

#### 14. *Viscosities of Aqueous Solutions of Amino-acids, with Some Conductivity Values.*

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Jones and Talley (*J. Amer. Chem. Soc.*, 1933, **55**, 624) have concluded that viscosity-concentration considerations classify dissolved substances into non-electrolytes, showing a linear relationship and a continuous increase of viscosity with concentration, and electrolytes, which show deviation from linearity and ultimately lower the viscosity below that of pure water. Solutions of amino-acids have now been examined to see if such ampholytes exhibit the properties of either of these two classes or if they show distinctive class properties of their own.

Although viscometrically glycine and alanine appear to be non-electrolytes this is not considered to suggest the non-existence of dual ions.

Sulphanilic acid and betaine hydrochloride are included for comparison and seem to behave similarly to electrolytes. Certain conductivity values are included and appear to agree with the viscosity conclusions.

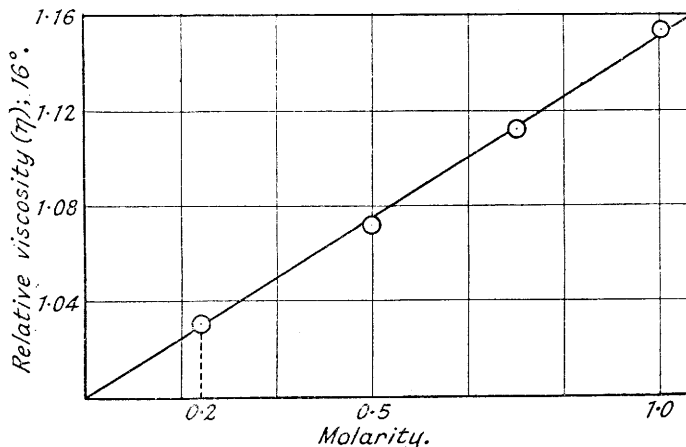
GLASSTONE ("Text Book of Physical Chemistry", Macmillan, London, 1940) states that simple aliphatic amino-acids are thought to exist in solutions mainly in the form of dual ions and he quotes  $K_a = 5 \times 10^{-3}$  for the acidic dissociation constant of glycine, on the assumption that a considerable proportion of dual ions exist. On general grounds such dual ions might be expected to produce effects similar to strong electrolytes, the viscosity-concentration peculiarities of which are attributed by Jones and Talley (*loc. cit.*) to inter-ionic effects of the kind envisaged by the Debye-Hückel theory. The present investigations sought to show if dual ions did produce such effects. Glycine and alanine were selected as examples which would be expected to be similar, and sulphanilic acid and betaine hydrochloride were included as ampholytes of marked one-sided weakness which might allow of useful comparison. No previous data exist apart from a few isolated measurements of solutions of glycine and alanine by Hedestrand (*Z. anorg. Chem.*, 1922, **124**, 153) and we have substantially confirmed these.

The table gives our values for concentrations, densities, and relative viscosities of solutions. Fig. 1 shows a linear variation of relative viscosity with concentration of glycine up to 1.0 M at 16°. Similar linearity is shown by glycine solutions at 40° and by alanine solutions at 16°. Evidently, these solutions behave as the non-electrolytes of Jones and Talley (*loc. cit.*) but the non-existence of dual ions does not necessarily follow. It may be that the positive and negative charges on a dual ion are so close together that the distortion of the ionic atmosphere by a shearing force perpendicular to the direction of the velocity gradient (see Falkenhagen, "Electrolytes", Oxford Univ. Press, 1934) does not occur and may be nullified by the superimposition of atmospheres appropriate to a positive and a negative ion. Thus the usual unequal distribution of charge in the ionic atmosphere may not exist.

Viscosities of 2.0M-glycine at 16° and 40° are much greater than would be expected by

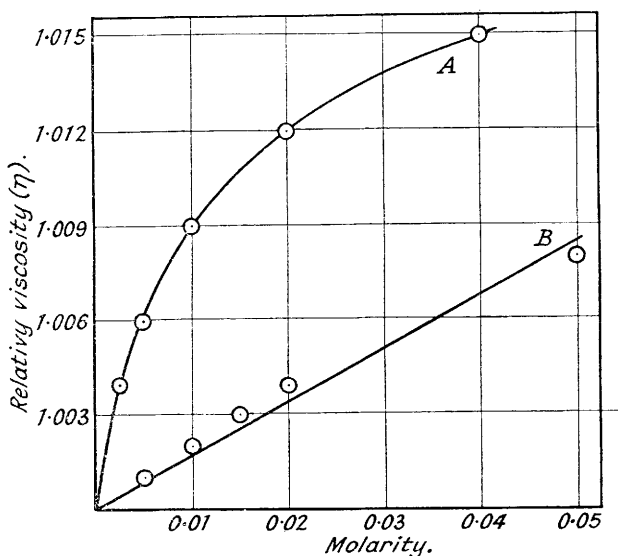
extrapolating curves as in Fig. 1. These greater values, whilst differing from the non-electrolytes of Jones and Talley (*loc. cit.*), certainly do not in any way resemble the electrolytes which these authors report as ultimately lowering viscosity at quite small concentrations. 2.0M-Glycine is a concentrated solution in which some new factors probably become operative. Fig. 2 shows sulphanilic acid (A) to differ from glycine (B) and non-electrolytes but to resemble the strong

FIG. 1.



electrolyte potassium bromate (Jones and Talley, *loc. cit.*) although neither with sulphanilic acid nor with potassium bromate is there an ultimate concentration at which the viscosity begins to decrease. The concentration ranges investigated may have been insufficient, but solubility limitations prevented further study of sulphanilic acid. Betaine hydrochloride gives viscosity variations similar to sulphanilic acid and both show some resemblance to strong electrolytes but

FIG. 2.



differ from non-electrolytes. Thus the four amino-acids under review appear to fall into two groups, with glycine and alanine in one group and sulphanilic acid and betaine hydrochloride in the other. It was thought that conductivity data might help to confirm this classification, but there do not seem to be any data except for some equivalent conductivity values for sulphanilic acid by Boyle (*J.*, 1919, 115, 1505).

We have therefore made some measurements of equivalent conductivity and our results are given in the table. They appear to confirm the conclusions from the viscosity, *viz.*, that glycine and alanine are virtually non-conductors, but the other two acids, whilst less than strong electrolytes, are definite conductors of the same order as, *e.g.*, chloroacetic acid. Allowance being made for the difference in temperature of investigation, our results for sulphanilic acid are in fair agreement with those of Boyle (*loc. cit.*).

	M.	Density.		Relative viscosity ( $\eta$ )*		Equiv. conductivity (ohm <sup>-1</sup> ) at 18°.
		At 16°.	At 40°	At 16°.	At 40°.	
Glycine	0.0025	0.99893	—	1.0005	—	—
	0.005	0.99912	—	1.001	—	—
	0.010	0.99921	—	1.002	—	0.085
	0.015	0.99937	—	1.003	—	—
	0.020	0.99955	0.99275	1.004	1.003	0.043
	0.050	1.00050	0.99375	1.008	1.008	0.023
	0.080	1.00180	0.99450	1.013	1.012	—
	0.100	1.00220	0.99525	1.015	1.015	0.013
	0.150	1.00360	0.99660	1.022	1.023	—
	0.200	1.00550	0.99820	1.029	1.031	0.077
	0.500	1.01508	1.00755	1.071	1.076	—
	0.750	1.02309	—	1.112	—	—
	1.000	1.03110	1.02260	1.153	1.165	—
	2.000	1.06097	1.05204	1.359	1.713	—
	Alanine	0.010	0.99920	—	1.003	—
0.020		0.99950	—	1.005	—	0.050
0.050		1.00017	—	1.016	—	0.037
0.100		1.00082	—	1.030	—	0.032
0.200		1.00326	—	1.056	—	0.027
Betaine hydrochloride	0.010	—	—	—	—	41.0
	0.020	0.99960	—	1.014	—	36.0
	0.050	1.00090	—	1.020	—	29.0
	0.100	1.00220	—	1.028	—	23.0
Sulphanilic acid †	0.0025	0.99841	—	1.004	—	88.64
	0.005	0.99863	—	1.006	—	64.10
	0.010	0.99911	—	1.009	—	48.70
	0.020	0.99983	—	1.012	—	36.70
	0.040	1.00166	—	1.015	—	27.10

\*  $\eta = \eta_s/\eta_0$ , where  $\eta_s$  = viscosity of solution,  $\eta_0$  = viscosity of water.

† Data for density and  $\eta$  relate to 20°.

#### EXPERIMENTAL.

"AnalaR" Glycine was recrystallised from water and dried in a vacuum desiccator. Pure alanine was twice dissolved in water and crystallised by addition of  $\frac{1}{3}$  vol. of ethyl alcohol. "AnalaR" Sulphanilic acid was recrystallised from boiling water and dried to constant weight in a vacuum desiccator. Betaine hydrochloride was dissolved in a minimum of warm concentrated hydrochloric acid, cooled under water, and an equal volume of acetone added slowly. Further cooling gave a deposit of fine crystals which were vacuum-filtered and dried at 100° for 2½ hours.

The determinations of relative viscosities and densities were by the methods described by Glass and Madgin (*J.*, 1934, 145, 1124), their No. 2 viscometer and silica pycnometers being used. Each viscosity value in the table is the average of three concordant results (agreeing to  $\pm 0.001$ ) and this has required many measurements because of the rapid growth of moulds in amino-acid solutions (especially at 40°). Even before these growths are visible they give rise to marked irregularities, and therefore freshly made samples of solutions are frequently necessary for repeat experiments. During actual use the viscometer was sealed (cf. Applebey, *J.*, 1910, 97, 2000) to exclude dust and, as far as possible, to avoid infection by spores. Guard filters were placed on either side of the viscometer and a short circuit air tube joined them. The temperature variation was  $\pm 0.05^\circ$  at 16° and 20°, but, in the prevailing supply conditions, it was  $\pm 0.20^\circ$  at 40°.

Conductivity measurements were made with a simple metre bridge, a valve oscillator, and a non-inductively wound resistance box. No more is claimed for the results than that they are of the right order of magnitude; in the case of sulphanilic acid fair agreement with Boyle (*loc. cit.*) is noted above. Since no other values are available, the present results are of use to enable a comparison to be made among the four compounds concerned.

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