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Some Physical Properties of Aqueous L-Ascorbic Acid Solutions

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Abstract

The density, viscosity and refractive index of aqueous L-ascorbic acid solutions, in the concentration range 0·01–1·20 M, have been measured at 25°C. The partial molal volume of the undissociated acid at infinite dilution has been found to be 105·74 cm^3 mol^{-1}. Equations which describe the density and relative viscosity of the solutions have also been given.

The physiological and medicinal aspects of L-ascorbic acid (vitamin C) have been investigated in great detail but the physicochemical data on this compound are meagre. This communication describes the densities, viscosities and refractive indices of aqueous ascorbic acid solutions.

Experimental

Analytical reagent grade L-ascorbic acid was dried over silica gel in a vacuum desiccator and was analysed for purity by potentiometric titration against carbonate-free potassium hydroxide solution. The compound was found to be 99·9% pure. Solutions were prepared by weighing the required quantity of the dried acid and dissolving it in degassed and nitrogen-flushed conductivity water ($\kappa < 1 \times 10^{-6}$ S cm^{-1}) in 500-ml flasks whose outer surfaces were painted black; these solutions were used soon after their preparation. They were made up at 25°C and all masses were corrected for the density of air. Solutions were pushed into the pyknometers or viscometer, which were covered with aluminium foil, directly from the painted flask by nitrogen gas pressure. The thermostat tank, set at $25 \pm 0·05$°C and controlled to $\pm 0·005$°C, was itself covered with black paper except for a small opening to handle pyknometers and viscometer. A red light of very low intensity (5-W bulb) was used to observe the levels. The solutions were protected from air and light thus preventing oxidation.[1]

Two narrow-necked (3 mm internal diameter) flask-type pyknometers of approximately 40 ml capacity were used to determine the density of each solution. The masses were corrected in the usual way and the reproducibility was better than 4×10^{-5} g cm^{-3} in the density.

An Ubbelohde viscometer was mounted on a brass frame and was always held in a vertical position in the thermostat bath. The flow time was measured to $\pm 0·1$ s. The viscometer was calibrated by using doubly distilled water and triply distilled ethanol. The absolute viscosities[2,3] of water

[1] Oser, B. L., 'Hawk's Physiological Chemistry' 14th Edn, p. 697 (McGraw–Hill: New York 1968).
[2] 'Handbook of Chemistry and Physics' 55th Edn, p. F-49 (Chemical Rubber Co.: Cleveland, Ohio, 1974–75).
[3] Stokes, R. H., and Mills, R., 'The International Encyclopedia of Physical Chemistry and Physics' Vol. 3, Appendix 1.3, p. 76 (Pergamon Press: London 1965).

and ethanol were taken as 0·8904 and 1·075 cP respectively. The flow time for pure water at 25°C was about 500 s. Kinetic energy corrections were made to the viscosity data.

An Abbe instrument, with a sodium lamp, was used to measure the refractive indices of the solutions. Water at 25°C was circulated through the refractometer by a pump. The results of the three measurements are given in Table 1.

Table 1. Density, viscosity and refractive index of aqueous L-ascorbic acid solutions at 25°C

x, mole fraction of ascorbic acid; n, refractive index; α, degree of dissociation: calculated by successive approximations from the equations

$$K_1 = [c\alpha^2/(1-\alpha)]f_{\pm}^2 \qquad \log f_{\pm}^2 = -1{\cdot}0196(c\alpha)^{1/2}/[1+Ba^{\circ}(c\alpha)^{1/2}]$$

where $K_1 = 5{\cdot}741\times10^{-5}$, $B = 0{\cdot}329$ and $a^{\circ} = 5$ Å [K_2 being very small: pK_2 11·57 (from Birch, T. W., and Harris, L. J., *J. Biochem.*, 1933, **27**, 595; Kumler, W. D., and Daniels, T. C., *J. Am. Chem. Soc.*, 1935, **57**, 1929)]. Values for K_1 and B have been taken from ref. 4 and from Robinson, R. A., and Stokes, R. H., 'Electrolyte Solutions' 2nd Edn, Appendix 7.1, p. 468 (Butterworths: London 1959) respectively

c (mol dm^{-3})	m (mol kg^{-1})	Mass (%)	x	α	ρ (g cm^{-3})	η/η°	n
0·008152	0·008182	0·1439	0·00015	0·0894	0·99774	1·0018	—
0·09906	0·10041	1·7377	0·00181	0·0273	1·00405	1·0231	1·3360
0·20313	0·30821	3·5376	0·00374	0·0194	1·01134	1·0488	1·3385
0·40002	0·41899	6·8726	0·00749	0·0140	1·02516	1·1044	1·3444
0·50135	0·53114	8·5547	0·00948	0·0126	1·03221	1·1352	1·3469
0·60273	0·64590	10·2143	0·01150	0·0116	1·03932	1·1697	1·3496
0·70455	0·76393	11·8594	0·01358	0·0108	1·04636	1·2058	1·3521
0·79447	0·87044	13·2931	0·01544	0·0102	1·05265	1·2430	1·3546
0·90090	0·99950	14·9690	0·01769	0·0096	1·06003	1·2894	1·3573
1·00692	1·13127	16·6146	0·01997	0·0091	1·06743	1·3384	1·3605

Results

The densities in g cm^{-3} of the solutions in the entire concentration range are given by the equation

$$\rho = 0{\cdot}99707+0{\cdot}07105c-0{\cdot}00025c^2$$

with an average deviation of $\pm 0{\cdot}00004$ g cm^{-3} where c is the molar concentration.

In the concentration range 0·10–1·2 M the acid undergoes 3–1% dissociation; to a first approximation therefore, it may be assumed to be in an undissociated state. Thus at infinite dilution the partial molal volume of the undissociated acid has been found to be 105·74 cm^3 mol^{-1}. However, at 0·01 M the dissociation is 9% and the partial molal volume shows a big drop. More experimental points at low concentrations are therefore needed to obtain the partial molal volume of the ionized species.[5] Traube contributions for the constituent atoms and groups etc. add up to 106·4 cm^3 mol^{-1}.

The relative viscosities, in the range 0·01–0·70 M, have been fitted to an extended form of the Jones–Dole equation; the equation

$$\eta/\eta^{\circ} = 1+0{\cdot}0035c^{1/2}+0{\cdot}210c+0{\cdot}1110c^2$$

represents η/η° values within $\pm 0{\cdot}0002$. The A-coefficient corresponds[4] well to $\lambda^{\circ} = 30{\cdot}59$ S cm^2 mol^{-1} for the ascorbate ion and the positive B-coefficient indicates

[4] Shamim, M., and Salah, M. A. B., unpublished data.

[5] Klotz, I. M., and Eckert, C. F., *J. Am. Chem. Soc.*, 1942, **64**, 1879.

strong interaction with the solvent molecules. Diffusion[4] studies have also shown the structure making nature of the acid. At 0·008152 M where the volume fraction is small (0·000769), Einstein's equation

$$\eta/\eta^{\circ} = 1+2\cdot5c\overline{V}$$

yields a value of 1·0019 for the relative viscosity.

The relative viscosities are lower than for anhydrous citric acid solutions.[6] A 3·8 mass % solution of citric acid is about as viscous as a 6·9 mass % solution of ascorbic acid.

The refractive index measurements probably were accurate within ±0·0002: the molar refraction, $[R]_D$, at infinite dilution therefore cannot be calculated with accuracy but it is approximately 36·4 $cm^3\ mol^{-1}$.

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[6] Levien, B. J., *J. Phys. Chem.*, 1955, **59**, 640.