

VISCOSITY OF AQUEOUS SOLUTIONS OF FORMIC, CYANOACETIC AND OXALIC ACIDS.

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Viscosities of aqueous solutions of formic, cyanoacetic and oxalic acids have been measured at 35°. The viscosity of these solutions is represented quite well by either of the two equations proposed by the authors, but the values of viscosity constants are not of the expected order. The results are also represented by the Jones and Dole equation, but the constants have no theoretical significance for weak electrolytes.

The authors derived an equation,

$$\frac{\eta - \eta_0}{\eta_0} = A \sqrt{\alpha c} + \beta(1 - \alpha)c \quad \dots (1)$$

connecting viscosity, concentration 'c' and the degree of dissociation 'α' of an aqueous solution of a weak electrolyte, on the assumption that the increase in relative viscosity $\frac{\eta - \eta_0}{\eta_0}$ of such a solution was due to two additive factors, one

$$\frac{\Delta_1}{\eta_0} = A \sqrt{\alpha c} + B\alpha c,$$

due to the dissociated part (electrolyte) and the other,

$$\frac{\Delta_2}{\eta_0} = \beta(1 - \alpha)c$$

due to the undissociated part (non-electrolyte) (*Trans. Faraday Soc.*, 1938, 34, 1139). In the case of dilute solutions of very weak electrolytes the term 'B α c' could be neglected as the value of 'α' and 'c' are very small. The equations represented the results satisfactorily in the case of very weak electrolytes (*loc. cit.*), but the experimental values of 'A' did not agree with the theoretical value (Falkenhagen and Vernon, *Phil. Mag.*, 1932, 14, 537).

It was considered desirable to extend the work to a few more weak electrolytes for some of which the term 'B α c' could be taken into account due to their fairly large degree of dissociation. In such cases the equation would assume the form,

$$\frac{\eta - \eta_0}{\eta_0} = A \sqrt{\alpha c} + B\alpha c + \beta(1 - \alpha)c \quad \dots (2)$$

With this object the viscosities of dilute solutions of formic, cyanoacetic and oxalic acids have been measured.

E X P E R I M E N T A L.

Measurements were made at $35^{\circ} \pm 0.005^{\circ}$ in a thermostat described in the previous communication (*loc. cit.*). Particulars about the viscometer used are given below.

Approx. time of flow for water	= 2141 sec.
Approx. capacity of bulb on the capillary side	= 7.5 c.c.
Length of capillary tube	= 10.5 cm.
Diameter of the capillary bore	= 0.28 mm.

No kinetic energy correction was found to be necessary. On account of the design of the viscometer, surface tension correction was eliminated (*Trans. Faraday Soc.*, 1939, **35**, 374). The time of flow was measured to an accuracy of 0.2 second by means of a Zenith stop-watch for formic and cyanoacetic acids and by a Venner time-switch (marked off in tenths of seconds) for oxalic acid. Density measurements were made with two pycnometers of approximate capacity of 20 c.c. and 63 c.c., the smaller one for formic and cyanoacetic acid and the larger for oxalic acid. The maximum error in viscosity measurements, calculated on the basis of an error of 0.2 second in measuring time of flow and 0.001 g. in determining the mass of the pycnometer, works to 0.0002. The mean of three to five readings for time and two readings for mass were taken for calculating the viscosity.

Kahlbaum's formic acid was redistilled before use. Solutions of oxalic acid were made from Kahlbaum's 'pro analysi' sample after crystallisation. Cyanoacetic acid (Merck's quality marked for scientific purposes) of m.p. 64° was used as such.

The values of the dissociation constants, 'K' were taken from the Landolt-Bornstein Tabellen. The constants in equation (1) were evaluated graphically by plotting $\frac{\eta}{\eta_0} - 1 / \sqrt{\alpha c}$ against $(1 - \alpha) \sqrt{c} / \alpha$, the slope of the straight line giving the value of ' β ' and the intercept at the ordinate, the value of A . The constants in equation (2) were obtained by solving simultaneous equations. In the following tables concentration in g. mols. per litre, density in g./c.c., relative viscosity observed $\frac{\eta}{\eta_0}(0)$, and viscosity calculated by equation (1), $\frac{\eta}{\eta_0}(1)$ and equation (2), $\frac{\eta}{\eta_0}(2)$ are given,

TABLE I.

Formic acid.

$$K = 2.4 \times 10^{-4}. \quad A = 0.00. \quad \beta = 0.048.$$

Conc.	Density.	$\frac{\eta}{\eta_0}$ (0).	$\frac{\eta}{\eta_0}$ (1).	Conc.	Density.	$\frac{\eta}{\eta_0}$ (0).
0	0.99406					
0.01086	0.99440	1.0007	1.0005	0.21842	0.99535	1.0084
0.02184	0.99448	1.0011	1.0009	0.32763	0.99548	1.0124
0.03271	0.99451	1.0013	1.0014	0.45584	0.99898	1.0164
0.04361	0.99463	1.0018	1.0020	0.56980	0.99984	1.0195
0.05452	0.99467	1.0021	1.0025	0.68376	1.00133	1.0236
0.06542	0.99477	1.0029	1.0030	0.79772	1.00255	1.0276
0.07632	0.99503	1.0037	1.0035	0.91168	1.00371	1.0310
0.08722	0.99512	1.0042	1.0040	1.02560	1.00482	1.0347
0.09813	0.99524	1.0047	1.0045	1.13960	1.00616	1.0381
0.10921	0.99531	1.0048	1.0050			

TABLE II.

Cyanoacetic acid.

$$K = 3.7 \times 10^{-3}; \quad (1) \quad A = 0.018, \quad \beta = 0.13.$$

$$(2) \quad A = 0.00, \quad B = 0.172, \quad \beta = 0.122.$$

Conc.	Density.	$\frac{\eta}{\eta_0}$ (0).	$\frac{\eta}{\eta_0}$ (1).	$\frac{\eta}{\eta_0}$ (2).
0.00800	0.99417	1.0014	1.0010	1.0012
0.02500	0.99463	1.0037	1.0038	1.0035
0.03500	0.99467	1.0047	1.0050	1.0048
0.04500	0.99496	1.0063	1.0063	1.0061
0.05594	0.99537	1.0075	1.0077	1.0074
0.06500	0.99564	1.0088	1.0088	1.0086
0.07513	0.99580	1.0095	1.0100	1.0099
0.08500	0.99609	1.0110	1.0112	1.0112
0.10000	0.99643	1.0131	1.0131	1.0131
0.24903	0.99946	1.0282		
0.40847	1.00256	1.0442		
0.70306	1.00824	1.0673		
1.16350	1.01712	1.1242		

TABLE III.

Oxalic acid.

$$K = 3.8 \times 10^{-2}. \quad (1) \ A = 0.022, \ \beta = 0.31$$

$$(2) \ A = 0.025, \ B = -0.024, \ \beta = 0.33.$$

Conc.	Density.	$\frac{\eta}{\eta_0}$ (0).	$\frac{\eta}{\eta_0}$ (1).	$\frac{\eta}{\eta_0}$ (2).
0.005013	0.99426	1.0016	1.0016	1.0017
0.010026	0.99450	1.0028	1.0026	1.0027
0.015039	0.99474	1.0034	1.0035	1.0036
0.020052	0.99497	1.0047	1.0045	1.0046
0.030078	0.99539	1.0062	1.0065	1.0064
0.035091	0.99552	1.0073	1.0073	1.0075
0.040104	0.99585	1.0085	1.0083	1.0085
0.045117	0.99604	1.0098	1.0094	1.0096
0.057843	0.99653	1.0122	1.0121	1.0123

DISCUSSION.

As seen from the foregoing tables, the results are represented satisfactorily in all cases. Equation (2) was not applied to formic acid as the values ' αc ' are small. The equations fail in the sense that the experimental values of A do not agree with the theoretical value, *i.e.*, about 0.003. In view of this wide difference the authors propose to test the correctness of the fundamental assumption (simple additivity of the viscosity of dissociated and undissociated parts) by measuring the viscosity of solutions of dextrose and some electrolytes, separately and together.

The Jones and Dole equation (*J. Amer. Chem. Soc.*, 1929, 51, 2950) represents the results in all cases but the values of A could have no theoretical significance for weak electrolytes.

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