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Viscosity Behavior of 18-Crown-6 in Aqueous and Carbon Tetrachloride Solutions at Different Temperatures and at Ambient Pressure

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The relative viscosity (η_r) and the viscosity *B*-coefficients in the equation $\eta_r = 1 + Bc + Dc^2$, with c = concentration of 18-crown-6 (18C6) in aqueous and carbon tetrachloride solutions (0.02 to 0.3 mol L^{-1}), have been determined in the temperature range (293.15 to 308.15) K and at ambient pressure. The values of the *B*- and *D*-coefficients are found to be high compared to those obtained for simple nonelectrolyte solutions. These values are further found to decrease and increase, respectively, as a function of temperature in aqueous solutions, while the value of the *B*-coefficient remains more or less constant in the case of CCl_4 solutions in the studied temperature range.

1. Introduction

18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) is an archetype of the family of macrocyclic polyether compounds known as crown ethers and represents a treatable model compound.[1,2] The most prominent feature of 18-crown-6 (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 nonaqueous organic phases. Further, 18C6 is able to bind neutral polar guest molecules such as water, CH_3OH, CH_3CN, NH_3, and so forth through H-bonds and dipolar forces ("molecular recognition"). The study of host−guest interactions involving 18C6 as a host may shed light on the complex biological processes involving enzyme specific binding activities, molecular transport, and molecular recognition.[3] The size and shape of the guest molecule should be compatible with the cavity size of the host for the complex to be more stable; thus, the specificity of the host molecule toward a guest is governed by such factors. It has been found that the stability of the 18C6/K^+ complex is higher in methanol than in water, meaning that 18C6−H_2O interactions are comparatively stronger in methanol.[4] In this context, several researchers have investigated 18C6−H_2O interactions using theoretical[5−9] as well as experimental techniques. X-ray diffraction[10] and Raman spectroscopic[11] studies have revealed that 18C6 forms various hydrates in the solid state (1:4, 1:8, 1:12) which exist in the D_{3d} conformation in the hydrates. The conformation of 18C6 in pure solid form is C_i; thus, some energy is expended in the conformational change from C_i to D_{3d} during complexation. The results of X-diffraction studies show that at least four water molecules are H-bonded with the oxygen atoms of 18C6 and can be distinguished into two types: (i) doubly H-bonded or bridged water molecules (two) which form H-bonds simultaneously with two oxygen atoms of 18C6 and (ii) singly H-bonded water molecules (two). The NIR spectral investigations by Patil and Pawar[12] have indicated that similar H-bonding exists even in the solution phase. This study and the studies of partial molar volume,[13] viscosity measurements,[14] and activity coefficients[15] at 298.15 K of aqueous solutions of 18C6 reveal that, in addition to these four H-bonded water molecules, there is large hydrophobic hydration of the 18C6 molecule. This is also revealed from many simulation studies. In particular, the molecular dynamic study of Kowall and Geiger shows that the hydrophobic hydration of 18C6 plays an important role in governing the conformational dynamics of the 18C6 molecule in aqueous solutions.[16] The ab initio studies carried out by Gadre et al. have shown that the cooperative electrostatic interactions govern the hydration pattern of 18C6 in aqueous solutions.[17] The study of viscosity of aqueous 18C6 solutions reported earlier from this laboratory was carried out at 298.15 K, and the radius of the solvated 18C6 molecule, brownon, was found to be 0.50 nm. Interpretation of viscosity results is not straightforward; therefore, complete interpretation of such results is possible when one has as much information as possible about the dependence of viscosity on various experimental parameters such as temperature variation or use of a nonaqueous solvent such as CCl_4 and so forth. In this communication we report the measurements of viscosity of solutions of 18C6 in the concentration range 0.02 to 0.3 M and at different temperatures in aqueous and CCl_4 solvent media (293.15 to 308.15 K). The *B*- and *D*-coefficients for 18C6 have been evaluated at these temperatures in both the solvent media: in water as well as in CCl_4.

The data obtained from these measurements have been utilized to evaluate parameters such as V_e (effective volume of the flowing unit), the radius of the flowing unit, and the hydration number of 18C6 (in aqueous solutions), which are discussed in terms of solute−solvent as well as hydrophobic interactions.

2. Experimental Section

18C6 (99% pure) procured from Merck-Schuchardt was used without further purification. The contact with atmospheric moisture was avoided by handling 18C6 in a drybox fabricated in our laboratory. All the solutions, either in water (doubly glass distilled) or CCl_4 (HPLC grade, Merck), were prepared on a molality basis and converted to the

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Table 1. Viscosity Data for 18-Crown-6 + H_2O Solutions at Different Temperatures

T	c	d		B	D	V_e	$10^{-3}\phi_V$	
K	mol dm^{-3}	kg m^{-3}	η_r	dm^3 mol^{-1}	$(dm^3\ mol^{-1})^2$	dm^3 mol^{-1}	mm^3 mol^{-1}	n
293.15	0	998.21	1	0.8577	0.2857	0.352[a]	222.2[a]	7.2
	0.0406	999.92	1.0358			0.334		
	0.07841	1001.5	1.0713			0.329		
	0.12086	1003.25	1.1064			0.306		
	0.17819	1005.57	1.1605			0.297		
	0.20794	1006.75	1.1892			0.292		
	0.25276	1008.52	1.2325			0.285		
	0.32027	1011.12	1.3015			0.277		
298.15	0	997.05	1	0.8069	0.3059	0.326[a]	223.8[a]	5.7
	0.04054	998.67	1.0335			0.315		
	0.07831	1000.21	1.0658			0.307		
	0.1207	1001.91	1.1008			0.292		
	0.17794	1004.16	1.1535			0.286		
	0.20764	1005.32	1.1792			0.28		
	0.25239	1007.03	1.2217			0.275		
	0.31978	1009.57	1.2874			0.268		
303.15	0	995.65	1	0.7534	0.3425	0.297[a]	224.9[a]	4
	0.04049	997.39	1.0308			0.291		
	0.0782	998.84	1.0606			0.284		
	0.12053	1000.51	1.0959			0.28		
	0.17768	1002.72	1.1438			0.271		
	0.20734	1003.84	1.1709			0.269		
	0.25201	1005.51	1.2113			0.264		
	0.31928	1008	1.274			0.258		
308.15	0	994.03	1	0.7012	0.3439	0.284[a]	226.6[a]	3.2
	0.04042	995.61	1.0294			0.279		
	0.07806	997.09	1.0561			0.266		
	0.12031	998.72	1.0901			0.265		
	0.17736	1000.89	1.1341			0.256		
	0.20695	1001.99	1.1592			0.254		
	0.25154	1003.65	1.1979			0.251		
	0.31867	1006.08	1.2584			0.246		

[a] Extrapolated values to infinite dilution.

Table 2. Viscosity Data for 18-Crown-6 + CCl_4 Solutions at Different Temperatures

T	c	d		B	V_e	$10^{-3}\phi_V$
K	mol dm^{-3}	kg m^{-3}	η_r	dm^3 mol^{-1}	dm^3 mol^{-1}	mm^3 mol^{-1}
293.15	0.00000	1593.39	1.0000	0.7084	0.284[a]	233.8[a]
	0.06567	1586.34	1.0514		0.291	234.0
	0.09829	1582.87	1.0697		0.257	234.1
	0.12825	1579.71	1.0886		0.245	234.3
	0.18563	1573.71	1.1304		0.238	234.5
	0.24642	1567.44	1.1727		0.229	234.7
	0.32561	1559.42	1.2326		0.221	234.9
298.15	0.00000	1583.71	1.0000	0.6999	0.269[a]	232.9[a]
	0.06528	1576.94	1.0471		0.269	233.1
	0.09771	1573.63	1.0681		0.254	233.1
	0.12751	1570.6	1.0894		0.249	233.2
	0.18459	1564.86	1.1292		0.238	233.4
	0.24507	1558.88	1.1738		0.231	233.5
	0.32389	1551.22	1.2247		0.216	233.7
303.15	0.00000	1574.2	1.0000	0.6912	0.265[a]	232.3[a]
	0.06490	1567.64	1.0441		0.255	232.8
	0.09714	1564.39	1.0680		0.255	233.1
	0.12677	1561.42	1.0877		0.246	233.3
	0.18351	1555.75	1.1282		0.238	233.7
	0.24364	1549.77	1.1700		0.228	234.2
	0.32198	1542.04	1.2204		0.214	234.8
308.15	0.00000	1564.65	1.0000	0.6883	0.261[a]	231.7[a]
	0.06453	1558.35	1.0432		0.251	232.0
	0.09662	1555.25	1.0668		0.252	232.2
	0.12611	1552.41	1.0846		0.239	232.3
	0.18265	1547.01	1.1255		0.234	232.6
	0.24261	1541.36	1.1700		0.229	232.9
	0.32085	1534.08	1.2197		0.215	233.2

[a] Extrapolated values to infinite dilution.

molarity scale using the density data at different temperatures. The uncertainty in composition of solutions is negligibly small and is of the order of $\pm 5 \times 10^{-5}$ mol L^{-1}.

The density measurements of 18C6−CCl_4 solutions (0.0 to 0.3 mol L^{-1}) were made using an Anton Paar digital densitometer (model DMA 60/602) at different temperatures (293.15−308.15 K). The reproducibility of values was found to be better than $\pm 1 \times 10^{-2}$ kg m^{-3}. The density data are given in Table 2. The details about the density measurements and the calculations of partial molar volumes of 18C6 in aqueous solutions are described elsewhere.[13]

A setup was constructed for the measurements of viscosity. A bath of 60 L capacity was used to suspend either an Ubbelohde or a Tuan-Fuoss viscometer. The temperature of the bath was maintained constant (±0.005 K) by circulating thermostated liquid from a U-10 ultrathermostat through an electroplated copper coil suspended in the bath. The temperature fluctuations were monitored using a Beckman thermometer.

The flow times of water for the Ubbelohde and Tuan-Fuoss viscometers are (1093.1 ± 0.1) s and (1020.1 ± 0.1) s, respectively, at 298.15 K, the time being monitored using a stopwatch with 0.1 s as the smallest increment. It was essential to use a Tuan-Fuoss viscometer for CCl_4 solutions (the flow time for pure CCl_4 is 659.1 s at 298.15 K), as CCl_4 evaporates, causing variation in the time of flow when an Ubbelohde viscometer is used.[18] Since the Tuan-Fuoss type viscometer was constructed using stoppered standard joints, the evaporation of CCl_4 could be prevented and a constant time of flow value could be determined. All the flow time measurements reported in this work are averaged over three separate measurements of the same solutions. The calibration of a Ubbelohde viscometer has been described earlier.[14] The uncertainty in viscosity measurements with reference to water is estimated using the guide to the expression of uncertainty in measurements (Inter-

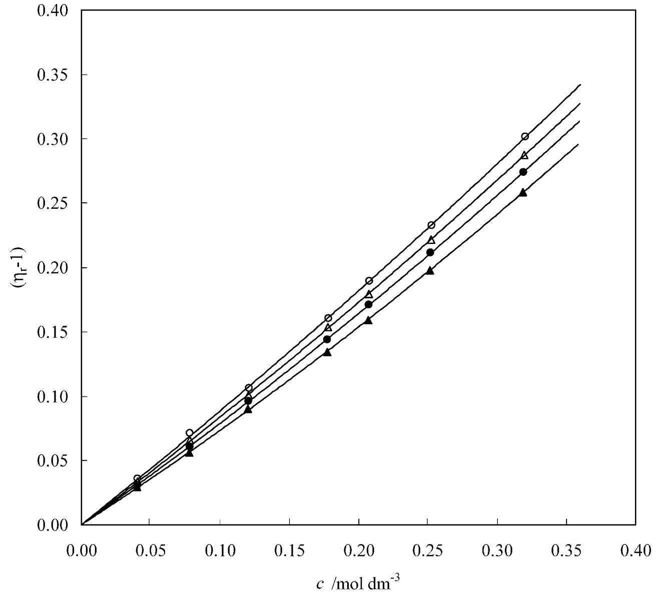

Figure 1. Variation of the relative viscosity of 18-crown-6 in aqueous solutions at different temperatures: ○, 293.15 K; △, 298.15 K; ●, 303.15 K; ▲, 308.15 K.

national Organization for Standardization, Geneva) to be of the order of ±0.000 15 mPa s.

3. Results and Discussion

The relative viscosities (η_r) of solutions of 18C6 in CCl_4 or water were evaluated using an expression[19]

$$\eta_r = \frac{1}{\eta_0} = \frac{td}{t_0 d_0} K \tag{1}$$

where η, t, and d are the viscosity, time of flow, and density, respectively, of the solution while η_0, t_0, and d_0 are respectively the viscosity, time of flow, and density of the solvent. The kinetic energy correction was found to be negligible, and the correction factor (K) is taken to be unity. The relative viscosity of the solutions can be expressed as a sum of terms in different powers of concentration (c), as given by

$$\eta_r = 1 + Bc + Dc^2 \tag{2}$$

The B-coefficient is a measure of hydrodynamic or size and shape effects, solvation effects, and structural effects, while the D-coefficient includes the contribution due to the higher terms of the hydrodynamic effects and interactions arising from changes in solute−solute interactions with concentration.[20]

The relative viscosity data of 18C6 in aqueous and CCl_4 solutions at different temperatures as a function of 18C6 concentrations are shown in Figures 1 and 2, respectively. It can be seen that the variation of η_r as a function of concentration of 18C6 in CCl_4 at all the temperatures is linear; therefore, it is sufficient to retain only the B-coefficient in eq 2 for representation of these data. The D-coefficient values for these solutions are found to be negligible. Thus, the slopes of the straight lines in Figure 2 yield the B-coefficient for 18C6−CCl_4 solutions. However, the η_r data in the case of aqueous 18C6 solutions show deviations from linearity at all temperatures. The B- and D-coefficients in this case were determined by plotting (η_r − 1)/c against c, whereby the intercept yields the B-coefficient and the slope is the measure of the D-coefficient.

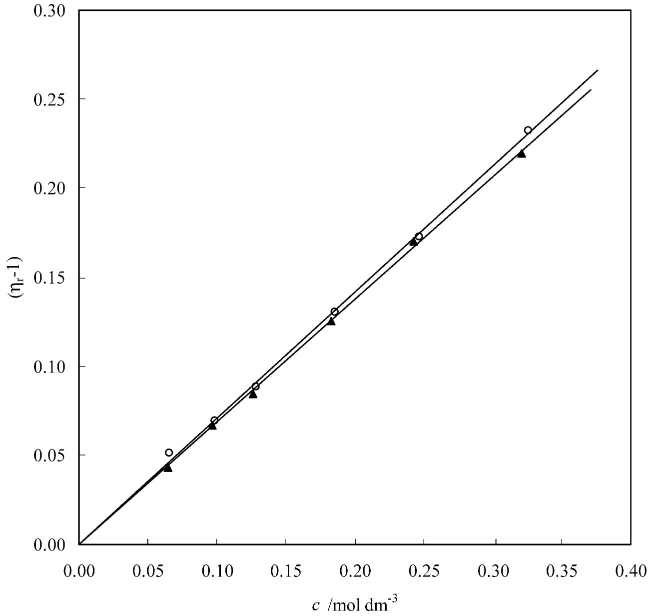

Figure 2. Variation of the relative viscosity of 18-crown-6 in CCl_4: ○, 293.15 K; ▲, 308.15 K.

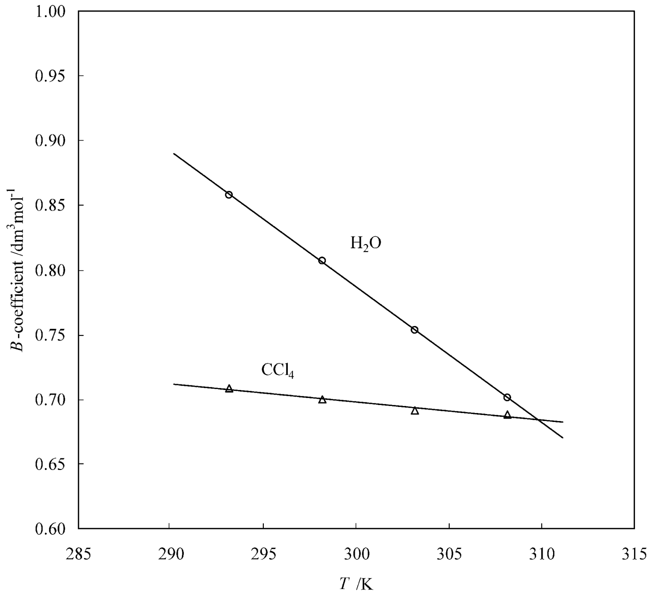

Figure 3. Variation of the B-coefficient as a function of temperature for 18C6 in H_2O and in CCl_4.

The data of these coefficients obtained are collected in Tables 1 and 2, respectively, for aqueous and CCl_4 solutions. The values of the B- and D-coefficients for 18C6−H_2O solutions decrease and increase, respectively, with temperature, while the B-coefficient values in the case of 18C6−CCl_4 remain almost constant (Figure 3).

The hydrodynamic effects can be expressed in the form of an equation derived by Einstein as

$$\eta_r = 1 + 2.5\phi \tag{3}$$

where ϕ is the volume fraction of the solute and can be replaced by the product $V_h c$; V_h is the hydrodynamic volume in dm^3 mol^{-1}. However, in the case of the solvated molecules, their covolumes include the contribution from the solvent molecules attached or encaged in the solute molecule cavities (for example, 18C6); hence, V_h can be replaced by V_e, the effective volume of the flowing unit.

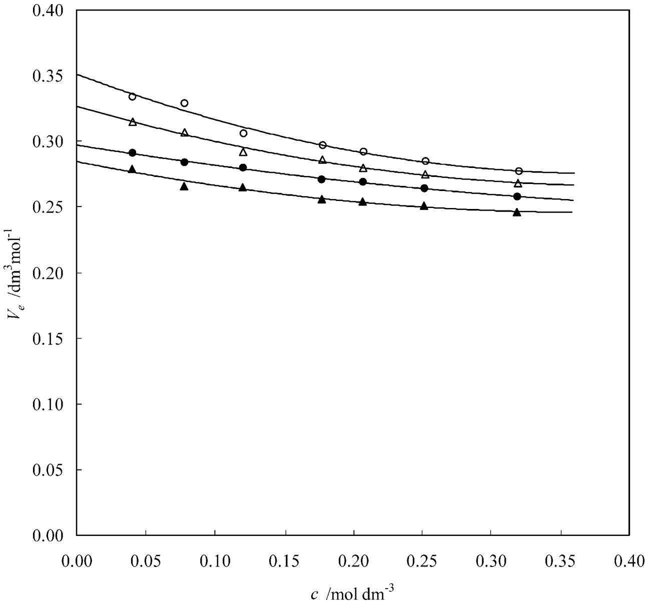

Figure 4. Variation of the effective volume of the flowing unit as a function of concentration of 18C6 in water at different temperatures: ○, 293.15 K; △, 298.15 K; ●, 303.15 K; ▲, 308.15 K.

The Einstein equation is applicable for spherical solutes[21] only, and therefore, we have utilized the Breslau−Miller equation[22] (derived from the Thomas equation[23] [$\eta_r = 1 + 2.5V_e c + 10.05V_e^2c^2$]), which is applicable for solutes with nonspherical shapes as well.

$$V_e = \frac{\{-2.5c + [(2.5c)^2 - 4(10.05c^2)(1 - \eta_r)]^{1/2}\}}{2(10.05c^2)} \quad (4)$$

Comparison of the Thomas equation with eq 2 reveals that

$$B = 2.5V_e \quad (5)$$

As noted earlier, V_e values for 18C6 are concentration dependent in the case of 18C6 solutions (Figure 4); therefore, we have extrapolated the V_e against c plot to zero concentration to obtain V_e°.[24] Equation 5 becomes

$$B = 2.5V_e^\circ \quad (6)$$

The V_e° values thus obtained are collected in Table 1. It is found that V_e° values decrease with increase in temperature (this is in harmony with the variation of the B-coefficient in 18C6 solutions). The V_e values for 18C6 in 18C6−CCl_4 solutions are almost constant as a function of concentration (Figure 5); therefore, the same methodology was applied to obtain V_e° values (Table 2) by linearly extrapolating to infinitely dilute solution.

The density data of solutions of 18C6 in CCl_4 were utilized for the evaluation of the derived property apparent molar volume (ϕ_V) of 18C6, which is collected in Table 2 as a function of concentration and at different temperatures. The uncertainty in the calculated ϕ_V data was found to be $\pm 0.5 \times 10^3$ mm^3 mol^{-1} at the lowest concentration. The limiting apparent molar volume (ϕ_V°) of 18C6 at a given temperature was obtained by smooth extrapolation of ϕ_V against concentration data at a particular temperature to infinite dilution (zero concentration). These ϕ_V° values are also collected in Table 2 while ϕ_V° values for 18C6 in H_2O are incorporated in Table 1. The details of ϕ_V data are summarized in a separate publication.[13]

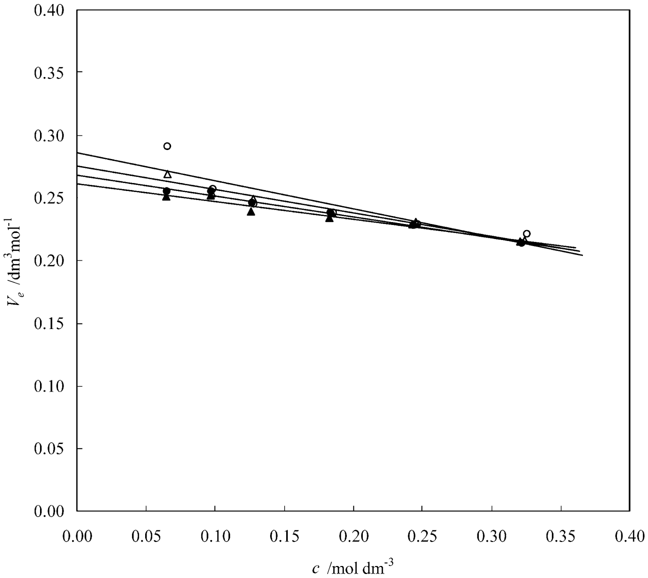

Figure 5. Variation of the effective volume of the flowing unit as a function of concentration of 18C6 in CCl_4 at different temperatures: ○, 293.15 K; △, 298.15 K; ●, 303.15 K; ▲, 308.15 K.

Examination of the viscosity data for 18C6−CCl_4 and 18C6−H_2O, summarized in Tables 1 and 2, reveals that the B-coefficients of aqueous 18C6 solutions are found to be high as compared to those for simple nonelectrolytes such as urea (0.038 dm^3 mol^{-1}),[25] ethanol (0.230 dm^3 mol^{-1}),[26] *tert*-butyl alcohol (0.373 dm^3 mol^{-1}),[27] dioxane (0.125 dm^3 mol^{-1}),[28] and *tert*-butylamine (0.394 dm^3 mol^{-1} at 293.15 K) and are of comparable magnitude to that of a polyfunctional solute such as sucrose (0.8786 dm^3 mol^{-1} at 298.15 K).[28] The value of the B-coefficient obtained for aqueous 18C6 solutions at 298.15 K (0.8069 dm^3 mol^{-1}) is in excellent agreement with the value (0.798 dm^3 mol^{-1}) reported earlier from this laboratory.[14] Kawaizumi et al. have reported a B-coefficient value of aqueous 18C6 solutions (0.846 dm^3 mol^{-1}) at 298.15 K only,[29] which is much more than that of the value obtained in present study. We believe that this may be due to handling of hygroscopic 18C6, which results in the higher B-coefficient value reported, in the said report. The high positive value of the B-coefficient indicates large hydrophobic hydration of 18C6 in aqueous medium. These values obtained are comparable to those of large hydrophobic ions such as R_4N^+.[30] These ions also exhibit negative dB/dT, indicating that more structure water (a greater number of hydrogen bonds) around the ion is broken down (breaking of H-bonds) as the temperature is increased. A similar effect of temperature was noted by Patel et al. for structure forming amines in water.[31]

A significant observation of the present work is that the values of the B-coefficient are large positive and more or less constant in the studied temperature range (293.15 to 308.15 K) for CCl_4 solutions, indicating that there are no significant (or appreciable) 18C6−CCl_4 interactions, or in the presence of 18C6 molecules, the structure of CCl_4 remains unaltered (probably a continuum) and only the volume effect is responsible for the increase in viscosity. However, the comparison of the B-coefficient in CCl_4 with that in aqueous solution is questionable on the molarity or molality scale, since the number of moles in 1 kg of the two solvents is strikingly different for CCl_4 and H_2O. This can be explained when we estimate the values of the B-coefficient for both the systems, aqueous 18C6 and

18C6−CCl_4, on the basis of the mole fraction scale instead of molarity or molality. It was found that values of the *B*-coefficient for the 18C6−CCl_4 system are significantly small as compared to those in water.

The *D*-coefficient values of aqueous 18C6 solutions are found to be of higher magnitude as compared to that reported by Herskovits and Kelly for several nonelectrolytes in aqueous media. For example, the values for *tert*-butyl alcohol, urea, tetramethyl urea, and glycine are 0.036, 0.007, 0.034, and 0.022 $(dm^3\ mol^{-1})^2$, respectively.[27] It was also observed that the values increase as the temperature is increased. The interpretation of *D*-coefficient values is not straightforward and is rather difficult. The large values of the *D*-coefficient probably indicate the existence of solute−solute interactions along with solute−solvent interactions. Further, the increase of *D*-coefficient with temperature may suggest that the interaction contribution to solute−solute interactions increases with increase in temperature. This may be taken as a beautiful observation indicative of solute−solute (hydrophobic) interactions, which must increase as temperature increases.

The values of the effective volume of the flowing unit (V_e), calculated using eq 4, decrease with increase in concentration of 18C6 for both the systems. Similar decreases in V_e values for the aqueous tetraalkylammonium bromide solutions have been reported by Eagland and Pilling.[24] Further, the V_e° values decrease as a function of temperature for aqueous 18C6 solutions, supporting the observed variation in *B*-coefficient values as a function of temperature.[24] This dependence of V_e on concentration and temperature can be attributed to the hydrodynamic behavior of the 18C6 in aqueous medium. In the case of the 18C6−CCl4 system, though the V_e values decrease as a function of concentration, they are found to change very little with increase of temperature. This is consistent with the observed *B*-coefficient values, indicating that there is no appreciable effect of temperature on the structural characteristics of CCl_4 as a solvent.

The hydration number, that is, the number of water molecules associated with one 18C6 molecule, has been estimated using eq 7 and reported in Table 1

$$n = \frac{V_e^\circ - \phi_V^\circ}{V_{H_2O}} \tag{7}$$

where V_{H_2O} is the molar volume of water. The V_e°, the limiting value of the effective volume of the flowing unit (18C6 + nH_2O), and ϕ_V° values are also included in Table 1. The hydration number is a vague concept, as different values are obtained by using different physical properties.[33] Generally, the calculations involving the viscosity parameter yield values ranging from 5 to 1 for molecules such as sucrose, glucose, alcohol, amines, and so forth. The molecules quoted above contain at least one or more functional groups, which can interact through H-bonding or dipole−dipole interactions with solvent molecules. In 18C6, since the exterior of the molecules contains only the hydrophobic surface, the strong interactions between 18C6 and water molecules are possible only through the oxygen atoms of the 18C6 ring pointing inward and forming the cavity. We proposed earlier that four water molecules can be stabilized by H-bonds in 18C6 cavities.[14] Since the calculations indicate slightly higher values of hydration number (~7 at 20 °C), it is also certain that some peripheral water molecules are affected by the structure making effect of 18C6. Such attachments should be labile on the time scale used and must be temperature sensitive. This is amply supported by the data of hydration number at higher temperature (~3 at 308.15 K). Thus, the 18C6 molecule with these H-bonded water molecules (18C6 + nH_2O) constitutes a kinetic entity whose size goes on decreasing as a function of temperature.

The radius, *r*, of the flowing entity (18C6 + *n*H2O) has been estimated using the relation

$$B = 2.5(^4/_3)(\pi r^3 N) \tag{8}$$

where *N* is Avogadro's number. The value comes out to be 0.5 nm at 298.15 K, which is in excellent agreement with that reported earlier from this laboratory.[14] There is a change in 0.01 nm in the radius of the flowing entity per 5 °C change of temperature. The value at 293.15 K is found to be 0.51 nm, and it becomes 0.48 nm at 308.15 K. This decrease in radii as a function of temperature indicates that there might be some alteration in the conformational changes due to thermal agitation. We did not attempt the radius calculations in CCl_4 solutions, as eq 9 involves the assumption of a spherical entity of 18C6.

4. Conclusions

The results of viscosity studies for aqueous and CCl_4 solutions of 18C6 at different temperatures and at ambient pressure are analyzed using the Jones−Dole equation. The observed temperature independence of the viscosity *B*-coefficient and V_e° values for 18C6 in CCl_4 throughout the studied temperature range suggests that there is no conformational change for 18C6 in going from pure solid state to solution state in CCl_4. In contrast to these observations, in aqueous 18C6 solutions the viscosity *B*-coefficient and V_e° values decrease with increase in temperature, which may be due to the fact that in aqueous solutions 18C6 exists in the D_{3d} conformation, since the complex formation with water molecules is only possible when all the oxygen atoms of crown molecules are oriented inside the cavity for H-bond interactions to occur. Such an equilibrium conformational state thus seems to be temperature sensitive.

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