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 ($V^\phi$) and viscosity B-coefficients were estimated for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L-proline from measured solution density ($\rho$) and viscosity ($\eta$) 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 $\text{sign}(\partial Q^0/\partial T)$.

Keywords: potassium chloride, potassium bromide and potassium iodide, L-proline, ion-solvent interaction

1. Introduction

Studies on densities ($\rho$) and viscosities ($\eta$) of electrolyte solutions are of great importance in characterizing the properties and structural aspects of solutions. The addition of an electrolyte to an aqueous L-proline solution alters the pattern of ion solvation and causes phenomenal changes in the behaviour of the dissolved electrolyte. The viscosity data of solutions for the electrolytes in L-proline have been analyzed using Jones–Dole equation and A and B-coefficients obtained from the equation are good indicative of ion-solvent and ion-ion interactions respectively. 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]. L-proline is often used as asymmetric catalyst and
therefore it is used in many biotechnological reactions [4]. It has been found by a number of workers [5–7] 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 ($\phi^0$), experimental slopes ($S^*$) 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 ($\eta$) and density ($\rho$) measurements.

2. Experimental Methods

2.1. Materials

L-proline (SD. Fine Chemicals) was purified by standard methods [8]. The purity of the solvent was checked by measuring the viscosity ($\eta$) and density ($\rho$) at 298.15 K which was in good agreement with the literature values. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \ \text{Ω}^{-1} \ \text{cm}^{-1}$ 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 dessicator over P$_2$O$_5$ for 24 h before use. The experimental values of viscosity ($\eta$) and density ($\rho$) of aqueous mixtures of 0.01 M, 0.03 M and 0.05 M L-proline at different temperatures are listed in Table 1.

2.2. Apparatus and procedure

Densities ($\rho$) were measured with an Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 g/cm$^3$. The calibration was done by double-distilled water and dry air and uncertainty in density was $\pm 0.00005$ g cm$^{-3}$.

The measurements were done in a thermostat bath controlled to $\pm 0.01$ K. Viscosity ($\eta$) 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 298K using
density and viscosity values from the literature [9-11]. 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.

3. Results and Discussion

3.2. Density calculation

The apparent molar volumes (\( \phi_v \)) were determined from the solution densities using the following Eq. [3]:

\[
\phi_v = \frac{M}{\rho} - \left( \rho - \rho_0 \right) \frac{1}{c} \rho \rho_o
\]

where M is the molar mass of the solute, c is the molarity of the solution; \( \rho_0 \) and \( \rho \) are the densities of the solvent and the solution respectively. The limiting apparent molar volumes \( \phi_v^0 \) were calculated using a least-square treatment to the plots of \( \phi_v \) versus \( \sqrt{c} \) using the following Masson equation [12]:

\[
\phi_v = \phi_v^0 + S_v^* \cdot \sqrt{c}
\]

where (\( \phi_v^0 \)) is the apparent molar volume at infinite dilution and (\( S_v^* \)) is the experimental slope. The plots of (\( \phi_v^0 \)) against square root of molar concentration (\( \sqrt{c} \)) were found to be linear as depicted graphically in Figs. 1–9 with negative slopes. Values of \( \phi_v^0 \) 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. $\phi^0_V$ can be used to interpret ion–solvent interactions. Table 3 showed that $\phi^0_V$ values are generally 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.

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 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) [13]. This suggests that ion–solvent interactions dominate over ion–ion interactions in all the solutions and at all experimental temperatures.

The variation of $\phi^0_V$ with temperature of potassium chloride, potassium bromide and potassium iodide in aqueous mixture of L-proline follows the polynomial,

$$\phi^0_V = a_0 + a_1T + a_2T^2$$

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 ($\phi^0_E$) can be obtained by the following equation:

$$\phi^0_E = (\partial \phi^0_V / \partial T)_p = a_1 + 2a_2T$$

The values of $\phi^0_E$ for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5.
potassium chloride increases with the increase in the amount of L-proline in the mixture. However, for potassium bromide and potassium iodide the $\phi_E^0$ values were found to be rather complicated to explain. During the past few years it has been emphasized by a number of workers that $S_p^*$ is not the sole criterion for determining the structure making or breaking tendency of any solute. Hepler [14] 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

$$(-\partial \phi_E^0 / \partial T)_p = 2a_2$$  \hspace{1cm} (5)

If the sign of $(\partial \phi_E^0 / \partial T)_p$ is positive or small negative [15,16] 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, 0.03 M, 0.05 M L-proline have been analyzed using Jones–Dole [17] equation:

$$(\eta / \eta_0 - 1) / \sqrt{c} = A + B \sqrt{c}$$  \hspace{1cm} (6)

where $\eta_0$ and $\eta$ are the viscosities of the solvent and solution respectively. A and B are the coefficients 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 [18,19]. 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 type 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 $\phi^0_v$ values discussed earlier. It has been reported in a number of studies [20, 21] 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.

4 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 intermediary 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.

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Tables:

Table 1. Density ($\rho$, kg m$^{-3}$) and viscosity ($\eta$, mPa.s) of aqueous mixtures of 0.01 M L-proline, 0.03 M L-proline, 0.05 M L-proline at different temperatures
### Table 2

The concentration ($c$), density ($\rho$), viscosity ($\eta$), apparent molar volume ($V_\phi$), and $(\eta/\eta_b-1)/c^{\frac{1}{2}}$ of 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.

| Temperature (K) | $\rho \times 10^3$ (kg m$^{-3}$) | $\eta$ (mPa.s) | $V_\phi \times 10^6$ (m$^3$ mol$^{-1}$) | $(\eta/\eta_b-1)/c^{\frac{1}{2}}$ (kg$^{1/2}$ mol$^{-1/2}$) |
|----------------|-------------------------------|----------------|---------------------------------------|-------------------------------------------------|
| **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 2. The concentration ($c$), density ($\rho$), viscosity ($\eta$), apparent molar volume ($V_\phi$), and $(\eta/\eta_b-1)/c^{\frac{1}{2}}$ of 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.
| Temperature | Component Concentration | Property 1 | Property 2 | Property 3 |
|-------------|-------------------------|------------|------------|------------|
| 298.15K     | 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 0.01 M L-proline** |

| Temperature | Component Concentration | Property 1 | Property 2 | Property 3 |
|-------------|-------------------------|------------|------------|------------|
| 308.15K     | 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 0.01 M L-proline** |

| Temperature | Component Concentration | Property 1 | Property 2 | Property 3 |
|-------------|-------------------------|------------|------------|------------|
| 318.15K     | 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 0.01 M L-proline

| Temperature (K) | Concentration (M) | Reaction Rate Constant (s⁻¹) | Reaction Order | Initial Rate (M/s) |
|-----------------|-------------------|------------------------------|---------------|-------------------|
| 298.15K         | 0.0153            | 0.99853                      | 0.922         | 53.5574           |
|                 | 0.0303            | 0.99959                      | 0.931         | 50.8657           |
|                 | 0.0454            | 1.00071                      | 0.940         | 48.7479           |
|                 | 0.0607            | 1.00189                      | 0.948         | 46.9048           |
|                 | 0.0759            | 1.00311                      | 0.957         | 45.1597           |
|                 | 0.0912            | 1.00438                      | 0.966         | 43.5138           |

| Temperature (K) | Concentration (M) | Reaction Rate Constant (s⁻¹) | Reaction Order | Initial Rate (M/s) |
|-----------------|-------------------|------------------------------|---------------|-------------------|
| 308.15K         | 0.0153            | 0.99692                      | 0.783         | 62.1030           |
|                 | 0.0303            | 0.99796                      | 0.792         | 55.8276           |
|                 | 0.0454            | 0.99911                      | 0.801         | 51.3776           |
|                 | 0.0607            | 1.00036                      | 0.810         | 47.6963           |
|                 | 0.0759            | 1.00168                      | 0.819         | 44.4546           |
|                 | 0.0912            | 1.00305                      | 0.828         | 41.8137           |

| Temperature (K) | Concentration (M) | Reaction Rate Constant (s⁻¹) | Reaction Order | Initial Rate (M/s) |
|-----------------|-------------------|------------------------------|---------------|-------------------|
| 318.15K         | 0.0153            | 0.99542                      | 0.651         | 69.3779           |
|                 | 0.0303            | 0.9964                       | 0.661         | 61.4873           |
|                 | 0.0454            | 0.99754                      | 0.671         | 55.3595           |
|                 | 0.0607            | 0.9988                       | 0.681         | 50.4901           |
|                 | 0.0759            | 1.00015                      | 0.690         | 46.2727           |


| Temperature | Concentration | Value 1 | Value 2 | Value 3 | Value 4 |
|-------------|--------------|---------|---------|---------|---------|
| 298.15 K    | 0.0912       | 1.00162 | 0.701   | 42.2061 | 0.321   |
|             | 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   |
| 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   |
| 308.15 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   |
Potassium chloride in aqueous mixture 0.03 M L-proline

| Temperature  | Activity Coefficient | Mole Fraction | Molal Potential (J/mol) | Molar Entropy (J/mol-K) |
|--------------|----------------------|---------------|-------------------------|-------------------------|
| 298.15K      |                      |               |                         |                         |
| 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 0.03 M L-proline

| Temperature  | Activity Coefficient | Mole Fraction | Molal Potential (J/mol) | Molar Entropy (J/mol-K) |
|--------------|----------------------|---------------|-------------------------|-------------------------|
| 308.15K      |                      |               |                         |                         |
| 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 0.03 M L-proline

| Temperature  | Activity Coefficient | Mole Fraction | Molal Potential (J/mol) | Molar Entropy (J/mol-K) |
|--------------|----------------------|---------------|-------------------------|-------------------------|
| 318.15K      |                      |               |                         |                         |
| 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                   |
| Temperature (K) | Potassium bromide in aqueous mixture 0.03 M L-proline |  |  |  |
|----------------|-----------------------------------------------------|---|---|---|
| 298.15K        |                                                    |   |   |   |
| 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 |
| 308.15K        |                                                    |   |   |   |
| 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 |
| 318.15K        |                                                    |   |   |   |
| 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 0.03 M L-proline

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Potassium iodide in aqueous mixture 0.03 M L-proline

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Potassium iodide in aqueous mixture 0.03 M L-proline

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Potassium iodide in aqueous mixture 0.03 M L-proline

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Potassium iodide in aqueous mixture 0.03 M L-proline

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Potassium iodide in aqueous mixture 0.03 M L-proline

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Potassium iodide in aqueous mixture 0.03 M L-proline

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| Temperature  | Potassium chloride in aqueous mixture 0.05 M 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                  |
| 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                  |
| 318.15 K    |                                                   |
|             |Potassium chloride in aqueous mixture 0.05 M L-proline |
|            |            |            |            |            |
|------------|------------|------------|------------|------------|
| 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 0.05 M 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 0.05 M 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 0.05 M L-proline
| Temperature (K) | Concentration | pH | Conductivity (µS/cm) | Antimony (ppm) |
|----------------|---------------|----|----------------------|----------------|
| 318.15         | 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 0.05 M L-proline

| Temperature (K) | Concentration | pH | Conductivity (µS/cm) | Antimony (ppm) |
|----------------|---------------|----|----------------------|----------------|
| 298.15         | 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 0.05 M L-proline

| Temperature (K) | Concentration | pH | Conductivity (µS/cm) | Antimony (ppm) |
|----------------|---------------|----|----------------------|----------------|
| 308.15         | 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 |
Table 3.

Limiting apparent molar volumes ($\phi^0_V$) and experimental slopes ($S^e_V$) of 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 | $\phi^0_V \times 10^6$ | $S^e_V \times 10^6$ |
|-----------------------|------------------------|---------------------|
|                       | (m$^3$·mol$^{-1}$)      | (m$^2$·mol$^{-3/2}$ L$^{1/2}$) |
| 298.15 K | 308.15 K | 318.15 K | 298.15 K | 308.15 K | 318.15 K |
| Potassium chloride    |                       |                     |
| 0.01  | 46.56 | 52.19 | 56.59 | -46.89 | -68.46 | -84.87 |
| 0.03  | 71.52 | 81.51 | 85.63 | -73.76 | -102.01 | -167.33 |
| 0.05  | 77.16 | 89.67 | 90.59 | -90.67 | -196.92 | -208.7 |
|Potassium bromide
| 0.01  | 46.56 | 52.19 | 56.59 | -46.89 | -68.46 | -84.87 |
| 0.03  | 71.52 | 81.51 | 85.63 | -73.76 | -102.01 | -167.33 |
| 0.05  | 77.16 | 89.67 | 90.59 | -90.67 | -196.92 | -208.7 |
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, 0.05 M L-proline at different temperatures

| Molarity of L-proline | $a_0$ (m$^3$·mol$^{-1}$) | $a_1$ (m$^3$·mol$^{-1}$·K$^{-1}$) | $a_2$ (m$^3$·mol$^{-1}$·K$^{-2}$) |
|-----------------------|--------------------------|----------------------------------|----------------------------------|
| **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                  | 84.48                    | 113.90                           | -58.75                           |
| 0.03                  | 203.81                   | 218.21                           | -460.91                          |
| 0.05                  | 212.82                   | 217.51                           | -489.42                          |
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

\begin{table}[h]
\centering
\begin{tabular}{cccc}
\hline
Molarity of L-proline & \( \phi_E^0 \) & \( (\partial \phi_E^0 / \partial T)_P \) & \( \phi_E^0 \) \\
\hline
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 \\
\hline
\end{tabular}
\end{table}
| Molarity of L-proline | Potassium chloride | | Potassium bromide | | Potassium iodide |
|----------------------|--------------------|-------------------|-------------------|-------------------|
|                      | 298.15 K           | 308.15 K          | 318.15 K          | 298.15 K          | 308.15 K          | 318.15 K          |
| 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             |
| 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             |
| 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 0.01 M L-proline, 0.03 M L-proline, 0.05 M L-proline at different temperatures.
Figures:

**Figure 1:** The apparent molar volume \( \phi_V \) 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 ($\phi_\gamma$) 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 ($\phi_v^o$) 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 ($\phi_v$) 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 ($\phi_v$) 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 (—▲—).
Figure 6: The apparent molar volume ($\phi_v$) and the square root of concentrations ($\sqrt{c}$) 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 ($\phi_v$) and the square root of concentrations ($\sqrt{c}$) 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 ($\phi_V$) and the square root of concentrations ($\sqrt{c}$) for potassium iodide in different aqueous mixtures 0.03 M L-proline at 298.15 K (—♦—), 308.15 K (—■—) and 318.15 K (—▲—).
Figure 9: The apparent molar volume ($\phi_v$) and the square root of concentrations ($\sqrt{c}$) for potassium iodide in different aqueous mixtures 0.05 M L-proline at 298.15 K (♦—), 308.15 K (■—) and 318.15 K (▲—).