240. *Viscosities of Aqueous Solutions of Electrolytes. Part I. Sodium Sulphate Solutions over the Temperature Range* 25—40°.

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VISCOMETRIC evidence of the existence of hydrated ferric chloride in unsaturated solutions is adduced by Smits, Lande, and Bouman (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 969). In the cases of solid hydrates (*e.g.*, sodium sulphate) which have a definite transition temperature, it is of interest to know whether a similar definite transition occurs at about the same temperature in unsaturated solutions of these salts. We have therefore measured vicosities of sodium sulphate solutions over a wide range of concentrations and at temperatures near the transition point (32·5°) of the solid hydrate.

Jones and Talley (*J. Amer. Chem. Soc.*, 1933, **55**, 624) claim that the relative viscosities of very dilute solutions of electrolytes can be represented by

$$\eta = 1 + A\sqrt{C} \pm BC \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the applicability of this formula to sodium sulphate solutions has now been tested.

EXPERIMENTAL.

Sodium sulphate (A.R.) was purified by recrystallisation from water until analysis of the anhydrous salt showed 100 (± 0·01) % purity. The crystals were dehydrated by heating at 120° for several hours, and stored in a desiccator. The water used in making up solutions was prepared as described by Robinson and Briscoe (J., 1925, **127**, 138); its specific conductivity was 1×10^{-6} mho.

Solutions of approximately regularly varying compositions were prepared, filtered through sintered glass, and analysed; the molalities (*m*) are shown in Table I. Their viscosities were measured over composition ranges extending as near to the saturation limit as possible, measurements being made by Applebey's method (J., 1910, **97**, 2000), with slight modifications, as indicated below. Two viscometers (Nos. 1 and 2; Ostwald type) were constructed as recommended by Applebey, and duplicate determinations of viscosity were made for each solution by using both viscometers. In addition, measurements of very dilute solutions were also made in a viscometer (No. 3) of the type used by Washburn and Williams (*J. Amer. Chem. Soc.*, 1913, **35**, 737). All viscometers were of Pyrex glass and dimensional details were as follows :

Viscometer.	Length of capillary, cm.	Vol. of upper bulb, c.c.	Radius of capillary, mm.	Mean head of liquid, cm.	Working volume, c.c.
1	17·5	8·74	0·23	16·08	11·5
2	17·1	9·31	0·23	14·15	12·5
3	17·5	11·02	0·23	15·0	50

The viscometers were first tested with pure water at 40°, by Applebey's method, and found to obey Poiseuille's law. Since all solutions had a greater viscosity than water and other temperatures were below 40°, this law was necessarily obeyed in all determinations now reported.

Bingham ("Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922) applied a kinetic-energy correction represented by the second term in the formula $\eta = \pi g P R^4 t / 8 l V - m \rho V / 8 \pi l t$, but if Poiseuille's law holds for any given solution (η constant), the first term is constant and therefore the kinetic energy term must be negligible; for this reason we have not applied such a correction.

In actual determinations the viscometer was held firmly in a holder of the Applebey type, modified so as to fix the position of the capillary limb, and immersed in a glass-sided thermostat, the temperature of which was electrically controlled; the variation was ± 0·01° at 40° and less at lower temperatures. The time interval between make and break on the electrical control was uniformly 60 secs., and, following Joy and Wolfenden (*Proc. Roy. Soc.*, **1931**, *A*, **134**, 413), we estimate that the maximum error thereby involved in timing is insignificant, owing to the rhythmical nature of this heating and cooling effect.

Before a viscometer was filled, the solution (of known composition and contained in a glass-stoppered flask) and a filling pipette (in a glass container) were immersed in the thermostat for 1 hour. The size of the pipette was such as to fill the viscometer from the middle of the upper to the middle of the lower limb (cf. Applebey, *loc. cit.*). When the viscometer was in position in the thermostat, the pipette was quickly filled from the stoppered flask and the content delivered into the viscometer, in which the level of the solution was adjusted before a run, precisely as described by Applebey.

Time of flow was found with a Venner stop-watch, readable to 0·03 sec., and four timings (in agreement to 0·1 sec.) were taken for each solution. They were independent of the state of winding of the watch, which therefore could be used for solutions of longer time of flow than pure water. Measurement of time of flow for any one solution was preceded and followed by a measurement on pure water, in the same viscometer, to ensure that no contamination (*e.g.*, by dust) had occurred. Some indication of the time of flow is given by the following results, which represent extreme values.

	Temp. 40°.		Temp. 25°.	
Viscometer 1.	Pure water	501·6 secs.	Pure water	679·0 secs.
	Solution A	1570·4 ,,	Solution B	1387·1 ,,
Viscometer 2.	Pure water	663·6 ,,	Pure water	900·4 ,,
	Solution A	2076·2 ,,	Solution B	1838·5 ,,
Viscometer 3.			Pure water	812·3 ,,

Molalities: Solution A, 3·27; solution B, 2·0.

Viscometers were cleaned and dried between determinations, by washing several times with dust-free distilled water, until no trace of sulphate could be detected in the last two washings. A final washing with redistilled absolute alcohol was followed by 1 hour's passage of a current of cleaned, dried air. As a further precaution, viscometers were cleaned with a sulphuric–chromic acid mixture after each six determinations.

In calculating relative viscosities (η) we have used Applebey's formula

$$\eta = \eta_s/\eta_0 = \frac{t}{t_0} \times \frac{S - \lambda}{S_0 - \lambda} \times \frac{H - K\gamma_s/S}{P}$$

where η_s = viscosity of solution, η_0 = viscosity of water,
H = mean difference of level (cm. H_2O),
P = hydrostatic pressure as measured in standardisation (cm. H_2O),
K = a constant depending on the form of the viscometer,
and γ_s = surface tension of solution.

Densities for sodium sulphate solutions at various temperatures are given by Gibson (*J. Physical Chem.*, **1927**, **31**, 496) and in Int. Crit. Tables, Vol. III, 81. From these, by interpolation, we have found the densities (S) for the temperatures we used. Combined with densities of pure water (S_0) (*op. cit.*, p. 25) and air (λ) (*op. cit.*, Vol. I, 71) for these same temperatures, the apparent relative densities $(S - \lambda)/(S_0 - \lambda)$ have been calculated. Check determinations of certain apparent relative densities were made at each temperature and agreed with those calculated from Gibson's data to within ± 0·00002.

No suitable data are available for very dilute solutions (less than 1%), and we now give values (Table II) for the apparent relative densities (D) of such solutions. All our determinations were made with the procedure and silica pyknometers described by Peel, Madgin, and Briscoe (*J. Physical Chem.*, **1928**, **32**, 285).

The surface tensions of all solutions were determined as follows. The differences in equilibrium levels (h) in the capillary limb and the lower viscometer bulb, in conjunction with density data, for solutions and water were applied in the simple surface-tension formula, *viz.*, $\gamma_s/\gamma_0 = h_s(S - \lambda)/h_0(S_0 - \lambda)$, where the subscripts s and 0 refer to solutions and water respectively. γ_0 values are from Int. Crit. Tables and thus γ_s can be found. The relative surface-tension results from two different viscometers agree to within ± 0·002, and since relative surface tension varies but little with temperature, we give only one set of values, which are for 40°.

The surface-tension correction is so small that results to 0·001 are adequate; nevertheless, the correction is useful, since it brings the results from two different viscometers into much closer agreement.

For convenience in presenting results, Table I gives values from one viscometer only (*viz.*, that requiring the smallest surface-tension correction). In all cases, corresponding results from a second viscometer agreed to ± 0·0001 or better. On account of the very small variations of K, only the two extreme values are given.

Some isolated values for the viscosities of sodium sulphate solutions are available (Int. Crit. Tables, Vol. V, 15) and, where comparison is possible, they are in good agreement with those now reported.

DISCUSSION OF RESULTS.

The results of the present work are most suitably treated by considering the variation of viscosity with temperature for each solution of constant composition. Four representative examples are given in the fig., where A, B, and C show a negative temperature coefficient of viscosity but D shows a slight positive coefficient. Solutions more dilute than D also show a positive coefficient (cf. Table I).

TABLE I.

Relative viscosities of sodium sulphate solutions at various temperatures.

	Temp.	40°.	38°.	36°.	34°.	33°.	32°.	31°.	29°.	27°.	25°.
	H	16·016	16·041	16·048	16·050	16·051	16·052	16·075	16·080	16·101	16·112
	P	15·936	15·961	15·967	15·969	15·970	15·971	15·993	15·998	16·019	16·029
	K	0·00114									0·001144
		Relative viscosities (η).									
m.	γ (40°).										
0·01783	1·000	1·0096	1·0092	1·0088	1·0085	1·0085	1·0083	1·0083	1·0080	1·0079	1·0079
0·07156	1·003	1·0348	1·0342	1·0335	1·0329	1·0326	1·0323	1·0321	1·0318	1·0316	1·0313
0·14437	1·007	1·0673	1·0663	1·0654	1·0647	1·0644	1·0641	1·0636	1·0634	1·0630	1·0626
0·29296	1·015	1·1343	1·1335	1·1328	1·1321	1·1318	1·1315	1·1312	1·1307	1·1301	1·1296
0·44938	1·022	1·2091	1·2087	1·2081	1·2077	1·2074	1·2073	1·2070	1·2066	1·2064	1·2062
0·61247	1·030	1·2960	1·2957	1·2955	1·2953	1·2951	1·2950	1·2949	1·2947	1·2945	1·2943
0·78607	1·038	1·3910	1·3913	1·3917	1·3920	1·3923	1·3925	1·3928	1·3933	1·3938	1·3944
0·95279	1·044	1·5014	1·5020	1·5026	1·5037	1·5041	1·5047	1·5054	1·5069	1·5086	1·5106
1·34412	1·058	1·7715	1·7748	1·7776	1·7804	1·7826	1·7848	1·7870	1·7939	1·8024	1·8095
1·55108	1·064	1·9333	1·9377	1·9423	1·9474	1·9501	1·9527	1·9558	1·9626	1·9691	1·9779
1·77155	1·073	2·1271	2·1321	2·1386	2·1473	2·1514	2·1568	2·1632	2·1788	2·1945	2·2155
2·00111	1·082	2·3550	2·3615	2·3730	2·3830	2·3913	2·3985	2·4060	2·4272	2·4498	2·4844
2·24276	1·093	2·6120	2·6219	2·6337	2·6507	2·6601	2·6710	2·6831	2·7113	2·7459	—
2·50123	1·102	2·9228	2·9439	2·9653	2·9928	3·0045	3·0202	3·0352	3·0671	—	—
3·01142	1·128	—	—	—	—	—	3·8391	3·8792	—	—	—
3·27607	1·140	4·1399	4·1706	4·2240	4·2850	4·3193	—	—	—	—	—

$\gamma = \gamma_s/\gamma_0$ (relative surface tension). m = molality (g.-mol. per 1000 g. of water).

TABLE II.

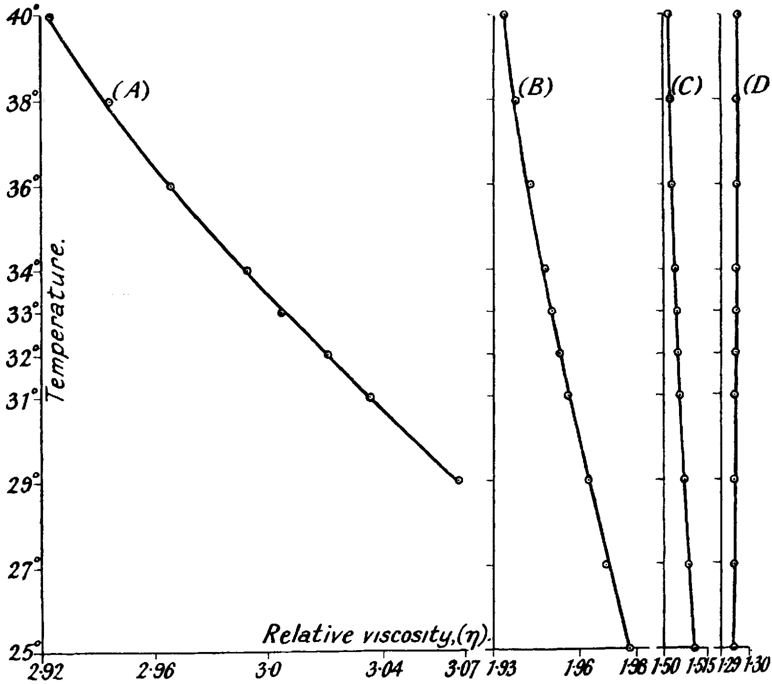
Relative viscosities of dilute sodium sulphate solutions at 25°.

Molarity (C)	0·00050	0·00099	0·00251	0·00501	0·01000	0·01777	0·02500	0·07125
Apparent relative density (D)	1·00007	1·00013	1·00034	1·00065	1·00128	1·00216	1·00323	1·00912
Relative viscosity (η)	1·0005	1·0009	1·0017	1·0029	1·0055	1·0079	1·0118	1·0313
$(\eta - 1)/\sqrt{C}$	0·0224	0·0286	0·0339	0·0410	0·0550	0·0593	0·0746	0·1172

Viscometers 1 and 3 gave identical results. C = molarity (g.-mol. per l. of solution).

Hatschek (" The Viscosity of Liquids," Bell, London, 1928, p. 122) states that " the viscosity of electrolyte solutions . . . referred to water at the same temperature, increases with rising temperature," but our results for concentrated solutions, down to a molality of 0·78, show that the reverse is the case, and similar behaviour is shown by aqueous solutions of sodium carbonate and calcium chloride (Int. Crit. Tables, Vol. V). In addition, other solutions of electrolytes (*e.g.*, salts of lithium, magnesium, and copper) show a negative temperature coefficient for all known concentrations (*ibid.*).

A possible explanation of the negative viscosity–temperature coefficients for the sodium sulphate solutions here reported is given by Rabinowitsch (*J. Amer. Chem. Soc.*, 1922, **44**, 954), who considers that, in solution, highly hydrated salts show negative viscosity–temperature coefficients, owing to the progressive decomposition of hydrates as temperature rises. It is commonly supposed that, at constant temperature, there occurs a similar progressive variation of hydration with composition such that, as concentration increases, the hydration per molecule decreases but the total hydration increases. In addition, Applebey (*loc. cit.*) considers that a dissolved electrolyte will cause a depolymerisation of the solvent water, and he states that this effect will " slowly decrease with successive additions of salt."



Molalities. $A = 2{\cdot}50123$, $B = 1{\cdot}55108$, $C = 0{\cdot}95279$, $D = 0{\cdot}61247$.

The effect of depolymerisation is to decrease viscosity, but the concomitant hydration of the solute electrolyte will increase viscosity. The variation of viscosity with concentration thus depends on which effect predominates, and evidently it is possible for a negative viscosity to change over to a positive viscosity with increasing concentration and *vice versa*. The degree of polymerisation of solvent water would be expected to increase as temperature falls, and so the depolymerisation due to a constant amount of solute should be more marked at lower temperatures. This factor alone would cause relative viscosity to decrease as temperature is lowered, and such behaviour is shown by the positive temperature coefficients of very dilute solutions (cf. fig., curve D). This depolymerisation, coupled with hydration effects discussed above, can account for the different slopes of the curves obtained for sodium sulphate solutions (see fig.), and it seems that hydration effects predominate as concentration increases, but become less pronounced as temperature rises for any one concentration Thus, an explanation of the marked slope of curve A may be that hydration predominates very considerably at this concentration, since the sulphate ion is considered to depolymerise water less than other anions (Bancroft and Gould, *J. Physical Chem.*, 1934, **38**, 197). Some support for this view of the abnormal behaviour of the sulphate ion is given by the viscosities of aqueous solutions of salts of potassium, rubidium, and cæsium (Int. Crit. Tables, Vol. V), since the sulphates are the only salts of these metals which do not give aqueous solutions showing relative viscosities of less than unity at lower concentrations. Further, for concentrated solutions, the slopes of the curves (*e.g.*, A) decrease as temperature is lowered and this is ascribed to a corresponding increase in the coefficient of variation of hydration with temperature.

Although the results of the present work do not give any evidence of an abrupt transition of hydrates in solution, yet there seems justification for the conclusion that hydration occurs and that it varies with temperature and concentration. Gibson (*loc. cit.*) has drawn similar conclusions from different experimental evidence.

Sugden (J., 1926, 183) calculated molecular hydration values from distribution experiments, but was unable to calculate such values for sulphates in solution to show comparable consistency with those obtained for other salts.

With the exception of barium chloride solutions, equation (1) has only been applied to the viscosities of uni-univalent electrolyte solutions, and such measurements are in good agreement with the equation (cf. Jones and Talley, *loc. cit.*; Joy and Wolfenden, *loc. cit.*). Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 2950) have applied a form of equation (1) to viscosities of solutions of barium chloride, but the value obtained for A differed markedly from that calculated by the method of Falkenhagen and Vernon (*Phil. Mag.*, 1932, **14**, 537). Sodium sulphate, being of a similar valency type (uni-bivalent) to barium chloride, affords a useful example with which to test the validity of equation (1), which has been applied to our results for dilute solutions at 25° (Table II).

From these results, the constants A and B in the equation have been calculated by the method of least squares, and the values found are $A = 0{\cdot}0155$, $B = 0{\cdot}357$. By applying the method of Falkenhagen and Vernon (*loc. cit.*) a value, $A = 0{\cdot}0147$, has been obtained and thus the agreement between experimental and calculated values of A is comparable with that found by Jones and Talley (*loc. cit.*) for solutions of uni-univalent electrolytes.

The viscosities of solutions of concentrations exceeding $0{\cdot}1M$ are markedly greater than those calculated from equation (1), and the interpretation of such viscosities involves several indeterminate effects, which include the following: (*a*) The inter-ionic effect [$A\sqrt{C}$ of (1)]; (*b*) the relaxation of solvent dipole effect [BC of (1)], discussed by Finkelstein (*Physikal. Z.*, 1930, **31**, 130, 165); (*c*) the depolymerisation of the solvent, which is proportional to C^n, where $n < 1$: evidently the solute becomes decreasingly effective in promoting depolymerisation as concentration is increased (cf. Applebey, *loc. cit.*); (*d*) the effect of hydration of the solute in decreasing the amount of free water, whereby the viscosity is proportional to C^m, where $m > 1$.

SUMMARY.

1. Viscosities of sodium sulphate solutions have been measured at various temperatures from 25° to 40° and over a range of concentrations extending up to as near saturation as possible.

2. No evidence of a definite transition of hydrates in solution, comparable with the change which occurs in solid hydrated sodium sulphate at about 32·5°, has been found, but the existence of a less definite form of hydration is presumed.

3. The viscosity–temperature curves for each concentration are discussed, and a probable explanation of their slopes is given in terms of hydration of solute and depolymerisation of solvent.

4. It is concluded that there is a progressive increase in total hydration of solute as temperature is lowered.

5. The equation $\eta = 1 + A\sqrt{C} \pm BC$ has been applied to dilute solutions at 25°, and a value for A has been found which agrees satisfactorily with that calculated by applying the theory of Falkenhagen and Vernon.

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