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Viscosity *B*-Coefficients of L-Proline and L-Hydroxyproline and the Effect of added Methanol

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The viscosity *B*-coefficients for aqueous solutions of L-proline and L-hydroxyproline containing various concentrations of methanol have been determined at 298.15, 308.15 and 318.15 K. Viscosity *B*-coefficients for both the amino acids are positive and increase as the temperature is increased. The values of *B*-coefficients in the mixed solvents first decrease and then increase after attaining a minimum at about 20% (w/w) methanol–water mixture.

MIXED solvents are used intensively in chemistry, biology and industry to control factors such as solubility, stability of systems and kinetics of reactions. In continuation of our earlier work[1-4] on the aqueous and mixed aqueous solutions of amino acids, the measured viscosities of L-proline and L-hydroxyproline over a range of concentration in water and methanol–water mixtures have now been reported. The viscosity *B*- and *D*-coefficients and the differential activation energy $\Delta E^* = E^*_{soln} - E^*_{solvent}$ have been calculated from these data and discussed qualitatively.

Experimental

The amino acids (E. Merck, G.R.) were used as such. Methanol (AnalaR) was purified by the recommended method[5]. All the solutions were prepared on molar basis in double-distilled degassed water, and vacuum correction was made for each weight.

The viscosity measurements were carried out using Cannon–Ubbelhode viscometer in a thermostat (±0.01°) with a Beckmann thermometer. The flow time was determined with a stop-watch of 0.1 s least count. The efflux times of the viscometer were 609.9, 495.8 and 414.4 s for water at 298.15, 308.15 and 318.15 K, respectively. Viscosity was calculated from average flow time (t) and density (ρ), using the relation,

$$\eta = \rho\,(At - B/t) \qquad (1)$$

where, the calibrating constants A and B were evaluated by least-square fitting of efflux time of water of known viscosity and density at 298.15, 308.15 and 318.15 K to equation (1). The procedure for density measurements have been described before[4]. The accuracy of density and viscosity measurements were $\pm 2\times10^{-4}$ g cm^{-3} and $\pm 4\times10^{-4}$ centipoise, respectively.

Results and Discussion

The viscosity and relative viscosity of L-proline and L-hydroxyproline in methanol–water mixtures as a function of concentration at 298.15, 308.15 and 318.15 K are reported in Table 1. Experimental values of relative viscosity are fitted into equation (2) by the least-squares method,

$$\eta_r = \eta/\eta_0 = 1 + Bc + Dc^2 \qquad (2)$$

where, η is the viscosity of the solution and η_0 is that of the solvent, c is the molar concentration of the solute, and B and D are the empirical coefficients. Coefficient B measures the size and shape effect of the solute as well as the structural effects induced by the solute–solvent interactions[6] and is the major contributor to the relative viscosity in equation (2). The coefficient D is relatively small in magnitude and its significance is not clearly understood[7]. The derived values of *B*- and *D*-coefficients, together with the standard errors are given in Table 2 alongwith the literature values. The *B*-coefficients obtained for L-proline (0.277±0.004) and L-hydroxyproline (0.279±0.004) in aqueous system are in good agreement with those (0.279 and 0.281, respectively) obtained by Ogawa *et al.*[8]. However, lack of viscosity data at 308.15 and 318.15 K in the literature puts a limitation on the detailed comparative study of these amino acids. Tsangaris and Martin[9] reported *B*-coefficients for a large number of amino acids at 30, 35 and 40°, which are lower than the values reported by other workers[8,10,11]. Their values for L-proline and L-hydroxyproline are also in poor agreement with the present values.

It is evident from Fig. 1 that *B*-coefficient value of both the amino acids first decreases and then increases after attaining a minimum. The minimum in *B* value is obtained at 20% (w/w) of methanol. This region of solvent composition may be concluded to be the most structured region. The

TABLE 1—VISCOSITY AND RELATIVE VISCOSITY OF L-PROLINE AND L-HYDROXYPROLINE IN METHANOL – WATER AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Methanol % (w/w)	C mol dm^{-3}	$\eta \times 10^4$ kg^{-1} s^{-1} 298.15 K	η_r	C mol dm^{-3}	$\eta \times 10^4$ kg^{-1} s^{-1} 308.15 K	η_r	C mol dm^{-3}	$\eta \times 10^4$ kg^{-1} s^{-1} 318.15 K	η_r
	L-Proline								
0	0	8.909	—	0	7.190	—	0	5.963	—
	0.069 28	9.081	1.019 3	0.069 07	7.338	1.020 6	0.068 80	6.097	1.022 5
	0.088 51	9.133	1.025 2	0.088 38	7.383	1.026 8	0.088 04	6.135	1.028 9
	0.118 13	9.219	1.034 8	0.117 73	7.451	1.036 3	0.117 29	6.197	1.039 3
	0.147 61	9.294	1.043 2	0.147 10	7.519	1.045 8	0.146 53	6.258	1.049 5
	0.243 91	9.566	1.073 8	0.243 16	7.746	1.077 3	0.242 22	6.462	1.083 7
	0.339 10	9.849	1.105 6	0.338 03	7.987	1.110 8	0.336 71	6.674	1.119 2
	0.432 53	10.127	1.136 7	0.431 14	8.219	1.143 2	0.429 42	6.894	1.156 2
	0.523 64	10.448	1.172 7	0.521 91	8.453	1.175 7	0.519 87	7.123	1.194 5
10	0	11.511	—	0	9.078	—	0	7.386	—
	0.069 12	11.708	1.017 1	0.068 89	9.246	1.018 5	0.068 57	7.536	1.020 3
	0.088 82	11.764	1.022 0	0.088 52	9.299	1.024 3	0.088 14	7.579	1.026 2
	0.119 87	11.861	1.030 4	0.119 48	9.378	1.033 0	0.118 92	7.651	1.035 9
	0.145 11	11.952	1.038 3	0.144 55	9.448	1.040 8	0.143 93	7.712	1.044 2
	0.195 94	12.115	1.052 5	0.195 24	9.587	1.056 1	0.194 38	7.838	1.061 2
	0.240 43	12.268	1.065 8	0.239 52	9.722	1.070 9	0.238 44	7.952	1.076 6
	0.350 46	12.680	1.101 6	0.349 09	10.055	1.107 6	0.347 53	8.252	1.117 2
	0.516 71	13.384	1.162 7	0.514 76	10.632	1.171 2	0.512 41	8.753	1.185 1
20	0	14.123	—	0	10.901	—	0	8.706	—
	0.068 42	14.326	1.014 4	0.068 09	11.073	1.015 8	0.067 74	8.860	1.017 8
	0.087 06	14.387	1.018 7	0.086 67	11.124	1.020 5	0.086 22	8.907	1.023 1
	0.114 53	14.479	1.025 2	0.114 02	11.202	1.027 6	0.113 41	8.974	1.030 8
	0.143 81	14.573	1.031 9	0.143 13	11.281	1.034 9	0.142 39	9.047	1.039 2
	0.190 32	14 739	1.043 6	0.189 46	11.411	1.046 8	0.188 45	9.168	1.053 1
	0.283 79	15.093	1.068 7	0 282 47	11.690	1 072 4	0.280 96	9.429	1.083 1
	0 373 84	15.463	1.094 9	0.372 11	11.999	1.100 8	0.370 07	9.707	1.115 0
	0 462 51	15.887	1.124 9	0.460 29	12.321	1.130 3	0.457 84	10.002	1.148 9
30	0	15.576	—	0	12.032	—	0	9.564	—
	0.066 09	15.836	1.016 7	0.065 71	12.246	1.017 8	0.065 29	9.750	1.019 5
	0.086 37	15.920	1.022 1	0.085 86	12.313	1.023 4	0.085 35	9.811	1.025 8
	0.115 44	16.042	1.029 9	0.114 67	12.413	1.031 7	0.114 04	9.898	1.035 0
	0.142 02	16.155	1.037 2	0.141 20	12.509	1.039 7	0.140 32	9.979	1.043 4
	0.187 14	16.356	1.050 1	0.186 05	12.673	1.053 3	0.184 89	10.122	1.058 4
	0.278 74	16.797	1.078 4	0.277 07	13.016	1.081 8	0.275 36	10.424	1.089 9
	0.369 13	17.244	1.107 1	0.366 94	13.383	1.112 3	0.364 54	10.747	1.123 7
	0.458 71	17.747	1.139 4	0.456 02	13.770	1.144 5	0.453 12	10.084	1.158 9
	L-Hydroxyproline								
0	0	8.909	—	0	7.190	—	0	5.963	—
	0.077 02	9.107	1.022 2	0.076 79	7.362	1.023 9	0 077 49	6.112	1.025 0
	0.087 92	9.137	1.025 6	0.087 81	7.385	1.027 2	0.087 28	6.134	1.028 7
	0.124 35	9.230	1.036 1	0.124 01	7.469	1 038 8	0.123 56	6.207	1.041 0
	0.154 08	9 316	1.045 7	0.153 61	7.546	1.049 5	1.153 02	6.272	1.051 8
	0.196 56	9.449	1.060 6	0.195 39	7.648	1 063 7	0.195 20	6.361	1.066 8
	0.245 61	9.589	1.076 4	0 244 73	7.775	1.081 4	0.243 92	6.473	1.085 5
	0.341 11	9.885	1.109 6	0.340 01	8.021	1.115 6	0.338 69	6 689	1.121 8
	0.456 53	10.277	1.153 6	0.455 05	8.364	1.163 3	0.453 30	6.973	1.169 4
10	0	11.511	—	0	9.078	—	0	7.386	—
	0.068 24	11.708	1.017 1	0.067 99	9.243	1.018 2	0 067 77	7.530	1.019 5
	0.089 22	11.770	1 022 5	0.088 90	9.298	1.024 3	0.088 52	7.579	1.026 2
	0.127 61	11.893	1.033 2	0.127 14	9.402	1.035 7	0.126 59	7.668	1 038 2
	0 145 76	11.952	1.038 3	0.145 21	9.456	1.041 7	0.144 58	7.712	1.044 2
	0.192 12	12.106	1.051 7	0.191 41	9.595	1.057 0	0.190 61	7.826	1.059 6
	0.290 18	12.469	1.083 3	0.289 12	9.891	1.089 6	0.287 84	8.083	1.094 4
	0.380 95	12.835	1.115 0	0.379 51	10.201	1.123 7	0.377 91	8.341	1.129 3
	0.471 33	13.224	1.148 8	0.469 57	10.537	1.160 7	0.467 48	8.625	1.167 8
20	0	14.123	—	0	10.901	—	0	8.706	—
	0.070 31	14.329	1.014 6	0.069 99	11.075	1.016 0	0.069 61	8.864	1.018 1
	0.087 57	14.390	1.018 9	0.087 18	11.125	1.020 6	0.086 73	8.903	1.022 6
	0.113 78	14.480	1.025 3	0 113 27	11.199	1.027 4	0.112 66	8.965	1.029 8
	0.142 92	14.581	1.032 4	0.142 26	11.287	1.035 4	0.141 51	9.043	1.038 7
	0.216 76	14.862	1 052 3	0.215 74	11.519	1.056 7	0.214 63	9.235	1.060 8
	0.298 59	15.217	1.077 5	0.297 55	11.806	1.083 0	0.296 34	9.470	1.088 7
	0.383 29	15.607	1.105 1	0.381 53	12.132	1.112 9	0.379 49	9.738	1.118 5
	0.463 65	16.056	1.136 9	0.461 89	12.480	1.144 9	0.460 03	10.031	1.152 2

(Table 1 contd.)

30	0	15.576	—	0	12.032	—	0	9.564	—
	0.065 55	15.824	1.015 9	0.065 16	12.245	1.017 7	0.064 76	9.743	1.018 7
	0.084 52	15.901	1.020 9	0.084 03	12.310	1.023 1	0.083 49	9.798	1.024 5
	0.115 07	16.028	1.029 0	0.114 41	12.421	1.032 3	0.113 67	9.891	1 034 2
	0.142 54	16.144	1.036 5	0.141 72	12.518	1.040 4	0.140 83	9.972	1.042 7
	0.187 16	16.344	1.049 3	0.186 09	12.689	1.054 6	0.184 91	10.122	1.057 3
	0.277 71	16.771	1.076 7	0.276 08	13.055	1.085 1	0.275 09	10.416	1.089 1
	0.369 11	17.243	1.107 0	0.368 98	13.453	1.118 1	0.364 72	10.739	1.229 9

TABLE 2—THE VALUES OF VISCOSITY *B*- AND *D*-COEFFICIENTS, STANDARD ERRORS AND dB/dT VALUES OF L-PROLINE AND L-HYDROXYPROLINE IN METHANOL–WATER MIXTURES AT DIFFERENT TEMPERATURES

Methanol % (w/w)	*B* (dm^3 mol^{-1}) Temp. (K)			*D* (dm^6 mol^{-2}) Temp (K)			dB/dT dm^3 mol^{-1} K^{-1}
	298.15	308.15	318.15	298.15	308.15	318.15	
L-Proline							
0	0.277±0.004 (0.279)[a]	0.297±0.003	0.321±0.002	0.098±0.008	0.081±0.006	0.100±0.003	0.002 20
10	0.237±0 004	0.260±0.001	0.285±0.001	0.151±0 008	0.140±0.002	0.150±0.002	0.002 40
20	0.201±0.002	0.225±0.003	0 253±0.002	0.145±0.004	0.122±0.006	0.156±0 004	0 002 60
30	0.243±0 002	0.263±0.001	0.291±0.001	0.130±0.004	0.118±0.003	0.133±0.002	0.002 45
L-Hydroxyproline							
0	0.279±0.004 (0.281)[a]	0.300±0.003	0.318±0.002	0.128±0.008	0.127±0.007	0.123±0.004	0.001 95
10	0.233±0.002	0.258±0 003	0.281±0.002	0.165±0.003	0.180±0.007	0.168±0.004	0.002 15
20	0.195±0.004	0.217±0.002	0.245±0.002	0.213±0.009	0.209±0 004	0.181±0.005	0.002 50
30	0.234±0.001	0.262±0.002	0.280±0.003	0.152±0.002	0.160±0.005	0.156±0.007	0.002 25

[a]Ref. 8.

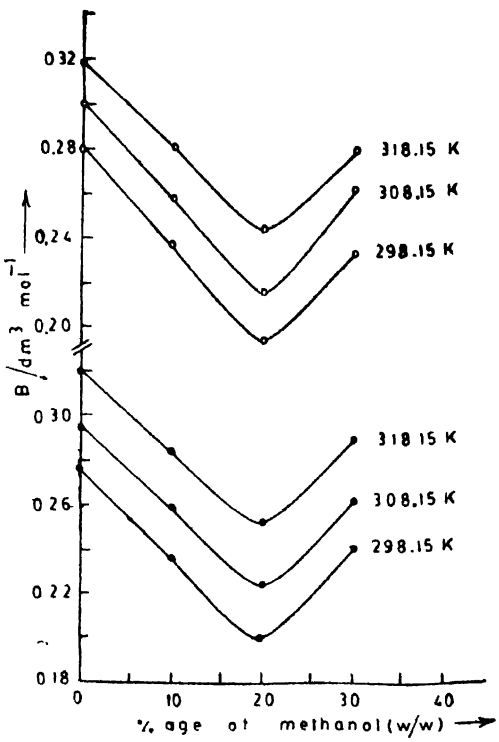

Fig. 1. Plots of viscosity *B*-coefficients vs percentage of methanol at different temperatures : (●) L-proline, (○) L-hydroxyproline.

minima in *B* values, indicating maximum solute–solute interactions, lead to maximum breaking of the solvent structure on addition of amino acids. Feakins *et al.*[12] studied the effect of added methanol on *B*-coefficient of the electrolytes and they observed that small amount of methanol enhanced the structure of the mixture compared with that of water and an increase in the structure-breaking effect caused a decrease in *B* values of the electrolytes.

Table 2 shows that the values of *B*-coefficients of both the amino acids increase with increase of temperature in aqueous and mixed aqueous solvent systems. The dB/dT values of the amino acids are also presented in Table 2. A positive dB/dT value indicates a structure-breaking solute, and a negative the structure-making one. The dB/dT values of both the amino acids are positive but the magnitude in presence of the added methanol is higher which goes on increasing till the solvent attained the maximum structure (Fig. 2). The results thus again support the interpretation that both the amino acids are even more effective as structure-breakers in methanol–water mixtures than in water, at least up to 20% (w/w) of methanol where maxima is observed for dB/dT values.

Activation energies (E^*) of viscous flow in the temperature range 25–45° of both the amino acids in methanol–water mixtures have been calculated at a single concentration (0.1 mol dm^{-3}) by using the Arrhenius equation[11]. The E^* values have

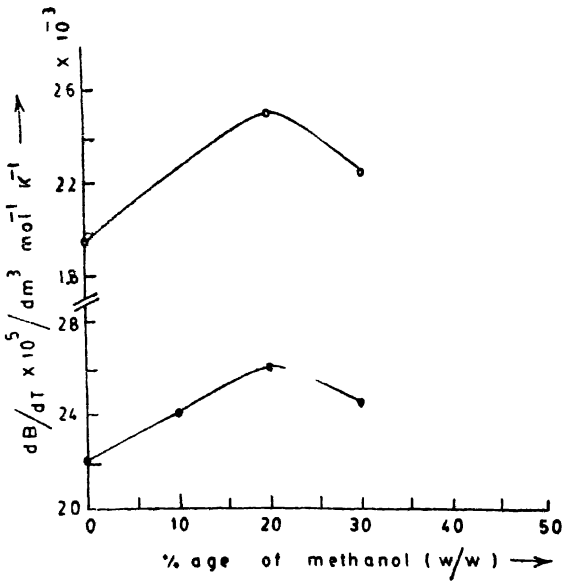

Fig. 2. Plots of dB/dT vs percentage of methanol: (●) L-proline and (○) L-hydroxyproline.

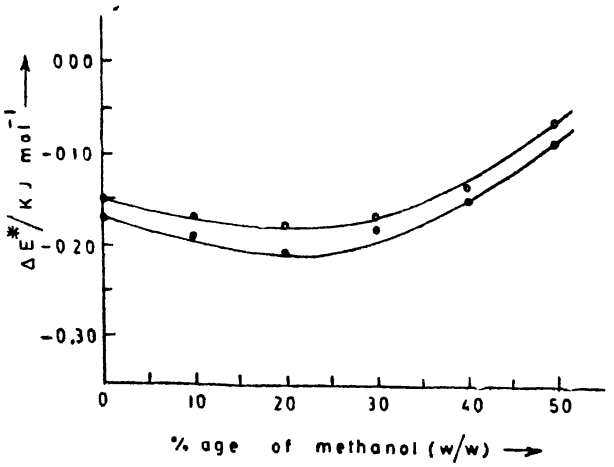

Fig. 3. Plots of ΔE^* vs percentage of methanol at 0.1 M: (●) L-proline and (○) L-hydroxyproline.

been used to calculate the differential activation energies of viscous flow (ΔE^*) using the relation,

$$\Delta E^* = E_{soln} - E^{\circ}_{solv} \qquad (3)$$

Fig. 3 shows the variation of ΔE^* against percentage of methanol. It is apparent that in the mixed solvents the ΔE^* values are more negative than those found in pure water, confirming the enhanced structure-breaking by both the amino acids in the presence of methanol. Thus upto 20% (w/w) of methanol, the viscosity data suggest that minima in B and ΔE^* values and the maxima in dB/dT values correspond to the maximum structure-breaking by the amino acids as a result of maximum solute–solvent interactions in methanol–water mixtures.

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