DOI: http://dx.doi.org/10.32571/ijct.726469 **E-ISSN: 2602-277X**

International Journal of Chemistry and Technology

http://dergipark.org.tr/ijct

Research Article

Partial molar volumes and thermodynamic properties of alkali metal halides in 10% (w/w) 2-(Ethoxy) ethanol water mixture

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Received: 24 April 2020; Final revised: 28 July 2020; Accepted: 30 July 2020

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Citation: Murthy, T. S. *Int. J. Chem. Technol.* **2020**, 4 (2), 109-120.

ABSTRACT

Apparent molar volumes of alkali metal halides in 10% (W/W) 2-(Ethoxy) ethanol-water mixture were calculated from the measured densities at 303.15K, 308.15K and 313.15K. Using Masson equation the partial molar volumes were obtained which are further divided into ionic components adopting the methods of Conway and Jolicoeur. A comparison of values of ionic partial molar volumes of alkali metal and halide ions with the values reported in pure water indicates a decrease in hydrophobic hydration, which may be due to the addition of co-solvent 2-(Ethoxy) ethanol. The conclusions drawn from viscosity studies confirm that the structure of water is reduced by the breaking of hydrogen bonds in 2-(Ethoxy) ethanol-water mixture. For all the ions, the $\bar{V}^{0}_{ion}$ values are divided into $\bar{V}^{0}_{stru}$ and $\bar{V}^{0}_{cage}$. Using the Padova's equation, the $\bar{V}^{0}_{intr}$ values of alkali metal salts were calculated and further divided into ionic contributions. Calculated dimensions of ions show that the classification of alkali metal halide salts into structure makers and structurebreakers based on the sign of $\bar{V}^{0}_{ion} - \bar{V}^{0}_{cryst}$ is not valid for the present solvent system.

Keywords: Molar volumes of electrolytes, alkali metal salts, 2-(Ethoxy) ethanol, liquid mixtures, solute-solvent interactions.

10% (w/w) 2-(Etoksi) etanol-su karışımında alkali metal tuzların kısmi molar hacimleri ve termodinamik özellikleri

ÖZ

10% (w/w) 2-(Etoksi) etanol-su karışımlarında alkali metal tuzların gözlenen molar hacimleri 303.15 K, 308.15 K and 313.15 K' de ölçülen yoğunluklardan hesplandı. Masson denklemini kullanarak, Conway ve Jolicoeur yöntemlerini benimseyen iyonik bileşenlere ayrılan kısmi molar hacimler elde edildi. Alkali metal ve halojenür iyonların İyonik kısmi molar hacimlerinin saf suda bildirilen değerlerle karşılaştırılması, hidrofobik hidrasyonda bir düşüşe işaret işaret etmektedir ki bu yardımcı çözücü 2- (Etoksi) etanolün eklenmesinden kaynaklanabilir. Viskozite çalışmalarından elde edilen sonuçlar, 2- (Etoksi) etanol-su karışımında hidrojen bağlarının kırılmasıyla suyun yapısının azaldığını doğrulamaktadır. Tüm iyonlar için, $\bar{V}^{0}_{ion}$ değerleri $\bar{V}^{0}_{stru}$ and $\bar{V}^{0}_{cage}$' e ayrılır. Padova denklemini kullanarak, alkali metal tuzlarının $\bar{V}^{0}_{intr}$ değerleri hesaplandı ve ayrıca iyonik katkılara bölündü. iyonların hesaplanan boyutları, alkali metal halojenür tuzlarının $\bar{V}^{0}_{ion} - \bar{V}^{0}_{cryst}$ işaretine göre yapı oluşturuculara ve yapı kırıcılara sınıflandırılmasının mevcut çözücü sistemi için geçerli olmadığını göstermektedir.

Anahtar Kelimeler: Elektrolitlerin kısmi molar hacimleri, alkali metal tuzlar, 2-(Etoksi) etanol, liquid mixtures, çözücü-çözünen etkileşimleri.

1. INTRODUCTION

Water-organic mixed solvents have been the subject of intense research conducted by many researchers all over the world. Knowledge of their structures and properties is very important on account of their application in various areas of chemistry and modern technologies.[1] Ion-ion and ion-solvent interactions are notable among the interactions that occur in solutions since these are connected with the physical and chemical properties of

DOI: http://dx.doi.org/10.32571/ijct.726469 **E-ISSN: 2602-277X**

the mixtures. Studies on thermo-chemical properties and transport properties such as viscosity, refractive index, ultrasonic velocity, adiabatic compressibility, density and conductivity of ionic solutions help to characterize the structures and properties of the solutions.[2-5]

n-(Alkoxy) ethanols also known as cello solves are good industrial solvents which are used as a component of solvents and co-emulgators and stabilizers of emulsion paints, lacquers and plastics. Cello solves are used as additives to gasoline due to their Octane enhancing and pollution-reducing properties.[6] n-Alkoxy alkanols are in fact monoalkyl ether of ethylene glycol. Therefore, its physicochemical properties are probably between dipolar aprotic and protic solvents. Previous studies have shown that they exist as molecular dispersion in water at low concentration of 2-alkoxy ethanol (at high concentration micelle–like aggregation occurs). It would be interesting to study the electrolyte behavior in such an uncharacteristic solvent medium. The study of thermal and transport properties of electrolytes in solutions would help indicate the use of cellosolves in various technologies like high energy batteries and ion exchangers.[7] Despite the potential applications of these solvents, there are relatively few solute-solvent interaction studies on substances in this class and their water mixtures. 2-(Butoxy)-ethanol and 2-(Methoxy)-ethanol are the solvents studied to some extent.[8-14]

Thermo chemical properties of electrolyte solutions in 2-alkoxyethanol–water mixtures have been reported with an emphasis on solution enthalpies. However no specific work has been reported so far on transport and quasi thermodynamic properties of electrolytes in 2-(Ethoxy)-ethanol water mixtures where some modifications are expected in the structure of water. The objective in selecting a 10% (W/W) 2-(Ethoxy) ethanol-water mixture in the present investigation is that the water-rich liquid mixtures are more economical and facilitates the desired properties required for the industry.

The purpose of the present study is to study the density, molar volumes and thermodynamic parameters of alkali metal halide salts in a 10% (W/W) 2-(Ethoxy) ethanol-water mixture. For this, it is aimed to do the following:

(i) To probe into the effect of temperature on the solvation process.

(ii) To study the effect of increasing both cation and anion size.

(iii) To compare the partial molar volumes of alkali metal salts with partial molar volumes and thermodynamic parameters of our previous work related to tetra alkyl ammonium bromides in the same 10% (W/W) 2-(Ethoxy) ethanol-water mixed solvent medium.[9]

2. EXPERIMENTAL

Sodium chloride, potassium chloride and potassium iodide (Sarabhai Chemicals G. R. grade), rubidium chloride (E.Merk analar grade) and potassium bromide (LOBA Chemie G. R. grade) were dried at 110°C in a hot air oven and stored in a desiccator. Electrolyte solutions of desired concentrations were prepared each time by mass with a precision of ± 0.0001 g.

2-(Ethoxy)-ethanol (E.Merk sample) was first refluxed for an hour with Tin II chloride to remove the traces of peroxide as per the procedure discussed in my earlier communication.[12] The refluxed solvent was then dried over anhydrous potassium carbonate and then fractionally distilled. The middle fraction distilling between 133-134°C was collected. 10% 2-(Ethoxy) ethanol-water mixture was prepared weight by weight. A bicapillary pycnometer of parker and parker type with minor modifications was used to determine densities. The uncertainty of the density measurements (95% confidence limits) was $\pm (8 \times 10^{-5})$ g cm^{-3}. The density value we measured at 298.15 K for pure 2-Ethoxy ethanol is 0.92407 g cm^{-3} which is in reasonable agreement with literature value: 0.9253 g cm^{-3}.[15]

3. RESULTS AND DISCUSSION

The experimentally measured densities of alkali metal halide salt solutions of 10% (w/w) 2-(ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K (temperature control was monitored to ± 0.001 K) were used to calculate the apparent molar volumes by using the equation where all the terms have their usual significance.[16] The densities along with the apparent molar volumes of the alkali metal halides are presented in Table 1.

$$\phi_V = \frac{M}{d_0} + \frac{1000(d_0 - d)}{d_0} \qquad (1)$$

The Debye–Huckel theory serves as a basis for the extrapolation of ϕ_V to infinite dilution. The recommended procedure for the extrapolation of ϕ_V to infinite dilution employs the Redlich–Meyer equation.[7]

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Table 1. Density (*d*) and apparent molar volume (ϕ_V) of alkali metal halides in 10% (w/w) 2-(Ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K

303.15 K			**308.15 K**			**313.15 K**		
$c\times10^3$	d	ϕ_v	$c\times10^3$	d	ϕ_v	$c\times10^3$	d	ϕ_v
				NaCl				
22.01	0.99636	13.0768	22.01	0.99436	12.6459	22.01	0.99215	15.4235
30.31	0.99672	13.6437	38.39	0.99504	14.5247	38.39	0.99284	15.8702
41.39	0.99720	14.0600	41.39	0.99518	14.3318	54.35	0.99348	16.6462
53.89	0.99774	14.3526	54.35	0.99568	15.6840	63.79	0.99386	16.8995
61.66	0.99805	14.8928	63.79	0.99606	16.0738	70.89	0.99414	17.1280
70.89	0.99840	15.6393	70.89	0.99630	16.9490	83.92	0.99462	17.3540
78.71	0.99871	15.9628	83.92	0.99684	16.9757	94.73	0.99510	17.4338
94.70	0.9993	16.9235	94.73	0.99728	17.0772	104.91	0.9955	17.6175
104.90	0.9997	17.1669	104.91	0.99766	17.4835	112.03	0.99580	17.5440
112.03	1.00004	16.7532	112.03	0.99804	16.6973			
				KCl				
28.30	0.99678	24.4969	28.30	0.99474	25.6137	28.30	0.99258	26.0257
41.20	0.99740	25.1662	41.20	0.99534	26.4348	41.20	0.99318	26.7370
52.00	0.99786	26.6055	52.00	0.99584	26.8539	52.00	0.99366	27.4942
61.70	0.99835	26.2214	61.70	0.99630	26.9270	61.70	0.99410	27.8030
71.20	0.99880	26.3678	71.2	0.99674	27.1280	71.20	0.99450	28.4621
82.20	0.99930	26.7523	82.2	0.99703	27.5412	82.20	0.99540	28.5828
91.04	0.9997	27.0139	91.04	0.99760	27.8427	91.04	0.99500	28.6788
100.09	1.00011	27.2291	100.09	0.99805	27.7870	100.09	0.99584	28.4521
110.50	1.00061	27.2179	110.60	0.99852	28.0012	110.6	0.99630	28.7004
119.6	1.00102	27.3626	119.60	0.99892	28.1754	119.60	0.99670	28.8270
				RbCl				
21.11	0.99732	28.224	21.11	0.99532	27.804	21.11	0.99310	31.167
29.59	0.99808	29.152	29.59	0.99608	28.871	29.59	0.99384	32.002
40.60	0.99902	30.936	40.60	0.99709	29.015	40.60	0.99482	32.059
50.98	0.99993	31.443	50.98	0.99796	30.717	50.98	0.99574	32.158
61.10	1.00082	31.725	61.10	0.99883	31.460	51.10	0.99663	32.354
70.50	1.00165	31.858	70.50	0.99964	31.932	70.50	0.99745	32.574
80.02	1.00248	32.111	80.02	1.00048	32.050	80.02	0.99828	32.750
90.80	1.00342	32.323	90.80	1.00143	32.167	90.80	0.99919	33.237
108.90	1.00500	32.569	108.90	1.00303	32.266	108.90	1.00077	33.355
120.40	1.00601	32.636	120.40	1.00404	32.368	120.40	1.00176	33.527
				KBr				
30.50	0.99786	36.557	30.50	0.99587	36.631	30.50	0.99366	37.373
39.86	0.99864	35.381	39.86	0.99664	36.705	39.86	0.99443	37.302
49.15	0.99949	35.750	49.75	0.99749	36.034	49.75	0.99522	37.735
61.40	1.00046	35.789	61.40	0.99845	36.189	61.40	0.99618	37.519
70.48	1.00126	35.178	70.48	1.00012	35.249	70.48	0.99699	36.615
80.80	1.00211	35.388	80.80	1.00100	35.459	80.80	0.99783	36.785
90.50	1.00301	34.419	90.50	1.00179	35.488	90.50	0.99870	36.013
100.87	1.00385	34.806	100.87	1.00256	35.515	100.87	0.99956	36.053
109.90	1.00453	35.097				109.90	1.000296	36.200
				KI				
20.90	0.9975	50.936	20.90	0.99578	48.631	20.90	0.99359	49.221
31.82	0.99903	50.279	31.82	0.99106	48.800	31.82	0.99490	48.273
40.08	1.00000	49.975	40.08	0.99807	47.816	40.08	0.99588	48.973
51.16	1.00136	48.566	51.76	0.99939	47.681	51.16	0.99720	47.983
60.30	1.00246	48.158	60.30	1.00047	47.755	60.30	0.99830	47.693
72.56	1.00395	47.571	72.56	1.00195	47.390	72.56	0.99978	47.355
80.57	1.00494	47.078	80.57	1.00288	47.674	80.57	1.00077	46.902
89.85	1.00607	46.807	89.85	1.00404	47.014	89.85	1.00190	46.668
102.27	1.00749	47.427	102.27	1.00559	46.343	102.27	1.00337	46.839
120.24	1.00967	47.051	120.24	1.00768	46.895	120.24	1.00552	46.831

Units: Molarity as $c\times10^3$ = (mol dm^{-3}); d = kg m^{-3}; ϕ_v = (cm^3 mol^{-1})

Table 2. Apparent molar volume at infinite dilution (ϕ_V) and the experimental slope (S_V^*) of electrolytes in 10% (w/w) 2-(OEt) EtOH-H_2O 303.15 K, 308.15 K and 313.15

Salt	**303.15 K**		**308.15 K**		**313.15 K**	
	ϕ_V^0 (cm^3 mol^{-1})	S_V^* (cm^3 mol$^{-3/2}$)	ϕ_V^0 (cm^3 mol^{-1})	S_V^* (cm^3 mol$^{-3/2}$)	ϕ_V^0 (cm^3 mol^{-1})	S_V^* (cm^3 mol$^{-3/2}$)
NaCl	9.55	22.67	9.71	24.01	13.59	12.79
KCl	22.33	15.23	23.56	13.60	23.79	15.50
RbCl	26.08	20.70	24.85	23.87	29.84	10.65
KBr	37.76	-9.184	38.167	-8.87	39.569	-10.459
KI	53.92	-22.03	50.28	-10.65	50.70	-12.37

$$\phi_V = \phi_V^0 + S_V C^{1/2} + q_V C \qquad (2)$$

Where S_V is the theoretical limiting slope and q_V is a constant. However the calculation of a numerical value for S_V requires knowledge of pressure dependence of dielectric constant, which is not available for the present solvent system under investigation. For this reason, the Masson empirical equation of the form given below has been used for extrapolating the ϕ_V to an infinite dilution where S_V^* is an experimental slope.

$$\phi_V = \phi_V^0 + S^*{}_V C^{1/2} \qquad (3)$$

According to Masson's equation, the apparent molar volumes should vary linearly with square root of concentration of the salt and the data shall fit into Masson's relation.[18] The linear relation has been known to be followed by many small strong electrolytes in dilute solutions and to moderate concentrations for some other salts as well.[19] Values of ϕ_V & S_V^* obtained by the method of least squares are presented in Table 2. In all cases studied, ϕ_V vary linearly with $\sqrt{c}$ at all temperatures as shown in Figures 1-3. S_V^* values indicate the data available in different solvents including water, leads one to conclude that, in general, negative slope is favored; (i) if the dielectric constant of the medium is high, whether the solvent is hydrogen-bonded or non-hydrogen bonded. (ii) if electrostatic ion-ion interactions are weak due to large ion-size or due to very high dielectric constant.

On the other hand, a positive slope is observed if ion-ion interactions are strong due to the low dielectric constant of the medium or due to small ionic size. S_V^* values were found as positive at all temperatures for NaCl, KCl and RbCl indicating the presence of ion-ion interactions, even though the dielectric constant of the medium ismoderately high. In contrast, the negative slope was observed for KBr and KI salts, which were not unexpected due to the larger ionic size and in a medium of moderately high dielectric constant. This indicates that the strong ion-solvent interactions weaken the ion-ion interactions.

3.1. The limiting partial molar volumes (ϕ_V^0)

The limiting partial molar volume of solutes is regarded as a measure of solute-solvent interactions by many workers.[20,21] In the present study, ϕ_V^0 values of alkali metal halides exhibit the order $Rb^+ > K^+ > Na^+$ at all temperatures studied. This shows that the structure breaking effect or solute-solvent interactions decrease in the order $Na^+ > K^+ > Rb^+$ for cations. A similar trend has been reported in the study of partial molar volumes of alkali metal halides in tertiary butanol-water mixtures by Desnoyers.[21]

On the other hand, the order of ϕ_V^0 concerning anions follows the $I^- > Br^- > Cl^-$ which in turn indicates that structure breaking effect decreases in the order $Cl^- > Br^- > I^-$. The comparatively small ϕ_V^0 values for sodium chloride can reasonably be explained based on the small size of the cation which causes greater electrostriction and thus gives small ϕ_V^0 values.

Many researchers have inferred that the maxima in plots of ϕ_V^0 versus t (in °C) indicate the presence of strong solute-solvent interactions, while the minima suggest the presence of ion-ion interactions.[20-26] In the case of rubidium chloride, a deep minima was observed, indicating the presence of ion-ion interaction also supported by positive S_V^* values. For other salts, ϕ_V^0 increased with an increase in temperature.

DOI: http://dx.doi.org/10.32571/ijct.726469 **E-ISSN: 2602-277X**

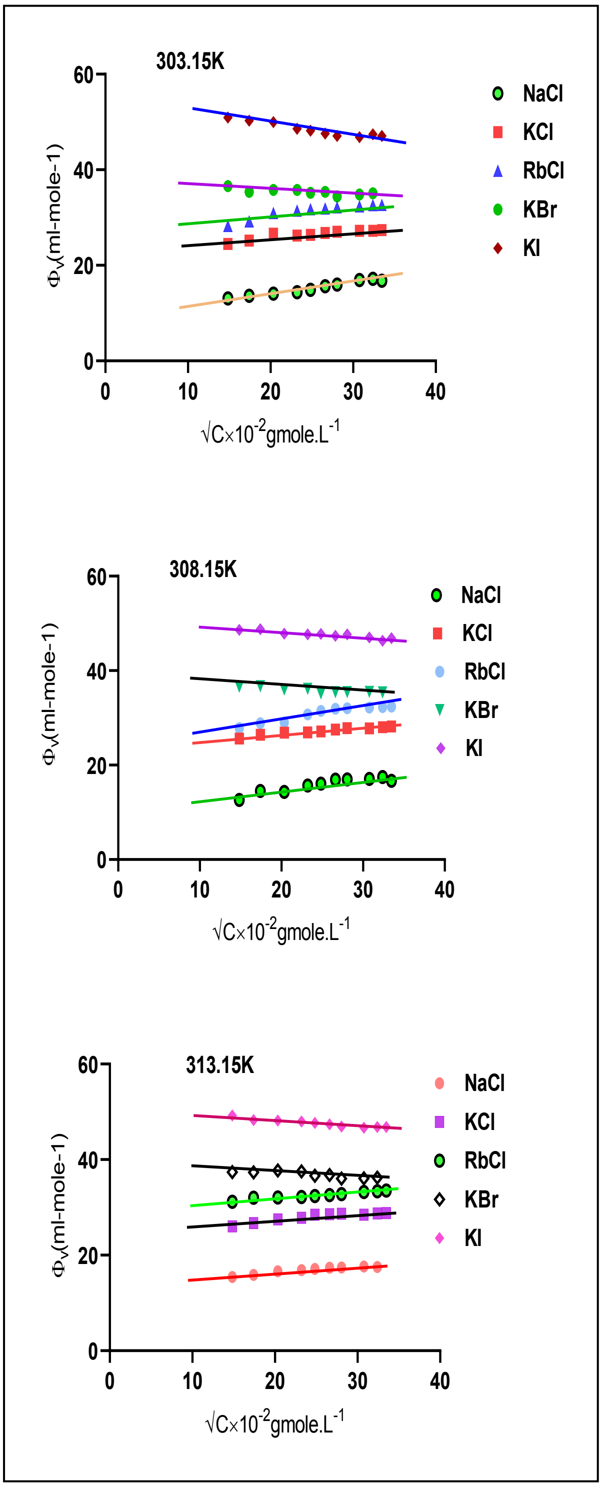

Figure 1. Apparent molar volume (ϕ_V) as a function of √C of Alkali metal halides in 10% (w/w) 2-(Ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K.

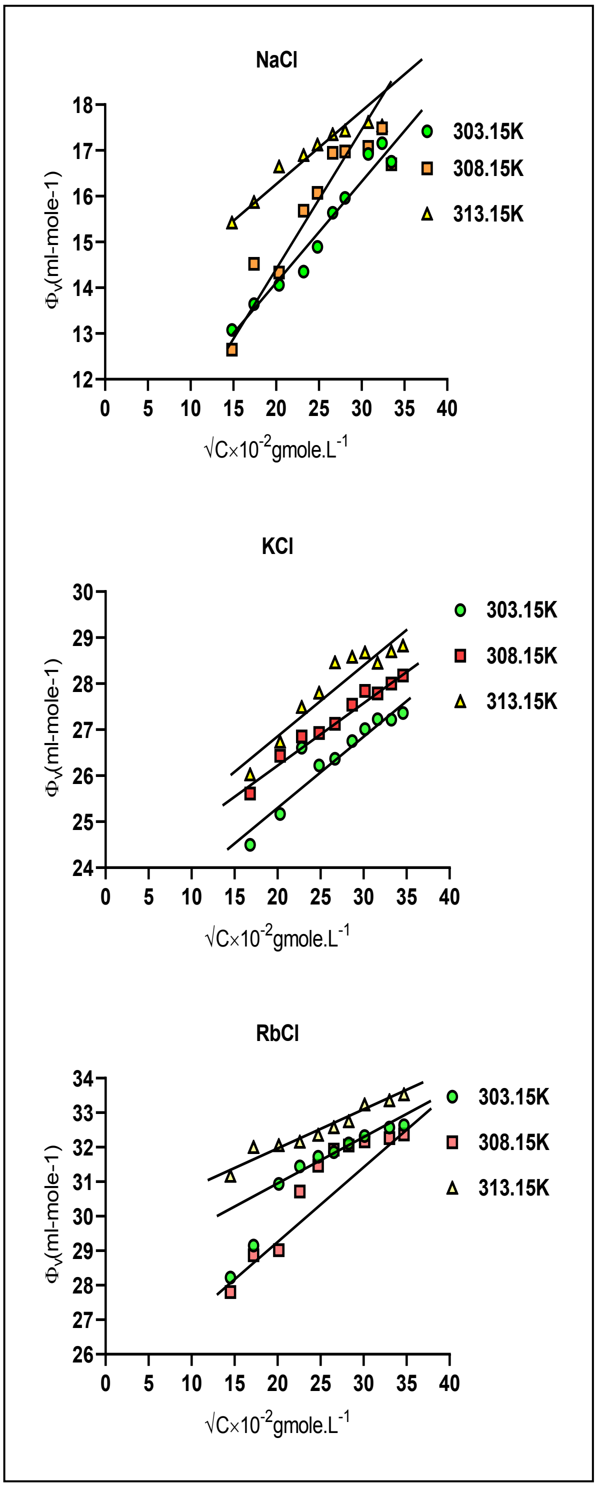

Figure 2. Apparent molar volume (ϕ_V) as a function of √C of NaCl, KCl and RbCl in 10% (w/w) 2-(Ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K.

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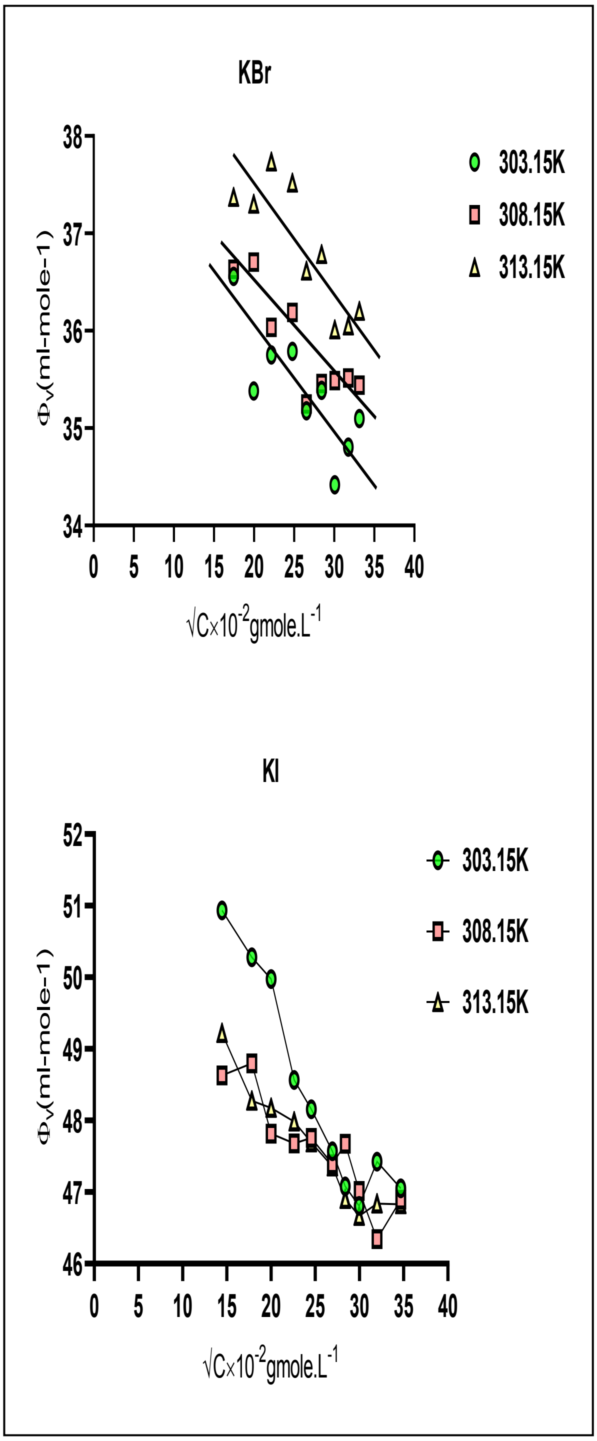

Figure 3. Apparent molar volume (ϕ_V) as a function of √C of KBr and KI in 10% (w/w) 2-(Ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K.

3.2. Limiting ıonic partial molar volumes

Ion-solvent interactions manifest themselves in all molar functions obtained by extrapolation to infinite dilutions. It is possible to assign the contribution of cation and anion by separating the limiting molar functions into ionic contributions. Two methods were used in the current research:[27] (i) Convey and co-workers and (ii) Jolicoeur and co-workers for the purpose of comparison. A detailed discussion on the separation of limiting molar volumes is presented in our previous publication.[9] From the $\bar{V}^0_{Br^-}$ the $\bar{V}^0_{ion}$ values of other ions were calculated using the additive nature of limiting partial molar volumes of solutes. The data obtained are presented in Table 3.

From Table 3 it can be observed that the $\bar{V}^0_{Na^+}$ is negative at 303.15 K and 308.15 K. The negative partial molar volume of an ion means that, with the addition of the ion, the decrease in the solution volume due to ion-solvent interactions is more than the increase in the solution volume due to the intrinsic ionic volume. From an observation of the $\bar{V}^0_{Na^+}$ values at 303.15 K, 308.15 K and 313.15 K, it is clear that as the temperature increases the sign of $\bar{V}^0_{Na^+}$ becomes positive at 313.15 K, indicating that at this temperature the decrease in solution volume due to ion-solvent interactions is less than the increase in the solution volume due to the intrinsic ionic volume.

The short-range solvating properties of ions have been discussed by considering the sign of the difference $(\bar{V}^0_{ion} - \bar{V}^0_{cryst})$.[28] An ion is considered as an electrostatic positive solvating (structure making) ion if $(\bar{V}^0_{ion} - \bar{V}^0_{cryst})$ is negative, and as a negative solvating (structure breaking) ion if $(\bar{V}^0_{ion} - \bar{V}^0_{cryst})$ is positive. It is assumed that this classification is valid even to the present aqua-organic mixed solvent system as it is water rich.

Data in Table 4 show that $(\bar{V}^0_{ion} - \bar{V}^0_{cryst})$ is negative for Na^+ and Cl^- ions at all temperatures (except for Na^+ at 313.15 K). It is a proven fact that the small ions with high charge density act as net structure makers.

The negative sign of $(\bar{V}^0_{ion} - \bar{V}^0_{cryst})$ agrees with this fact and proves that these ions are structure makers. The other alkali metal and halide ions (i.e. K^+, Rb^+, Br^- and I^-) have positive $(\bar{V}^0_{ion} - \bar{V}^0_{cryst})$ values showing that these ions are structure breaking ions. These facts are in accordance with the observations of other workers.[29]

Table 3. Limiting partial molar volumes of various ions in 10% (w/w) 2-(Ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K from I: the method of Convey and co-workers, II: the method of Jolicoeur and and co-workers

	Method I , ϕ_V (cm^3 mol^{-1})			Method II, ϕ_V (cm^3 mol^{-1})		
	303.15 K	**308.15 K**	**313.15 K**	**303.15 K**	**308.15 K**	**313.15 K**
Na$^+$	-3.04	-1.81	3.97	-23.19	-22.30	-16.72
K$^+$	9.74	12.04	14.17	-10.44	-8.45	-6.52
Rb$^+$	13.49	13.33	20.22	-6.66	-7.16	-0.47
C^{l-}	12.59	11.52	9.62	32.74	32.01	30.31
Br$^-$	28.02	26.13	25.40	48.17	46.62	46.09
I$^-$	44.18	38.24	36.53	64.36	58.73	57.24

Table 4. $(\bar{V}^{0}_{ion} - \bar{V}^{0}_{cryst})$ values for alkali and halide ions in 10% (w/w) 2-(Ethoxy) ethanol at 303.15 K, 308.15 K and 313.15 K

	$(\bar{V}^{0}_{ion} - \bar{V}^{0}_{cryst})$		
	303.15 K	**308.15 K**	**313.15 K**
Na$^+$	-5.20	-3.97	1.81
K$^+$	3.82	6.11	8.24
Rb$^+$	5.33	5.16	12.05
C^{l-}	-2.35	-3.42	-5.32
Br$^-$	9.33	7.44	6.71
I$^-$	18.78	12.84	11.13

3.3. Components of limiting ionic molar volumes

Using the multilayer hydration models of Gurney, Frank–Wen and Eigen-Wicke for ion–solvent interactions, Millero[28,30] has shown that the limiting ionic partial molar volume $\bar{V}^{0}_{ion}$ can be attributed to the following components.

$$\bar{V}^{0}_{ion} = \bar{V}^{0}_{\mathrm{int}\,r} + \bar{V}^{0}_{elect} + \bar{V}^{0}_{stru} + \bar{V}^{0}_{cage} \qquad (4)$$

Where $\bar{V}^{0}_{(\mathrm{int}\,r)}$ is the intrinsic partial molar volume (the positive increment in the $\bar{V}^{0}_{ion}$ due to the intrinsic ionic volume). $\bar{V}^{0}_{(elect)}$ is the electrostriction partial molar volume (the negative increment equals to the decrease in the molar solute volume due to ion-solvent electrostrictive interaction). $\bar{V}^{0}_{(\mathrm{int}\,r)}$ is the disordered or void space partial molar volume (the increment due to the destruction of solvent structure in the region of ionic co-sphere). $\bar{V}^{0}_{cage}$ is the caged partial volume (the negative increment is characteristic of hydrophobic “Structure making” ions such as R$_4$N$^+$ ions). $\bar{V}^{0}_{(\mathrm{int}\,r)}$ of the solutes are calculated adopting Padova equation[28] that makes use of both the molar volume and compressibility

$$\bar{V}^{0}_{\mathrm{int}\,r} = \phi^{0}_{V} + \left(-\phi^{0}_{K} \times \frac{S^{*}_{V}}{S^{*}_{K}} \right) \qquad (5)$$

Where ϕ^{0}_{V} is the partial molar volume of the solute, S^{*}_{V} is the experimental slope obtained from ϕ^{0}_{V} versus $\sqrt{c}$ graph, ϕ^{0}_{K} is the partial molar adiabatic compressibility and S^{*}_{K} is the experimental slope obtained from the ϕ_K versus $\sqrt{c}$ graph. Using the compressibility data[12] of our work, the $\bar{V}^{0}_{(\mathrm{int}\,r)}$ for the solutes are calculated only at 303.15 K (Table 5) (Since the compressibility data is available only 303.15 K in the present solvent system.

Table 5. $\bar{V}^0_{(\text{int}\,r)}$ calculated in 10% (w/w) 2-(OEt) EtOH-H_2O at 303.15 K

Salt	NaCl	KCl	RbCl	KBr	KI
$\bar{V}^0_{(\text{int}\,r)}$	28.61	35.80	48.88	28.30	46.04

Assuming that the method of Conway and co-workers for the separation of $\bar{V}^0$ values into ionic components is equally applicable to separate the $\bar{V}^0_{(\text{int}\,r)}$ values,[9] the $\bar{V}^0_{(\text{int}\,r)}$ value is calculated to be 26.37 for Br^- ion at 303.15K. Applying additive rule the $\bar{V}^0_{(\text{int}\,r)}$ values of the other ions along with the $\bar{V}^0_{ion}$ are calculated.

Hepler's semi-empirical equation[31] for the $\bar{V}^0_{ion}$ calculation in water is

$$\bar{V}^0_{ion} = Ar^3 - BZ^2/r \tag{6}$$

Where A, B are constants. Z and r are the charge and crystallographic radius of the ion, respectively. This equation is used to separate the geometric part from the electrostrictive part of the ionic volume.[32] The first term of the equation is equal to $\bar{V}^0_{\text{int}} + \bar{V}^0_{(disord)}$ and the second term is equal to $\bar{V}^0_{(elect)}$. For mono valent ions, the equation can be rearranged as

$$\bar{V}^0_{ion} r = Ar^4 - B \tag{7}$$

To separate the intrinsic size of an ion and the void space effect, the following semi-empirical equations have been proposed by Hepler.[31]

$$\bar{V}^0_{ion} = 2.52r^3 + (\text{A}-2.52)\text{r}^3 - Bz^2/r \tag{8}$$

$$\bar{V}^0_{ion} = 2.52r^3 + A'r^2 - B'Z^2/r \tag{9}$$

In these calculations, the void space is assumed to be equal to the surface of the ion, $A' \,\&\, B'$ are constants. *A*, *B* and *A′*, *B′* have been determined by plotting $\bar{V}^0_{ion} \times r$ against r^4 and $(\bar{V}^0_{ion} r - 2.52r^4)$ against r^3 respectively. From the graphs in Figures 4 and 5, it can be seen that in both cases the cations and the anions fall into two separate straight lines and giving different A, B and *A′*, *B′* values for the cations and the anions.

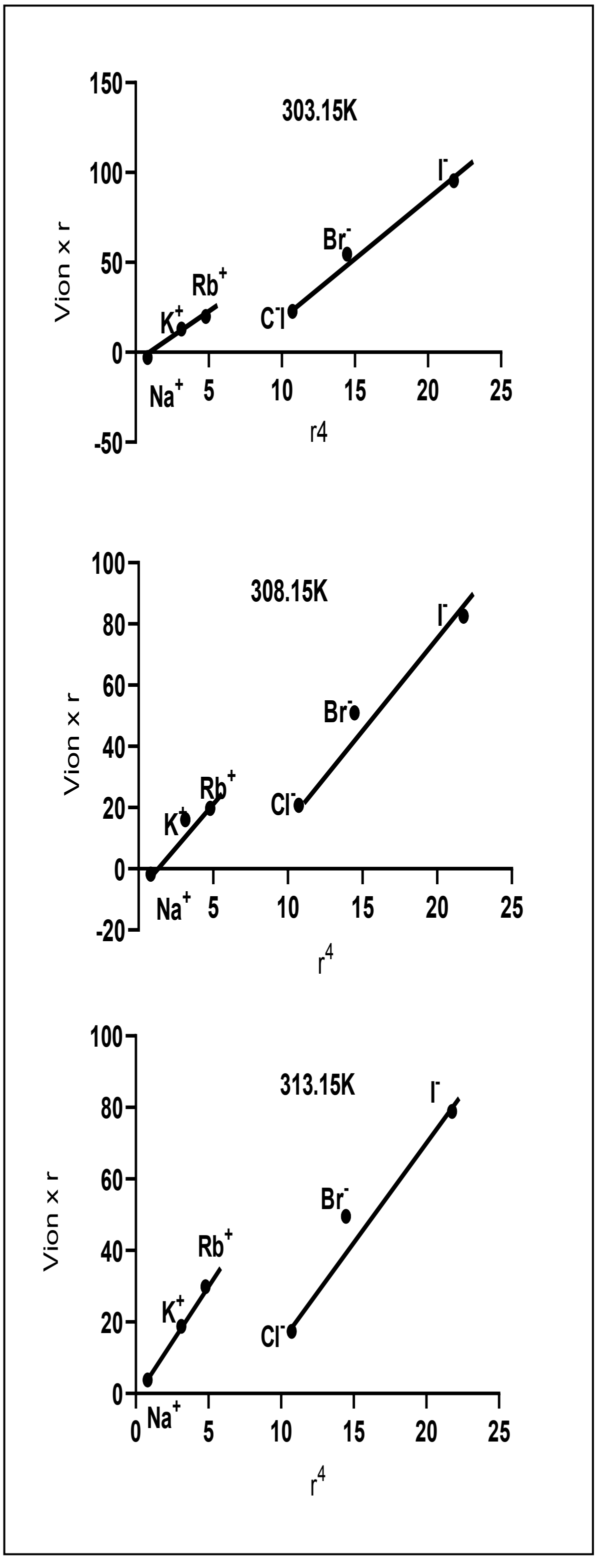

Figure 4. Plot of $V_{ion}.r$ against r^4 for alkali metal and halide ions in 10% (w/w) 2-(OEt) EtOH-H_2O mixture at 303.15 K, 308.15 K, and 313.15 K.

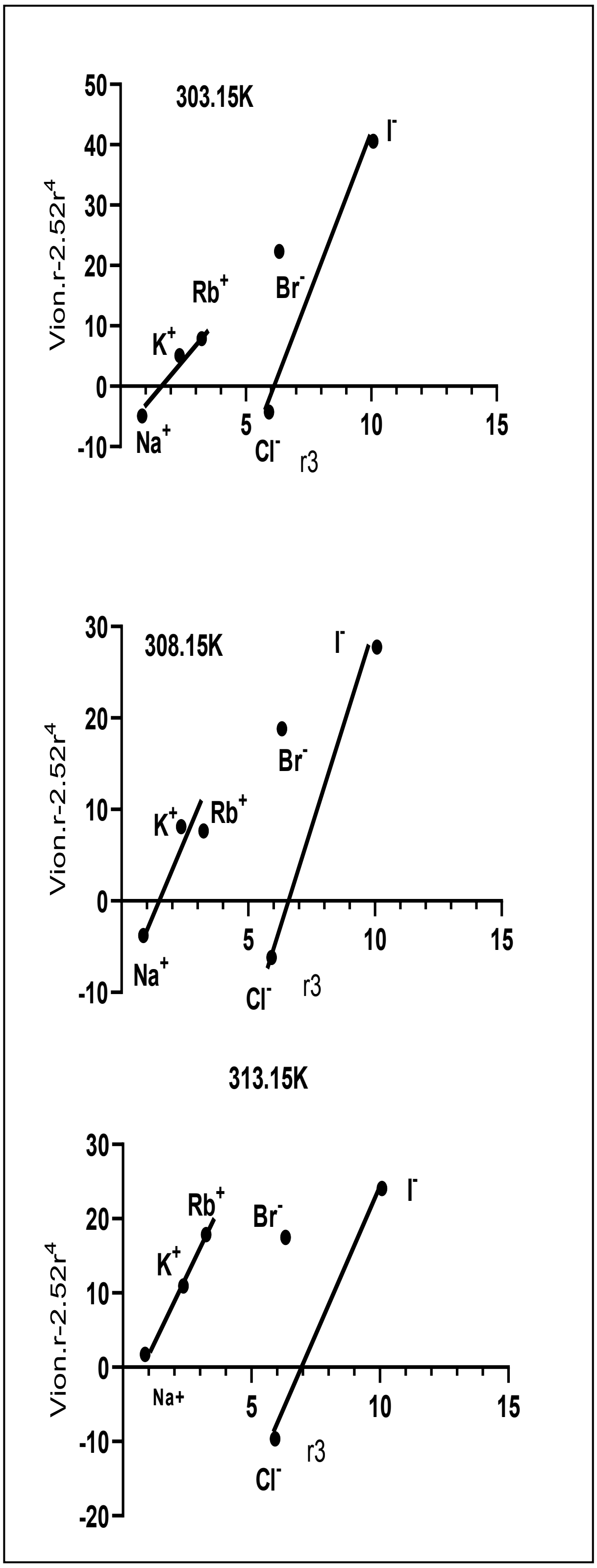

Figure 5. Plot of ($\bar{V}ion.r - 2.52\ r^4$) against r^3 for alkali metal and halide ions in 10% (w/w) 2-(Ethoxy) ethanol-water mixture at 303.15 K, 308.15 K and 313.15 K.

According to Hepler, [31] one should not expect plots of various functions of $\bar{V}^0_{ion}$, Z and r to give only one line for both cations and anions because radii of ion cavities are larger than corresponding crystal radii and also crystal radii are greater for cations than for anions.

From Table 7, it can be seen that *B* is larger for anions than cations. The larger *B* values for anions than cations indicate that the ion-solvent interactions are greater for anions than for cations of the same size and charge.

Table 6. $\bar{V}^0_{\mathrm{int}}$ of various ions along with $\bar{V}^0_{ion}$ in 10% (w/w) 2-(OEt) EtOH –H_2O at 303.15 K

	$\bar{V}^0_{\mathrm{(int)}}$	$\bar{V}^0_{ion}$
Na^+	-5.26	-3.04
K^+	1.93	9.74
Rb^+	15.01	13.49
C^{l-}	33.87	12.59
Br^-	26.37	28.02
I^-	44.11	44.18

Table 7. Values of A (cm^3 mol^{-1} (A^o)$^{-3}$) and B(cm^3 mol^{-1} A^o) from Eq. 6 and A′ (cm^3 mol^{-1} (A^o)$^{-2}$) and B′ (cm^3 mol^{-1} A^o) and from Eq. 9 of ions at 303.15 K, 308.15 K and 313.15 K

Ions		**303.15 K**	**308.15 K**	**313.15 K**
Alkali Metal Cations	A_+	5.8	4.60	5.2
	A'_+	5.4	7.3	7.2
	B_+	8.0	4.5	1.6
	B'_+	9.5	11.0	7.0
Halide Anions	A_-	6.5	5.4	5.4
	A'_-	10.5	8.0	8.0
	B_-	43.2	33.5	35.2
	B'_-	64.0	49.5	50.0

DOI: http://dx.doi.org/10.32571/ijct.726469 **E-ISSN: 2602-277X**

Table 8. Comparison of values of $\bar{V}^0_{(disor)}$ and $\bar{V}^0_{(electr)}$ of alkali and halide ions by two methods in 10% (w/w) 2-(OEt) EtOH-H_2O at 303.15 K, 308.15 K and 313.15 K

Ion	**303.15 K**		**308.15 K**		**313.15 K**		**303.15 K**		**308.15 K**		**313.15 K**	
	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii
	$\bar{V}^0_{(disor)}$						$\bar{V}^0_{(electr)}$					
Na^+	2.81	4.87	1.78	6.59	2.30	6.50	8.42	10.00	4.73	11.58	1.68	7.37
K^+	7.72	9.5	4.89	12.91	6.30	12.74	6.01	7.14	3.38	8.27	1.20	5.26
Rb^+	10.63	11.83	6.74	15.99	8.69	15.77	5.40	6.42	3.04	7.43	1.08	4.73
C^{l-}	23.60	39.40	17.08	26.21	17.08	26.21	23.86	35.36	18.51	27.35	19.45	27.62
Br^-	29.51	39.92	21.35	30.42	21.35	30.42	22.15	32.82	17.18	25.38	18.05	25.64
I^-	40.11	48.99	29.02	37.32	29.02	37.32	20.00	29.63	15.51	22.92	16.29	23.15

Note: i and ii indicate the methods.

Table 9. Dimensions of various ions (Radius in Å) in 10% (w/w) 2-(Ethoxy) ethanol-water mixture

Ion	**303.15 K**	**308.15 K**	**313.15 K**	**Pauling's crystallographic radius**[36]
Na^+	1.02	1.08	1.31	0.95
K^+	1.50	1.57	1.63	1.33
Rb^+	1.64	1.60	1.77	1.48
C^{l-}	1.58	1.55	1.50	1.81
Br^-	1.93	1.90	1.88	1.85
I^-	2.20	2.11	2.08	2.16

$\bar{V}^0_{(disord)}$ & $\bar{V}^0_{(elect)}$ are calculated from the constants A, B and A^1 and B^1 are presented in the table. The $\bar{V}^0_{(elect)}$ values obtained for the ions cannot be compared with the theoretical $\bar{V}^0_{(elect)}$ values from the Drude and Nerst equation[33] since the evaluation of theoretical $\bar{V}^0_{(elect)}$ requires the value of $\frac{\partial(\ln D)}{\partial P}$ which is not available for the solvent system studied.

3.4. Dimensions of ions

Padova and Conway's equations are used to estimate effective radii for various ions[34,35]

$$\text{(i)}\ \bar{V}^0_{ion} = 4.48 r^3_{ion} - 8.0 / r_{ion} \qquad (10)$$

$$\text{(ii)}\ \bar{V}^0_{ion} = 2.51 r^3_{ion} - 3.15 / r^2_{ion} \qquad (11)$$

Comparison of radius of the ions in the solution with effective crystallographic radius proposed by Pauling[36] shows that the cations are solvated to some extent however not much significantly, while the anions are either least solvated or un-solvated in the present solvent system.

4. CONCLUSIONS

The following results are obtained from this study.

- Positive values of the S^*_V for NaCl, KCl, and RbCl at all the temperatures indicate the presence of ion-ion interactions.
- The ϕ^0_V values for concerning cations are in the order $Rb^+ > K^+ > Na^+$ and structure breaking effects are in the oreder $Na^+ > K^+ > Rb^+$. For anions, the ϕ^0_V values are in the order $I^- > Br^- > Cl^-$ and structure breaking effect order is $Cl^- > Br^- > I^-$.

- $(\bar{V}^{o}_{ion} - \bar{V}^{o}_{cryst})$ are negative for Na$^+$ and Cl$^-$, which act as net structure makers. $(\bar{V}^{o}_{ion} - \bar{V}^{o}_{cryst})$ are positive for K$^+$, Rb$^+$, Br$^-$ and I$^-$, which act as net structure breakers.

ACKNOWLEDGEMENTS

The author is thankful to Mr. Sanjay ji Ghodawat (Chairman S.G.U), Shri Vinayak Bhosale (Trustee, S.G.U), Mr. Srinivas Konduti (Director SGIMA) and Mr. Sreedhar Gupta (Centre head SGIMA) for their support during this research work. The author express his thanks to his research colleague Mr. Maruthi Kavuri, Personnel Officer, Singareni Collieries Ltd., Telangana. The author records his gratitude to the research supervisor Late Dr. K. Lakshminarayna, Professor, Physico-Chemical Laboratories, Sri Venkateswara University, Tirupathi. (A. P) India.

Conflict of interests

Author declares that there is no a conflict of interest with any person, institute, company, etc.

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