

Study on Viscosity and density of Crown ether (15C5) Complexes in aqueous Solutions at 25oC

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Abstract :

This paper reports on the viscosity and density study of the 1,4,7,10,13pentaox-cyclopentadecane (15C5) as binary system and 15C5 in present of KBr(the ternary system) in aqueous solutions at 25oC. The results of the viscosity and density depends on type of system, and concentration rang. The relative viscosity obtain was fitted well by the use of Jones-Dole and Falkenhagen equations to the viscosity parameters i.e. the apparent molar volume and the effective rigid molar volume at infinite dilution. The results indicate that 4.2 mole of water are engaged in one mole of 15C5 and the complexation volume $0.015 \text{ dm}^3\text{mol}^{-1}$ K^+ with 15C5 has been determine. . The results are interpreted in terms of molecular and occupation of crown ether cavity by solvent molecules.

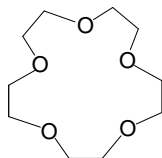
Introduction

After the discovery of crown ethers by Pederson, great number have been synthesized[1,2]. Numerous articles about the complex formation between cations and crown ethers have been published[3,4]. The interaction between solvent molecules and crown ethers have been reported, since the solvation plays a major role in molecular recognition processes by host-guest complexes, these results indicate that the interaction between the solvent and crown ether by hydrogen bonding and dipole interaction, which may be replaced by ion-dipole interaction in salt Solution [5,6]. The present study employs precision viscosity and density measurements of KBr with and without 15C5 in aqueous at 25°C, to examine molecular interaction.

Experimental

Crown ether (15C5) (Fluka) of high purity was used without further purification. Potassium bromide was recrystallized three time from a water and ethanol mixture and dried below their decomposition temperature then temporarily stored in a glass desiccators over P₂O₅.

Viscosity measurements were accomplished with ubbelohde viscometer from Schott-Gerate. The flow time was measured by photoelectric device. The apparatus used was Anton Paar digitah densitometry (model DMA 60/601) at 25°C.



15C5

Results and discussion

The parameters of viscosity i.e. η_r , A, B and D of solution were calculated using equations(1,2 and3) [7]

$$\eta_r = \frac{td}{t_o d_o} \quad (1)$$

Where t , d are respectively the

time of flow and density of solution while t_0 is the time of flow and d_0 is the density of water in binary system(15C5) and in ternary system KBr in 0.2M aqueous solution of 15C5

The Jones-Dole equation, which holds for electrolyte, different concentration of KBr and 0.2M15C5 aqueous 15C5 solutions is

$$\eta_r = 1 + A\sqrt{c} + Bc \quad (2)$$

Where A and B are a coefficient that depends on the long range coulombic forces and solvent –solute interaction. The relative viscosity data for binary (aqueous 15C5)non-electrolyte solutions treated using equation 3, which an additional term in second power of c

$$\eta_r = 1 + Bc + Dc^2 \quad (3)$$

Since D is constant reflects the dipole-dipole interaction.

The plots of $[(\eta_r-1)/c^{1/2}]$ versus c and $[(\eta_r-1)/c]$ versus c were found to be linear for binary and ternary system. The A and B coefficients obtained as intercepts of the straight line.

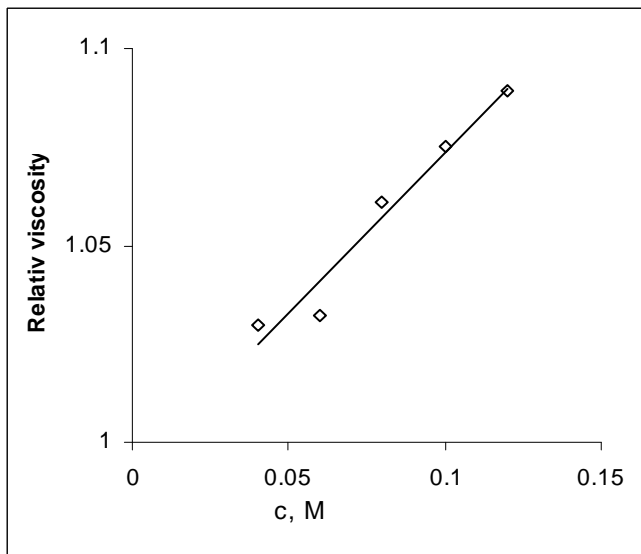


Figure 1. The variation of η_r as a function of concentration of 15C5 at 25°C

Table(1). The relative viscosity (η_r), density(d)and parameters viscosity of 15C5 in aqueous solution at 25°C

c dm ³ mol ⁻¹	η_r	d g mol ⁻¹	V _e dm ³ mol ⁻¹	ϕ_v dm ³ mol ⁻¹
0.04	1.0296	0.9974	0.283	0.179
0.06	1.0321	0.9981	0.201	0.181
0.08	1.0610	0.9991	0.280	0.179
0.10	1.0571	1.0005	0.271	0.173
0.12	1.0891	1.0034	0.264	0.175
0.14	-	1.0069	-	0.141
B=0.63 dm ³ mol ⁻¹				
D= 0.90(dm ³ mol ⁻¹) ² V _e ^o = 0.308 ϕ_v^o = 0.203				

It is apparent from Figure.1. and Table(1). that the relative viscosity (η_r) and density (d) were increased by increasing the concentration. The η_r values can be fitted well by the use of Jons-Doll and Falkenhagen equation(3).The B-coefficient value for 15C5(0.63 dm³ mol⁻¹), the high positive value clearly indicate a structure making action of 15C5 in water to form spherical entity(brownon). The high value of the D-coefficient reflects the increase co-oprative interaction amongst these spherical entities through molecules. The high value of B for 18C6 in water(0.789 dm³ mol⁻¹)[6] as compared with15C5 (0.630 dm³ mol⁻¹) may be due to the sex donor oxygen atoms of cavity 18C6 lead to increase structure making action.

Table(2). The viscosity (η_r), density(d) and parameters of different concentration KBr in aqueous 0.20M 15C5 solution at 25°C

c dm ³ mol ⁻¹	η_r	d gcm ⁻³	ϕ_v	A dm ³ mol ⁻¹	B (dm ³ mol ⁻¹) ²
0.08	0.9912	1.001	0.053	-0.0396	0.0338
0.12	0.9915	1.003	0.059		
0.16	1.005	1.006	0.055		
0.20	0.9900	1.008	0.058		
0.24	0.9911	1.012	0.052		
0.28	0.9902	1.015	0.051		
$\phi_v^o = 0.059$					

The η_r data of the ternary system(KBr in aqueous 0.2M 15C5 solutions) are represented in Table(2). The results in general indicate that η_r values are tend to unity in the concentration region[0.08-0.28] this may be due to the capture of potassium ion in cavity the ether which lead to the structure breaking character of aqueous system (i.e.dipole-dipole and hydrogen bonding interaction). The B-coefficient value($0.0338\text{dm}^3 \text{mol}^{-1}$)²) means that the charge on K^+ ion is effectively screened in the complexation process very low with 15C5 molecule.

The viscosity and density parameters effective rigid molar volume (V_e) and apparent molar volume (ϕ_v) were calculate using the following equations [6]

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

$$\phi_v = \frac{M_2}{d_o} + \frac{1000(d_o - d)}{cd_o} \quad (5)$$

where d_o and d are the densities of aqueous an solution respectively, c is molar concentration and M_2 is the molecular weight of the solute.

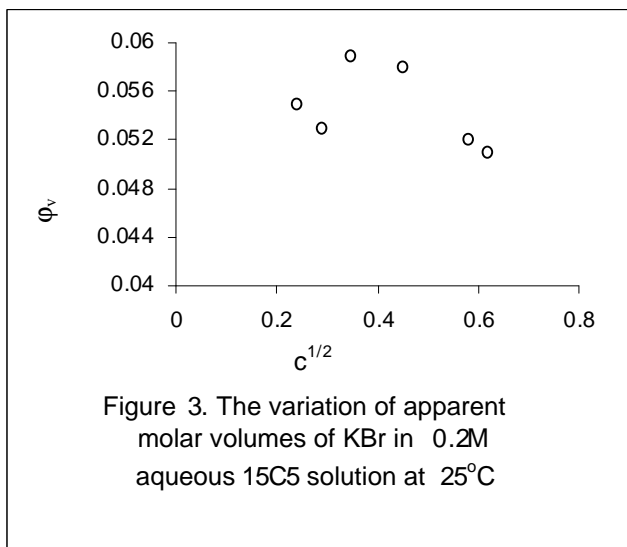
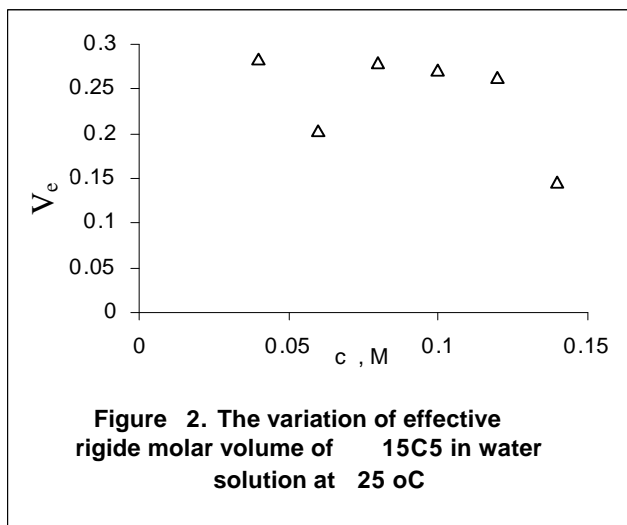
The variation of ϕ_v of 15C5 as a function of c is represent in Table(2). Since the d_o being the density of 0.2M aqueous 15C5 solution, and M_2 the molecular weight of KBr.

The viscosity and density parameters i.e. apparent molar volume at infinite dilution (ϕ_v^0) and effective rigid molar volume at infinite dilution (V_e^0) were calculated by plotting ϕ_v and V_e against $c^{1/2}$ and c respectively and curves were extrapolated to zero concentration as shown in Figures2.3. These values of (V_e^0) and (ϕ_v^0) in aqueous 15C5 solution were estimate that about 4.2 mole of water are engaged in one mole of the 15C5.This is a reasonable values when compared with 18C8 (4.9 mole) in which possess a more donor atoms in its molecules[6]

It can be proposed that the 15C5 molecules interact with aqueous molecules to form the kinetic entity, the increased size of the kinetic entity(15C5+H₂O), calculated by estimate radius(r), using B-coefficient(0.63 dm³ mol⁻¹), hence

$$B = 2.5\left(\frac{4}{3}\right)(\pi r^3 N_A) \quad (6)$$

N_A is Avogadro's number, which comes to be 0.46 nm, we can compare this value with unsolvated radius of 15C5(0.10nm)[2]. thus the assumed kinetic entity is justified with the H-bonded aqueous molecules and 15C5.



The (ϕ_v^0) data for ternary system(KBr+ aqueous 15C5) $0.059 \text{ dm}^3 \text{ mol}^{-1}$ and KBr in aqueous solution $0.034 \text{ dm}^3 \text{ mol}^{-1}$ [7], the different can be processed to yield the volume of complexation($0.05900 \text{ dm}^3 \text{ mol}^{-1} - 0.034 \text{ dm}^3 \text{ mol}^{-1} = 0.015 \text{ dm}^3 \text{ mol}^{-1}$) is obtained, the volume change due to complexation of K^+ ion with 15C5.

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