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Viscosity Behaviour of Cryptand C222 in Methanol Solution

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The viscosity measurements for potassium chloride solution contaning C222 in methanol at 25°C have been investigated. The relative viscosity in the studied concentration range was found to fit well with Jones-Dole and Falkenhagen equation. The results are interpreted in terms of molecular interaction and occuption of cryptand cavity by methanol molecules.

Key Words: Viscosity, Cryptand C222, Methanol solution.

INTRODUCTION

Pederson[1] and Len[2] were the first to synthesize the crown compounds (crown ethers and cryptands). Crown compounds show a remarkable range specifying for a wide variety of cations; it depends, in part, on the size of cavity, type of donor atoms and polarity of the solvent[3, 4]. Crown compounds display the extraordinary property of metal ions, including alkali cations, into non-aqueous and non-polar solvents[5]. It has been extensively studied from a theoretical and experimental point of view[6–9].

In recent years, the studies of hydration of 18C6 have attracted the attention of many research workers, since the solvation plays a major role in molecular recognition processes by host-gust complexes[10–12]. Previous studies of 18C6 and C222 uncomplexed in water led to the conclusion that dissolution of crystals should lead to conformational changes and hydrogen bonding between crown oxegen atoms and water molecules; partial molar volume indicated that hydrophobic hydration is important in the dilute concentration region in aqueous medium[13].

These results indicate the interaction between the solvent and crown compounds by hydrogen bonding and dipole interaction, which may be replaced by ion-dipole interaction in salt solution. Only a few results have been reported about the interaction between solvent molecules and cryptand. The present study employs precision viscosity and density measurements of KCl with and without cryptand in methanol at 25°C to examine molecular interaction.

EXPERIMENTAL

Cryptand C222 procured from Merck was used without further purification; methanol grade BDH was used as a solvent. Potassium chloride (Riedal-Dehean) was of commercial purity (99.8%) and was recrystallized three times from a water and ethanol mixture and dried below decomposition temperature, then temporarily stored in glass desiccators over P_2O_5.

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

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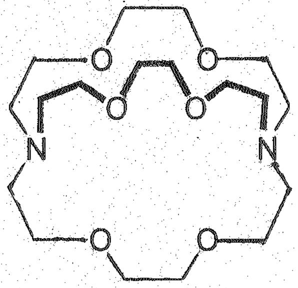
RESULTS AND DISCUSSION

The relative viscosity (η_r) of the solution was calculated using eqn. (1)[14].



[C222]

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

where t, d are respectively time of flow and density of solution and t_0, d_0 are respectively time of flow and density of solvent (methanol in binary and 0.11MC222 + methanol in ternary solution).

The Jones-Dole equation, which holds for electrolyte solution, is defined by eqn. (2).

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

where A is a coefficient that depends on the long range coulombic forces (adjustable parameter). The relative viscosity data for binary C222 + methanol solution was treated using eqn. (3), with an additional term in second power of c.

$$\eta_r = 1 + Bc + Dc^2 \tag{3}$$

It is apparent from Fig. 1 and Table-1 that the relative viscosity (η_r) increases with increasing the concentration. The η_r can fit well with Jones-Dole and Falkenhagen eqn. (3). The B-coefficient value for C222 (0.876 $dm^3\,mol^{-1}$), the high positive value, clearly indicates a structure making action of C222 in methanol to form spherical entity (brownon). The low value of the D-coefficient reflects the decreased cooperative interaction amongst these spherical entities through molecules.

TABLE-1
THE VISCOSITY (η_r) AND PARAMETERS VISCOSITY OF C222 IN METHANOL SOLUTION AT 25°C

c ($dm^3\,mol^{-1}$)	η_r	V_e ($dm^3\,mol^{-1}$)	B ($dm^3\,mol^{-1}$)	D ($dm^3\,mol^{-1}$)
0.01	1.0085	0.335		
0.06	1.0531	0.328		
0.09	1.0796	0.317	0.876	0.119
0.11	1.0996	0.318		
0.14	1.1280	0.311		
0.16	1.1540	0.284		
		$V_e^0 = 0.343$		

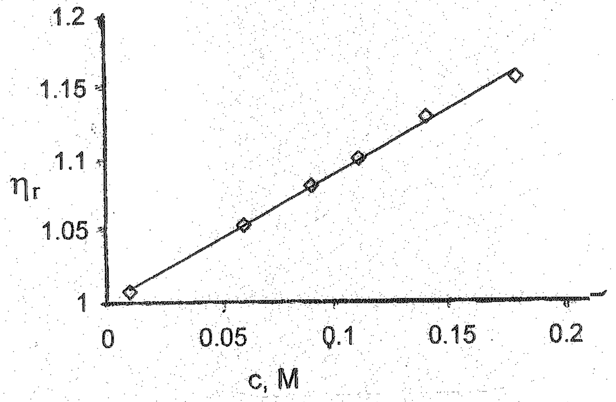


Fig. 1. The variation of η_r as a function of concentration of C222 at 25°C

TABLE-2
THE VISCOSITY (η_r), DENSITY(D) AND PARAMETERS OF DIFFERENT CONCENTRATION KCl AND 0.11 M OF C222 IN METHANOL SOLUTION AT 25°C

c (dm^3 mol^{-1})	η_r	d (g cm^{-3})	φ_v (dm^3 mol^{-1})	A (dm^3 mol^{-1})	B (dm^3 mol^{-1})
0.004	1.0009	0.79479	—		
0.010	0.9998	0.79513	—		
0.019	0.9996	0.79531	0.045	0.014	–0.088
0.020	1.0010	0.79579	0.041		
0.035	0.9998	0.79611	0.038		
0.040	0.9992	0.79624	0.041		
			$\varphi_v^0 = 0.056$		

The η_r data of system (KCl + 0.11 M C222) in methanol are represented in Table-2. These results in general indicate that the η_r values vary little from unity in the concentration region. This may be owing to capture of potassium ion to cavity cryptand, which leads to the structure breaking character of methanol system (dipole-dipole and hydrogen bonding interaction). The small A-coefficient value means that on complexation with C222 molecule the charge on K^+ ion is effectively screened. This behaviour is observed in some crown ether system in methanol[15].

The expression for the hydrophobic hydration was derived by Einstein, in case of brownons molecules[16].

$$\eta_r = 1 + 2.5V_hc \tag{4}$$

where V_h is the hydrodynamic volume in dm^3 mol^{-1}. In case of solvated molecules, their covolumes include the contribution from the solvent molecules attached to the solute; hence the hydrodynamic volume of solute is referred to as the effective rigid molar volume (V_e). The V_e of C222 at the studied concentration was calculated using the Breslu and Miller equation[17].

$$V_e = \frac{-2.5C + [(2.5C)^2 - 4(10.05C^2)(1 - \eta_r)]^{1/2}}{2(10.05C^2)} \tag{5}$$

The B-coefficient can be related to V_e as

$$B = 2.5V_e \tag{6}$$

The apparent molar volumes (φ_v) of C222 and (KCl + 0.11 M C222) in methanol were calculated using the equation

$$\varphi_v = \frac{M_2}{d_0} + \frac{1000(d_0 - d)}{Cd_0} \tag{7}$$

where d_0 and d are the densities of methanol and solution, respectively, C is molar concentration and M_2 is the molecular weight of the solute[18].

The variation of φ_v of C222 as a function of C is represented in Table-2, where d_0 is the density of 0.11 M C222 in methanol solution, and M_2 the molecular weight of KCl.

The parameters viscosity, apparent molar volume at infinite dilution (φ_v^0) and effective rigid molar volume at infinite dilution (V_e^0) were calculated from the extrapolations φ_v and V_e against concentration curve to zero concentration (Figs. 2, 3).

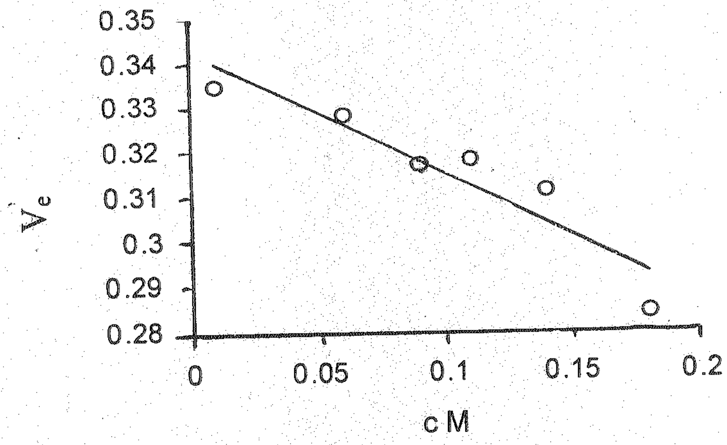


Fig. 2. The variation of effective rigid molar volumes of C222 in methanol solution at 25°C

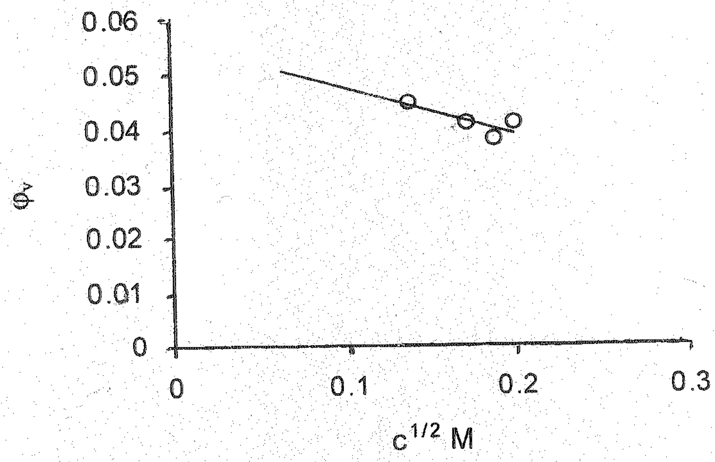


Fig. 3. The variation of apparent molar volumes of KCl in 0.11MC222ol solution at 25°C

(V_e^0) is used instead of V_e, that is independent of concentration[17]; hence eqn. (6) becomes

$$B = 2.5V_e^0 \tag{8}$$

It can be proposed that the C222 molecules interact with methanol molecules to form the kinetic entity. The increased size of the kinetic entity (C222 + methanol) is calculated by the estimation of the radius (r), using B-coefficient (0.876 $dm^3\ mol^{-1}$); hence

$$B = 2.5\left(\frac{4}{3}\right)(\pi_r^3 N_A) \tag{9}$$

where N_A is the Avogadro number, which comes to be 0.500 nm; we can compare this value with unsolvated radius of C222 (0.14 nm)[19]. Thus the assumed kinetic entity is justified with the H-bonded methanol molecules and C222.

The (φ_v^0) data for ternary system(KCl + C222 in methanol, 0.056 $dm^3\ mol^{-1}$), for binary system(KCl in methanol, 0.0113 $dm^3\ mol^{-1}$)[15] was found to be in good agreement with literature value (0.0101 $dm^3\ mol^{-1}$)[20]. The data of φ_v^0 of ternary system and binary system can be processed to yield the volume of complexation ($0.05600\ dm^3\ mol^{-1} - 0.01134\ dm^3\ mol^{-1} = 0.04534\ dm^3\ mol^{-1}$). This volume change is due to complexation of K^+ ion with C222.

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