THE VISCOSITIES OF AQUEOUS SOLUTIONS OF SOME AMINO ACIDS

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Viscosity measurements have been made at 298.15, 308.15 and 318.15° K on aqueous solutions of some amino acids. The viscosity B and D-coefficients have been calculated by a linear extrapolation using the least-squares method. The activation energy for viscous flow, E*, and the differential activation energy $\Delta E^* = E^*_{soln.} - E^*_{H_2O}$ have been calculated for solutions of these amino acids. The results have been used to discuss the solute-solvent interactions.

Amino acids, the building blocks of proteins retain the prime significance as models for determining the thermodynamic behaviour of proteins in aqueous solutions [1]. Hence, interest continues in the study of amino acids in understanding solute-solvent interactions and the effects of amino acids on structure of water. Amino acids exist as zwitterions in aqueous solutions and are highly polar [2-4], but contain structurally differing nonpolar side chains. Thus the changes in structure of water caused by amino acids should reflect whether the polar character of the zwitterion or the non-polar side chain predominates in determining the solute-solvent interactions.

It is known that viscosity measurements provide valuable information regarding the solute-solute and solute-solvent interactions. Such measurements have been made on amino acids in aqueous solutions by several workers [5-9]. However, adequate experimental data, especially about the temperature dependence, have not been available. To provide this information, we have examined the viscosities of aqueous solutions of 5 amino acids at different temperatures and concentrations.

The amino acids chosen are glycine (GLY), α-alanine (α-ALA), α-amino-n-butyric acid (β-ABA), α-amino-i-valeric acid (VAL) and ε-amino-n-caproic acid (ε-CAP). These amino acids are selected to observe the effect of increasing number of methylene groups in the alkyl chain, ε-CAP has been chosen to see the effect of charge separation.

EXPERIMENTAL

The purity of GLY (E.Merck, West Germany), α-ALA and VAL (Loba Chemie), β-ABA and ε-CAP (Sigma Chemicals, USA) was checked by noting their melting points. These were dried in vacuum for 40 hours, were stored over anhydrous calcium chloride in a vacuum desicator and used as such. All the solutions were prepared by weight on molar basis in doubly distilled, degassed water and vacuum correction was made for each weight.

The viscosities were measured with the help of modified ubbelohde type of viscometer with flow times for water at 298.15°, 308.15° and 308.15° K of 589.0, 477.4 and 398.6 sec. respectively, in a water thermostat controlled to ±0.01° K. Efflux times were measured with a ROCAR stop watch which could read up to ±0.1 sec. At least three readings of the flow times with variations not exceeding ±0.2 sec. were taken for each solution. The viscosities were calculated from the average flow times t, and densities, ρ, based on the equation.

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

where A and B are calibrating constants and were determined by least-squares fitting of the efflux times to the equation (1) and viscosities of water used were, 0.8903, 0.7195 and 0.5963 centipoise [10] at 298.15, 308.15 and 318.15 K respectively.

The densities were measured with 12 cm^3 'flask' type pyknometer calibrated with doubly distilled degassed water. The densities of water used were 0.99704, 0.99403 [11] and 0.99925 [12] at 298.15, 308.15 and 318.15°K respectively.

The reproducibility in viscosity and density measurements was found to be $\pm 4 \times 10^{-4}$ centipoise and $\pm 3 \times 10^{-5}$ g cm^{-3}

RESULTS AND DISCUSSION

The values of relative viscosities η_r & densi-

TABLE 1

EXPERIMENTAL DENSITIES ρ AND RELATIVE VISCOSITIES η_r OF SOME AMINO ACIDS AT 298.15, 308.15 AND 318.15 K IN AQUEOUS SOLUTIONS

298.15° K			308.15° K			318.15° K		
c/mol dm^3	ρ/g cm^3	η_r	c/mol dm^3	ρ/g cm^3	η_r	c/mol dm^3	ρ/g cm^3	η_r
Glycine								
0.04992	0.99868	1.0073	0.04976	0.99564	1.0073	0.04958	0.99184	1.0077
0.09947	1.00023	1.0041	0.09917	0.99716	1.0151	0.09880	0.99334	1.0152
0.14857	1.00177	1.0217	0.14813	0.99866	1.0225	0.14754	0.99482	1.0233
0.19777	1.00330	1.0293	0.19714	1.00017	1.0304	0.19640	0.99630	1.0314
0.26298	1.00534	1.0389	0.26218	1.00217	1.0409	0.26116	0.99827	1.0423
0.32764	1.00736	1.0491	0.32662	1.00415	1.0516	0.32534	1.00022	1.0534
0.42573	1.01043	1.0647	0.42376	1.00713	1.0669	0.42254	1.00317	1.0710
α-Alanine								
0.05594	0.99870	1.0143	0.05577	0.99566	1.0137	0.05556	0.99183	1.0136
0.11120	1.00023	1.0291	0.11088	0.99718	1.0282	0.11044	0.99336	1.0280
0.16628	1.00177	1.0426	0.16579	0.99869	1.0427	0.16515	0.99489	1.0423
0.22099	1.00329	1.0571	0.22033	1.00019	1.0564	0.21949	0.99640	1.0565
0.27518	1.00480	1.0724	0.27431	1.00168	1.0712	0.27326	0.99790	1.0712
0.34418	1.00672	1.0915	0.34377	1.00360	1.0901	0.34312	0.99985	1.0906
0.41358	1.00866	1.1117	0.41298	1.00550	1.1090	0.41226	1.00178	1.1097
α-amino butyric acid								
0.06035	0.99883	1.0196	0.06016	0.99571	1.0191	0.05994	0.99185	1.0187
0.11982	1.00035	1.0391	0.11947	0.99724	1.0386	0.11901	0.99339	1.0379
0.17897	1.00186	1.0596	0 17842	0.99876	1.0579	0.17777	0.99492	1.0581
0.23736	1.00336	1.0800	0.23667	1.00026	1.0786	0.23577	0.99643	1.0781
0.29548	1.00484	1.1015	0.29455	1.00175	1.0990	0.29347	0.99793	1.0995
0.39815	1.00747	1.1393	0.39746	1.00440	1.1375	0.39661	1.00062	1.1372
0.51319	1.01041	1.1837	0.51287	1.00737	1.1836	0.51201	1.00362	1.1833
α-amino isovaleric acid								
0.02721	0.99779	1.0114	0.02713	0.99481	1.0108	0.02702	0.99098	1.0102
0.05211	0.99845	1.0217	0.05196	0.99545	1.0210	0.05176	0.99162	1.0198
0.10372	0.99981	1.0442	0.10340	0.99678	1.0425	0.10301	0.99294	1.0399
0.12924	1.00049	1.0551	0.12874	0.99743	1.0529	0.12835	0.99360	1.0507
0.15442	1.00115	1.0664	0.15394	0.99808	1.0640	0.15335	0.99424	1.0607
0.19409	1.00220	1.0844	0.19359	0.99910	1.0815	0.19302	0.99527	1.0776
ε-amino -caproic acid								
0.07543	0.99912	1.0394	0.07520	0.99607	1.0384	0.07491	0.99226	1.0369
0.15894	1.00136	1.0860	0.15848	0.99831	1.0843	0.15788	0.99451	1.0808
0.23573	1.00340	1.1302	0.23500	1.00026	1.1278	0.23411	0.99650	1.1238
0.35462	1.00643	1.2014	0.35377	1.00319	1.1995	0.35310	0.99943	1.1928
0.45329	1.00891	1.2647	0.45273	1.00562	1.2644	0.45201	1.00183	1.2567
0.52316	1.01074	1.3118	0.52273	1.00736	1.3115	0.52198	1.00357	1.3027

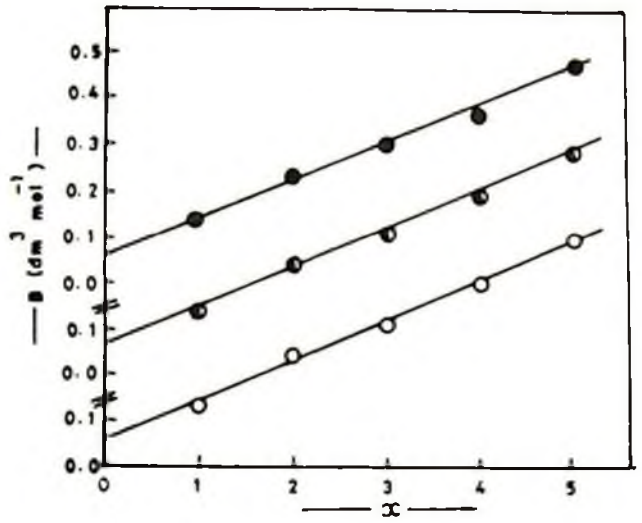


Fig.1 Plots of B-coefficients vs ○-298.15 K, ●-308.15 K, ●-318.15 K

ties P , as a function of concentration and temperature are presented in Table-1. The viscosity of solution of dipolar ions is represented by the Jones-Dole equation of the form:

$$\eta_r = \eta / \eta_o = 1 + B c + D c^2 \quad .....(2)$$

where c is the molar concentration of the solute, and B is an empirical constant which is called usually the Jones-Dole viscosity B-coefficient. This is known to depend on the size of the solute particle and also on the interactions between the solute and solvent molecules [13]. D is another empirical constant, which cannot be interpreted unambiguously [14]. By rearranging the equation [2] we obtain:

$$(\eta_r - 1)/c = B + D c \quad .....(3)$$

The viscosity coefficients B- and D- are calculated by linear extrapolation using the least-squares fit to the equation[3]. Since c is expressed in terms of molarity, the units for B-coefficients can be written as dm^3 /mol. The derived values of B and D coefficients along with the standard errors, are summarised in Table-2. The literature values of B-coefficients have also been included for comparison.

It is evident that present B-coefficients of these amino acids at 25°C agree very well with most of the literature values. 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. Tsangris and Martin[7] reported B-coefficients for large number of amino acids at 303.15, 308.15 and 318.15 K which are much lower than the values reported by other workers [5,9].

The B-coefficients of the amino acids studied are positive. As shown in Fig.1, the viscosity B-coefficients increase linearly with 'X', the number of CH_2 groups. The average increments per CH_2 group, ΔB, at 298.15°, 308.15° and 318.15° K are found to be 0.092, 0.088 and 0.082 dm^3/mol respectively. These values of increments are higher than the value (0.038 dm^3/mol) expected from the volume, 15.2 cm^3/mol of CH_2 group (9), if fitted in the following equation:

$$B = aV \quad .....(4)$$

where V is the volume of CH_2 group (dm^3 /mol) and a is a constant which depends on the shape of the particles (i.e., 2.5 for spherical solutes). The large increments in B-values

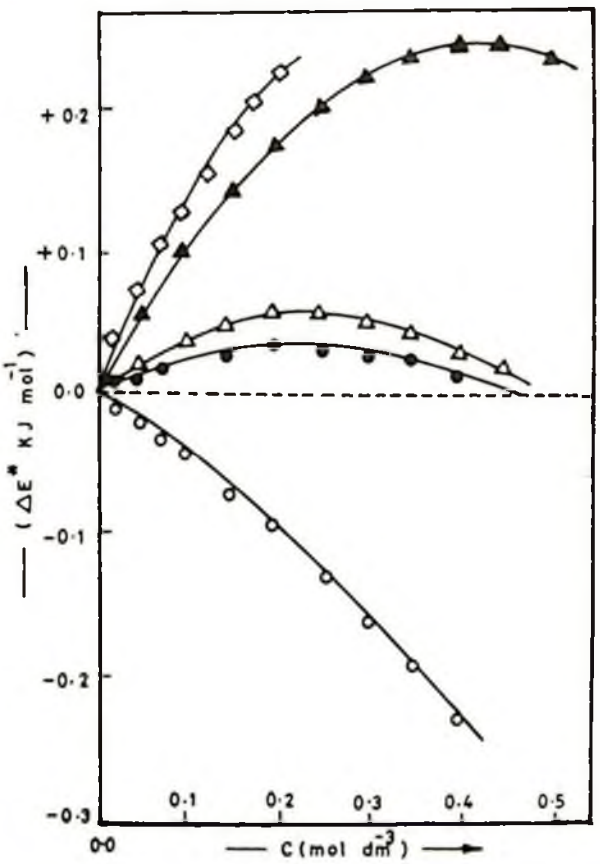


Fig. 2 Plots of E* vs C (o-GLY, ●- α-ALA, Δ- ABA, □-VAL, ▲- CAP)

suggest that the CH_2 groups lead to structure promotion as a result of hydrophobic hydration [15-17]. The value of average increment decreases with rise in temperature which indicates that structure formation or hydrophobic hydration at higher temperature is reduced.

Effect of Temperature on the B-cofficients

Tsangaris and Martin [7] were the first to emphasise the importance of sign and magnitude of dB/dT instead of the sign and magnitude of the B-coefficient. Tyrrell and Kennerlay [8] also held the same view that dB/dT is a much more revealing parameter in determining the water structure making and breaking propoerties of a solute. The positive value of dB/dT is normally associated with structure breaking while the negative value with the structure making [13]. The dB/dT values of the amino acids are presented in Table-2. The dB/dT value of GLY is positive while for α-ALA, β-ABA, VAL and ϵ-CAP, its value is negative. It suggests that GLY is a structure breaker while other 4 dipolar ions of Table-2 are structure makers in water.

Energies of Activation

The Arrhenius equation expressing viscosity as a function of temperature [13] may be written as

$$\ln \eta = \alpha + (E^*/RT) \qquad .....(5)$$

where E^* is the activation energy for viscous flow expressed in KJ/mol. The E^* value calculated for the temperature interval, 298.15 - 318.15 K have been used to calculate the differential activation energies of vicous flow (ΔE^*) using the relation:

$$\Delta E^* = E^*_{Solution} - E^*_{H_2O} \qquad .....(6)$$

where $E^*_{H_2O}$ is the energy of activation of viscous flow for water, (calculated from data in ref 10) and found to be 15.81 KJ/mol. Since activation energy is related to structural order [5], the differential activation energies, ΔE^*, may be interpreted in terms of strengthening or weakening effects of these amino acids on the water structure. In Fig. 2, the plots of differential activation energies

TABLE 2

THE VALUES OF VISCOSITY B- AND D-COEFFICIENTS, STANDARD ERRORS AND dB/dT OF SOME AMINO ACIDS IN AQUEOUS SOLUTIONS AT 298.15, 308.15 AND 318.15° K

B in dm^3/mol^{-1}			D in dm^6/mol^{-2}			dB/dT ($dm^3\ mol^{-1}\ K^{-1}$)
298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	
Glycine						
0.143±0.001	0.148±0.001	0.152±0.001	0.021±0.006	0.028±0.005	0.037±0.003	+0.00045
0.14193 [5]	0.14470 [5]					
0.143 ± 0.002 [9]	0.139 [7]					
Alanine						
0.253±0.002	0.247±0.002	0.245±0.002	0.037±0.009	0.044±0.008	0.054±0.007	-0.00040
0.25253 [5]	0.23633 [5]					
α-amino butyric acid						
0.319±0.001	0.311±0.001	0.307±0.001	0.077±0.003	0.089±0.004	0.100±0.004	-0.00040
α-amino isovaleric acid						
0.414±0.002	0.396±0.001	0.374±0.002	0.105±0.015	0.128±0.011	0.146±0.016	-0.00200
0.4052 [6]						
ϵ-amino -caproic acid						
0.513±0.002	0.499±0.002	0.480±0.002	0.150±0.006	0.186±0.006	0.192±0.006	-0.00165
0.479 [9]	0.348 [7]					

of viscous flow (ΔE^*) vs the concentration of the amino acids are depicted. As expected, GLY that exhibits positive temperature dependence of B-coefficients also diplays negative differential activation energies of vicous flow (Fig.2). The other 4 amino acids which have negative dB/dT values, display positive differential activation energies of viscous flow. This confirms the earlier conclusions drawn from dB/dT values that GLY is a structure breaker while other amino acids are structure makers in water.

In Fig. 2, the curve of ε-CAP lies below that of VAL. ε-CAP has a longer side chain than that of VAL. But NH_2 group taking same positive charge from NH_3^+ in α position increases the structure breaking properties of ε-CAP due to the removal of partial overlap of the positive and negative charges. The other possible reason for this behaviour may be due to a larger dipole moment of ε-CAP than that of VAL that the former interacts more strongly with water molecules that does VAL.

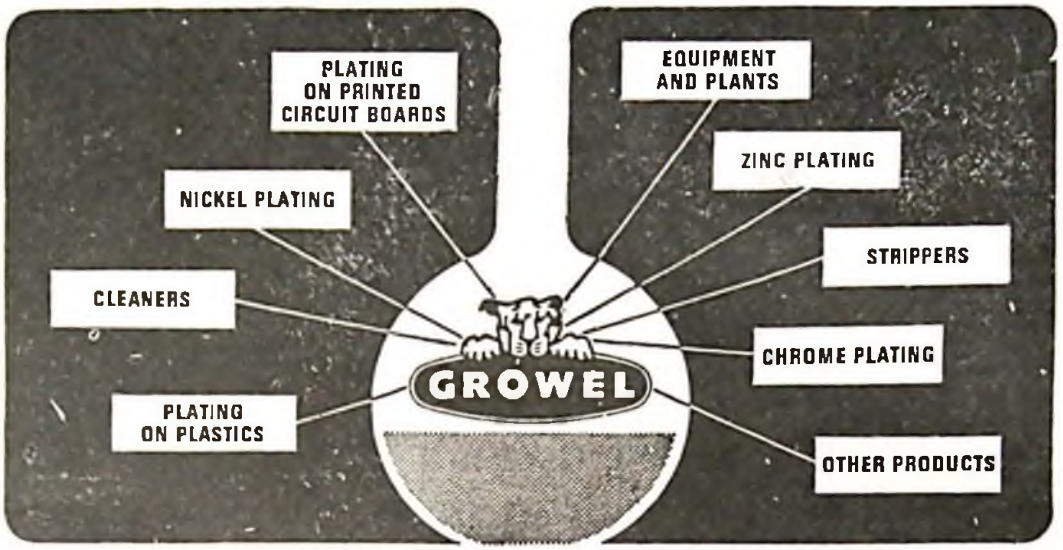
The conclusion drawn from dB/dT and ΔE^* values for GLY, VAL and ε-CAP is generally in accordance with the findings of earlier worker [5,9], but present results of ΔE^* as well as dB/dT show that α -ALA is a structure maker. This conclusion is in agreement with the view of Mason et al. [5] and Dey et al [18], but does not agree with the view of Devine and Lowe [9] and Phang [19] who proposed that alanine is a structure breaker. The controversy seems to arise from the structure promotion caused by the apolar groups and the structure breaking by NH_3^+ and CO_2^- groups, the net effect of which might vary under experimental conditions as pointed out earlier by Dey [18].

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