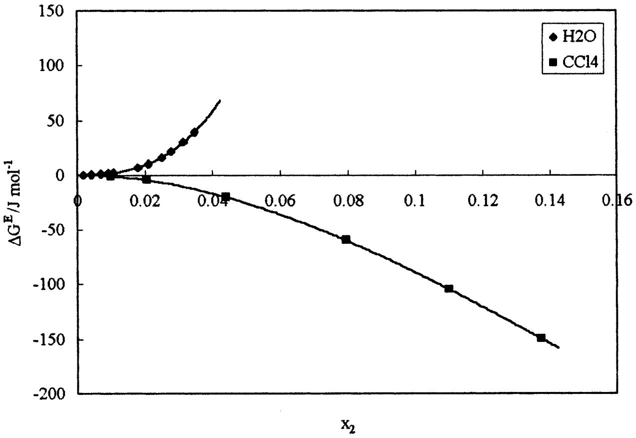

Figure 4. Variation of excess free energy of 18C6 in aqueous and CCl_4 solutions as a function of mole fraction of 18C6 at 25 °C.

aqueous 18C6 solutions, the decrease is more pronounced as compared to that in aqueous sucrose solutions.

It has been shown that

$$\ln \gamma_2 = (\Phi - 1) + \int_0^m (\Phi - 1) \mathrm{d} \ln m \tag{5}$$

where γ_2 is the solute activity coefficient. Since the osmotic coefficient is expressed as a power series on the molality scale of the solute by the equation

$$\Phi = 1 + \sum_{i=1}^{n} A_i m^i \tag{6}$$

where the coefficient A_i can be obtained by the method of least-squares; eq 5 takes the form, after solving the right-hand side integral, as

$$\ln \gamma_2 = \sum_{i=1}^{n} \left(\frac{i+1}{i}\right) A_i m^i \tag{7}$$

The data for the solute activity coefficient γ_2 for aqueous 18C6 and 18C6−CCl_4 solutions are collected in Tables 1 and 2, respectively. The dependence of solute activity coefficient on the solute concentration are shown in Figure 3 for aqueous and CCl_4 solutions. The activity data, which have been converted into the mole fraction scale, were used to calculate free energy change of mixing 18C6 with water and CCl_4 ΔG_{mix}. This enabled us further to calculate the excess free energy change ΔG^{E} using standard equations. It is observed that ΔG_{mix} is negative in the studied concentration range for both solvent media, while the excess free energy change ΔG^{E} is positive in aqueous solutions and is negative in CCl_4 solutions. The values of ΔG^{E} are also incorporated in Tables 1 and 2 for aqueous and CCl_4 solutions, respectively, while their variation as function of mole fraction of 18C6 at 25 °C is shown in Figure 4.

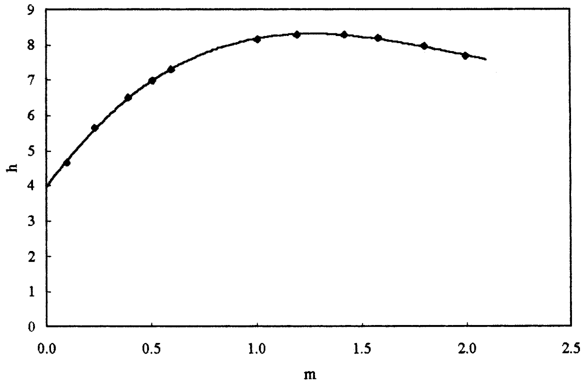

Figure 5. Variation of hydration number of 18C6 as a function of molality of 18C6 at 25 °C.

4. Discussion

Solute−Solvent Interactions. If hydration is the only cause for departure from ideality of an aqueous nonelectrolyte solution, the water activity of the solution is given by[16]

$$a_{\mathrm{w}} = \frac{1 - 0.018hm}{1 - 0.018(h-1)m} \tag{8}$$

where a_{w} is the water activity and h is the hydration number. By expanding $\ln a_{\mathrm{w}}$ in a series and converting to the osmotic coefficient, the equation has the form

$$\Phi = 1 + 0.018\left(h - \frac{1}{2}\right)m + 0.018^2\left(h^2 - h + \frac{1}{3}\right)m^2 \tag{9}$$

Comparing eqs 1 and 9 hydration number h was found to be 4.17 for 18C6, then the second term of eq 9 should have coefficient of 0.0044. Clearly there is a contribution of $0.1312m^2$ to Φ which cannot be accounted only by the hydration. Thus at higher concentrations the deviation from ideality is not only due to the hydration but also other factors may have significant contribution. At low concentrations, the major contribution to the nonideality is the hydration. Robinson and Stokes pointed out this in case of aqueous sucrose solutions.[16]

This value of hydration number ($h = 4.17$) estimated using activity data for aqueous 18C6 solutions is in very good agreement with that obtained from NIR study[9] and viscosity measurements[18,19] at 25 °C. Thus it is necessary to have at least four water molecules attached to one 18C6 molecule. From Figure 2 it is observed that the deviation from ideality is more pronounced in aqueous 18C6 solutions than that in aqueous sucrose solutions indicating that the water−18C6 interactions are stronger than sucrose−water interactions. The hydration numbers calculated using eq 8 at various concentrations of 18C6 are graphically exhibited in Figure 5. It is observed that h, the hydration number, increases from 4 to 8 in the studied concentration range. Hydration number is a vague concept, and many workers have reported different values using different solution properties for electrolytes. However, our experience in this field made us confident that hydration number obtained from activity data and compressibility data for electrolyte

TABLE 3: Attractive Contributions to Solute−Solvent Interaction Coefficients at 25 °C

	$10^{-3} \times \bar{V}_2$/ mm^{3}mol^{-1}	$10^{-3} \times RT\kappa$/ mm^{3}mol^{-1}	$10^{-3} \times NB_{11}^{*}$/ mm^{3}mol^{-1}	$10^{-3} \times NS$/ mm^{3}mol^{-1}	$10^{-3} \times (-N\Phi^A)$/ mm^{3}mol^{-1}
18C6+H_2O	223.17	1.11	222.06	699	477
sucrose +H_2O[a]	211.49	1.11	210.38	476	266
glucose + H_2O[a]	112.2	1.11	111.10	358	246
hexamethylene-tetramine + H_2O[a]	110.58	1.11	109.47	300	191
urea[a]	44.2	1.11	43.10	176	143

[a] Data from refs 31 and 32.

solutions agree closely if sufficiently accurate data is obtained in the low concentration region.[20] For ions and nonelectrolytes, such as alcohols,[21−23] the hydration number generally decreases with increase in concentration of solute. However, in this work we observe an increase in h initially and a more or less constant value of 7 or 8 at higher studied concentration. Such behavior can be attributed to successive hydrate formation of variable stoichiometry in liquid-state analogous to that reported in solid phase.[5]

Gottlieb and Herskowitz have studied water activities in aqueous 18C6 solutions at higher concentrations (> 3m) by isopiestic measurements and have shown that γ_1 goes through a minimum at about $x_2 = 0.15$ of 18C6.[24] This behavior is similar to that observed for *tert*-BuOH−water system at 10 °C.[25] The solution properties of aqueous *tert*-BuOH solutions have been explained in terms of hydrophobic hydration and interaction by several workers using different properties as well as spectroscopic properties.[26] W. Zielenkiewicz and et al. have discussed the enthalpic coefficient of solute−solute interactions for aqueous 18C6 solutions in terms of hydrophobic solute−solute interactions.[27] The positive ΔG^E obtained in aqueous solutions show similarity with the behavior of aqueous nonelectrolyte (e.g., alcohols, amines, ethers, etc.) solutions exhibiting water structure making effect. Brigner and Wadso have reported the enthalpy change of mixing for 18C6−water system.[28] The data of ΔG_{mix} and enthalpy change indicate that the entropy change for mixing is negative. However, the enthalpy term is more dominating term. The solvation of hydrophobic moieties is charaterized by a large increase in heat capacity and the large $C^{o}_{p,2}$ values found for 18C6 reflect a short-range effect on the water structure.[28]

The solute−solvent cluster integral $b_{11}{}^0$ is related to the partial molecular volume of the solute at infinite dilution by[22−23,29−30]

$$b_{11}{}^{0} = -\upsilon_2{}^{0} + kT\kappa \qquad (10)$$

where k is the Boltzmann constant, T is the absolute temperature, and κ is the isothermal compressibility coefficient of the pure solvent. The values for solute−solvent interaction $NB_{11}{}^{0*}$ (where $B_{11}{}^{0*} = -b_{11}{}^{0}$) for aqueous 18C6 solutions calculated using eq 10 are given in Table 3. The values for other nonelectrolytes in aqueous solutions at 25 °C are also included in Table 3 for comparison.

The solute−solvent cluster integral in the above equation is related to the potential of mean force ω^{11} between one molecule of solute and one of solvent in the pure solvent by the expression

$$b_{11}{}^{0} = -4\pi\int_0^{\infty} [1 - \exp(-\omega^{11}/kT)]\, r^2\, \mathrm{d}r \qquad (11)$$

where r is the distance between the centers of the molecules. It was shown that this integral could be split into attractive and repulsive parts as

$$B_{11}{}^{0*} = 4\pi\int_0^{R} [1 - \exp(-\omega^{11}/kT)]\, r^2\, \mathrm{d}r + \int_R^{\infty} [1 - \exp(-\omega^{11}/kT)]\, r^2\, \mathrm{d}r \qquad (12)$$

$$= S + \Phi^A \qquad (13)$$

where R is the distance of closest approach of the two molecules, S is the repulsive, and Φ^A is the attractive contribution.

If the form of potential ω^{11} is known, then the integration could be performed to yield $B_{11}{}^{0*}$. The simplest potential function regards the molecules as rigid spheres. For two hard spheres of diameters R_1 and R_2,

$$S = \frac{\pi}{6}(R_1 + R_2)^3 \qquad (14)$$

The self-diffusion coefficient[8] study and viscosity measurement[18,19] of aqueous 18C6 solutions at 25 °C have shown that the radius of 18C6 in aqueous solutions is 0.5 nm. The water molecule can be considered to be a sphere of diameter 0.304 nm (although one may use the diameter of water as 0.276 nm, however we retained the value equal to 0.304 nm as the comparison of the data for other solutes can be made). Then the repulsive contribution to the solute−solvent interaction comes out as $NS = 699$ cm^3 mol^{-1} and the attractive contribution at 25 °C can be obtained as

$$N\Phi^A = NB_{11}^{*0} - NS = -477\ \mathrm{cm}^3\,\mathrm{mol}^{-1}$$

The data of attractive and repulsive contributions to the solute−solvent interaction in water for other H-bonding nonelectrolytes at 25 °C are given in Table 3 for the comparison. It is interesting to note that the attraction between the 18-crown-6 and water molecules is significantly larger than that for sucrose + water and for other nonelectrolytes and water. It would have been better to compare these contributions for poly(ethylene glycol)s, which are linear analogues of crown ether, however, we could not find the osmotic coefficient values in the studied concentration range. Furthermore, it will be difficult to obtain the values of diameter for long chain flexible molecules in solution phase to complete the calculations. The attractive contribution increases in the order urea < hexamethylenetetramine < glucose < sucrose <18-crown-6. Thus the attractive contribution is in the order of increase of H-bonding sites. Urea−water hydrogen bond interactions exists but are very short-lived. The interactions between glucose (probably five H-bond sites available) and water are only slightly less than that for the sucrose (with more H-bonding sites available) and water. Hence, the 18C6 should have greater H-bonding ability than the sucrose. The hydration numbers for sucrose (∼4.6) and 18C6 (∼4.2) at 25 °C are nearly the same. The strong interactions between 18C6 and water indicates that along with the four firmly attached water

TABLE 4: Attractive Contributions to Solute−Solute Interaction Coefficients at 25 °C

	NB_2^*	$N^2B_3^*$	$-A_{2\text{min}}$	$R_{2\text{min}}$	$-A_{3\text{ min}}$	$R_{3\text{min}}$
18C6+CCl_4	−201	16700	1410	1611	552344	535644
18C6+H_2O	278	226998	615	893	498048	271051
sucrose + H_2O[a]	286	87000	558	783	360000	447000
glucose + H_2O[a]	117		403	520		
hexamethylene-tetramine + H_2O[a]	338		58	396		
urea[a]	1	3800	178	179	16000	19800

[a] Data from refs 31 and 32.

molecules to the 18C6 molecule there is large hydrophobic hydration. Thus, some peripheral water molecules gets affected due to the structure making ability of 18C6. The same conclusion was also revealed from viscosity measurements.[19]

Solute−Solute Interactions. According to the theory of McMillan and Mayer[14] for a solution of a solute in a solvent, the osmotic pressure π is given by

$$\frac{\pi}{kT} = n + B_2^* n^2 + B_3^* n^3 + ... \tag{15}$$

where n is the number density. It can be shown that the osmotic second and third virial coefficient, B_2^* and B_3^*, respectively, for the osmotic pressure of nonelectrolyte solutions can be calculated from experimental activity data and the partial molar volume of solute and solvent as[15]

$$B_2^* = \frac{1}{N}\left[(\bar{V}_2^{\,0} - V_1^{\,0}) + V_1^{\,0}\left(\frac{1}{2} - B\right)\right] \tag{16}$$

$$B_3^* = \frac{1}{N^2}[(b/V_1^{\,0}) + g + (V_1^{\,0} - \bar{V}_2^{\,0})^2 - V_1^{\,0}(1 - 2B)(V_1^{\,0} - \bar{V}_2^{\,0}) + (V_1^{\,0})^2\left(\frac{1}{3} - C\right)] \tag{17}$$

where V_1^0 and $\bar{V}_2^0$ are the partial molar volumes of solvent and solute respectively at infinite dilution, B and C are the coefficients in eq 3, while b and g are the coefficients in the following equations

$$\bar{V}_1 = V_1^{\,0} + aC_2 + bC_2^{\,2} \tag{18}$$

$$\bar{V}_2 = \bar{V}_2^{\,0} + gC_2 + hC_2^{\,2} \tag{19}$$

Here $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of solvent and solute respectively at concentration C_2. The coefficients a, b, g, and h have been evaluated using the density data of aqueous 18C6 solutions at 25 °C.

Kozak et al.[15] have shown that the osmotic second virial coefficient can decomposed into attractive and repulsive components. The minimum attractive $A_{2\text{min}}$ and minimum repulsive $R_{2\text{min}}$ contributions to the osmotic second virial coefficient can be calculated by following equations

$$R_{2\text{min}} = f(4V_2^{\,0}) \tag{20}$$

$$A_{2\text{min}} = R_{2\text{min}} - NB_2^* \tag{21}$$

where f is the factor which is measure of the ellipticity of the molecule. For spherical molecule f is unity. 18C6 in aqueous medium exists in D_{3d} conformation and may be assumed as a spherical entity. In CCl_4 medium, it exists in C_i conformation with axial ratio of ∼1.5. In much the same way as the second virial coefficient, the third virial coefficient can be decomposed into attractive and repulsive components. The minimum attractive $A_{3\text{min}}$ and minimum repulsive $R_{3\text{min}}$ contributions of these two components have been calculated by using the following equations

$$R_{3\text{min}} = 10(V_2^{\,0})^2 \tag{22}$$

$$A_{3\text{min}} = R_{3\text{min}} - N^2B^*{}_3 \tag{23}$$

The values of osmotic second and third virial coefficients as well as the minimum attractive and repulsive contributions to the solute−solute interactions are given in Table 4. The data for other nonelectrolytes in aqueous medium, collected from the literature, are also included in Table 4 for the comparison. Although much reliance cannot be placed on the absolute values for $A_{3\text{min}}$, $R_{3\text{min}}$, and B_3^* due to assumption in the original theory and the accuracy of the data, these can serve as a guideline for comparison purposes.

The minimum attractive contribution to the solute−solute interactions for 18C6 in aqueous solutions is found to be −615 cm^3 mol^{-1} which is a measure of pairwise interactions between two 18C6 molecules in water. As seen from Table 4, the attraction between two solute molecules decreases in the series 18-crown-6 > sucrose > glucose > urea > hexamethyltetramine. Since the magnitude of the attractive contribution increases with the number of functional groups capable of H-bonding as well as hydrophobic interactions with another solute molecules, it reveals that one 18C6 molecule may interact strongly with another 18C6 molecule by means of hydrophobic interactions. Comparing the magnitude of the attractive contribution to the solute−solute interactions of 18C6 and sucrose in aqueous medium, the crown−crown interactions are much larger than the sucrose−sucrose interactions.

The attractive contribution to third virial coefficient is found to be greater for 18C6 than the other nonelectrolytes as mentioned above in the presence of water. So the greater attractive contribution to the third virial coefficient indicate the existence of triplate interactions as well of 18C6 in aqueous medium and may be indicative of water mediated stacking type of interactions.

The decrease of the solute activity coefficient as a function of solute concentration in 18C6−CCl_4 medium indicates that solute−solvent interactions are favorable than solute−solute interactions. 18C6 in CCl_4 may associate and the association constant has been evaluated from the osmotic coefficient data using the expression as[33]

$$K = (1 - \Phi)/m\Phi^2 \tag{24}$$

where K is the association constant which is found to be 0.8 ± 0.1 m^{-1}. Thus the low value of association constant indicates that the solute−solute interactions are weak and may be of stacking type. All these results pointed out that the conformational characteristics of 18C6 depend on the solvent. The proper orientation of water molecules via hydrogen-bond and electrostatic interactions along with the stronger 18C6−18C6 hydrophobic interactions governs the properties of such solutions.

5. Conclusions

The results of present study reveal that 18C6 dissolve in water with structure making effect i.e., hydrophobic hydration and interaction. The hydration number of 18C6 calculated using activity data is in good agreement with the values obtained from spectral data. The hydration number value of ∼4 may be indicative of similarity with that of ice-like structures (the coordination number of water molecule is 4 in ice). The comparison of excess free energy change in aqueous and CCl_4 medium indicates different kinds of interactions on the basis of conformational characteristic of 18C6. The applications of MacMillan−Mayer theory shown that the minimum attractive contributions to second and third virial coefficients are large negative indicating the presence of pairwise and triplet interactions of 18C6. The attractive contribution to the solute−solvent interaction in aqueous 18C6 solutions is also found to be large compared to other nonelectrolytes. These results have been interpreted as in aqueous 18C6 solutions the formation of bridged hydrogen bonds, i.e., solute−solvent interaction, to form a suitable D_{3d} conformation is essential along with the hydrophobic hydration of nonpolar $>CH_2$ groups (peripheral hydration).

Acknowledgment. The authors are thankful to the referee for his constructive suggestions to modify this report.

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