Exploration of Solution Behaviour of Potassium Halides in Mixtures of L-Proline and Water at 298.15, 308.15 and 318.15 K

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Abstract

Apparent molar volume (ϕ_V) and viscosity B-coefficients were estimated for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L-Proline from measured solution density (ρ) and viscosity (η) at 298.15, 308.15 and 318.15 K at various electrolyte concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data has been analyzed using Jones-Dole equation and the derived parameters, B and A, have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of sign $(\ \partial \phi_V^0 / \partial T\ )_P$.

Introduction

Studies on densities (ρ) and viscosities (η) of electrolyte solutions are of great importance in characterizing the properties and structural aspects of solutions. The addition of an electrolyte to an aqueous organic solution alters the pattern of ion solvation and causes phenomenal changes in the behaviour of the dissolved electrolyte. Hence studies on the limiting apparent molar volume and viscosity B-coefficients of electrolyte provide us valuable information regarding ion-ion, ion-solvent and solvent-solvent interactions [1-3]. It has been found by a number of workers [4-6] that the addition of an electrolyte could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various electrolyte concentrations and temperature.

In this paper we have attempted to report the limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*) and viscosity B-coefficients for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L-Proline at 298.15, 308.15 and 318.15 K. Since potassium ion being a common cation for all of the electrolytes under investigation, the present work enables us to have a qualitative comparison of the role of anion in aqueous L-Proline in terms of various derived parameters obtained from viscosity (η) and density (ρ) measurements.

Experimental Methods

Materials

L-Proline (SD. Fine Chemicals) was purified by standard methods [7]. The purity of the solvent was checked by measuring the viscosity (η) and density (ρ) at 298.15 K which was in good agreement with the literature values. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6}/\Omega/cm$ was used. Potassium chloride, potassium bromide and potassium iodide (Sigma-Aldrich, Germany) were purified by re-crystallizing twice from conductivity water and then dried in a vacuum desiccator over P_2O_5 for 24 h before use. The experimental values of viscosity (η) and density (ρ) of aqueous mixtures of 0.01 M, 0.03 M and 0.05 M L-Proline at different temperatures are listed in Table 1.

Apparatus and procedure

Densities (ρ) were measured with an Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 g/cm³. The calibration was done by double-distilled water and dry air and uncertainty in density was ± 0.00005 g/cm.

The measurements were done in a thermostat bath controlled to ± 0.01 K. Viscosity (η) was measured by means of Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 having an accuracy of 1.0% and fitted to a Brookfield Digital Bath TC-500 at 298 K using density and viscosity values from the literature [8-10]. The uncertainty in viscosity measurements is within ± 0.003 mPa s. The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation loses during the actual measurements.

The electrolyte solutions studied here were prepared by mass and the conversion of molality into molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

Results and Discussion

Density calculation

The apparent molar volumes (ϕ_V) were determined from the solution densities using the following Equation [3]:

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$$\phi_V = M / \rho - (\rho - \rho_o) / c\rho\rho_o \qquad (1)$$

Where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volumes ϕ_V^0 was calculated using a least-squares treatment to the plots of ϕ_V versus $\sqrt{c}$ using the following Masson equation [11]:

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \qquad (2)$$

Where (ϕ_V^0) is the apparent molar volume at infinite dil ution and (S_V^*) is the experimental slope. The plots of (ϕ_V^0) against square root of molar concentration ($\sqrt{c}$) were found to be linear as depicted graphically in Figures 1-9 with negative slopes. Values of ϕ_V^0 and S_V^* are reported in Table 3.

In these systems the ion-solvent and ion-ion interactions can be interpreted in terms of structural changes between various components of the solvent and solution systems. ϕ_V^0 can be used to interpret ion-solvent interactions. A perusal of Table 3 reveals that the ϕ_V^0 values are positive and increase with a rise in both the temperature and amount of L-Proline in the mixtures. This indicates the presence of strong ion-solvent interactions and these interactions are further strengthened at higher temperatures and higher molar mass of L-Proline in the mixtures, suggesting larger electrostriction at higher temperatures and in enhanced amount of L-Proline.
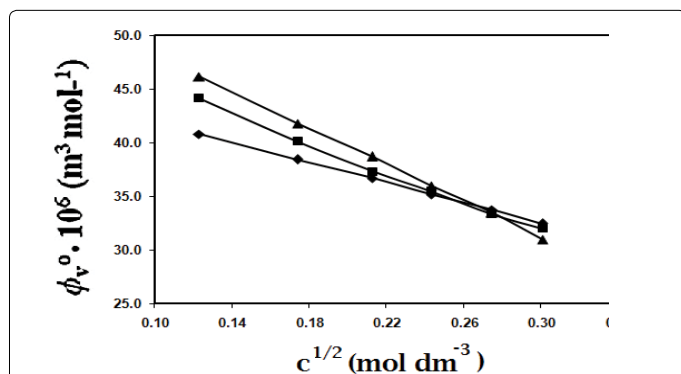

Figure 1: The apparent molar volume (ϕ_V) and the square root of concentrations ($\sqrt{c}$) for potassium chloride in different aqueous mixtures 0.01 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

Figure 2: The apparent molar volume (ϕ_V) and the square root of concentrations ($\sqrt{c}$) for potassium chloride in different aqueous mixtures 0.03 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

Figure 3: The apparent molar volume (ϕ_V) and the square root of concentrations ($\sqrt{c}$) for potassium chloride in different aqueous mixtures 0.05 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

Figure 4: The apparent molar volume (ϕ_V) and the square root of concentrations ($\sqrt{c}$) for potassium bromide in different aqueous mixtures 0.01 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

Figure 5: The apparent molar volume (ϕ_V) and the square root of concentrations ($\sqrt{c}$) for potassium bromide in different aqueous mixtures 0.03 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

A perusal of Table 3 also reveals that the S_V^* values are negative for all the solutions at all the experimental temperatures and S_V^* values decrease as the experimental temperature and amount of L-Proline in the mixtures increases. Since S_V^* is a measure of ion-ion interactions, the results indicate the presence of weak ion-ion interactions in the
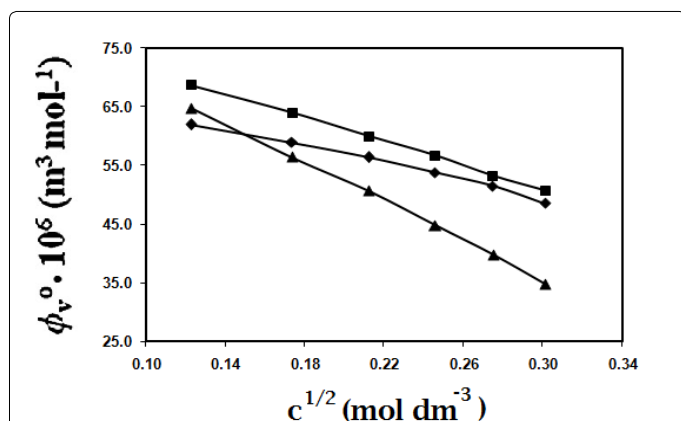
Figure 6: The apparent molar volume (ϕ_V) and the square root of concentrations (√c) for potassium bromide in different aqueous mixtures 0.05 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

Figure 7: The apparent molar volume (ϕ_V) and the square root of concentrations (√c) for potassium iodide in different aqueous mixtures 0.01 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

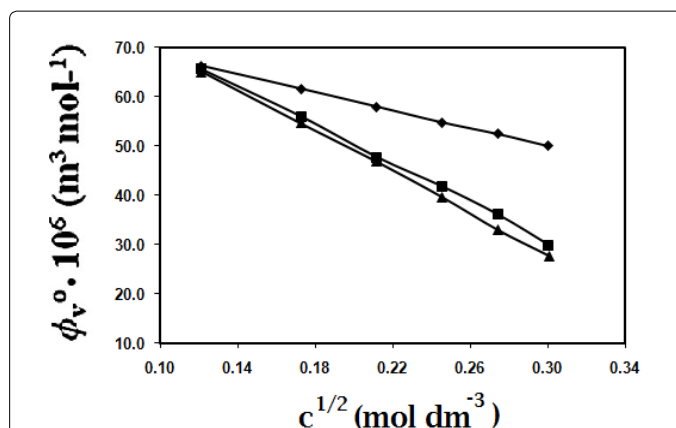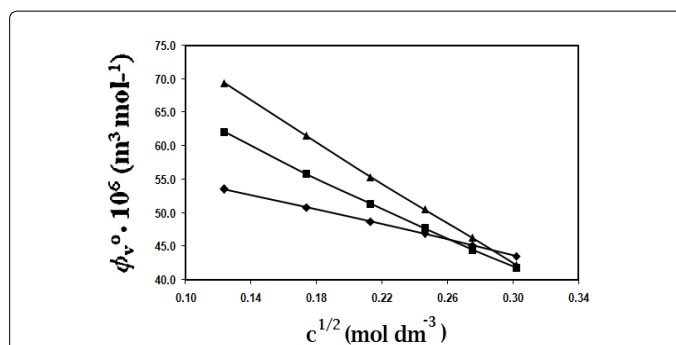**Figure 8:** The apparent molar volume (ϕ_V) and the square root of concentrations (√c) for potassium iodide in different aqueous mixtures 0.03 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).

solutions at all the experimental temperatures and these interactions further decrease with a rise in temperature and increase in molar mass L-Proline in the mixtures. In other words, it may be said that the solvation of electrolyte/ions increases with the increase of L-Proline content in water. This is probably due to more violent thermal agitation

at higher temperatures, resulting in diminishing the force of ion-ion interactions (ionic-dissociation) [12]. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and at all experimental temperatures.

The variation of ϕ_V^0 with temperature of potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L-Proline follows the polynomial,

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \tag{3}$$

Over the temperature range under study where T is the temperature in K. Values of coefficients of the above equation for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L- Proline are reported in Table 4.

The apparent molar expansibilities (ϕ_E^0) can be obtained by the following equation:

$$\phi_E^0 = (\ \partial \phi_V^0 / \partial T\ )_P = a_1 + 2a_2 T \tag{4}$$

The values of ϕ_E^0 for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. From the table it is evident that the values of ϕ_E^0 for potassium chloride increases with the increase in the amount of L- Proline in the mixture. However, for potassium bromide and potassium iodide the ϕ_E^0 values were found to be rather complicated to explain. During the past few years it has been emphasized by a number of workers that S_V^* is not the sole criterion for
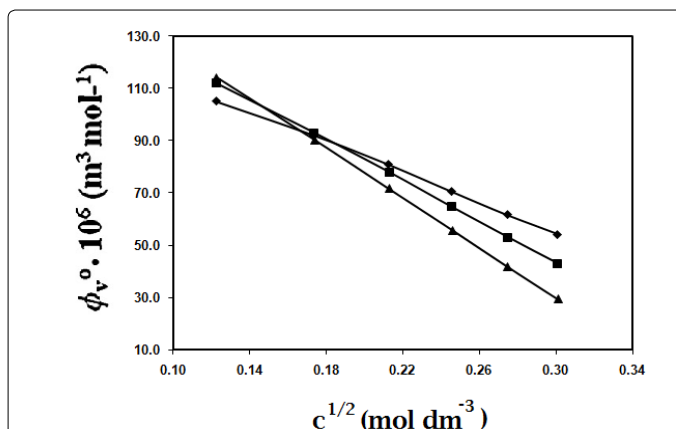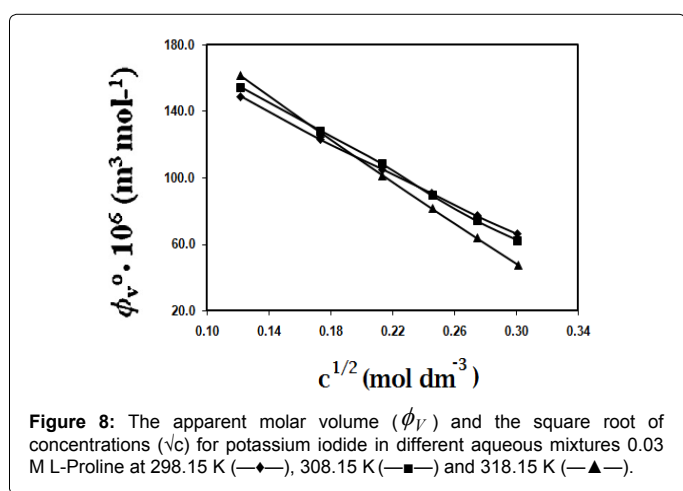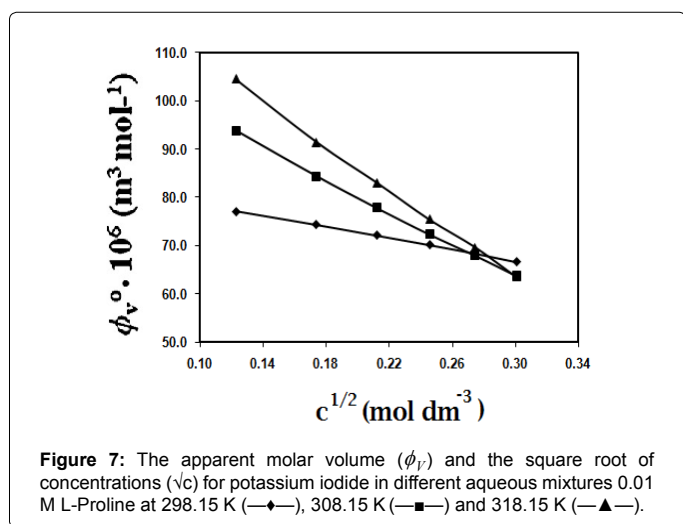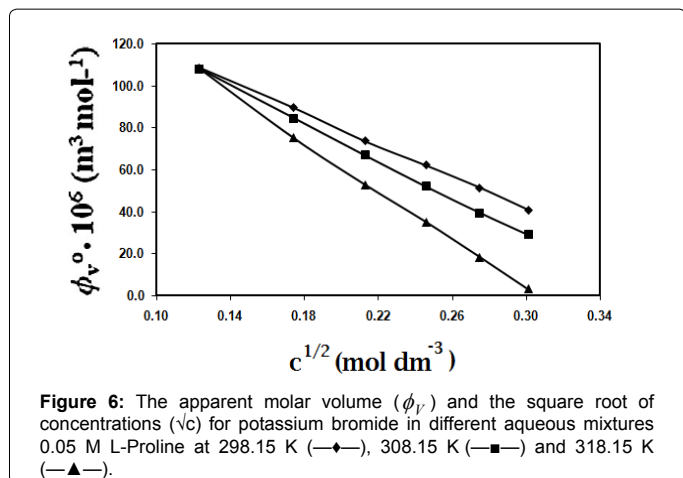

Figure 9: The apparent molar volume (ϕ_V) and the square root of concentrations (√c) for potassium iodide in different aqueous mixtures 0.05 M L-Proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).
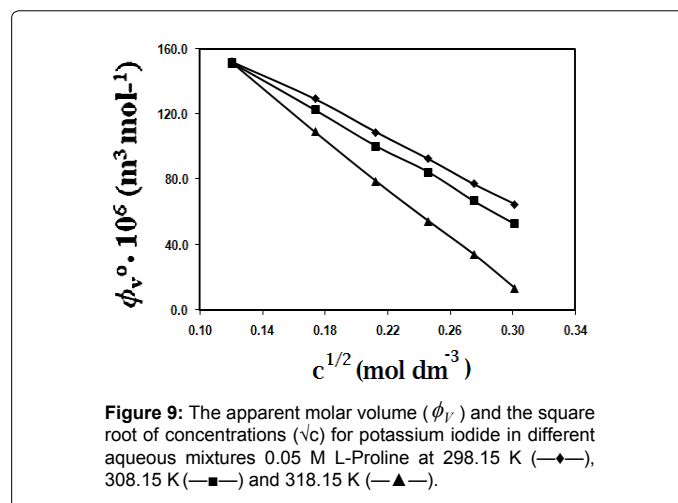
Temperature (K)	$\rho \times 10^{-3}$(kg/m)	η (mPa.s)
0.01 M L-proline		
298.15 K	0.99753	0.909
308.15 K	0.99605	0.771
318.15 K	0.99466	0.639
0.03 M L-proline		
298.15 K	0.99902	0.916
308.15 K	0.99763	0.778
318.15 K	0.99604	0.645
0.05 M L-proline		
298.15 K	1.00045	0.923
308.15 K	0.99941	0.786
318.15 K	0.99772	0.652

Table 1: Density (ρ, kg/m) and viscosity (η, mPa.s) of aqueous mixtures of 0.01 M L-proline, 0.03 M L-proline, 0.05 M L-proline at different temperatures.

c (mol/dm³)	$\rho \times 10^{-3}$ (kg/m)	η (mPa.s)	$\phi_V \times 10^6$ (m³/mol)	$(\eta/\eta_0-1)/c^{1/2}$ (kg$^{1/2}$ mol$^{-1/2}$)
Potassium chloride in aqueous mixture 0.01M L-proline				

c (mol/dm³)	$\rho \times 10^{-3}$ (kg/m)	η (mPa.s)	$\phi_V \times 10^6$ (m³/mol)	$(\eta/\eta_0-1)/c^{1/2}$ (kg$^{1/2}$ mol$^{-1/2}$)
Potassium chloride in aqueous mixture 0.01M L-proline				
298.15 K				
0.0151	0.99804	0.918	40.7724	0.081
0.0302	0.99862	0.923	38.4219	0.089
0.0452	0.99924	0.927	36.6533	0.093
0.0590	0.99985	0.931	35.1369	0.100
0.0752	1.00059	0.935	33.7388	0.104
0.0903	1.00132	0.938	32.4331	0.106
Potassium chloride in aqueous mixture 0.01M L-proline				
308.15 K				
0.0151	0.99651	0.779	44.1206	0.084
0.0302	0.99709	0.784	40.0940	0.097
0.0452	0.99773	0.789	37.3202	0.110
0.0590	0.99835	0.793	35.4719	0.117
0.0752	0.99914	0.798	33.3263	0.128
0.0903	0.99988	0.802	31.9725	0.134
Potassium chloride in aqueous mixture 0.01M L-proline				
318.15 K				
0.0151	0.99509	0.647	46.1479	0.102
0.0302	0.99565	0.653	41.7753	0.126
0.0452	0.99628	0.659	38.6617	0.147
0.0590	0.99693	0.664	35.9803	0.161
0.0752	0.99774	0.670	33.4493	0.177
0.0903	0.99858	0.675	30.9510	0.187
Potassium bromide in aqueous mixture 0.01M L-proline				
298.15 K				
0.0153	0.99853	0.922	53.5574	0.116
0.0303	0.99959	0.931	50.8657	0.139
0.0454	1.00071	0.940	48.7479	0.160
0.0607	1.00189	0.948	46.9048	0.174
0.0759	1.00311	0.957	45.1597	0.192
0.0912	1.00438	0.966	43.5138	0.208
Potassium bromide in aqueous mixture 0.01M L-proline				
308.15 K				
0.0153	0.99692	0.783	62.1030	0.126
0.0303	0.99796	0.792	55.8276	0.156
0.0454	0.99911	0.801	51.3776	0.183
0.0607	1.00036	0.810	47.6963	0.205
0.0759	1.00168	0.819	44.4546	0.226
0.0912	1.00305	0.828	41.8137	0.245
Potassium bromide in aqueous mixture 0.01M L-proline				
318.15 K				
0.0153	0.99542	0.651	69.3779	0.152
0.0303	0.9964	0.661	61.4873	0.198
0.0454	0.99754	0.671	55.3595	0.235
0.0607	0.9988	0.681	50.4901	0.267
0.0759	1.00015	0.690	46.2727	0.290
0.0912	1.00162	0.701	42.2061	0.321
Potassium iodide in aqueous mixture 0.01M L-proline				
298.15 K				
0.0151	0.99887	0.926	77.1285	0.152
0.0302	1.00029	0.941	74.3642	0.203
0.0451	1.00175	0.955	72.0751	0.238
0.0604	1.00329	0.968	70.1716	0.264
0.0755	1.00486	0.982	68.3442	0.292
0.0906	1.00647	0.995	66.6517	0.314
Potassium iodide in aqueous mixture 0.01M L-proline				

308.15 K				
0.0151	0.99714	0.788	93.7994	0.179
0.0302	0.99851	0.803	84.3485	0.239
0.0451	1.00001	0.818	77.8489	0.287
0.0604	1.00168	0.833	72.2998	0.327
0.0755	1.00341	0.847	67.9012	0.359
0.0906	1.00525	0.861	63.7203	0.388
Potassium iodide in aqueous mixture 0.01M L-proline				
318.15 K				
0.0151	0.99559	0.656	104.5438	0.217
0.0302	0.99691	0.672	91.3819	0.297
0.0451	0.99839	0.688	82.9873	0.361
0.0604	1.00010	0.703	75.4455	0.408
0.0755	1.00189	0.718	69.5956	0.450
0.0906	1.00387	0.733	63.5555	0.489
Potassium chloride in aqueous mixture 0.03M L-proline				
298.15 K				
0.0150	0.99921	0.923	61.9450	0.062
0.0301	0.99949	0.927	58.9421	0.069
0.0451	0.99984	0.931	56.3604	0.077
0.0603	1.00027	0.935	53.7704	0.085
0.0754	1.00075	0.938	51.5348	0.087
0.0907	1.00137	0.942	48.5495	0.094
Potassium chloride in aqueous mixture 0.03M L-proline				
308.15 K				
0.0151	0.99772	0.785	68.7139	0.073
0.0301	0.99795	0.790	64.0361	0.089
0.0451	0.99829	0.795	59.9847	0.103
0.0603	0.99871	0.799	56.6853	0.110
0.0754	0.99924	0.804	53.2104	0.122
0.0907	0.99979	0.808	50.6903	0.128
Potassium chloride in aqueous mixture 0.03M L-proline				
318.15 K				
0.0151	0.99619	0.652	64.8067	0.088
0.0302	0.99659	0.658	56.4412	0.116
0.0451	0.99712	0.664	50.6549	0.139
0.0604	0.99784	0.669	44.7281	0.151
0.0756	0.99866	0.675	39.7752	0.169
0.0907	0.99964	0.679	34.7144	0.175
Potassium bromide in aqueous mixture 0.03M L-proline				
298.15 K				
0.0150	0.99923	0.928	105.1030	0.107
0.0301	0.99983	0.938	92.0902	0.138
0.0452	1.00074	0.947	80.8570	0.159
0.0603	1.00193	0.956	70.5692	0.178
0.0754	1.00332	0.965	61.7272	0.195
0.0905	1.00486	0.975	54.1642	0.214
Potassium bromide in aqueous mixture 0.03M L-proline				
308.15 K				
0.0151	0.99774	0.790	111.9319	0.126
0.0302	0.99842	0.802	92.8868	0.178
0.0453	0.99948	0.812	78.0739	0.205
0.0604	1.00089	0.822	64.8203	0.230
0.0755	1.00258	0.832	53.1259	0.253
0.0906	1.00448	0.842	42.9908	0.273
Potassium bromide in aqueous mixture 0.03M L-proline				
318.15 K				
0.0151	0.99612	0.657	114.1186	0.152
0.0302	0.99691	0.669	90.3578	0.214
0.0453	0.99818	0.680	71.7285	0.255
0.0604	0.99985	0.691	55.7207	0.290

0.0755	1.00185	0.702	41.6985	0.322
0.0906	1.00412	0.713	29.3384	0.350
Potassium iodide in aqueous mixture 0.03M L-proline				
298.15 K				
0.0149	0.99928	0.934	148.6430	0.161
0.0302	1.00032	0.950	122.8749	0.214
0.0456	1.00180	0.965	104.7895	0.251
0.0604	1.00356	0.980	90.4247	0.284
0.0755	1.00571	0.996	76.8781	0.318
0.0906	1.00802	1.012	66.0675	0.348
Potassium iodide in aqueous mixture 0.03M L-proline				
308.15 K				
0.0149	0.99781	0.796	154.2313	0.190
0.0302	0.99878	0.813	127.9890	0.259
0.0456	1.00027	0.829	107.9414	0.307
0.0605	1.00225	0.845	89.2142	0.350
0.0756	1.00455	0.861	73.9113	0.388
0.0907	1.00701	0.879	61.9273	0.431
Potassium iodide in aqueous mixture 0.03M L-proline				
318.15 K				
0.0149	0.99612	0.663	161.2379	0.229
0.0302	0.99723	0.680	126.7934	0.312
0.0456	0.99899	0.697	101.1548	0.378
0.0605	1.00115	0.714	81.1575	0.435
0.0756	1.00374	0.731	63.5879	0.485
0.0907	1.00674	0.749	47.3012	0.535
Potassium chloride in aqueous mixture 0.05M L-proline				
298.15 K				
0.0147	1.00058	0.931	66.1920	0.071
0.0298	1.00085	0.937	61.6009	0.088
0.0449	1.00122	0.942	57.8579	0.097
0.0602	1.00167	0.947	54.7120	0.106
0.0754	1.00215	0.952	52.4210	0.114
0.0904	1.00271	0.957	49.9364	0.123
Potassium chloride in aqueous mixture 0.05M L-proline				
308.15 K				
0.0147	0.99955	0.794	65.5701	0.084
0.0298	0.99998	0.800	55.9323	0.103
0.0449	1.00064	0.806	47.6291	0.120
0.0602	1.00141	0.812	41.7613	0.135
0.0754	1.00234	0.817	36.1032	0.144
0.0903	1.00348	0.823	29.8654	0.157
Potassium chloride in aqueous mixture 0.05M L-proline				
318.15 K				
0.0147	0.99787	0.660	64.9810	0.101
0.0298	0.99833	0.667	54.6447	0.133
0.0449	0.99899	0.674	46.7675	0.159
0.0603	0.99985	0.681	39.6604	0.181
0.0754	1.00089	0.688	32.9022	0.201
0.0904	1.00199	0.695	27.6887	0.219
Potassium bromide in aqueous mixture 0.05M L-proline				
298.15 K				
0.0152	1.00061	0.935	108.4123	0.105
0.0304	1.00135	0.945	89.2875	0.137
0.0454	1.00251	0.954	73.4616	0.158
0.0605	1.00389	0.964	61.9252	0.181
0.0756	1.00556	0.974	51.1534	0.201
0.0907	1.00753	0.983	40.6693	0.216
Potassium bromide in aqueous mixture 0.05M L-proline				
308.15 K				
0.0152	0.99958	0.798	107.8545	0.124

0.0304	1.00046	0.809	84.4013	0.168
0.0454	1.00177	0.820	66.8686	0.203
0.0605	1.00345	0.830	52.0043	0.228
0.0756	1.00542	0.841	39.2430	0.254
0.0907	1.00756	0.851	28.8720	0.275
Potassium bromide in aqueous mixture 0.05M L-proline				
318.15 K				
0.0152	0.99789	0.664	108.0181	0.149
0.0304	0.99906	0.676	74.8907	0.211
0.0454	1.00072	0.687	52.7317	0.252
0.0605	1.00279	0.698	34.9094	0.287
0.0756	1.00533	0.709	18.0126	0.318
0.0907	1.00822	0.721	2.9450	0.351
Potassium iodide in aqueous mixture 0.05M L-proline				
298.15 K				
0.0146	1.00065	0.941	152.2114	0.161
0.0303	1.00155	0.959	129.5148	0.224
0.0452	1.00301	0.976	109.0648	0.270
0.0607	1.00488	0.993	92.6019	0.308
0.0759	1.00713	1.009	77.4794	0.338
0.0908	1.00958	1.025	64.8759	0.367
Potassium iodide in aqueous mixture 0.05M L-proline				
308.15 K				
0.0146	0.99962	0.804	151.6684	0.190
0.0303	1.00072	0.823	122.6546	0.270
0.0452	1.00236	0.841	100.5065	0.329
0.0607	1.00433	0.859	84.5345	0.377
0.0759	1.00688	0.876	67.0643	0.416
0.0908	1.00963	0.893	52.8721	0.452
Potassium iodide in aqueous mixture 0.05M L-proline				
318.15 K				
0.0146	0.99794	0.670	151.2114	0.228
0.0303	0.99944	0.690	109.1685	0.335
0.0453	1.00165	0.709	78.8492	0.411
0.0607	1.00446	0.728	54.4682	0.473
0.0759	1.00769	0.746	34.0835	0.523
0.0908	1.01154	0.764	13.2989	0.570

Table 2: The concentration (c), density (ρ), viscosity (η), apparent molar volume (ϕ_V), and $(\eta/\eta_0-1)/c^{1/2}$ of potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01M L-proline , 0.03M L-proline, 0.05M L-proline at different temperatures.

Molarity of L-proline	a_0 (m^3/mol)	a_1 (m^3/mol/K)	a_2 (m^3/mol/K)
Potassium chloride			
0.01	-686.321	4.2917	-0.0062
0.03	-2922.861	18.7939	-0.0293
0.05	-5619.977	36.3861	-0.0579
Potassium bromide			
0.01	-1817.842	10.9216	-0.0155
0.03	-2976.151	18.7747	-0.0279
0.05	4075.112	-26.5645	0.0451
Potassium iodide			
0.01	-6181.141	38.5014	-0.0586
0.03	2016.222	-13.3537	0.0244
0.05	9044.573	-58.7362	0.0976

Table 3: Limiting apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*) of potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01M L-proline , 0.03M L-proline, 0.05M L-proline at different temperatures.

Molarity of L-proline	a_0 (m³/mol)	a_1 (m3/mol/K)	a_2 (m³/mol/K)
Potassium chloride			
0.01	-686.321	4.2917	
0.03	-2922.861	18.7939	
0.05	-5619.977	36.3861	
Potassium bromide			
0.01	-1817.842	10.9216	-0.0155
0.03	-2976.151	18.7747	-0.0279
0.05	4075.112	-26.5645	0.0451
Potassium iodide			
0.01	-6181.141	38.5014	-0.0586
0.03	2016.222	-13.3537	0.0244
0.05	9044.573	-58.7362	0.0976

Table-4: Values of the coefficients of Eq. (4) for potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M L-proline, 0.03 M L-proline, 0.05M L-proline at different temperatures.

Molarity of L-proline	ϕ_E^0 (m³/mol)			$(\partial\phi_E^0 / \partial T)_P$ (m³/mol/K)
	298.15 K	308.15 K	318.15 K	
Potassium chloride				
0.01	0.0595	0.47064	0.34664	-0.0124
0.03	1.3223	1.7363	0.1505	-0.0586
0.05	1.8603	0.7023	-0.4556	-0.1158
Potassium bromide				
0.01	1.6789	1.3690	1.0589	-0.0310
0.03	2.1379	1.5799	1.0220	-0.0558
0.05	0.3286	1.2306	2.1326	0.0902
Potassium iodide				
0.01	3.5582	2.3862	1.2142	-0.1172
0.03	1.1960	1.6840	2.1720	0.0488
0.05	-0.5373	1.4146	3.3666	0.1952

Table-5: Limiting partial molar expansibilities for potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M L-proline , 0.03 M L-proline, 0.05 M L-proline at different temperatures.

Molarity of L-proline	B-coefficient (dm³/²/mol¹/²)			A-coefficient (dm³/mol)		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Potassium chloride						
0.01	0.149	0.283	0.488	0.062	0.048	0.042
0.03	0.179	0.308	0.496	0.039	0.035	0.029
0.05	0.278	0.403	0.658	0.038	0.034	0.020
Potassium bromide						
0.01	0.511	0.669	0.938	0.050	0.041	0.035
0.03	0.588	0.810	1.103	0.034	0.031	0.019
0.05	0.625	0.849	1.116	0.027	0.019	0.013
Potassium iodide						
0.01	0.903	1.177	1.525	0.043	0.035	0.031
0.03	1.037	1.325	1.706	0.032	0.026	0.016
0.05	1.137	1.451	1.889	0.025	0.016	0.004

Table-6: Values of A and B coefficients for potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01M L-proline , 0.03M L-proline, 0.05M L-proline at different temperatures.

determining the structure making or breaking tendency of any solute. Hepler [13] developed a technique of examining the sign of $(\partial\phi_E^0 / \partial T)_P$ for the solute in terms of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows

$$(\partial\phi_E^0 / \partial T)_P = 2a_2 \qquad (5)$$

If the sign of $(\partial\phi_E^0 / \partial T)_P$ is positive or small negative [14,15] the electrolyte is a structure maker and when the sign of $(\partial\phi_E^0 / \partial T)_P$ is negative, it is a structure breaker. As is evident from Table 5, the electrolyte under investigation generally acts as a structure breaker.

The viscosity data of solutions for the electrolytes in 0.01 M, 0.03M, 0.05M L-Proline have been analyzed using Jones-Dole [16] equation:

Where η_0 and η are the viscosities of the solvent and solution respectively. A and B are the constants estimated by least square method and are reported in Table 6. From the table it is evident that the values of the A-coefficient are very small for all the solutions under investigation at all experimental temperatures. These results indicate the presence of weak ion-ion interactions, and these interactions further decrease with both rise of experimental temperatures and amount of L-Proline suggesting an increase in ion-solvation. Interestingly, values are found to be smallest for Potassium iodide and hence it may be concluded that solubility in aqueous L-Proline solutions is maximum for Potassium iodide and minimum for Potassium chloride.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B-coefficient [17,18]. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B-coefficient of potassium chloride, potassium bromide and potassium iodide in the studied solvent systems are more positive than A-coefficients, thereby suggesting the presence of strong ion-solvent interactions, and these types of interactions are strengthened with a rise in both temperature and amount of L-Proline in solutions. These conclusions are in excellent agreement with those drawn from ϕ_V^0 values discussed earlier. It has been reported in a number of studies [19,20] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 6 that the values of the B-coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of potassium chloride, potassium bromide and potassium iodide in the solvent systems.

Conclusion

Extensive study of potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L- Proline reveals that potassium iodide is more associated in L-Proline than the other two halides. The ion-association is found minimum in the case of potassium chloride in L- Proline. The said interaction of potassium bromide arises in the intermediacy of potassium iodide and potassium chloride. The present study reveals the predominance of ion-solvent interaction over the ion-ion interaction in all the solution under investigation.

Acknowledgements

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