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Anion effect on selectivity in 18-crown-6 ether interaction with alkali metal cations

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Abstract

The Selectivity complexation of alkali metal cations by 18-crown-6 ether was investigated with particular focus on the effect of various cations at 298.15K using viscosity and density study elucidates how different anions influences the interaction ability and selectivity of alkali metal ions. The presence and nature of anions were found to modulate the host-guest interaction energies, impacting the structural confirmation of common ether complex as well as salvation and electrostatic effects. The excess parameters such as excess molar volume (V_E), viscosity deviation ($\Delta\eta$), apparent molar volume (ϕ_v) were calculated from the experimental data of viscosity and density at 298.15K. These excess calculated data reveals that anions identify significantly changes the thermodynamic parameters and binding selectivity these finding contributes to a deeper understanding of ion recognition mechanism in 18-crown-6 ether system and suggest strategic manipulation of anions for enhanced the selectivity in applications such as ion extraction sensing and catalyst at 298.15K.

Keywords: Alkali metals cations, 18-crown-6, anion, viscosity, density, interaction.

Introduction

The study of effect of anion on selectivity of cation with 18-Crown-6 at 298.15K. Crown ethers are macrocyclic polyether known for their tendency to selectively bind their alkali metal ions. Among all of crown ether, 18-Crown-6 strong interaction for the ions due to closely matched size of K^+ ion and size of holes of 18-Crown-6 ether[1-4]. The extensively studies has been carried out on alkali metal cation and crown ether interaction, However adequate study on the role of anion in the complexation and interaction of alkali metal cation with crown ether. The anion affect on solvation, ion-pairing and indirectly on the stability of cation-crown ether interaction and complexation.

This present investigation has scope to study how chloride (Cl^-) and bromide (Br^-) anion affect the selectivity of potassium ion (K^+) with aqueous solution of 18-Crown-6 ether at various concentration since the size polarizability and hydration ability of Cl^- and Br^- anions different from each other. Due to different size of Cl^- and Br^- ions, to affect the physico-chemical properties of the alkali metal cation-18-Crown-6 complex[5-6]. This research work are vital for clearing our understanding of crown ether chemistry and for applications in supramolecular recognition, ion separation technique and sensing[7].

This investigation carried out by measurement the viscosities and densities of aqueous solution of alkali metal salts with various mole fractions of 18-Crown-6 at 298.15K. From these values of viscosities and densities used to calculate the excess parameters, which used for understanding influence of anions on the interaction of alkali metal ions with 18-Crown-6[8].

This research work indicated bromide has larger size anion and more polarizable than chloride, it affects significantly interaction of cation-18-Crown-6 ether that is complexation. This work reveal that anions only acts as spectators but also considered as active participants in determining the selectivity and interaction strength of 18-Crown-6 with K^+ ion in aqueous solutions[9-11].

Theory: Excess parameter has been calculated from experimental data of density and viscosity [12-13].

$$V^E = \frac{(X_1M_1+X_2M_2)}{\rho} - (x_1v_1 + x_2v_2) \quad (1)$$

Where, x_1 and x_2 are the mole fractions, M_1 and M_2 are the molecular weight, v_1 and v_2 are molar volume of water and 18-Crown-6 respectively.

The excess viscosities ($\Delta\eta$) of binary liquid systems were calculated by measuring flow time of the mixture [14-15].

$$\Delta\eta = \eta - \{X_1\eta_1 + X_2\eta_2\} \quad (2)$$

η viscosity of binary liquid mixture. $\eta_1$and η_2 are the viscosities of aqueous solution of alkali metal salt (1) and 18-crown-6 (2)

$$\text{Apparent molar volume } V_\phi = \frac{M}{d_0} - \frac{1000}{C}\left[\frac{d-d_0}{d_0}\right] \quad (3)$$

M is the molecular weight of solute, d and $d_0$are the densities of solution and pure solvent. C is the concentration in mol dm^{-3}

Materials and Methods

In the present investigation all the required chemical were analytical grades (AR) having purity 99.9% purchase from Spectrochem. The various concentrations solutions of binary liquid mixtures were prepared in airtight umber colour stoppered bottles[16]. The density and time flow of liquid measured as a function of binary system (18-crown-6 + aqueous 1 millimoles alkali metal salts solution).

Density measurements: The pycnometer having bulb capacity 10×10^{-6} m^3 with graduated used for determination density of solutions. It was calibrated with primary standard toluene, benzene and tripled distilled water[17].

Viscosity measurement: Measurement viscosity of liquid mixture using ubbelohde viscometer (20 ml) was used. For measurement flow time using digital clock having an accuracy of ± 0.1S. It was calibrated with primary standard toluene, benzene and tripled distilled water[18].

Results and Discussion

Densities (ρ) and viscosities (η) of aqueous 1 millimole solution of KCl (1) + 18-Crown-6 (2) and aqueous 1 millimole solution of KBr (1) + 18-Crown-6 (2) at 298.15K. are listed in table 1 and 2. The negative value of V^E and positive value of Δη in these binary system, there is more negative value of V^E and more positive value of Δη in the aqueous solution of KBr (1) + 18-Crown-6 (2) system, indicated that there is more interaction and complexation. This is due to chloride ion (Cl^-) is significantly smaller than the bromide ion (Br^-). The Cl^- ion has higher charge density and generally more strongly hydrated than Br^-. Therefore Cl^- form close contact with (crown ether- K^+) complex as compared to less hydrated anion (Br^-).Thus the complexation stability of 18-crown-6 ether with K^+ in KBr solution is generally very close to that in KCl solution. The positive values of apparent molar volume in both system, the value of ϕ_v higher, It also reveals that more interaction of K^+ with 18-crown-6 in KBr solution. The graphical presentation of VE of binary system varied concentration of 18-crown-6 with aqueous solution of one milli mole of alkali metal salts at 298.15K.

Table-1: Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and apparent molar volume for the Aqueous Solution of KCl (1) + 18-crown-6 ether (2) System at 298.15K.

Temp	m (g cm^{-3})	X_1	ρ(gcm^{-3})	η(mPa s)	V^E (cm mol^{-1})	Δη	ϕ_v
298.15K	0	1	0.9962	0.9003	0	0	18.0686
	0.00125	0.999977	0.9968	0.9074	-0.00971687	0.00712	18.0589
	0.0025	0.999954	0.9970	0.9131	-0.01218168	0.01284	18.0564
	0.005	0.999909	0.9972	0.9175	-0.01348751	0.01728	18.0551
	0.01	0.999819	0.9974	0.9221	-0.01247264	0.02196	18.0561

Table-2: Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and apparent molar volume for the aqueous solution of KBr (1) + 18-crown-6 ether (2) System at 298.15K.

Temp	m (g cm^{-3})	X_1	ρ(gcm^{-3})	η(mPa s)	V^E (cm mol^{-1})	Δη	ϕ_v
298.15K	0	1	0.9959	0.9038	0	0	18.0741
	0.00125	0.999977	0.9969	0.9115	-0.01697161	0.00772	18.0571
	0.0025	0.999954	0.9971	0.9155	-0.01943613	0.01174	18.0546
	0.005	0.999909	0.9973	0.9199	-0.02074210	0.01618	18.0533
	0.01	0.999819	0.9975	0.9266	-0.01972825	0.02296	18.0541

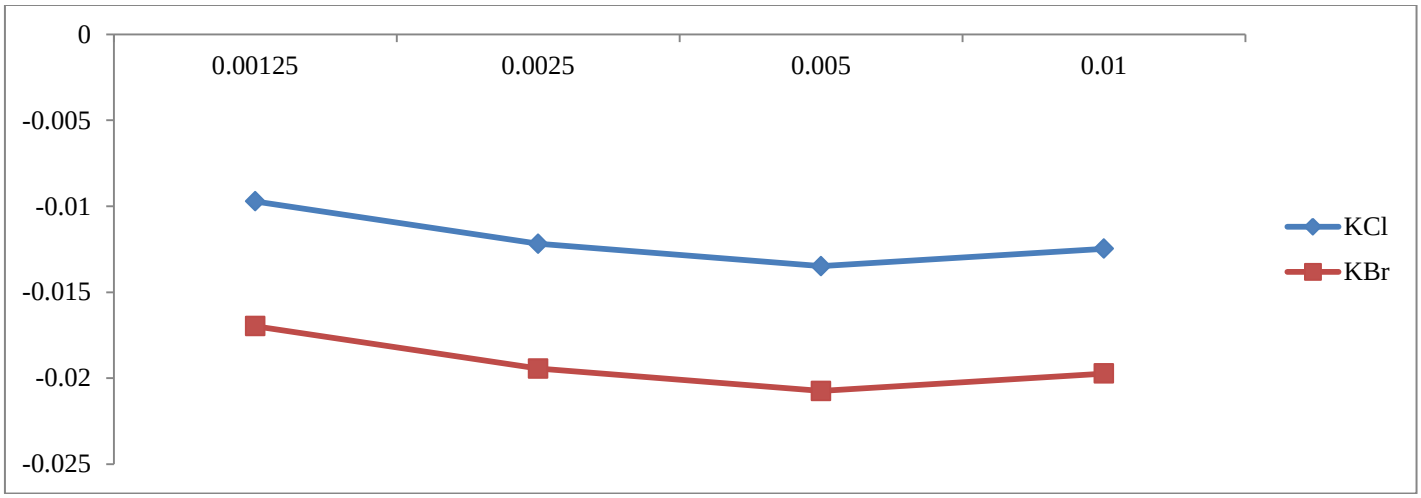

Figure-1: Excess molar volume (VE) for the Binary System 18-Crown-6 (1) + aqueous solution of one milli mole alkali metal salt (2) at 298.15K.

The graphical presentation of Δη of binary system varied concentration of 18-crown-6 with aqueous solution of one milli mole of alkali metal salts at 298.15K.

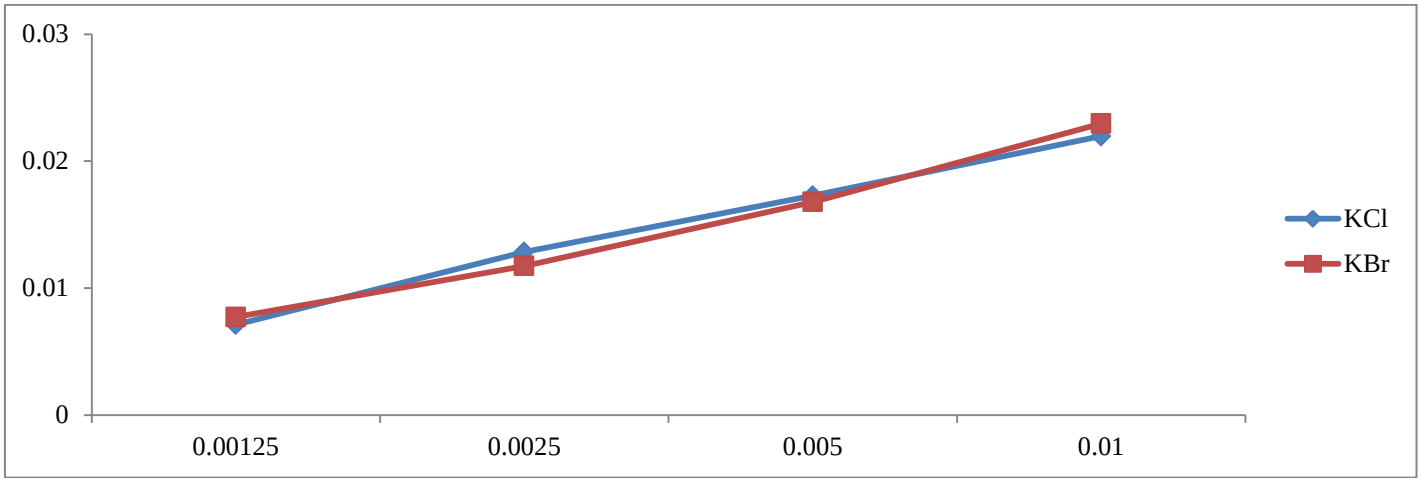

Figure-2: Viscosity deviations (Δη) for the Binary System 18-Crown-6 (1) + aqueous solution of one milli mole alkali metal salt at 298.15K.

Conclusion

The sequence of interaction or complexation of K^+ with 18-crown-6 in binary system at 298.15K as – KBr -18-crown-6 > KCl- 18-crown-6. Thus, K+ ion of KBr salt interact strongly with 18-crown-6 than KCl

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