VISCOSITY B-COEFFICIENTS FOR L-SERINE AND L-THREONINE IN METHANOL-WATER MIXTURES

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The relative viscosities and densities of L-serine in water, 10%, 20% and 30% w/w methanol-water mixtures and of L-Threonine in water, 10%, 15% and 20% w/w methanol-water mixtures have been measured at 25°C, 35°C and 45°C respectively. The variation of the relative viscosity with molarity has been fitted to the Jones-Dole equation by the method of least squares and the viscosity B-coefficients calculated. The values of B-coefficient of both the solutes decrease with increase in solvents, but in case of L-serine increase after attaining minimum at about 20% w/w methanol-water mixture. The dB/dT values are positive for both the amino acids and indicate structure breaking behaviour of these amino acids in methanol-water mixtures.

Aqueous solutions have always received good attention especially with regard to the exceptional properties of water as solvent. Most of the studies on dipolar ions, particularly of amino acids have been carried out by a number of workers [1-4] in aqueous solutions. Recently mixed aqueous solvents have been used extensively in chemistry and other fields to control factors e.g. stability and reactivity of systems. In continuation with our studies on the aqueous and mixed aqueous solutions of amino acids [5,6], the systematic variation of viscosities and viscosity B-coefficients of L-serine and L-Threonine are reported over a range of concentrations in water and methanol-water mixtures. As the temperature effect on solvation has not been extensively studied, the amino acids have been studied at three temperatures.

EXPERIMENTAL

L-Serine and L-Threonine of extra pure quality were obtained from Sigma Chemicals, U.S.A. and were dried without any further purification in an air oven at 150°C for an hour and then under vacuum for 24 hours. These were then kept over anhydrous calcium chloride in a vacuum desicator desicator till required for use. Freshly distilled solvents were used in each experiment. Methanol (A.R., B.D.H.) was purified by recommended method. Doubly distilled water was used for making up the solutions and buoyancy corrections were applied to all weighings. L-Threonine was studied up to 20% methanol due to solubility limitations, serine was was studied upto 30% methanol.

Viscosity measurements were made with Cannon-Ubbelhode viscometer in the thermostat constant to $\pm$ 0.01 C. The flow time was determined with a stop watch of 0.1 s least count. The efflux times of the viscometer were 612.0, 414.0, 495.9 sec. for water at 25°C, 35°C and 45°C respectively, so as to minimise the kinetic energy correction. At least 6 determinations were made for each solution and difference of any two readings did not exceed 0.3 sec.

The densities of solutions, were determined with the aid of a single stem pyknometer of about 14 cm^3 capacity, accuracy being $\pm$ 2×10^{-4} g cm^{-3} and these were used to calculate relative viscosities.

RESULTS AND DISCUSSION

The results are given in Table 1 and 2. The data for the relative viscosities are fitted by the least-square method to the extended Jones-Dole equation [8].

$$\eta / \eta_0 = 1 + BC + DC^2 \quad .. \; .. \quad (1)$$

where B is the coefficient for solute-solvent Interaction and D for solute-solute interaction, and C is the molarity of solute.

The calculated B-coefficients together with standard deviation, and values for the temperature effect on the coefficients (dB/dT) are listed in Table 3. The B-coefficients obtained for L-serine (0.223$\pm$0.001) and L-Threonine (0.331$\pm$0.001) in aqueous system are in good agreement with those (0.225, 0.335 respectively) obtained by Ogawa, Yasuda and Mizutani [9] L-Serine and L-Threonine are hydroxy amino acids i.e substitution of H by OH group in alanine and α-amino-n-butyric acid gives rise to L-Serine and L-Threonine. In order

TABLE 1

DENSITY, VISCOSITY AND RELATIVE VISCOSITY OF L-SERINE IN METHANOL-WATER MIXTURES AT DIFFERENT TEMPERATURES AND CONCENTRATIONS

[Amino acid] (mol dm^{-3})	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} sec^{-1})	η/η_o	[Amino acid] (mol dm^{-3})	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} sec^{-1})	η/η_o	[Amino acid] (mol dm^{-3})	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} sec^{-1})	η/η_o
	at 25°C				at 35°C				at 45°C		
0 % methanol											
0	997.07	8.909	——	0	994.06	7.190	——	0	990.25	5.963	——
0.07438	1000.36	9.048	1.0156	0.07415	993.33	7.312	1.0170	0.07387	993.50	6.079	1.0194
0.14814	1003.59	9.216	1.0345	0.14769	1000.52	7.453	1.0366	0.14713	996.70	6.210	1.0414
0.19723	1005.73	9.344	1.0488	0.19664	1002.68	7.555	1.0508	0.19589	998.88	6.300	1.0505
0.24603	1007.89	9.465	1.0624	0.24528	1004.80	7.655	1.0647	0.24434	1000.97	6.383	1.0704
0.29525	1010.02	9.593	1.0768	0.29285	1006.88	7.759	1.0791	0.29173	1003.05	6.468	1.0847
0.34168	1012.02	9.711	1.0900	0.34064	1008.94	7.857	1.0928	0.33936	1005.14	6.558	1.0998
0.43529	1016.08	9.977	1.1199	0.43396	1012.99	8.071	1.1225	0.43231	1009.14	6.738	1.1300
0.53093	1020.17	10.259	1.1515	0.52935	1017.13	8.302	1.1546	0.52737	1013.32	6.920	1.1605
0.62169	1024.10	10.573	1.1868	0.61984	1021.06	8.527	1.1859	0.61745	1017.11	7.105	1.1915
10% methanol											
0	980.15	11.401	——	0	976.78	8.922	——	0	972.65	7.447	——
0.08879	984.20	11.614	1.0187	0.08848	980.80	9.098	1.0197	0.08811	976.66	7.623	1.0236
0.13479	986.26	11.740	1.0297	0.13433	982.87	9.205	1.0317	0.13376	978.74	7.702	1.0342
0.17454	988.10	11.841	1.0386	0.17393	984.69	9.287	1.0409	0.17320	980.52	7.795	1.0467
0.25449	991.75	12.048	1.0567	0.25358	988.19	9.466	1.0610	0.25254	984.14	7.963	1.0693
0.33543	995.36	12.281	1.0772	0.33427	991.92	9.639	1.0804	0.33285	987.71	8.126	1.0912
0.42819	999.52	12.539	1.0998	0.42671	996.05	9.852	1.1042	0.42490	991.83	8.321	1.1174
0.52234	1003.65	12.816	1.1241	0.52054	1000.20	10.071	1.1288	0.51830	995.89	8.528	1.1451
0.61188	1007.94	13.114	1.1502	0.60957	1004.14	10.282	1.1524	0.60704	999.97	8.713	1.1700
20% methanol											
0	964.93	13.789	——	0	960.70	10.563	——	0	955.77	8.800	——
0.05230	967.37	13.937	2.0107	0.05207	963.15	10.685	1.0115	0.05181	958.21	8.919	1.0135
0.08742	968.99	14.055	1.0193	0.08704	964.77	10.783	1.0208	0.08659	959.83	9.007	1.0235
0.13272	971.14	14.174	1.0279	0.13213	966.84	10.883	1.0303	0.13146	961.89	9.109	1.0351
0.18161	973.38	14.329	1.0392	0.18082	969.13	11.008	1.0421	0.17989	964.17	9.223	1.0481
0.23786	975.95	14.515	1.0526	0.23683	971.74	11.156	1.0561	0.23561	966.73	9.368	1.0645
0.33032	980.20	14.824	1.0750	0.32890	976.00	11.415	1.0806	0.32719	970.92	9.596	1.0904
0.42171	984.38	15.159	1.0993	0.41987	980.10	11.672	1.1050	0.41769	975.01	9.831	1.1172
30% methanol											
0	949.45	15.353	——	0	944.25	11.710	——	0	938.04	9.716	——
0.07093	952.75	15.595	1.0158	0.07055	947.57	11.898	1.0160	0.07008	941.34	9.911	1.0201
0.08602	953.49	15.638	1.0186	0.08590	952.20	11.945	1.0201	0.08498	942.03	9.947	1.0238
0.09495	953.89	15.676	1.0210	0.09444	948.72	11.968	1.0220	0.09384	942.77	9.973	1.0264
0.13059	955.52	15.803	1.0293	0.12988	950.33	12.069	1.0306	0.12902	944.09	10.072	1.0366
0.17869	957.72	15.971	1.0402	0.17772	952.52	12.212	1.0429	0.17656	946.29	10.214	1.0512
0.20641	958.98	16.066	1.0464	0.20530	953.82	12.295	1.0499	0.20396	947.59	10.291	1.0592
0.23404	960.29	16.171	1.0533	0.23277	955.08	12.385	1.0576	0.23124	948.79	10.375	1.0678
0.24655	968.82	16.213	1.0560	0.24523	955.67	12.415	1.0602	0.24362	949.38	10.406	1.0710
0.30032	963.25	16.415	1.0692	0.29871	958.10	12.586	1.0748	0.29675	951.80	10.568	1.0877

TABLE 2

DENSITY, VISCOSITY AND RELATIVE VISCOSITY OF L-THREONINE IN METHANOL-WATER MIXTURES AT DIFFERENT TEMPERATURES AND CONCENTRATIONS

[Amino acid] (mol dm^{-3})	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} sec^{-1})	η/η_o	[Amino acid] (mol dm^{-3})	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} sec^{-1})	η/η_o	[Amino acid] (mol dm^{-3})	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} sec^{-1})	η/η_o
	at 25°C				at 35°C				at 45°C		
0 % methanol											
0	997.07	8.909	———	0	994.06	7.190	———	0	990.25	5.963	———
0.04991	999.16	9.060	1.0169	0.04976	996.14	7.318	1.0178	0.04957	992.35	6.078	1.0193
0.08907	1000.84	9.173	1.0296	0.08880	997.83	7.420	1.0320	0.08846	994.01	6.172	1.0350
0.09966	1001.21	9.224	1.0353	0.09937	998.21	7.445	1.0360	0.09899	994.40	6.196	1.0391
0.14775	1003.20	9.387	1.0536	0.14731	1000.21	7.588	1.0553	0.14675	996.40	6.314	1.0589
0.18851	1004.90	9.536	1.0704	0.18796	1001.94	7.704	1.0715	0.18724	998.09	6.419	1.0765
0.23478	1006.82	9.711	1.0900	0.23409	1003.84	7.842	1.0907	0.23320	1000.02	6.534	1.0957
0.30925	1009.92	10.012	1.1238	0.30833	1006.94	8.068	1.1221	0.30716	1003.08	6.728	1.1283
0.34898	1011.55	10.171	1.1416	0.34795	1008.56	8.204	1.1410	0.34663	1004.73	6.834	1.1461
0.37730	1012.71	10.298	1.1559	0.37609	1009.73	8.302	1.1546	0.37466	1005.87	6.918	1.1601
0.42210	1014.58	10.502	1.1788	0.42087	1011.60	8.447	1.1748	0.41925	1007.72	7.039	1.1804
10 % methanol											
0	980.15	11.401	———	0	976.78	8.922	———	0	972.65	7.447	———
0.04907	982.39	11.714	1.0274	0.04890	979.00	9.067	1.0162	0.04870	974.88	7.579	1.0177
0.08758	984.10	11.821	1.0368	0.08728	980.79	9.181	1.0290	0.08691	976.64	7.688	1.0324
0.11652	985.44	12.085	1.0600	0.11612	982.06	9.271	1.0391	0.11563	977.92	7.770	1.0434
0.14533	988.55	11.924	1.0459	0.14483	983.38	9.358	1.0489	0.14423	979.31	7.855	1.0548
0.18545	986.80	12.264	1.0757	0.18480	985.12	9.485	1.0631	0.18403	981.02	7.963	1.0693
0.23100	990.62	12.567	1.1023	0.23019	987.13	9.632	1.0796	0.22925	983.08	8.103	1.0881
0.30435	993.90	12.649	1.1095	0.30326	990.36	9.872	1.1065	0.30203	986.33	8.327	1.1182
0.32564	994.88	12.649	1.1095	0.32447	991.31	9.942	1.1143	0.32315	987.27	8.398	1.1277
0.37687	997.17	12.885	-	0.37549	993.51	10.120	1.1343	0.37386	989.21	8.562	1.1497
15 % methanol											
0	971.53	12.750	———	0	987.55	9.740	———	0	963.46	8.124	———
0.05801	974.39	12.906	1.0122	0.05778	970.42	9.740	1.0134	0.05753	966.25	8.248	1.0153
0.07186	975.05	12.933	1.0143	0.07157	971.05	9.910	1.0174	0.07126	966.88	8.283	1.0196
0.08684	975.77	12.991	1.0189	0.08648	971.78	9.943	1.0208	0.08611	967.58	8.311	1.0230
0.13499	978.10	13.142	1.0307	0.13444	974.12	10.062	1.0330	0.13385	969.85	8.419	1.0363
0.18053	980.30	13.297	1.0429	0.17980	976.34	10.184	1.0456	0.17900	972.00	8.524	1.0492
0.22914	982.62	13.481	1.0573	0.22822	978.65	10.322	1.0597	0.22719	974.26	8.647	1.0644
0.26509	984.36	13.603	1.0669	0.26403	980.43	10.423	1.0701	0.26283	975.95	8.729	1.0745
0.30482	986.22	13.766	1.0797	0.30362	982.34	10.545	1.0826	0.30222	977.82	8.826	1.0864
0.32974	987.39	13.888	1.0892	0.32846	983.54	10.622	1.0905	0.32693	978.97	8.890	1.0943
20 % methanol											
0	964.93	13.789	———	0	960.70	10.562	———	0	955.77	8.800	———
0.05036	967.51	13.895	1.0077	0.05014	963.24	10.658	1.0091	0.04988	958.30	8.897	1.0110
0.05763	967.88	13.897	1.0078	0.05737	963.59	10.684	1.0115	0.05708	958.67	8.907	1.0121
0.07139	968.91	13.957	1.0122	0.07107	964.32	10.709	1.0139	0.07071	959.38	8.941	1.0160
0.08626	969.34	14.003	1.0155	0.08588	965.03	10.745	1.0173	0.08544	960.09	8.973	1.0196
0.13411	971.77	14.160	1.0269	0.13351	967.42	10.874	1.0295	0.13283	962.46	9.085	1.0324
0.17938	974.07	14.347	1.0405	0.17857	969.68	11.029	1.0442	0.17766	964.70	9.209	1.0465
0.22772	976.55	14.575	1.0570	0.22668	972.08	11.199	1.0603	0.22552	967.07	9.356	1.0632
0.26347	978.34	14.771	1.0712	0.26227	973.88	11.342	1.0738	0.26092	968.85	9.466	1.0757
0.30015	980.18	14.990	1.0871	0.29877	975.68	11.510	1.0897	0.29723	970.66	9.591	1.0899

TABLE 3

VISCOSITY B-COEFFICIENT AND dB/dT OF L-SERINE AND L-THREONINE IN METHANOL-WATER MIXTURES

%(wt/wt) methanol	Temperature (°C)	B/dm³/mol⁻¹		dB/dT/dm³/mol⁻¹ K⁻¹	
		L-Serine	L-Threonine	L-Serine	L-Threonine
0	25	0.223+0.001	0.331+0.001	+0.00260	+0.00275
	35	0.239+0.001	0.353+0.001		
	45	0.275+0.001	0.386+0.001		
10	25	0.212+0.001	0.302+0.001	+0.00275	+0.00295
	35	0.219+0.004	0.327+0.001		
	45	0.267+0.001	0.362+0.001		
15	25	-	0.199+0.002	-	+0.00310
	35	-	0.225+0.001		
	45	-	0.261+0.001		
20	25	0.200+0.000	0.130+0.002	+0.00305	+0.00355
	35	0.220+0.001	0.161+0.001		
	45	0.261+0.001	0.202+0.001		
30	25	0.219+0.001	-	+0.00285	-
	35	0.225+0.001	-		
	45	0.275+0.001	-		

to see the effect quantitatively and qualitatively of two functional groups, comparison has been made with B-coefficient of alanine (0.2525) [1] and amino-n-butyric acid (0.3606)[10] at 25°C. It is evident that the magnitude of B-coefficients of hydroxy amino acids are less than those having one-functional group. It may be due to the fact that hydroxyl groups reduce the hydrophobic propensity of the neighbouring alkyl group[11-13].

It can be seen from Tables that B-coefficients of both amino acids decrease with the addition of methanol except in 30% w/w methanol-water mixture in case of L-serine. The decrease can be attributed to the fact that the structure breaking properties of both amino acids are enhanced in methanol-water mixtures. In terms of structural temperature methanol can be interpreted as having lowered the structural temperature of the solutions, and therefore may be considered as a structure maker. In case of serine it is observed that minimum in B value is obtained corresponding to 20% methanol. This region of solvent composition is reported to be more structured [14,15]. Thus more structured the solvent, greater will be the structure breaking.

The values of B-coefficients of both amino acids increase with increase of temperature in aqueous and mixed aqueous solvent systems as can be seen in Table 2. The positive dB/dT is normally associated with structure breaking, while the negative dB/dT is associated with structure making in

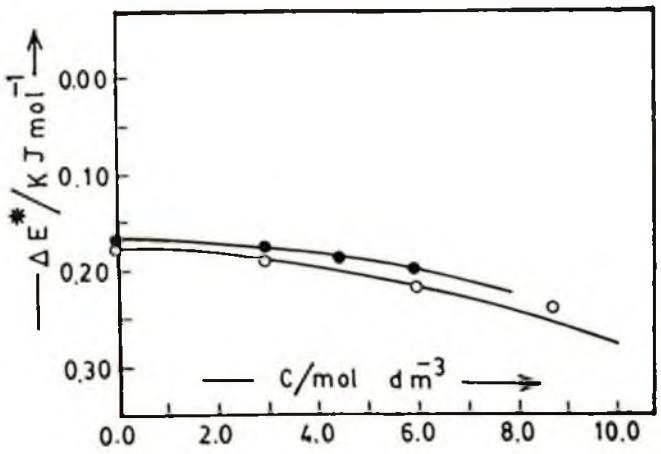


Fig. 1 Plot of E^* of L-Serine and L-Threonine at 0.1 mol dm vs. molarity of methanol (o-L-Threonine, o-L-Serine)

structured solvents [4,16]. In Table 3 all dB/dT values are positive but the magnitude in the presence of co-solvent is higher which goes on increasing till the solvent has attained the maximum structure. The results are again indicative of large structure breaking effect in the presence of co-solvent.

If the assumption is made that Arrhenius equation is valid over a temperature range, say 25-45°C, $E^*_{H_2O}$ may be calculated from the equation which

expresses the viscosity as a function of temperature as:

$$\ln \eta = \alpha + E^*/RT \quad \ldots\ldots\ldots(2)$$

where E* is the activation energy for viscous flow expressed in kilo joules per mole. From equation(2), the differential activation energies, $\Delta E^* = E^*_{Solution} - E^*_{Solvent}$ for both the amino acids are computed at a given concentration (0.1 mol dm) and plotted against the molarity of methanol (Fig. 1). ΔE^* values are more negative in mixed solvents than those found in aqueous medium, confirming the enhanced structure breaking of both the amino acids in the presence of methanol.

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