The Conductance of Tetraalkylammonium Iodides in Aqueous Proline and Hydroxyproline Solutions

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The density, viscosity and dielectric constant of aqueous proline and hydroxyproline solutions have been determined at 25 °C. The results appear to indicate that the two aminoacids have a destructive effect on the molecular water aggregates.

The equivalent conductance of tetramethylammonium iodide and tetrabutylammonium iodide in aqueous proline and hydroxyproline solutions has been measured at 25 °C. The aminoacids increase the viscosity of the solutions and decrease the limiting equivalent conductance of the two electrolytes. Electrostatic interactions of the iodide ions with the water molecules and hydrophobic interactions of the tetraalkylammonium ions with the aminoacids also seem to affect the conductometric behaviour of the electrolytes.

Introduction

If aminoacids are added to aqueous electrolytes, the viscosity η generally increases and the limiting equivalent conductance Λ_0 decreases, while the Walden product $\Lambda_0\eta$ increases. The latter trend is believed to be due to a reduction of dielectric relaxation effects and has been observed for alkali halides [1] and tetraalkylammonium bromides in water-glycine and water-β-alanine [2].

KCl and CsI in water-α-alanine and water-serine solutions [3] exhibit $\Lambda_0\eta$ values which decrease with aminoacid content up to 0.1–0.2 mol kg^{-1} and increase above this concentration. Their electrolytic conductance is lower in the water-serine than in the water-α-alanine solutions.

Proline and hydroxyproline differ by an –OH group, as do alanine and serine. It seemed interesting to extend the conductometric investigations to their solutions.

As our attention was focussed on the solvation of the iodide ion, tetramethylammonium iodide (Me_4NI) and tetrabutylammonium iodide (Bu_4NI) have been chosen as electrolytes, because the large cations involved interact only little with the water dipoles via electrostatic forces.

To analyze the conductometric data, the variations in density, viscosity and dielectric constant at various aminoacid concentrations have also been measured.

Experimental

C. Erba dl-hydroxyproline and Fluka dl-proline were purified by recrystallization from water-ethanol 3:1 and dioxane-ethanol 1:1 mixtures, respectively.

Tetramethylammonium and tetrabutylammonium iodides (Merck) were recrystallised from ethyl acetate containing a small amount of ethanol [4].

Aminoacids and iodides were dried under high vacuum, at 50–60 °C, for several days in the dark.

Conductivity water was passed through a cation-anion exchanging bed and maintained out of contact with air. Its specific conductivity was found to be $\chi = 1 \times 10^{-7}$ ohm^{-1} cm^{-1}.

Johson and Adams pycnometers were used; their volume was measured by weighing degassed conductivity water ($d^{25°}_{H_2O} = 0.99707$ gr cm^{-3}).

Ubbelohde-type viscosimeters were used and kinetic energy corrections calculated ($\eta^{25°}_{H_2O} = 0.8903$ cP).

Dielectric constants, D, were measured using 1 cm^3 of aqueous aminoacid solutions in a cell with large, closely-spaced platinum electrodes, with a HP mod. 427 A automatic capacitance bridge, at 25 ± 0.1 °C. The D values were virtually constant

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in the frequency range used, 50—500 kHz, thus assuring that dielectric relaxation phenomena may be neglected.

Conductance measurements were carried out using a Daggett-Kraus cell and a Jones bridge (Leeds and Northrup).

The bath was maintained at 25 ± 0.002 °C and controlled with a Müller bridge. Operating techniques were as described previously [5].

Results

A least-squares analysis of the experimental density d (g cm^{-3}), viscosity η (cP) and dielectric constant D of 22 proline (Pro) and 18 hydroxyproline (HP) solutions gave the following equations:

$$d_{\mathrm{Pro}} = 0.99707 + 0.03336\,M - 0.003266\,M^2\,, \quad (1)$$

$$\eta_{\mathrm{Pro}} = 0.8903 + 0.2501\,M + 0.0401\,M^2\,, \quad (2)$$

$$D_{\mathrm{Pro}} = 78.54 + 20.83\,M\,, \quad (3)$$

and

$$d_{\mathrm{HP}} = 0.99707 + 0.04509\,M\,, \quad (4)$$

$$\eta_{\mathrm{HP}} = 0.8903 + 0.2482\,M + 0.0528\,M^2\,, \quad (5)$$

$$D_{\mathrm{HP}} = 78.54 + 20.89\,M\,, \quad (6)$$

where M is the molal concentration.

The measurements were carried out on solutions with concentrations ranging between zero and 0.8 molal.

The partial molar volumes, $\bar{V}_{\mathrm{Pro}}$ and $\bar{V}_{\mathrm{HP}}$ were found to be 81.8 cm^3 and 86.1 cm^3. Comparing these data with Traube predicted volumes, the electrostriction was $E_{\mathrm{Pro}} = 13$ cm^3 and $E_{\mathrm{HP}} = 11$ cm^3. Cohn and Edsall [6] found $\bar{V}_{\mathrm{Pro}} = 81.0$ cm^3 and $\bar{V}_{\mathrm{HP}} = 84.4$ cm^3.

Tsangaris [7] measured the viscosities of proline and hydroxyproline solutions at 30°, 35° and 40 °C. By a rough extrapolation to 25 °C, the linear viscosity coefficients of proline and hydroxyproline solutions were estimated to be $B_{\mathrm{Pro}} = 0.432$ cP molal^{-1} and $B_{\mathrm{HP}} = 0.184$ cP molal^{-1}. These values are not in agreement with our viscosity coefficients, $B_{\mathrm{Pro}} = 0.2501$ and $B_{\mathrm{HP}} = 0.2482$ of (2) and (5).

Using a different apparatus, Wyman [8] found dielectric molar increments $\Delta_{\mathrm{Pro}} = 21.0$ molar^{-1} and $\Delta_{\mathrm{HP}} = 22.2$ molar^{-1}. From (3) and (6) the molar increments were found to be $\Delta_{\mathrm{Pro}} = 22.12$ and $\Delta_{\mathrm{HP}} = 21.87$.

Table 1. Physical properties of water-proline and water-hydroxyproline systems; M = aminoacid molality, μ = aminoacid ionic strength, D = dielectric constant, η = viscosity of solutions.

Aminoacid	M molal	μ molal	D	η cP
Proline	0.05026	0.272	79.59	0.9029
	0.15131	0.762	81.69	0.9290
	0.29980	1.469	84.78	0.9689
	0.6187	2.931	91.43	1.0603
	0.05127	0.277	79.61	0.9032
	0.10514	0.539	80.73	0.9170
	0.15160	0.764	81.70	0.9290
	0.25410	1.253	83.83	0.9564
	0.7133	3.351	93.40	1.0890
Hydroxy-proline	0.04947	0.690	79.57	0.9027
	0.14540	1.833	81.58	0.9275
	0.29390	3.567	84.68	0.9678
	0.44840	5.328	87.90	1.0122
	0.04850	0.677	79.55	0.9024
	0.05022	0.698	79.59	0.9029
	0.14791	1.863	81.65	0.9282
	0.30680	3.715	84.95	0.9714
	0.5274	6.211	89.56	1.0359

Table 1 shows the molal concentrations, ionic strengths μ, dielectric constants and viscosities of the aminoacid solutions used as solvents for Me_4NI and Bu_4NI, and Table 2 shows the limiting equivalent conductances, standard deviations σ_Λ and Fuoss-Skinner constants S, E, E_1 and L obtained. These parameters are obtained by analysing the experimental conductometric results by the equation [9]

$$\Lambda = \Lambda_0 - S\sqrt{c} + E\,c\ln(6E_1\,c) + L\,c\,, \quad (7)$$

where c is the equivalent concentration of the electrolyte.

A contribution [10]

$$\Delta\Lambda = S\,(\sqrt{\mu + c} - \sqrt{c})\,, \quad (8)$$

which takes into account the effect of aminoacid ions on the equivalent conductance of electrolytes, was added to each experimental Λ value. To evaluate the ionic strength of the proline and hydroxyproline solutions, the aminoacids were assumed to be at the isoelectric point, and the following equilibrium constants were used [11]:

$$K_{1(\mathrm{Pro})} = [\mathrm{H^+}][\mathrm{NH_3^+RCOO^-}]/[\mathrm{NH_3^+RCOOH}] = 1.0233 \times 10^{-2}\,,$$

$$K_{2(\mathrm{Pro})} = [\mathrm{H^+}][\mathrm{NH_2RCOO^-}]/[\mathrm{NH_3^+RCOO^-}] = 0.25 \times 10^{-10}\,, \quad (\mathrm{pH} = 5.06 \times 10^{-7})$$

Table 2. Conductance parameters: limiting equivalent conductance, Λ_0; Fuoss-Skinner constants S, E, L; standard deviation, σ_Λ; Walden product, $\Lambda_0\eta$; iodide Walden product, $\Lambda_0^-\eta$; ionic association constant, K_A, of tetramethylammonium and tetrabutylammonium iodides Me_4NI and Bu_4NI.

Solution	M	Λ_0	σ_Λ	S	E	L	$\Lambda_0\eta$	$(\Lambda_0^-\eta)$	K_A
Me_4NI-Pro-H_2O	0.0000	121.42	0.01	88.35	18.94	50.1	1.0810	0.6840	—
	0.05026	119.01	0.01	86.02	17.68	86.5	1.0745	0.6799	—
	0.15131	115.44	0.02	81.82	15.64	63.9	1.0724	0.6786	—
	0.29980	110.50	0.02	76.19	13.18	54.9	1.0706	0.6775	—
	0.6187	100.66	0.01	65.47	9.121	71.4	1.0673	0.6754	—
Bu_4NI-Pro-H_2O	0.0000	96.13	0.04	82.56	13.14	−159.7	0.8558	0.6840	4.1
	0.05127	94.17	0.01	80.41	12.20	−131.1	0.8505	0.6798	4.6
	0.10514	92.98	0.02	78.28	11.33	−105.3	0.8471	0.6770	4.3
	0.15160	90.99	0.03	76.53	10.66	−108.0	0.8453	0.6756	4.3
	0.25410	88.11	0.02	72.85	9.35	−158.3	0.8426	0.6735	4.4
	0.7133	76.90	0.03	58.96	5.34	−107.3	0.8374	0.6693	3.8
Me_4NI-HP-H_2O	0.04947	119.37	0.02	86.13	17.77	62.5	1.0775	0.6818	—
	0.14540	116.01	0.01	82.15	15.82	69.3	1.0760	0.6809	—
	0.29390	111.22	0.03	76.39	13.31	45.8	1.0765	0.6812	—
	0.44840	106.74	0.01	70.99	11.21	− 13.7	1.0804	0.6837	—
Bu_4NI-HP-H_2O	0.04850	94.85	0.02	80.66	12.38	−233.7	0.8562	0.6844	5.7
	0.05022	94.83	0.02	80.59	12.35	−252.0	0.8562	0.6844	5.6
	0.14791	91.91	0.03	76.82	10.87	−170.2	0.8531	0.6819	4.9
	0.30680	87.74	0.04	71.22	8.933	−170.1	0.8523	0.6812	4.8
	0.5274	82.29	0.02	64.21	6.849	−158.6	0.8524	0.6813	4.5

* $n_-(Me_4NI) = \Lambda_0^-/\Lambda_0(H_2O) = 76.84/121.42 = 0.6328$.
* $n_-(Bu_4NI) = \Lambda_0^-/\Lambda_0(H_2O) = 76.84/\ 96.13 = 0.7993$.

and

$$K_{1(HP)} = [H^+][NH_3^+RCOO^-]/[NH_3^+RCOOH] = 1.0233 \times 10^{-2},$$

$$K_{2(HP)} = [H^+][NH_2RCOO^-]/[NH_3^+RCOO^-] = 2.24 \times 10^{-10} \quad (pH = 1.86 \times 10^{-6}).$$

The limiting equivalent conductances of Me_4NI and Bu_4NI in pure water, at 25 °C, 121.42 and 96.13 $ohm^{-1}\,cm^2\,equiv^{-1}$, are in good agreement with the results of Evans and Kay's [12], 121.39 and 96.16, and with those of Justice and Justice [13], 121.41 and 96.18, respectively.

Table 2 lists also Walden products $\Lambda_0\eta$, ionic products $\Lambda_0^-\eta$ and ion-pair association constants K_A.

Discussion

First some conclusions may be drawn from the experimental results obtained for the binary systems Pro-H_2O and HP-H_2O.

The dielectric molal increment coefficients, $\delta_{(Pro)} = 20.83$ and $\delta_{(HP)} = 20.89$ are quite similar. As a close relation exists between dielectric effects and the dipole moment of the solute molecule [14] (and, hence, molecular charge distance), $-COO^-$ and $-NH_3^+$ groups seem to be localized at the same distance in proline and hydroxyproline molecules, despite the known conformational differences between these two molecules in water [15].

Proline and hydroxyproline have the same densimetric behaviour as most aminoacids (cf. Table 3). The increase in density may be due to the bigger size of the aminoacid molecules as compared to water. Other effects can not be excluded, since the increase for the small serine is greater than that for the bigger proline molecule. Presumably the hydrophobic ring of proline enhances the water

Table 3. The b coefficients of the density equation: $d = d_{H_2O} + bM - dM^2$ and the B coefficients of the viscosity equation: $\eta = \eta_{H_2O} + BM + DM^2$.

Aminoacid	b g cm^{-3} $molal^{-1}$	B cP $molal^{-1}$
Glycine [1]	0.03150	0.1127
Alanine [2]	0.02907	0.2248
Serine [3]	0.04232	0.1616 x
Proline	0.03336	0.2501
Hydroxyproline	0.04509	0.2482

structure, thus causing a rather limited increases in density of proline solutions.

The hydrophobic interactions must be stronger for proline than for hydroxyproline because of the presence of an —OH group in the latter. In fact, the density coefficient of proline solutions is smaller than that of hydroxyproline solutions while the viscosity of proline solutions is greater than that of hydroxyproline solutions.

The above suggestions are supported by the results of Kennerley et al. [16] on the entropies and heat capacities of transfer of some aminoacids, including proline and hydroxyproline. The thermodynamic evidence is in agreement with the "structure-making" properties of these aminoacids.

A macroscopic consequence of the higher viscosity of aminoacid solutions is a lowering of the electrolytic conductance of Me_4NI and Bu_4NI as the aminoacid concentration increases (see the Λ_0 values of Table 2).

Not only the viscosity can reduce the ionic mobility; in fact, the Walden product $\Lambda_0\eta$ of Me_4NI and Bu_4NI also decreases markedly as the aminoacid concentration increases, up to about 0.2—0.3 mol kg^{-1} (Figure 1).

The reduced mobility of electrolytes in very dilute aminoacid solutions may be attributed to solvation effects.

At higher aminoacid concentration, most electrolytes show an increase in $\Lambda_0\eta$ due, presumably, to a decrease in the dielectric relaxation effect. Both, the ionic solvation and the dielectric relaxation, invoked to interpret the trend in the Walden function, mainly concern the small iodide ion and affect the large organic cations very little.

Fig. 1 shows that only the Walden functions of the Me_4NI-HP and Bu_4NI-HP solutions conform with the above general features. The proline solutions, however, show an anomalous decrease of $\Lambda_0\eta$ with increasing aminoacid concentration. This feature is particularly unexpected because the hydrophobic proline is supposed to reduce the free water molecules responsible for relaxation effects.

With the aim of partitioning the contributions of the anion and cation to the conductance, Λ_0^- and $\Lambda_0^-\eta$ values were calculated and listed in Table 2, assuming

$$\Lambda_0^- = n_- \Lambda_0 ,$$

where $n_- = \Lambda_0^-{}_{(H_2O)}/\Lambda_{0(H_2O)}$.

$\Lambda_0^-{}_{(H_2O)}$ at 25 °C is assumed to be 76.84 [17]. The $\Lambda_0^-\eta$ values of both electrolytes in the same aminoacid solutions would be expected to lie on the same curve if cation-solvent interactions were negligible.

Instead, $\Lambda_0^-\eta(Me_4NI)$ and $\Lambda_0^-\eta(Bu_4NI)$ differ, as may be seen in Figure 2.

On the above evidence, we assume that cation-solvent interactions play a role in the transport process of tetraalkylammonium iodides. Considering that a chemical affinity exists between organic cations and hydrophobic aminoacids, it may be assumed that tetraalkylammonium ions are surrounded by aminoacid molecules in solution and, consequently, that an increased hydrodynamic hindrance of the cation causes a decrease in $\Lambda_0^-\eta$ values.

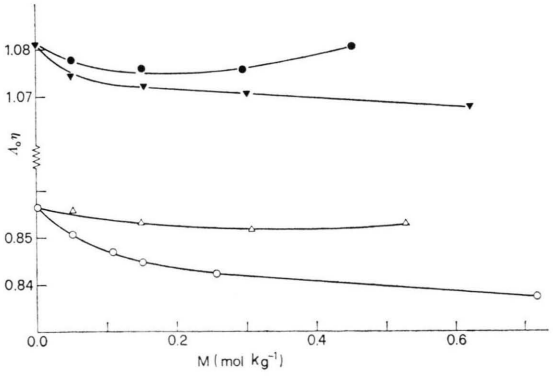

Fig. 1. Walden product $\Lambda_0\eta$ vs. molality of aminoacid, M, of Me_4NI in H_2O-Pro, ▼, of Me_4NI in H_2O-HP, ●, of Bu_4NI in H_2O-Pro, ○, and of Bu_4NI in H_2O-HP, △.

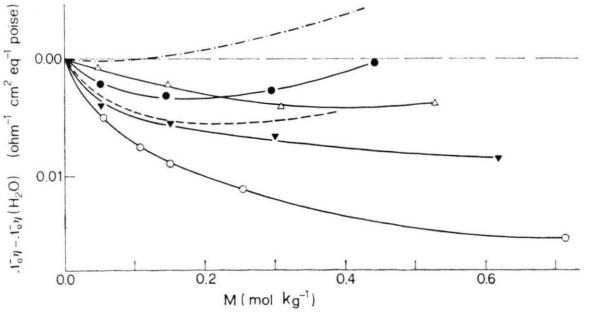

Fig. 2. Ionic products differences between $\Lambda_0^-\eta$ of water aminoacid solutions and $\Lambda_0^-\eta$ of water solutions vs. molal aminoacid concentration, M, concerning $I^-(Me_4NI\text{-}Pro\text{-}H_2O)$, ▼, $I^-(Me_4NI\text{-}HP\text{-}H_2O)$, ●, $I^-(Bu_4NI\text{-}Pro\text{-}H_2O)$, ○, and $I^-(Bu_4NI\text{-}HP\text{-}H_2O)$, △. Dashed curves (– · – · –) and (– – – –) refer to I^-(CsI-H_2O-alanine) and I^-(CsI-H_2O-serine) systems.

These effects are expected to be stronger in the more hydrophobic proline solution than in the hydroxyproline solution. Indeed, the $\Lambda_0{}^-\eta(H_2O\text{-HP})$-$\Lambda_0{}^-\eta(H_2O)$ differences are smaller than the $\Lambda_0{}^-\eta(H_2O\text{-Pro})$-$\Lambda_0{}^-\eta(H_2O)$ ones (Fig. 2). Moreover, curves of the ionic product difference of I^- with the larger and more hydrophobic tetrabutylammonium cation lie below that of I^- with tetramethylammonium cation.

For comparison the $\Lambda_0{}^-\eta(H_2O\text{-serine})$-$\Lambda_0{}^-\eta(H_2O)$ and $\Lambda_0{}^-\eta(H_2O\text{-}\alpha\text{-alanine})$-$\Lambda_0{}^-\eta(H_2O)$ differences for the I^-(CsI) ion are also plotted in Figure 2. These curves exhibit a marked increase above the 0.1—0.2 mol kg^{-1} concentration, which is stronger for hydrophobic alanine solutions than for serine solutions. Therefore, when organic cations are absent, the Walden products for the iodide ion follow the general behaviour.

Tetraalkylammonium iodides are known to form ion-pairs [12]. This association is anomalous because it is enhanced as the cation becomes larger and is due in part to a preference of organic cations to be surrounded by halide ions, rather than by water molecules [18]. Physical or chemical changes of the water structure can influence the associative behaviour of these salts. Justice [2] made a systematic study of tetraalkylammonium bromides and found a decrease in the association constant K_A with increase in the content of glycine in water.

The K_A values of Bu_4NI in H_2O-Pro and in H_2O-HP solutions, calculated by means of a simplified equation for associated electrolytes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + E\,c\ln(6E_1\,c) + L\,c - K_A\,c\,\Lambda \quad (9)$$

with the Fuoss method [19], range between 4.4 and 5.1 $molal^{-1}$ for proline and hydroxyproline systems, respectively (Table 2). The reinforcement of the water structure, due to the presence of the hydrophobic aminoacid, seems to compensate the weakness of the electrostatic ion-ion interactions in highly polar mixtures.

A preliminary study of the ionic association in Me_4NI gave less tractable results which were not further elaborated.

Further work is in progress.

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