LIV.—*The Viscosity and Density of Rubidium Nitrate Solutions.*

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The following measurements, carried out in 1922, were undertaken to complete our knowledge of the viscosity and density of aqueous solutions of the alkaline nitrates. Grüneisen (*Wiss. Abh. Phys. Tech. Reichsanstalt*, 1904, **4**, 239) has made measurements on the nitrates of sodium and potassium, and lithium and cæsium nitrates have been studied in this laboratory by Applebey (J., 1910, **97**, 2000) and Merton (*ibid.*, p. 2454) respectively.

Experimental.

Materials.—The rubidium nitrate used was Merck's pure salt; spectroscopic examination showed it to be free from all but negligible amounts of the other alkali metals. The salt was dried to constant weight at 210° immediately before use in every case. The conductivity of the water used in making up solutions and in washing out pyknometers and viscometers ranged from 0·5 to 2 gemmhos.

Temperature Control.—All the measurements were carried out in two electrically controlled thermostats. The temperatures of the baths were determined by a thermometer which had been standardised by the Reichsanstalt and whose ice-point was confirmed in the course of the present work. The corrected temperatures of the two baths were 18·00° ± 0·005° and 25·01° ± 0·005° and the fluctuations from the mean did not exceed 0·003°.

Results.

TABLE I.—*Viscosities at* 18·00° *and* 25·01°.

			t_s/t_w at 18°.				t_s/t_w at 25·01°.		
Soltn.	N_w.	N_v at 18°.	Viscometer B 2.	Viscometer G 3.	*R.V.* at 18°.	N_v at 25·01°.	Viscometer B 2.	Viscometer G 3.	*R.V.* at 25·01°.
A	0·09244	0·09321	0·98281	0·98300	0·99251	0·09306	0·98473	0·98464	0·99422
B	0·14440	0·14641	0·97303	0·97272	0·9877	0·14616	0·97604	0·97637	0·99100
C	0·18531	0·18870	0·96475	0·96487	0·98386	0·18838	0·96955	0·96957	0·98850
D	0·25122	0·25762	0·95283	0·95278	0·97846	0·25716	0·95934	0·95825	0·98490
F	0·47418	0·49800	0·91556	0·91525	0·96278	0·49702	0·92635	0·92626	0·97383
G	0·47581	0·49988	0·91460	0·91460	0·96225	0·49888	0·92564	0·92531	0·97326
H	0·71402	0·76984	0·87821	0·87821	0·94826	0·76815	0·89256	0·89266	0·96308
I	0·89168	0·98051	0·85463	0·85431	0·94100	0·97821	0·87130	0·87130	0·95877
J	0·98708	1·09699	0·84238	0·84206	0·93740	1·09434	0·86000	0·85982	0·95629
K	1·26927	1·4566	0·81010	0·81041	0·93128	1·4528	0·83109	0·83107	0·95421
L	1·5505	1·8391	0·78330	0·78334	0·9306	1·8341	0·80639	0·80682	0·95715
M	1·78637	2·1799	0·76418	0·76398	0·93388	2·1735	0·78976	0·78977	0·96394

TABLE II.—*Densities at* 18·00° *and* 25·01° $(d_{t^\circ}^{t^\circ})$.

		Values at 18·00°.				Values at 25·01°.			
Soltn.	N_w.	Pyknometer M.	Pyknometer P.	Pyknometer X.	Mean.*	Pyknometer M.	Pyknometer P.	Pyknometer X.	Mean.*
A	0·09244	1·009766	1·009767		1·00977	1·009665	1·009664		1·00966
B	0·14440		1·015309		1·01531	1·015144	1·015165		1·01515
C	0·18531	1·01973	1·01978		1·01973	1·01955	1·01960		1·01955
D	0·25122	1·02690			1·02690	1·02663			1·02663
E	0·36593		1·039536	1·039535	1·03954		1·039159	1·039152	1·03916
F	0·47418	1·051702	1·051752		1·05170	1·051239	1·051265		1·05124
G	0·47581		1·052038		1·05204		1·051564		1·05156
H	0·71402	1·07970	1·07967		1·07967	1·07899	1·07897		1·07897
I	0·89168	1·101144	1·101189		1·10114	1·100267	1·100329		1·10027
J	0·98708		1·112880	1·112882	1·11288		1·111923	1·111941	1·11193
K	1·26927	1·149196	1·149225		1·14920	1·147982	1·148016		1·14798
L	1·5505		1·18783		1·18783		1·18637		1·18637
M	1·78637		1·221956		1·22196		1·220275		1·22028

* See p. 409.

Viscosity Measurement.—The method of measurement and the viscometers and holders used were similar to those described by Applebey and by Merton. Every solution was measured in two viscometers, both of which the late Mr. G. A. Hutchinson had shown by the constancy of the pressure–time product to obey Poiseuille's law. The time intervals, ranging from 600 to 950 seconds, were measured on a stop-watch, graduated in fifths of a second and fitted with an electromagnetic release. The results are given in Table I, in which N_w and N_v are respectively the weight normality (mols. per 1000 g. of solution) and the volume normality (mols. per litre), t_s and t_w are respectively the times of flow of solution and of water, and *R.V.* is the mean relative viscosity (see below).

Density Measurement.—The density of every solution was measured in two pyknometers of about 25 c.c. capacity, the technique of Hartley and Barrett (J., 1911, **99**, 1072) being followed. The results are shown in Table II.

Discussion of Results.

Viscosity.—The relative viscosity of the solutions was calculated from the formula

$$R.V. = \frac{t_s}{t_w} \times \frac{\Delta_{\text{solution}} - \Delta_{\text{air}}}{\Delta_{\text{water}} - \Delta_{\text{air}}}.$$

Following the practice of Applebey and of Merton, no kinetic-energy correction was introduced. No correction was made for surface tension, but the error involved is probably within the error of time measurement for solutions less concentrated than $N/4$.

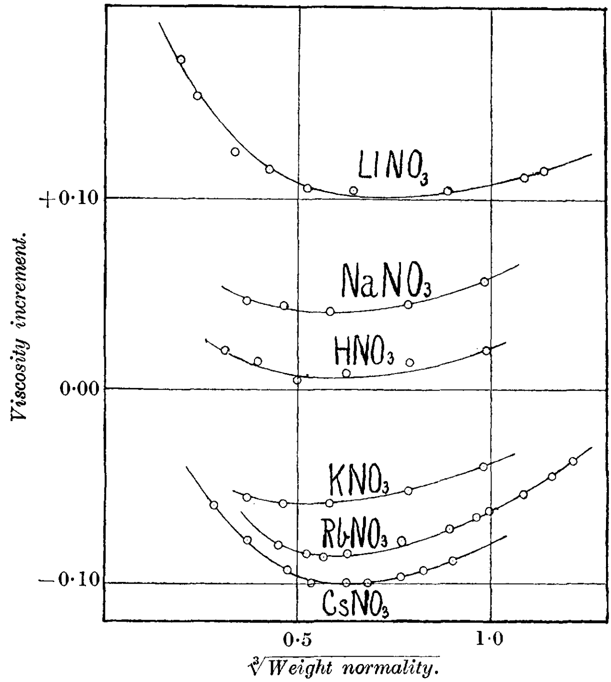
The agreement between independent determinations of the same solution in both viscometers suggests an average error of about one part in 10,000 parts in the measurements of relative viscosity. This compares favourably with the concordance recorded by other observers who have used more than one viscometer.

The form of the viscosity–concentration curves at both temperatures is similar to that of Grüneisen's curves for potassium nitrate and of Merton's curves for cæsium nitrate. When the viscosity increment, defined as $(R.V. - 1)/N_w$, is plotted against the cube root of the weight normality the curve shows the minimum which Grüneisen obtained with a number of salts. In Fig. 1 the viscosity increments for the completed series of alkaline nitrates and for nitric acid at 18° are plotted against the cube root of the weight normality; it will be seen that the value of the increment decreases regularly with increase of atomic number.

The inadequacy of most of the attempts to represent the relative viscosity–concentration curve of an electrolyte solution by an equation is well known. Thus the equations of Einstein (*Ann.*

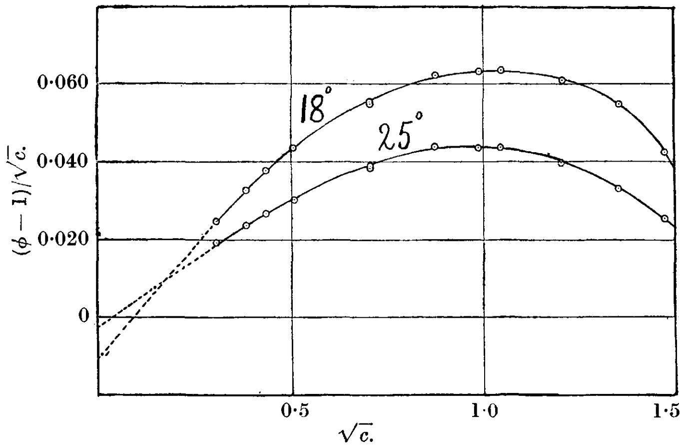
Physik, 1906, **19**, 289) and of Herz (*Z. anorg. Chem.*, 1917, **99**, 132) do not admit of the possibility of "negative viscosity"; that of Arrhenius (*Z. physikal. Chem.*, 1888, **1**, 285) predicts no minimum in either relative viscosity or viscosity increment; that of Applebey (*loc. cit.*) predicts a viscosity increment minimum but, when applied to our results for rubidium nitrate, postulates an average hydration number for the two ions of about −3; the semi-empirical equation of Grüneisen (*loc. cit.*) is equally unsatisfactory when applied to our results since, in spite of its three arbitrarily fixed constants, it fails to reproduce with anything approaching the experimental accuracy the form of the viscosity increment–concentration curve.

FIG. 1.



A much more promising form of equation correlating the viscosity and concentration of an electrolyte solution has recently been put forward by Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 2950), whose experimental data for the fluidity of barium chloride solutions were adequately represented over a concentration range 0·005—1·00*M* by the equation $\phi = 1 + A\sqrt{c} + Bc$, where c is expressed in mols. per litre. They further showed that their equation is equally applicable to all the other published data on salts which increase the viscosity of water. In the case of cæsium nitrate, which diminishes the viscosity of water, they found that the equation was obeyed over a more limited concentration range up to 0·2N. Moreover, qualitative arguments based on the Debye–Hückel theory were advanced for believing that the coefficient A must always be negative, *i.e.*, that the relative viscosity of all electrolytes must be greater than unity at sufficiently high dilution. Dole and Falkenhagen (*Physikal. Z.*, 1929, **30**, 611) have developed this point of view mathematically and evaluated the constant A for the special case of a binary electrolyte whose ions have equal mobilities. Experimental confirmation has recently been obtained by Joy and Wolfenden (*Nature*, 1930, **126**, 994) in the case of dilute aqueous solutions of potassium chloride.

FIG. 2.



In view of these considerations, it is of interest to compare the present experimental results with the Jones–Dole equation. As these authors point out, the most convenient way of testing the validity of the equation is to plot $(\phi - 1)/\sqrt{c}$ against $\sqrt{c}$ and to see if a straight line is obtained with a negative intercept on the axis of zero concentration. The data recalculated in this way are shown in Table III and plotted in Fig. 2.

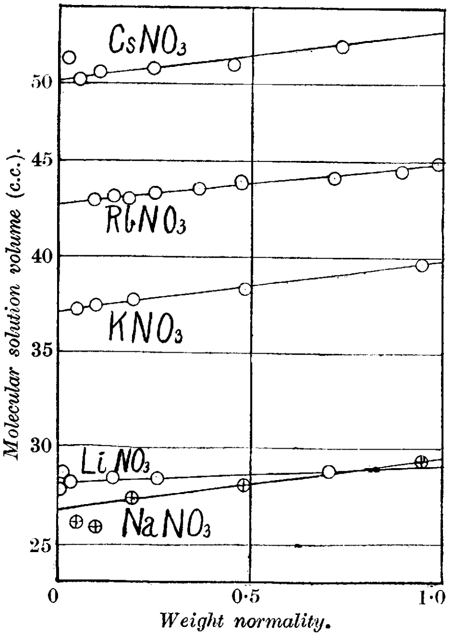
It is clear from the figure that the intercept (which is numerically equal to A) is negative at 18°, diminishes with rising temperature, and is probably still negative at 25°. The curves show convergence to linearity as the dilution increases but, as in the case of cæsium nitrate, the Jones–Dole equation is valid only at concentrations less than about 0·2N.

Density.—The concordance between the densities determined in the different pyknometers is in all cases well within the probable

TABLE III.

	18·00°.			25·01°.		
Soltn.	$\sqrt{c}$.	ϕ.	$(\phi - 1)/\sqrt{c}$.	$\sqrt{c}$.	ϕ.	$(\phi - 1)/\sqrt{c}$.
A	0·3053	1·00755	0·0247	0·3050	1·00581	0·01905
B	0·3826	1·01244	0·0325	0·3823	1·00908	0·02375
C	0·4344	1·01640	0·0378	0·4340	1·01163	0·0268
D	0·5075	1·02201	0·0434	0·5071	1·01533	0·0302
F	0·7057	1·03866	0·0548	0·7050	1·02687	0·0381
G	0·7070	1·03923	0·0555	0·7063	1·02747	0·0389
H	0·8774	1·05456	0·0622	0·8764	1·03833	0·0437
I	0·9902	1·06270	0·0633	0·9890	1·04300	0·0435
J	1·0473	1·06678	0·0637	1·0459	1·04571	0·0437
K	1·2069	1·07379	0·0611	1·2052	1·04799	0·0398
L	1·3560	1·07457	0·0550	1·3542	1·04477	0·0331
M	1·4765	1·07080	0·0425	1·4741	1·03741	0·0254

FIG. 3.



error of the viscosity measurement to which they are auxiliary. With the exception of solutions A, E, and J, the concordance is, however, less satisfactory than might be expected in accurate pyknometry. This is attributable to the fact that the limited amount of rubidium nitrate available compelled us, with all except the above-mentioned solutions, to transfer the same quantity of solution from the first to the second pyknometer instead of making simultaneous determinations in two pyknometers. The evaporation incidental to this transfer and the second filling invariably caused an increase in the density as measured in the second pyknometer. We have therefore adopted the lower (and earlier) density value whenever the density of the solution was not measured on independent portions of the solution in the two pyknometers.

We have calculated from the density results the contraction on solution of 1 mol. of rubidium nitrate at various concentrations. More significant results are obtained by calculating the " molecular solution volume " of the salt at various concentrations, since the latter method has the substantial advantage that the density of the solid salt and the anomalies introduced by polymorphism, etc., are not involved in the calculation. Table IV shows the molecular solution volume of rubidium nitrate at 18° and 25·01° over the concentration range measured, and in Fig. 3 this function for the completed series of alkaline nitrates at 18° is plotted against weight normality. The values for lithium nitrate are calculated from the data of Applebey, those for sodium and potassium nitrates from the data of Grüneisen, and those of cæsium nitrate from the data of Merton.

TABLE IV.

		Molecular solution vol. (c.c.).	
Soltn.	N_w.	At 18·00°.	At 25·01°.
A	0·09244	42·91	44·09
B	0·14440	43·08	44·22
C	0·18531	42·98	43·98
D	0·25122	43·26	44·34
E	0·36593	43·57	44·61
F	0·47418	43·87	44·81
G	0·47581	43·83	44·82
H	0·71402	44·18	45·08
I	0·89168	44·54	45·40
J	0·98708	44·98	45·82
K	1·26927	45·65	46·06
L	1·5505	45·54	46·27
M	1·78637	46·27	46·76

(The molecular volume of solid rubidium nitrate is 47·64 c.c.)

Summary.

(1) The relative viscosity and the relative density of aqueous solutions of rubidium nitrate have been measured at 18° and 25° over the concentration range 0·092—1·786*N*.

(2) The relative viscosity of rubidium nitrate solutions can be represented by the Jones–Dole equation at concentrations below 0·2*N*, and the coefficient *A* of those authors is shown to have the negative value and negative temperature coefficient which they postulate.

(3) The molecular solution volume of rubidium nitrate is shown to fall in the normal periodic sequence of the alkaline nitrates.

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