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Densities And Viscosities Study Of Intermolecular Interaction In 18-Crown-6 With Alkali Metal Cation's At 298.15K.

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Abstract:-

The present research aim to examination the intermolecular interactions between various concentration of 16-crown-6 with alkali metal ions (Li^+, Na^+, $K+^+$) in their aqueous solutions using the measurements of viscosity and density at 298.15K and 308.15K. Viscosities were measured by using an Ubbelohde viscometer, while densities were determined using Pycnometer. The experimental data used to calculate the Excess volume (V^E), Viscosity deviation ($\Delta\eta$), Apparent molar volume(ϕ_v), to evaluate the strength of interaction and complexation between alkali metal ion with 18-crown-6. The results indicate significant variations in interaction and complexation with concentration of 18-crown-6. The sequence of interaction strength was found in accordance with the size of alkali metal ions and binding strength of 18-crown-6 with K^+ ions showing stronger interaction and complexation effect as compared to Na^+And Li^+ ions. At higher temperature viscosity and densities decreases, reveals weakened interactions due to increased kinetic movement. General conclusion confirms that, 18-crown-6 ether with alkali metal ion complexation play an important role in regulating 18-crown-6 behaviours and provides valuable understanding into alkali metal ion-macrocyclic interactions in aqueous medium.

Key Words:- Density, Viscosity, 18-crown-6, Alkali metal ion, Interaction, Complexation.

Introduction:-

Crown ether is one of the most well-known host molecules. Which shows binding selectivity for alkali metal and alkaline earth metal cations in binary liquid system.

Intermolecular interaction in the binary liquid system understanding has been focus in solution chemistry similar to this study examines physico-chemical properties like solvation of ions, transport behaviours and molecular recollection. 18-crown-6 is famous macrocyclic ligands with which are synthesized by Pedersen in 1967[1] Selective cavities size has been responsible for interaction of alkali metal ion. The study of 18-crown-6 ether interaction with alkali metal ions in a binary system give understanding host-guest chemistry that is, alkali metal ions-18-crown-6, which has application in the ion separation technique, supramolecular chemistry, delivery of drug. The measurement of viscosity and densities are used

to study the interaction and complexation. The thermodynamic stability of complex of 18-crown-6 with alkali metal ion is evaluate at the same time with variations of temperatures [2-5].

The main focus of this research is the investigation the effect of temperature and concentration on the interaction and complexation of 18-crown-6 with alkali metal ions. (Li^+, Na^+, K^+). This data useful to determine solution properties [6].

18-crown-6 ether has ability to complexation with alkali metal ion studies have reported that, potassium ion (K^+) preferred for interaction with 18-crown-6 due to same size of cavities of 18-crown-6 and K^+ ion. However, this selectivity is modify by solvent (water) molecules[7-8].

Viscosity and density studies have been studies to examine the interaction and complexation of 18-crown-6 with alkali metal ions. Excess volume, apparent molar volume, viscosity deviation have been used to understanding ion-crown ether interactions. Many researcher have also marked that Li^+ ion tend to show stronger hydration effects. Where as K^+ ion is the best for complexation with 18-crown-6at constant temperature [9-10].

It is hypothesized that the density and viscosities of binary system of 18-crown-6 with alkali metal ion will vary with variation of temperature and concentrations of 18-crown-6.

To examine these hypothesis, by measurement of viscosities and densities of binary systems of 18-crown-6 with alkali metal ions were carried out at various concentration and temperatures. Using data density and viscosities excess and thermodynamics parameters were calculated. These parameters gives important information on interaction and complexation and of crown ether with alkali metal ions. This research analysis also provide the comparable information about role of cation and solvation energy along with selectivity of crown ether.

This research work indicated the following sequence of interaction strength-

$Li^+ > Na^+ > K^+$ ……. In terms of solvation.

While, $K^+ > Na^+ > Li^+$……. In terms of complexation.

This research not only reveals that the role of alkali metal ion is an important for the modulating the physico-chemical behaviour of aqueous solution of 18-crown-6 ether but also major understanding the metal ion-crown ether complexation which is main role for separation of ions, drug separation and for supramolecular design[11-12].

Experimental:-

Material and method:-

All the chemical used in this research were analytical reagent (AR)grade having 99.9 percent purity purchased from spectrochem and were used without further purification. All the mass measurement were performed on an electric balance having sensitivity ±0.001 mg. The binary liquid mixture of different known concentration were prepared in air tight, umber coloured stopper bottles. The viscosity and density of 18-crown-6 with 1 millimole of alkali metal salt in water were measured at 298.15K and 308.15K. The pycnometer and ubbelohde viscometer were calibrated with triple distilled water, benzene and toluene [13].

Density measurement:-

The density of various concentration solution were determined by using pycnometer (10 ml) capacity with graduated marking scale [14].

Viscosity measurement:-

An ubbelohde viscometer (25 ml) was used for the measurement of viscosity of various composition at different temperature and efflux time was measured using a digital electronic clock having an accuracy ±0.1 S [15].

Theory:-

Using the experimental data the following excess and interaction parameters has been calculated.

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

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.

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

η viscosity of binary liquid mixture.
$\eta_1$and η_2 are the viscosities of salts solutions and 18-crown-6

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

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 ($\Delta\eta$) and apparent molar volume (ϕ_V) values at various concentration ranges and at various temperature are reported in table 1, 2, 3, 4, 5 & 6.

Observation Table:-

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

Temp	m (g cm^{-3})	X_1	ρ(gcm^{-3})	η (mPa s)	V^E (cm mol^{-1})	$\Delta\eta$	ϕ_v
298.15K	0	1	0.9959	0.9015	0	0	18.0741
	0.00125	0.999977	0.9964	0.9033	-0.007908	0.001820	18.0661
	0.0025	0.999954	0.9966	0.9072	-0.010373	0.005740	18.0637
	0.005	0.999909	0.9968	0.9112	-0.011677	0.009781	18.0624
	0.01	0.999819	0.9970	0.9153	-0.010656	0.013962	18.0634
308.15K	0	1	0.9935	0.7377	0	0	18.1177
	0.00125	0.999977	0.9939	0.7668	-0.006115	0.029116	18.1116
	0.0025	0.999954	0.9941	0.7699	-0.008583	0.032233	18.1091
	0.005	0.999909	0.9943	0.7722	-0.009876	0.034566	18.1078
	0.01	0.999819	0.9945	0.7743	-0.008812	0.036733	18.1089

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

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	0.9960	0.8886	0	0	18.0722
	0.00125	0.999977	0.9966	0.8925	-0.009720	0.003920	18.0625
	0.0025	0.999954	0.9968	0.8966	-0.012185	0.008040	18.0601
	0.005	0.999909	0.9970	0.9006	-0.013489	0.012080	18.0587
	0.01	0.999819	0.9972	0.9047	-0.012471	0.016260	18.0598
308.15K	0	1	0.9936	0.7243	0	0	18.1159
	0.00125	0.999977	0.9941	0.7645	-0.007936	0.040216	18.1080
	0.0025	0.999954	0.9943	0.7667	-0.010404	0.042432	18.1055
	0.005	0.999909	0.9945	0.7689	-0.011697	0.044665	18.1042
	0.01	0.999819	0.9947	0.7721	-0.010637	0.047930	18.1053

Table:-3 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.

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	0.9961	0.9003	0	0	18.0704
	0.00125	0.999977	0.9968	0.9074	-0.011530	0.007120	18.0589
	0.0025	0.999954	0.9970	0.9131	-0.013995	0.012840	18.0564
	0.005	0.999909	0.9972	0.9175	-0.015301	0.017281	18.0551
	0.01	0.999819	0.9974	0.9221	-0.014286	0.021962	18.0561
308.15K	0	1	0.9937	0.7308	0	0	18.1141
	0.00125	0.999977	0.9943	0.7782	-0.009756	0.047416	18.1043
	0.0025	0.999954	0.9945	0.7823	-0.012224	0.051532	18.1018
	0.005	0.999909	0.9947	0.7861	-0.013518	0.055365	18.1005
	0.01	0.999819	0.9949	0.7898	-0.012461	0.059131	18.1016

Table:- 4 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.

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	0.9038	0	0	18.0686
	0.00125	0.999977	0.997	0.9131	-0.013340	0.009320	18.0553
	0.0025	0.999954	0.9972	0.9192	-0.015804	0.015440	18.0528
	0.005	0.999909	0.9974	0.9232	-0.017111	0.019481	18.0515
	0.01	0.999819	0.9976	0.9283	-0.016099	0.024663	18.0525
308.15K	0	1	0.9938	0.7173	0	0	18.1122
	0.00125	0.999977	0.9945	0.7802	-0.011575	0.062916	18.1007
	0.0025	0.999954	0.9947	0.7853	-0.014043	0.068032	18.0982
	0.005	0.999909	0.9949	0.7906	-0.015338	0.073364	18.0969
	0.01	0.999819	0.9951	0.7956	-0.014284	0.078429	18.0980

Table:- 5 Densities, Viscosities, Excess Molar Volumes, Deviation in Viscosities and apparent molar volume for the aqueous solution of LiCl (1) + 18-crown-6 ether (2) system.

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	0.9957	0.9165	0	0	18.0777
	0.00125	0.999977	0.9960	0.8913	-0.004281	-0.025179	18.0734
	0.0025	0.999954	0.9962	0.8957	-0.006747	-0.020758	18.0709
	0.005	0.999909	0.9964	0.8998	-0.008049	-0.016617	18.0696
	0.01	0.999819	0.9966	0.9041	-0.007021	-0.012234	18.0707
308.15K	0	1	0.9933	0.7364	0	0	18.1214
	0.00125	0.999977	0.9935	0.7221	-0.002469	-0.014283	18.1189
	0.0025	0.999954	0.9937	0.7269	-0.004938	-0.009466	18.1164
	0.005	0.999909	0.9939	0.7312	-0.006229	-0.005133	18.1151
	0.01	0.999819	0.9941	0.7352	-0.005159	-0.001067	18.1162

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

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	0.9958	0.91	0	0	18.0759
	0.00125	0.999977	0.9962	0.8898	-0.006095	-0.020179	18.0698
	0.0025	0.999954	0.9964	0.8939	-0.008560	-0.016059	18.0673
	0.005	0.999909	0.9966	0.8982	-0.009864	-0.011717	18.0660
	0.01	0.999819	0.9968	0.9024	-0.008839	-0.007435	18.0670
308.15K	0	1	0.9934	0.7413	0	0	18.1195
	0.00125	0.999977	0.9937	0.7599	-0.004292	0.018616	18.1152
	0.0025	0.999954	0.9939	0.7621	-0.006761	0.020833	18.1128
	0.005	0.999909	0.9941	0.7641	-0.008053	0.022866	18.1115
	0.01	0.999819	0.9943	0.7674	-0.006986	0.026233	18.1126

Result and discussion:-

The experimental values of density and viscosity, calculated values of interaction parameters of binary systems are in table number 1 to 6.

Excess molar volume (V^E) value of all the systems gives the strength of interaction between 18-crown-6 + alkali metal ions. In all the V^E values are Negatives, however Negative V^E values decreases with increase the concentration of 18-crown-6. It indicate that interaction and complexation of 18-crown-6 with alkali metal ion increases.

Positive viscosity deviation (Δη) of all the systems, increases with increase the concentration of 18-crown-6 ether. However it decreases with increase the temperature. The positive deviation indicates there is a interaction in between 18-crown-6 and alkali metal ions.[16]

At lower concentration, the value of apparent molar volume higher, suggest that alkali metal ions are well accommodated inside the cavity of 18-crown-6 ether, while at higher concentration ϕ_v value low,

suggest that poor fit of the alkali metal ion inside the crown ether cavity. It implies that ion-solvent interaction dominates over alkali metal ion-crown ether interaction[17-19].

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