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Effect of Temperature on the interaction of Alkali metal ions and 18-crown-6 ether in Binary system

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Abstract

18-crown-6 ether is widely accepted for their selectivity complexation and interaction with higher alkali metal ion, even their binding and complexation efficiency is strongly influenced by the temperature. In this research work, we investigate the effect of Variation of temperature on the stability of the complex and interaction between 18-crown-6 and alkali metals (Rb^+ & Cs^+) in a binary liquid systems. Viscosity and density measurements were employed to determine molecular interaction and thermodynamic parameters like $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ over a temperature range 298.15K, 308.15K. The excess molar volume (V^E), Viscosity deviation ($\Delta\eta$)and other interaction parameters data indicate that at lower temperature rise the binding affinity and complexation due to reduce the molecular movement. The complexation and interaction of 18-crown-6 and alkali metal ion depending on the ion type. The interaction and thermodynamic parameters data revealed that alkali metal ions & 18-crown-6 accepted processes in supramolecular chemistry and recommend possible applications in selective alkali metal ion extraction, drugs separation and design the sensors. In this results the sequence of interaction of 18-crown-6 with alkali metal salts as RbBr > RbCl > CsBr > CsCl.

Keywords: 18-crown-6, temperature, alkali metal ions, viscosity, density, interaction, complexation.

Introduction

Pedersen discovered various crown ethers; they have ability to selectively binding with positive ions of metals through size contentious cavities. Hence crown ethers play an important role in the development of supramolecular chemistry. Among all of crown ethers, 18-crown-6 is the best crown ether and indicates exceptional affinity towards alkali metal ions, particularly Cs^+ & Rb^+ [1,2]. The 18-crown-6 ether making model system to study complexation and interaction with alkali metal ions. This research of such ions-crown ether interaction importance in co-ordination chemistry[3,4]. As well as in catalysis process material design applicability in ion transport phase transfer catalysis and membrane mimicking systems[5-10]. The interaction of alkali metal ion with 18-crown-6 is strongly affected by temperature variation. The increasing temperature reduces alkali metal ions and 18-crown-6 ether thus altering the selectivity of crown ether[11]. This research work is therefore fascinated on studying the combining effect of temperature and concentration variations on the interactions of 18-crown-6 with higher alkali metal ions (Rb^+ & Cs^+) both in binary systems (Rb^+ + 18-crown-6 & Cs^+ + 18-crown-6)[12]. This research work applicable to determination of thermodynamics parameters likes enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG) and also for evaluation of interaction parameters at variation of temperature. This comprehensive research has been dedicated to the interaction properties of 18-crown-6 with higher alkali metal ions. Pederson's investigating research work for established the models for alkali metal ion selectivity with crown ethers their after studies stability constant of complex in various solvents. It has been reported that the interaction affinity of crown ether depends on the metal ion size, dielectric constant of solvent, and temperature[13-15].

The investigators have revealed that the complex stability reduced or enhance depends on the temperature variation and concentration of 18-crown-6 ether with alkali metal ions. The lack of data published on the combined effect of temperature variation and concentration, especially in systematic correlation of binary liquid systems. This gap in the literature gives the reasoning for the present research[16,17].

The interaction strength and selectivity of higher alkali metal ions with 18-crown-6 will differ significantly with temperature variations. It is due to changes in salvation and 18-crown-6 flexibility.

The interaction in between 18-crown-6 and alkali metal ions complex and its stability constant were determined by density and viscosity measurement methods were employed.

Theory: Using the experimental data the following excess and interaction parameters has been calculated[18,19].

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

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 (Δη) of binary liquid systems were calculated by measuring flow time of the mixture.

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

η viscosity of binary liquid mixture. η_1 and η_2 are the viscosities of salts solutions and 18-crown-6

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

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}.

The experimental value of density (ρ), viscosity (η) and calculated value of excess molar volume (V^E), viscosity deviation (Δη) and apparent molar volume (ϕ_V) values at various concentration ranges and at various temperature are reported in Table-1, 2, 3 and 4.

Table-1: Values of Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and Apparent molar volume for the 18-Crown-6 (1) + aqueous solution of RbCl salt binary System.

Temp (K)	Concentration	ρ × 10^{-3} (Kgm^{-3})	η M(PaS)	$V^E \times 10^6$ ($M^3 mol^{-1}$)	Δη (M PaS)	V_ϕ
298.15	0	0.9970	0.8900	-	-	-
	0.00125	0.9971	0.8985	-0.00065353	0.0085	184.874624
	0.0025	0.9975	0.9037	-0.00673918	0.0137	64.5135406
	0.005	0.9979	0.9082	-0.01166797	0.0182	84.5737212
	0.01	0.9983	0.9129	-0.01428689	0.0229	134.724173
398.15	0	0.9940	0.7191	-	-	-
	0.00125	0.9941	0.7237	0.001175098	0.0046	265.888744
	0.0025	0.9946	0.7276	-0.00675725	0.0085	64.7017403
	0.005	0.9949	0.7323	-0.00987293	0.0132	104.939141
	0.01	0.9952	0.7359	-0.01064190	0.0168	155.235892

Table-2: Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and Apparent molar Volume for the 18-Crown-6 (1) + aqueous solution of RbBr salt (2) binary System.

Temp (K)	Concentration	ρ × 10^{-3} (Kgm^{-3})	η M (PaS)	$V^E \times 10^6$ ($M^3 mol^{-1}$)	Δη (M PaS)	V_ϕ
298.15	0	0.9970	0.8900	-	-	-
	0.00125	0.9972	0.9021	-0.00246439	0.0121	104.633902
	0.0025	0.9976	0.9063	-0.00854915	0.0163	24.3931795
	0.005	0.9980	0.9101	-0.01347760	0.0201	64.5135406
	0.01	0.9984	0.9128	-0.01609730	0.0228	124.694082
398.15	0	0.9940	0.7191	-	-	
	0.00125	0.9943	0.7259	-0.00246815	0.0068	104.939141
	0.0025	0.9948	0.7295	-0.01039796	0.0104	-15.773061
	0.005	0.9951	0.7334	-0.01351369	0.0143	64.7017403
	0.01	0.9955	0.7369	-0.01610593	0.0178	125.057841

Table-3: Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and Apparent molar volume for the 18-Crown-6 (1) + aqueous solution of CsCl salt (2) binary System.

Temp (K)	Concentration	$\rho \times 10^{-3}$ (Kgm^{-3})	η M (PaS)	$V^E \times 10^6$ ($M^3 mol^{-1}$)	Δη (M PaS)	V_ϕ
298.15	0	0.9970	0.8900	-	-	-
	0.00125	0.9966	0.8937	0.008406225	0.0037	586.078235
	0.0025	0.9970	0.9011	0.002316095	0.0111	265.115346
	0.005	0.9974	0.9060	-0.00261437	0.0160	184.874624
	0.01	0.9978	0.9112	-0.00522938	0.0212	184.874624
398.15	0	0.9940	0.7191	-	-	-
	0.00125	0.9932	0.7188	0.017587871	-0.0003	990.161956
	0.0025	0.9937	0.7227	0.009644061	0.0036	426.838346
	0.005	0.9942	0.7268	0.002881246	0.0077	245.770043
	0.01	0.9947	0.7312	-0.00152786	0.0121	205.532643

Table-4: Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and Apparent molar volume for the 18-Crown-6 (1) + aqueous solution of CsBr salt System.

Temp (K)	Concentration	$\rho \times 10^{-3}$ (Kgm^{-3})	η M(PaS)	$V^E \times 10^6$ ($M^3 mol^{-1}$)	Δη (M PaS)	V_ϕ
298.15	0	0.9970	0.8900	-	-	-
	0.00125	0.9968	0.8945	0.004781231	0.0045	425.59679
	0.0025	0.9972	0.9019	-0.00130710	0.0119	184.874624
	0.005	0.9976	0.9068	-0.00623690	0.0168	144.754263
	0.01	0.9980	0.9120	-0.00885347	0.022	164.814443
398.15	0	0.9940	0.7191	-	-	-
	0.00125	0.9936	0.7221	0.010289634	0.003	668.26275
	0.0025	0.9941	0.7269	0.00235092	0.0078	265.888744
	0.005	0.9946	0.7312	-0.00440905	0.0121	165.295242
	0.01	0.9950	0.7352	-0.00699738	0.0161	175.354592

On the basis of theory of absolute reaction rates, the excess Gibbs energies ($G^{E\#}$) of activation of viscous flow were calculated are shown in Table-5 to 12.

$$\frac{\Delta G^{E*}}{RT} = \left\{\ln\left(\frac{\eta v}{\eta_2 v_2}\right) - x_1 \ln\left(\frac{\eta_1 v_1}{\eta_2 v_2}\right)\right\} \quad (3)$$

Thermodynamic parameters $\Delta G^{\neq}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ were determined using Erying and John's equation.

$$\eta = \frac{hN}{V} \exp\left[\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}\right] \quad (4)$$

Where, η is the viscosity of binary and ternary mixture, h, N,& V is the planks constant, Avogadro's number & molar volume respectively.

Plot the graph of ln (ηv/hN) against1/T, the calculate slope and intercept of graph[20].

The slope of graph is equal to $\Delta H^{\#}/R$ and intercept is equal to $-\Delta S^{\#}/R$ from the graph activation parameters were obtained. $\Delta G^{\neq}$ was calculated using the equation $\Delta G^{\neq} = \Delta H^{\#} - T\Delta S^{\#}$ and values are reported in Table-5 to 8.

Table-5: Thermodynamic Activation Parameters for 18-Crown-6 (1) + aqueous solution of RbCl salt (2) binary system.

Concentration	$\Delta H^{\#}$ (kJ mole^{-1})	$\Delta S^{\#}$ (JK^{-1} mole^{-1})	$\Delta G^{\#}$ (kJ mole^{-1})		$G^{E\#}$ (kJ mole^{-1})	
			298.15 K	308.15 K	298.15 K	308.15 K
0.00125	16306.25	-148.446	60565.56	62050.03	6908.611	6593.154
0.0025	16337.01	-148.397	60581.45	62065.42	6922.688	6606.427
0.005	16223.94	-148.812	60592.32	62080.45	6935.537	6623.732
0.01	16243.89	-148.796	60607.32	62095.28	6950.400	6638.430

Table-6: Thermodynamic Activation Parameters for 18-Crown-6 (1) + aqueous solution of RbBr salt (2) binary system.

Concentration	$\Delta H^{\#}$ (kJ mole^{-1})	$\Delta S^{\#}$ (JK^{-1} mole^{-1})	$\Delta G^{\#}$ (kJ mole^{-1})		$G^{E\#}$ (kJ mole^{-1})	
			298.15 K	308.15 K	298.15 K	308.15 K
0.00125	16380.24	-148.230	60575.11	62057.41	6918.276	6600.932
0.0025	16356.96	-148.347	60586.53	62070.00	6929.562	6613.625
0.005	16269.67	-148.679	60598.39	62085.18	6940.470	6628.094
0.01	16132.49	-149.170	60607.46	62099.16	6949.880	6642.682

Table-7: Thermodynamic Activation Parameters for 18-Crown-6 (1) + aqueous solution of CsCl salt (2) binary system.

Concentration	$\Delta H^{\#}$ (kJ mole^{-1})	$\Delta S^{\#}$ (JK^{-1} mole^{-1})	$\Delta G^{\#}$ (kJ mole^{-1})		$G^{E\#}$ (kJ mole^{-1})	
			298.15 K	308.15 K	298.15 K	308.15 K
0.00125	16415.99	-148.031	60551.37	62031.68	6896.574	6578.582
0.0025	16632.99	-147.374	60572.54	62046.28	6916.788	6591.947
0.005	16614.70	-147.482	60586.47	62061.29	6930.766	6606.733
0.01	16591.42	-147.615	60602.85	62079.00	6947.021	6624.072

Table-8: Thermodynamic Activation Parameters for 18-Crown-6 (1) + aqueous solution of CsBr salt (2) binary system.

Concentration	$\Delta H^{\#}$ (kJ mole^{-1})	$\Delta S^{\#}$ (JK^{-1} mole^{1})	$\Delta G^{\#}$ (kJ mole^{-1})		$G^{E\#}$ (kJ mole^{-1})	
			298.15 K	308.15 K	298.15 K	308.15 K
0.00125	16134.15	-148.987	60554.58667	62044.45547	6898.295	6589.287
0.0025	16258.03	-148.638	60574.35	62060.73	6918.49	6605.764
0.005	16221.45	-148.812	60589.83	62077.95	6932.458	6621.168
0.01	16241.40	-148.796	60604.82	62092.78	6948.699	6637.279

Materials and Methods

All the required chemical in the present investigation were analytical grade (AR) having purity 99.9% purchase from Spectrochem. The binary liquid mixtures of various concentrations were prepared in airtight umber colour stoppered bottles[21]. The density and time flow of liquid measured as a function of binary system (18-crown-6 + 1 millimoles alkali metal salts).

Density measurements: The density was determined using pycnometer of bulb capacity 8 $\times 10^{-6}$ m^3 with graduated stem. The pycnometer was calibrated with tripled distilled water, toluene and benzene[22,23].

Viscosity measurement: An ubbelohde viscometer (20 ml) was used for the viscosity measurement and flow time was determined using digital clock having an accuracy of ± 0.1S[24,25].

Results and Discussion

Binary system: 18-crown-6 ether solution + 1 milliloles salts of alkali metal.

Excess molar volume: From Table-1 and 2 of binary mixtures, the values of V^E are negative for RbCl and RbBr and negative values increasing with concentration of 18-crow-6 at 298.15K and 308.15K. This indicates that strong interaction and complexation of Rb^+ with 18-crown-6 for the entire mole fraction. The large negative value of V^E increases with increase the concentration of 18-crown-6 [26-27].

There were negative V^E values of RbBr higher than RbCl. Therefore the interaction of Rb^+ with 18-crown-6 is more in RbBr salt than RbCl solution.
RbBr + 18-crown-6 > RbCl + 18-crown-6
For the 18-crown-6 + CsCl binary system (Table-3, 4), the V^E values are less negative and V^E values increases with decrease the concentration of 18-crown-6 at 298.15 and 308.15K temperatures. These V^E values are higher than the V^E values of system 18-crown-6 + Rb^+. It reveals that there is less interaction in 18-crown-6 + CsCl and 18-crown-6 + CsBr system. Thus order of complexation and interaction of 18-crown-6 with alkali metal ions as $Rb^+ > Cs^+$.

Therefore, RbBr > RbCl > CsBr > CsCl.

With increase the temperature the V^E values increases in all concentration in binary system. The interaction of alkali metal ions with 18-crown-6 decreases but in same order as given above.

Deviation in viscosities (Δη): In a binary system the value Δη were reported in Table-1, 2, 3 and 4. The Δη values in binary system are all positives at temperature 298.15K and 308.15K viscosity deviation is a useful investigation for understanding the strength of complexation and interaction of 18-crown-6 ether with alkali metal ions[28]. A positive viscosity deviation indicates stronger complexation interaction and ordering in between unlike molecules. In this present investigation in binary system Δη values are positive at 298.15K and 308.15K[29-30]. The values decreasing in order as –
RbBr > RbCl > CsBr > CsCl.

Large size of Cs^+ ion than Rb^+ hence Cs^+ loose fit in 18-crown-6 ether and weaker interaction, smaller effect on viscosity deviation excess energy of activation for viscous flow values of binary system shown in the table no 5 to 8. The observed $\Delta G^{E\neq}$ indicate the specific interaction leading to complexation between 18-crown-6 and alkali metal ion.

Thermodynamic activation parameters ($\Delta H^{\#}$, $\Delta S^{\#}$ & $\Delta G^{\#}$) values are reported table no 5 to 8 for binary systems. The observed values of $\Delta H^{\#}$ and $\Delta G^{\#}$ for all the concentrations are positive values increases as RbBr < RbCl < CsBr < CsCl.

Lower the value of $\Delta H^{\#}$ & $\Delta G^{\#}$ formation of bond between metal cation and 18-crown-6. $\Delta S^{\#}$ values are negative for binary systems. It indicates that there is ordering means that interaction between alkali metal ions and 18-crown-6[31].

The graphical presentation Figure-1 and 2 of V^E of binary system varied concentration of 18-crown-6 with aqueous solution of one milli mole of alkali metal salts at 298.15K and 308.15K. The graphical presentation Figure-3 and 4 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 and 308.15K.

Table-9: The calibrated values of densities and viscosities were close agreement with literature values[24].

Chemicals	Temp K	Density		Viscosity	
		Literature	Experimental	Literature	Experimental
Water	298.15	0.9970	0.9970	0.8900	0.8900
	308.15	0.9940	0.9941	0.7191	0.7191
Toluene	298.15	0.8623	0.8619	0.5733	0.5731
	308.15	0.8550	0.8531	0.4662	0.4657
Carbon tetra chloride	298.15	1.5867	1.5861	0.9010	0.8589
	308.15	1.5989	1.5654	0.7928	0.8037

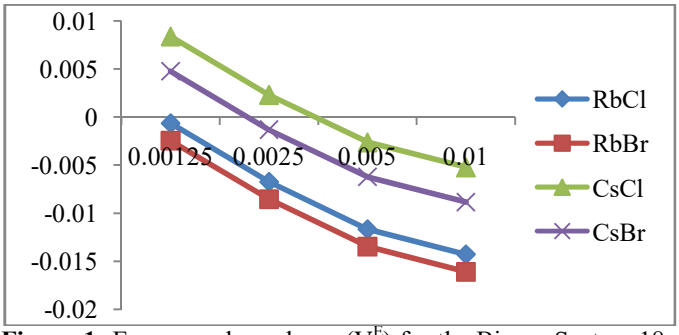

Figure-1: Excess molar volume (V^E) for the Binary System 18-Crown-6 (1) + aqueous solution of one milli mole alkali metal salt (2) at 298.15K.

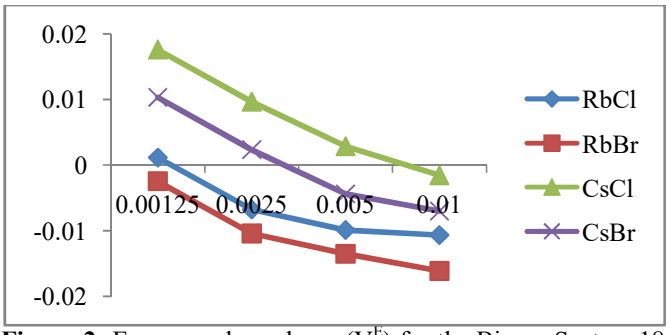

Figure-2: Excess molar volume (V^E) for the Binary System 18-Crown-6 (1) + aqueous solution of one milli mole alkali metal salt (2) at 308.15K.

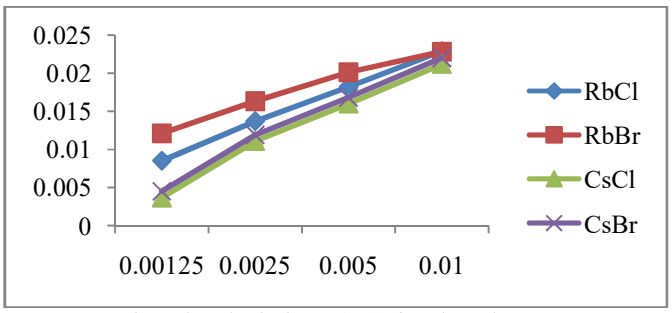

Figure-3: Viscosity deviations (Δη) for the Binary System 18-Crown-6 (1) + aqueous solution of one milli mole alkali metal salt at 298.15K.

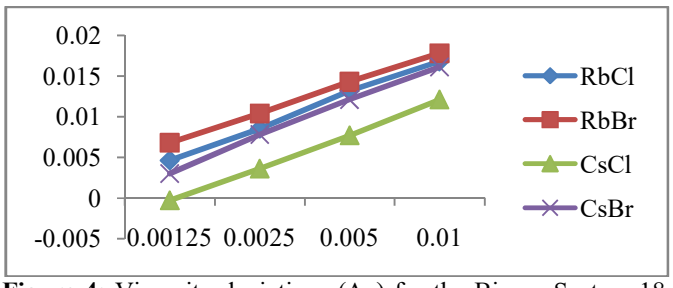

Figure-4: Viscosity deviations (Δη) for the Binary System 18-Crown-6 (1) + aqueous solution of one milli mole alkali metal salt at 308.15K.

Conclusion

Experimental data of density and viscosity of 18-crown-6 with alkali metal salts (binary system) have been measured over the entire composition range at 298.15K & 308.15K. It has been observed that negative deviations were observed for excess molar volume (V^E) and positive deviation were observed for viscosity deviation. It indicates that the existence of complexation and interaction in between 18-crown-6 and alkali metal ions at all concentration. The order of interaction in binary system as - RbBr > RbCl > CsBr > CsCl.

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