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Comparative Study Of Effect Of Surfactant And Temperature On The Thermodynamics And Transport Properties Of Ternary Liquid Mixtures.

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Abstract: -

This research work give a comparative investigate on the effect of temperature variation and surfactant on the thermodynamic and transport properties of binary and ternary system involving 18-crown-6 ether and alkali metal ions. The binary liquid system (18-crown-6 + 1 millimoles alkali metal salt) and ternary liquid system (18-crown-6 + 1 millimoles alkali metal salt + 1 cmc surfactant) were investigated at 298.15K, 308.15K. Thermodynamic parameters such as adiabatic compressibility (Ks), free length (L_f) and acoustic impedance (Z) were calculated to understand the complexation and interaction in between 18-crown-6 and alkali metal ions, while transport properties such as viscosity provided comprehension into 18-crown-6 ether and alkali metal ions mobility and dynamic behavior governing the host guest chemistry in binary and ternary systems and point up the influence of thermal condition and surfactant on supramolecular interaction.

In binary and ternary systems 18-crown-6 crown ether formed strong complexation with alkali metal ions as the following order RbBr > RbCl > CsBr > CsCl

Keywords:-

18-crown-6, surfactant, alkali metal ions, binary system, ternary system, temperature supramolecular interaction, complexation.

1. Introduction:-

The practical importance of binary and ternary liquid mixture rather than single liquid component has achieved much importance during the last 20 years in assessing the complexation interaction between 18-crown-6 and alkali metal ions and studying the physico-chemical behavior of such systems [1-3]

The study of 18-crown-6 ether and their interactions with alkali metal ions has been a main focus in supramolecular chemistry due to their capacity to form highly selective interaction and stable complexation as host-guest nature. In this research 18-crown-6 specific interest as proper its cavity size which is proper to accommodated higher alkali metals cations such as Rb^+ & Cs^+ the interaction between 18-crown-6 and alkali metal ions (Rb^+ & Cs^+) that is complexation depend on thermodynamic factors, salvation energy, environment of metal ions, temperature etc. Thermodynamics and transports properties of such systems are vital role for applications in extraction process, catalysis and delivery of drugs. [4-7]

Surfactants as detergent molecules play a vital role in altering not only the interaction in between 18-crown-6 ether and alkali metal ions but also complexation. In ternary system surfactant can change the polarity, viscosity, conductivity and potential of liquid so influencing 18-crown-6 ether + alkali metal ions interaction and their complexation. The merger of surfactant into host-guest systems inserts co operative effect that can change the thermodynamics and transport properties of system. [8]

The another important factor temperature that direct effect on the interaction of alkali metal cations and 18-crown-6, enthalpy of and entropy of the systems, complex stability, viscosity and ionic mobility [9]. Therefore for better understanding the stability of complexes, conductivity, interaction of alkali metal ion with 18-crown-6 ethers. That is thermodynamic properties controlling the temperature is most important even small variation in temperature it effects thermodynamics and transport properties of binary and ternary liquid mixture system. Therefore for systematic study of binary system (18-crown-6 + alkali metal ion) and ternary system (18-crown-6 + alkali metal ion + Surfactant) at temperature variation gives the dipper knowledge of molecular interaction of mechanism of complexation [10-11].

The main aim of this investigation to find out the combined effect of temperature and surfactant on the thermodynamics and transport properties of binary and ternary systems at 298.15K and 308.15K. It is carried out by studying the viscosity, adiabatic compressibility (Ks), free length (L_f), acoustic impedance (Z), Relative association (R_A), apparent molar volume (ϕ_V) etc. can established the modified role of surfactant and temperature in modulating interactions in between 18-crown-6 ether and alkali metal ions.

In this research paper we have made an attempt to investigate the interaction and complexation in between 18-crown-6 and alkali metal ions in presence and absence of surfactant and also studied of variation of temperature on the interaction at 298.15K and 308.15K.

Binary system - various concentrations of 18-crown-6 + 1 milliloles aqueous alkali metal salt (RbCl/ RbBr/ CsCl/ CsBr) solution.

Ternary system- various concentrations of 18-crown-6 + 1 milliloles aqueous alkali metal salt (RbCl/ RbBr/ CsCl/ CsBr) solution + 1 cmc surfactant (1-Decyl trimethyl ammonium bromide).

Experimental details:-

The chemicals used in this research work were analytical reagent (AR) grades with minimum assay of 99.9% purity were obtained from Spectrochem. The various concentrations of the binary and ternary liquid mixtures were prepared in terms of mole fraction. The mole fractions of 18-crown-6 were varied from 0.0 to 0.01 with 1 milliloles of aqueous alkali metal salt (RbCl / RbBr / CsCl / CsBr) solution. In the ternary system, the mole fractions of 18-crown-6 were varied from 0.0 to 0.01 with 1 millimole of aqueous alkali metal salts (RbCl/ RbBr/ CsCl / CsBr) solution and also 1 cmc surfactant. [12].

i) Ultrasonic velocity measurement:-

The ultrasonic velocity in binary and ternary liquid mixtures of all concentration has been measured using 2 MHz frequency ultrasonic interferometer with a high degree of accuracy. The measuring cell of interferometer is a specially designed double walled vessel with arrangement for constant temperature. A digital constant temperature bath with accuracy of ± 0.1K has been used to circulate water through the outer jacket of the double walled measuring cell containing measuring cell containing the experimental liquid [13].

ii) Density measurement:-

The density was determined using pycnometer of bulb capacity 8×10^{-6} m^3 with graduated stem. The pycnometer was calibrated with tripled distilled water, toluene and benzene. [14].

Viscosity measurement:-

An ubbelohde viscometer (20 ml) used for the viscosity measurement and flow time determined using digital clock having an accuracy of ± 0.1S.

The calibrated values of densities and viscosities were close agreement with literature values [15].

Calibration Table:-1

Chemicals	Temp	Density (ρ)		Ultrasonic velocity (U)	
		Literature	Calculated	Literature	Calculated
Water	298.15K	0.9970	0.9970	1497	1488
	308.15K	0.9940	0.9941	1522	1513.6
Carbon tetrachloride	298.15K	1.5867	1.5861	930	928
	308.15K	1.5989	1.5654	902	899.2
Toluene	298.15K	0.8623	0.8619	1308	1296.8
	308.15K	0.8550	0.8531	1288	1284

The experiments were repeated for consistency and the average value was considered.

Theory:-

The following thermodynamic parameters were calculated from Jacobson's relation. [16-18]

Adiabatic compressibility $K_s = \frac{1}{U^2 d_1}$ ---- (1)

Intermolecular free length (L_f) $= k\sqrt{Ks}$ ---- (3)

Ultrasonic velocity $U = \lambda f$ ----- (4)

Specific acoustic impedance $Z = U\,d_1$ ----- (5)

Where, λ is wavelength, f is frequency (2MH_Z), d_1 and d_0 measured densities of solution and pure solvent. U and U_0 are the experimental ultrasonic velocities of the solution and pure solvent respectively, Ks is the adiabatic compressibility of solution.

Result and discussion:-

The calculated physical and acoustic parameters of binary system are listed in table 2, 3, 4 & 5 and ternary systems are listed in table 6, 7, 8 & 9.

Table:- 2 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of RbCl binary system.

Temp	Conc	X_1	U (m/s)	ρ (Kg/m^3)	Ks $\times 10^{-7}$ (N/m^2)	Z	$L_f \times 10^{-10}$
298.15 K	0	1	1387.2	0.9971	5.2117	1383.17	6.71
	0.00125	0.9999774	1295	0.9972	5.9796	1291.37	7.19
	0.0025	0.9999549	1307	0.9975	5.8686	1303.73	7.12
	0.005	0.9999098	1326	0.9979	5.6993	1323.21	7.02
	0.01	0.9998195	1345	0.9983	5.5372	1342.71	6.92
308.15 K	0	1	1440.8	0.9940	4.8462	1432.15	6.47
	0.00125	0.9999774	1335	0.9942	5.6437	1327.25	6.99
	0.0025	0.9999549	1348.4	0.9946	5.5299	1341.11	6.92
	0.005	0.9999098	1368.8	0.9949	5.3646	1361.81	6.81
	0.01	0.9998195	1388.4	0.9952	5.2127	1381.73	6.71

Table:- 3 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of RbBr binary system**.**

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks ×10^{-7} (N/m^2)**	**Z**	**L_f ×10^{-10}**
298.15 K	0	1	1386.4	0.9963	5.2219	1381.27	6.72
	0.00125	0.9999774	1400.8	0.9973	5.1100	1397.01	6.65
	0.0025	0.9999549	1419.2	0.9976	4.9768	1415.79	6.56
	0.005	0.9999098	1438	0.9980	4.8456	1435.12	6.47
	0.01	0.9998195	1450	0.9984	4.7638	1447.68	6.42
308.15 K	0	1	1459.2	0.9933	4.7281	1449.42	6.39
	0.00125	0.9999774	1447.2	0.9943	4.8020	1438.95	6.44
	0.0025	0.9999549	1467.4	0.9948	4.6684	1459.76	6.35
	0.005	0.9999098	1487.6	0.9951	4.5411	1480.31	6.27
	0.01	0.9998195	1507.6	0.9955	4.4196	1500.81	6.18

Table:- 4 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of CsCl binary system

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks ×10^{-7} (N/m^2)**	**Z**	**L_f ×10^{-10}**
298.15 K	0	1	1432.8	0.9975	4.8833	1429.21	6.50
	0.00125	0.9999774	1248	0.9966	6.4424	1243.75	7.46
	0.0025	0.9999549	1254	0.9970	6.3784	1250.23	7.43
	0.005	0.9999098	1260	0.9974	6.3152	1256.72	7.39
	0.01	0.9998195	1266	0.9978	6.2530	1263.21	7.35
308.15 K	0	1	1465.6	0.9944	4.6817	1457.39	6.36
	0.00125	0.9999774	1295	0.9932	6.0038	1286.19	7.21
	0.0025	0.9999549	1300	0.9937	5.9547	1291.81	7.18
	0.005	0.999909	1305	0.9942	5.9061	1297.4	7.15

		8				3	
	0.01	0.999819 5	1310	0.9947	5.8582	1303.0 5	7.12

Table:- 5 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of CsBr binary system

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks ×10^{-7} (N/m^2)**	**Z**	**L_f ×10^{-10}**
298.15 K	0	1	1614. 4	0.9974	3.8469	1610.2 0	5.77
	0.0012 5	0.999977 4	1280. 2	0.9968	6.1212	1276.1 0	7.28
	0.0025	0.999954 9	1286. 4	0.9972	6.0599	1282.7 9	7.24
	0.005	0.999909 8	1292. 2	0.9976	6.0032	1289.0 9	7.21
	0.01	0.999819 5	1298. 4	0.9980	5.9436	1295.8 0	7.17
308.15 K	0	1	1813. 6	0.9945	3.0571	1803.6 3	5.14
	0.0012 5	0.999977 4	1322. 2	0.9936	5.7569	1313.7 4	7.06
	0.0025	0.999954 9	1328. 2	0.9941	5.7022	1320.3 6	7.02
	0.005	0.999909 8	1334. 4	0.9946	5.6465	1327.1 9	6.99
	0.01	0.999819 5	1340. 4	0.9950	5.5938	1333.6 9	6.96

Table:- 6 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of RbCl + 1-Decyl trimethyl ammonium bromide (D-TAB) surfactant ternary system

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks ×10^{-7} (N/m^2)**	**Z**	**L_f ×10^{-10}**
298.15 K	0	1	1387. 2	0.9971	5.2117	1383.1 7	6.71 E
	0.0012 5	0.999732 2	1300	0.9969	5.9355	1295.9 7	7.16
	0.0025	0.999709 7	1319. 2	0.9973	5.7617	1315.6 3	7.06
	0.005	0.999664 4	1338. 4	0.9977	5.5953	1335.3 2	6.96
	0.01	0.999573 8	1357	0.9981	5.4408	1354.4 2	6.86
308.15 K	0	1	1440. 8	0.9940	4.8462	1432.1 5	6.47

	0.00125	0.9997322	1325	0.9941	5.7297	1317.18	7.04
	0.0025	0.9997097	1344.8	0.9944	5.5606	1337.26	6.93
	0.005	0.9996644	1369.8	0.9947	5.3578	1362.54	6.81
	0.01	0.9995738	1394	0.9950	5.1719	1387.03	6.69

Table:- 7 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of RbBr + 1-Decyl trimethyl ammonium bromide (D-TAB) surfactant ternary system

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks $\times10^{-7}$ (N/m^2)**	**Z**	**L_f $\times10^{-10}$**
298.15 K	0	1	1386.4	0.9963	5.2219	1381.27	6.72
	0.00125	0.9997322	1419.6	0.997	4.9770	1415.34	6.56
	0.0025	0.9997097	1438.6	0.9974	4.8445	1434.85	6.47
	0.005	0.9996644	1457.4	0.9978	4.7184	1454.19	6.39
	0.01	0.9995738	1476.8	0.9982	4.5934	1474.14	6.30
308.15 K	0	1	1459.2	0.9933	4.7281	1449.42	6.39
	0.00125	0.9997322	1444.4	0.9942	4.8211	1436.02	6.46
	0.0025	0.9997097	1463.6	0.9945	4.6940	1455.55	6.37
	0.005	0.9996644	1482.4	0.9948	4.5743	1474.69	6.29
	0.01	0.9995738	1501.4	0.9951	4.4580	1494.04	6.21

Table:- 6 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of CsCl + 1-Decyl trimethyl ammonium bromide (D-TAB) surfactant ternary system

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks ×10^{-7} (N/m^2)**	**Z**	**L_f ×10^{-10}**
298.15 K	0	1	1432.8	0.9975	4.8833	1429.21	6.50
	0.00125	0.9997322	1262	0.9965	6.3009	1257.58	7.38
	0.0025	0.9997097	1268	0.9969	6.2389	1264.06	7.35
	0.005	0.9996644	1274	0.9973	6.1778	1270.56	7.31
	0.01	0.9995738	1280	0.9977	6.1175	1277.05	7.27
308.15 K	0	1	1465.4	0.9944	4.6830	1457.19	6.36
	0.00125	0.9997322	1296	0.993	5.9957	1286.92	7.20
	0.0025	0.9997097	1301	0.9935	5.9467	1292.54	7.17
	0.005	0.9996644	1306	0.994	5.8983	1298.16	7.14
	0.01	0.9995738	1311	0.9945	5.8504	1303.78	7.11

Table:- 7 Experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility(Ks), intermolecular free length (L_f), acoustic impedance(Z) for various concentration of 18-crown-6 in 1 millimole aqueous solution of CsBr + 1-Decyl trimethyl ammonium bromide (D-TAB) surfactant ternary system

Temp	**Conc**	**X_1**	**U (m/s)**	**ρ (Kg/m^3)**	**Ks ×10^{-7} (N/m^2)**	**Z**	**L_f ×10^{-10}**
298.15 K	0	1	1614.4	0.9974	3.8468	1610.20	5.77
	0.00125	0.9997322	1290.2	0.9967	6.0272	1285.94	7.22
	0.0025	0.9997097	1296.4	0.9971	5.9673	1292.64	7.18
	0.005	0.9996644	1302.4	0.9975	5.9101	1299.14	7.15
	0.01	0.9995738	1308.4	0.9979	5.8537	1305.65	7.12
308.15 K	0	1	1813.6	0.9945	3.0571	1803.62	5.14
	0.00125	0.9997322	1320.4	0.9935	5.7732	1311.81	7.07
	0.0025	0.9997097	1324.2	0.994	5.7372	1316.25	7.04
	0.005	0.999664	1328.	0.9945	5.6999	1320.8	7.02

		4	2			9	
	0.01	0.999573 8	1332. 3	0.9949	5.6622	1325.5 4	7.00

1) Density:-

In this investigation, densities of binary mixture were higher than ternary mixtures at all concentration of 18-crown-6, indicating stronger interaction in the absence of surfactant. Data also show that, density decreases with increase in temperature, reflecting weaker complexation RbCl salt showed higher density than CsCl thus Rb^{+} formed more stable complex and strong interaction with 18-crown-6 than Cs^{+} ion. [19].

Thus order of complexation and interaction of 18-crown-6 with alkali metal ions as

RbBr > RbCl > CsBr > CsCl

2) Ultrasonic velocity:-

Ultrasonic velocity of binary system decreases with increase the concentration of 18-crown-6 this reveals that due to structural modification in the solution there is complexation and interaction in between alkali metal ion and 18-crown-6. At higher temperature enhanced the molecular movement and weakening the interaction and complexation. In ternary system, due to effect of the surfactant ultrasonic velocity increases. [20].

3) Adiabatic Compressibility (Ks):-

In the present investigation, the compressibility decreases with increase in concentration of 18-crown-6 that mean increase the interaction and complexation in the system.

4) Free length (L_f):- intermolecular free length decreases with increase the concentration of 18-crown-6.In binary and ternary systems. This indicated stronger interaction in between alkali metal cations and 18-crown-6. In binary and ternary system the L_f values for RbBr lowers than other salts.

5) Acoustic impedance: - (z)

Acoustic impedance (z) to be almost reciprocal of adiabatic compressibility (βad) in this present work in binary and ternary systems acoustic impedance increases with increases the concentration of 18-crown-6, it indicating stronger interaction and complexation in alkali metal ions and 18-crown-6 [21,22].

Conclusion:-

This research reports experimental data for density and ultrasonic velocity for the binary system and ternary system. Over the entire range of mole fraction at 298.15K and 308.15K from these experimental data the related parameters were calculated. The existence of complexation and interaction in between 18-crown-6 and alkali metal ions more favored at lower temperature and in the absence of surfactants; It confirmed from the experimental and calculated data of ρ, U, L_f, Z, and Ks. The existence of strong complexation and interaction in the both systems as

RbBr > RbCl > CsBr > CsCl

The graphical presentation of adiabatic compressibility (Ks), intermolecular free length (L_f) of binary system and ternary systems at 298.25K and 308.15K

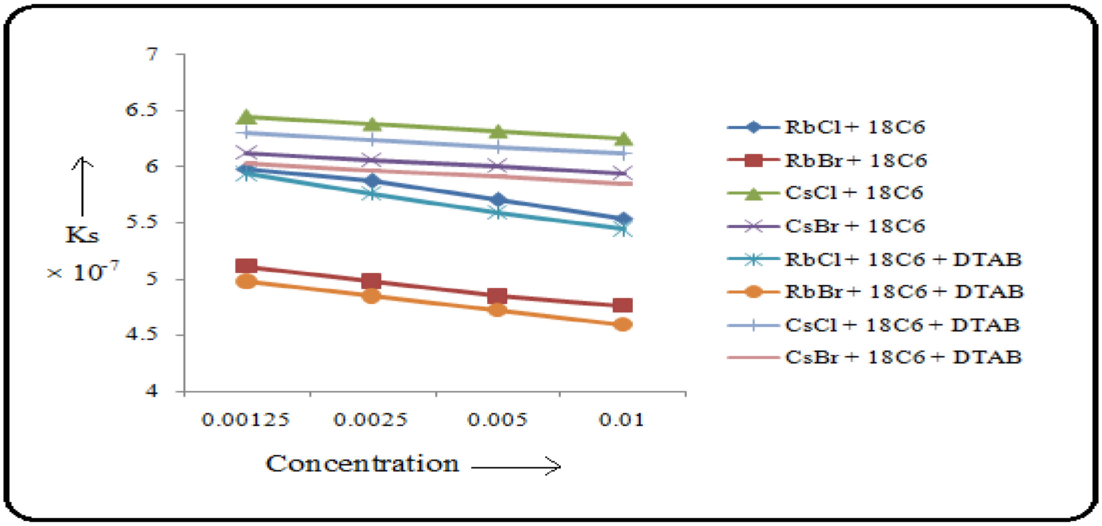

Fig:-1 Adiabatic compressibility (Ks) for the Binary and Ternary System at 298.15K

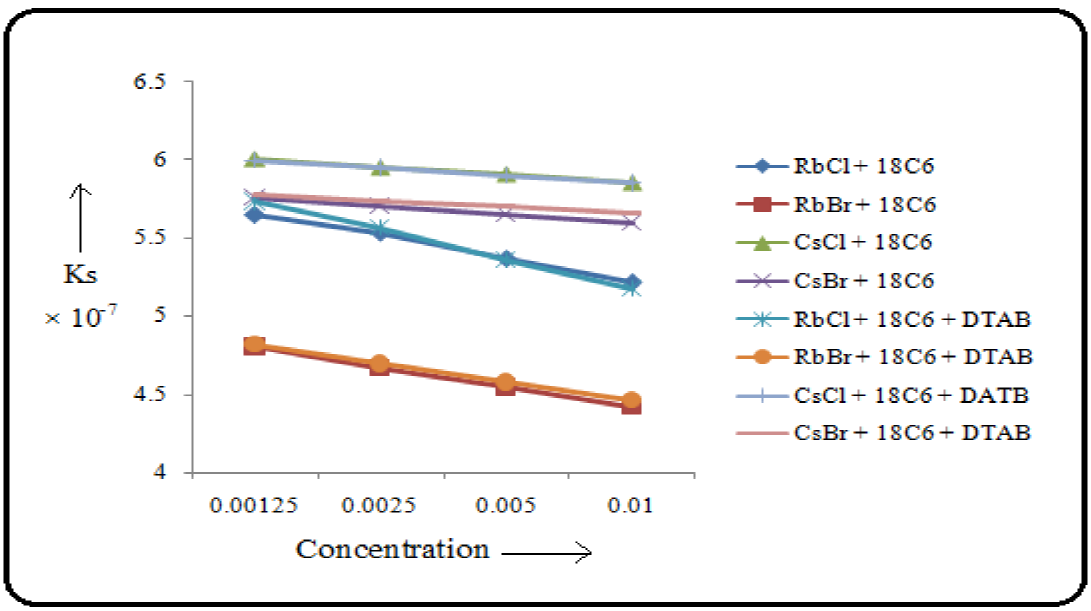

Fig:-2 Adiabatic compressibility (Ks) for the Binary and Ternary System at 308.15K

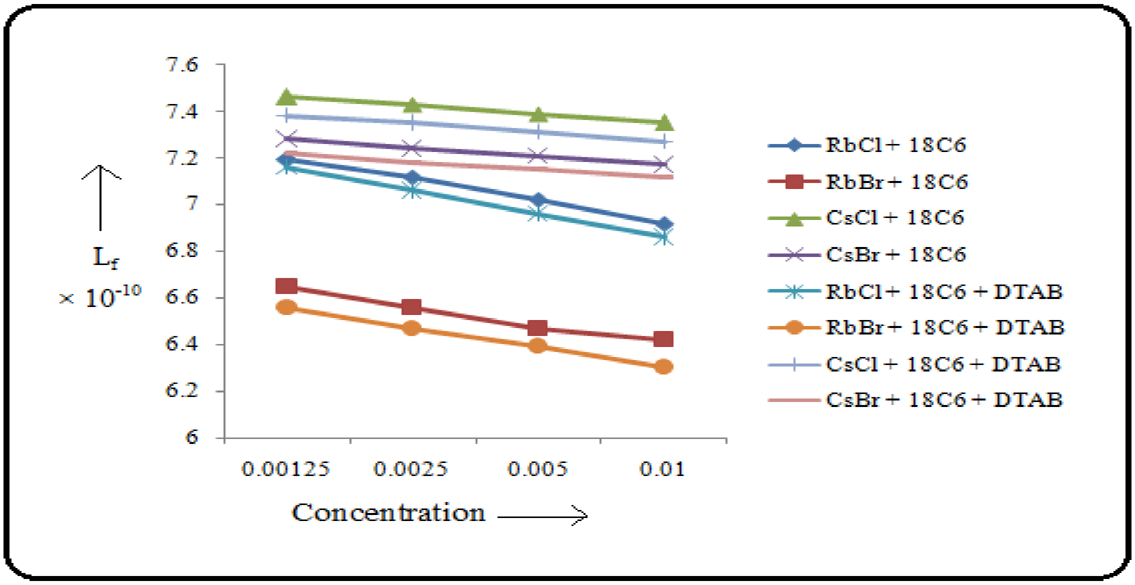

Fig:-3 Intermolecular free length (L_f) for the Binary and Ternary System at 298.15K

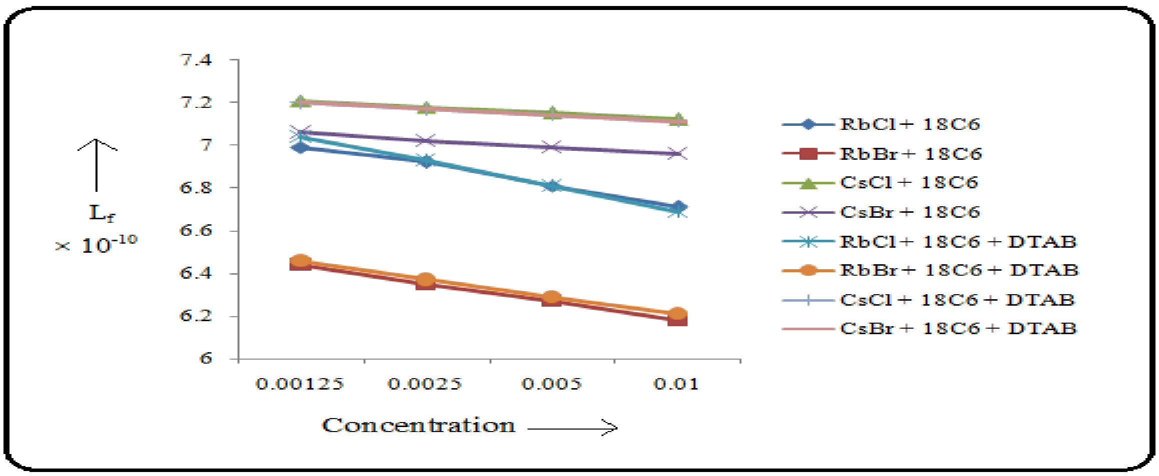

Fig:-4 Intermolecular free length (L_f) for the Binary and Ternary System at 308.15K

Conclusion:-

Experimental data of density and ultrasonic velocity of binary and ternary system have been measured over the entire composition range at 298.15K & 308.15K. It has been observed that ultrasonic velocity increases, adiabatic compressibility decreases, acoustic impendence increases, intermolecular free length also decreases with increase the concentration of 18-Crown-6 in both binary and ternary systems. This strength of U, Ks, Z and L_f indicate that the existence of complexation and interaction in between 18-crown-6 and alkali metal ions (Rb^+ and Cs^+) at all concentration. The interaction in between alkali metal ions and 18-crown-6 increases linearly with increase the concentration of 18-crown-6. Due to effect of surfactant in ternary system density (ρ), ultrasonic velocity (U), acoustic impendence (Z) and intermolecular free length (L_f) values are smaller in ternary mixture as compared to binary mixture at 298.15K and 308.15K. This indicates that less complexation in ternary systems. The order of interaction in binary system as - RbBr > RbCl > CsBr > CsCl.

It is the same order of interaction in ternary system However; it is lower due to effect of surfactant.

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