Jones[1] has pointed out the following general relations deduced from the study of a large number of data concerning temperature coefficients:

1. Those ions with the largest hydrating power have the largest temperature coefficients of conductivity.
2. Those substances having equal hydrating power have approximately the same temperature coefficients of conductivity.
3. At higher dilutions the temperature coefficients of conductivity, for any given substance, are greater than at lower dilutions.

In the present investigation all of these relations have been found to hold, with the few apparent exceptions which are noted in the above discussion.

Summary.

Eighteen more or less unusual salts were studied with reference to the conductivity, over a range of temperature from 0° to 35°, and, wherever possible, their dissociation has been calculated. Their temperature coefficients were also calculated in two sets of units.

The results of this investigation are, for the most part, in accord with the findings of other workers in this field in this laboratory. Three exceptions to the rule that dissociation decreases with increased temperature were found. Two apparent exceptions to the rule that large temperature coefficients are indicative of great hydration were noted, and possible explanations offered.

BALTIMORE, MD.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

THE VISCOSITIES OF SOLUTIONS OF CAESIUM SALTS IN MIXED SOLVENTS.[2]

BY P. B. DAVIS AND HARRY C. JONES.

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Introduction.

We have endeavored for some time to secure enough caesium salts to study their viscosity in pure and in mixed solvents, but only within the past year have we been successful. Through the courtesy of Professor James Lewis Howe, of Washington and Lee University, a quantity of caesium sulfate was placed at our disposal. This was converted first into the hydroxide, then into the carbonate, and finally into the chloride and nitrate; and with these salts this investigation was carried out.

Caesium is the most electropositive of all the elements, and is further distinguished by possessing the largest atomic volume, being followed in

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[1] *Am. Chem. J.*, 34, 357 (1905).

[2] This is part of an investigation which was carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones, and the results will be recorded in full in Publication No. 230 of that Institution.

this respect by rubidium and potassium, respectively. Since salts of the latter two elements are of great interest from the viscosity standpoint, it would be expected that caesium salts would possess, to a more pronounced degree, any peculiarities shown by salts of rubidium and potassium.

An examination of the literature bearing on viscosity shows that, in general, only the salts of the three metals mentioned above are known to lower the viscosity of water. The effect of potassium and rubidium salts on the viscosities of solvents other than water, and of mixtures of such solvents with one another and with water, has been the subject of earlier investigations in this laboratory; and this series of investigations can now be regarded as in a measure completed by the study of caesium salts in these solvents. The present investigation, therefore, has been made to comprise a study of the viscosity of the two caesium salts, chloride and nitrate, in water and in binary mixtures of methyl alcohol, ethyl alcohol, and acetone with water.

The results obtained with caesium salts in formamid as a solvent are now in press,[1] and further investigation of their behavior in glycerol and glycerol-water mixtures, as well as in mixed solvents containing formamid instead of water, is now in progress.

Historical Sketch.

Jones and Linsay,[2] in their work on binary mixtures of the alcohols with water, found that the molecular conductivities of solutions of salts in these solvents, were, in every case, less than the averages calculated from conductivities in the component solvents themselves. These results, interpreted in the light of the work of Dutoit and Aston, point to a lower degree of association in the case of the mixed solvents than in that of the pure solvents themselves.

Jones and Carroll,[3] in extending the above investigation, showed that the change in the viscosity of the medium was an important factor conditioning the decrease in conductivity of salts in such binary mixtures and liquids, the decrease in ionization due to changes in association being only one of the factors to be taken into account.

It, however, remained for Jones and Veazey[4] to offer a satisfactory explanation of the increase in viscosity which occurs when two highly associated liquids are mixed; and also to account for the phenomenon of negative viscosity, or the lowering of the viscosity of the solvent by a dissolved substance.

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[1] *Pub. Carnegie Inst. Wash.*, No. 230 (1915).

[2] *Am. Chem. J.*, 28, 329 (1902); *Pub. Carnegie Inst. Wash.*, No. 80, 24 (1907).

[3] *Am. Chem. J.*, 32, 409 (1904); *Pub. Carnegie Inst. Wash.*. No. 80, 43 (1907).

[4] *Ibid.*, 107 (1907); *Z. physik. Chem.*, 61, 641 (1908); 62, 44 (1908).

The work of Thorpe and Rodger having shown that viscosities depend largely upon the frictional surfaces of the physical particles in any solution, it followed that if these surfaces were increased or diminished by any means whatsoever, there would result a corresponding increase or decrease in the fluidity of the medium. The work of Jones and Murray[1] had brought out the fact that on mixing two highly associated liquids a material diminution in the association of both takes place. This would result in an increase in the number of ultimate particles in a given volume, with a corresponding decrease in their size, and therefore an increase in their frictional surfaces which would be exposed to one another. Consequently, the viscosity curves for the various mixtures should pass through a maximum, the position of which would depend upon the relative effects of the solvents upon one another.

The reason for the maximum in such viscosity curves and their relation to conductivity having been explained, the effect of certain salts in lowering the viscosity of the solvent remained to be interpreted. Potassium, rubidium and caesium salts, as has already been stated, were known to lower the viscosity of water. These elements occupy the highest maxima on the atomic volume curve, and, as Wagner[2] had shown, they possess negative viscosity coefficients in water, which vary directly as their volumes. The explanation offered by Jones and Veazey to account for these facts, was that salts of these metals lower the viscosity of the solvent by introducing into it ions which are so large that, when mixed with the molecules of the solvent, they lower the total fractional surfaces exposed to one another. That certain salts of potassium do not produce this effect is due to the fact that the viscosity of the solu-

TABLE I.

Viscosity of Caesium Chloride in Methyl Alcohol-Water Mixtures at 15°, 25°, 35°.

75% Methyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
0.50	0.01674	0.01309	0.01049
0.25	0.01637	0.01275	0.01021
0.10	0.01613	0.01243	0.00997
Solv.	0.01594	0.01235	0.01032

50% Methyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
0.50	0.02119	0.01547	0.01200
0.25	0.02084	0.01553	0.01197
0.10	0.02086	0.01531	0.01179
Solv.	0.02100	0.01535	0.01169

25% Methyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
0.50	0.01778	0.01338	0.01048
0.25	0.01828	0.01360	0.01047
0.10	0.01862	0.01358	0.01044
Solv.	0.01871	0.01359	0.01032

Water.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.01098	0.00877	0.0713
4	0.01111	0.00889	0.0716
10	0.01133	0.00884	0.0719
Solv.	0.01134	0.00891	0.0721

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[1] *Am. Chem. J.*, 30, 193 (1903).

[2] *Z. physik. Chem.*, 46, 867 (1903).

TABLE II.

Viscosity of Caesium Nitrate in Methyl Alcohol-Water Mixtures at 15°, 25°, 35°.

75% Methyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	...	...	...
4	...	...	...
10	...	0.01244	0.00987
Solv.	0.01594	0.01235	0.00978

50% Methyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	...	...	...
4	...	0.01520	0.01177
10	0.02072	0.01543	0.01182
Solv.	0.02100	0.01535	0.01169

25% Methyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	...	0.01300	0.01018
4	0.01795	0.01331	0.01028
10	0.01832	0.01346	0.01031
Solv.	0.01871	0.01359	0.01032

Water.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.01075	0.00858	0.00703
4	0.01102	0.00871	0.00705
10	0.01122	0.00885	0.00720
Solv.	0.01134	0.00891	0.00720

TABLE III.

Viscosity of Caesium Chloride in Ethyl Alcohol-Water Mixtures at 15°, 25°, 35°.

75% Ethyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.02777	0.02061	0.01590
4	0.02783	0.02039	0.01561
10	0.02761	0.01994	0.01500
Solv.	0.02762	0.01997	0.01537

50% Ethyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.03176	0.02245	0.01635
4	0.03346	0.02283	0.01666
10	0.03359	0.02274	0.01648
Solv.	0.03400	0.02286	0.01618

25% Ethyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.02381	0.01694	0.01262
4	0.02472	0.01738	0.01282
10	0.02522	0.01736	0.01276
Solv.	0.02585	0.01760	0.01270

Water.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.01098	0.0877	0.0713
4	0.01111	0.0889	0.0716
10	0.01133	0.0884	0.0719
Solv.	0.01134	0.0891	0.0720

TABLE IV.

Viscosity of Caesium Nitrate in Ethyl Alcohol-Water Mixtures at 15°, 25°, 35°.

25% Ethyl Alcohol.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	...	...	...
4	0.02424	0.01697	0.01261
10	0.02526	0.01745	0.01276
Solv.	0.02585	0.01760	0.01270

Water.

	Viscosities.		
Mol. conc.	η 15°.	η 25°.	η 35°.
2	0.01075	0.00858	0.00703
4	0.01102	0.00871	0.00705
10	0.01122	0.00885	0.00720
Solv.	0.01134	0.00891	0.00720

NOTE.—The salt was practically insoluble in the 75% and 50% mixtures.

TABLE V.

Viscosity of Caesium Chloride in Acetone-Water Mixtures at 15°, 25°, 35°.

75 % Acetone.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	. . .	. . .	. . .
4	0.01188	0.00930	0.00764
10	0.01135	0.00904	0.00740
Solv.	0.01125	0.00896	0.00732

50% Acetone.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	0.01785	0.01354	0.01060
4	0.01783	0.01337	0.01038
10	0.01777	0.01316	0.01029
Solv.	0.01766	0.01306	0.01009

25% Acetone.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	0.01647	0.01250	0.00983
4	0.01667	0.01254	0.00979
10	0.01677	0.01246	0.00978
Solv.	0.01690	0.01248	0.00964

Water.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	0.01098	0.00877	0.0713
4	0.01111	0.00889	0.0716
10	0.01133	0.00888	0.0719
Solv.	0.01134	0.00891	0.0720

TABLE VI.

Viscosity of Caesium Nitrate in Acetone-Water Mixtures at 15°, 25°, 35°.

75% Acetone.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	. . .	. . .	. . .
4	. . .	. . .	. . .
10	0.01143	0.00804	0.00737
Solv.	0.01119	0.00878	0.00680

50% Acetone.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	. . .	. . .	. . .
4	0.01759	0.01320	0.01030
10	0.01756	0.01307	0.01017
Solv.	0.01767	0.01304	0.01007

25% Acetone.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	0.01610	0.01216	0.00965
4	0.01655	0.01229	0.00971
10	0.01665	0.01244	0.00968
Solv.	0.01673	0.01232	0.00962

Water.

Mol. conc.	Viscosities. η 15°.	η 25°.	η 35°.
2	0.01075	0.00858	0.00703
4	0.01102	0.00871	0.00705
10	0.01122	0.00885	0.00720
Solv.	0.01134	0.00891	0.00720

tion is also a function of the anions as well as the cations. When the volume of the anion is very small, the negative effect on viscosity of the cation is more than overcome, and positive viscosity results.

Applying this hypothesis of Jones and Veazey to mixed solvents, Jones and his co-workers have been able to explain a number of facts which otherwise appear to be explicable. For a detailed discussion of this work and a description of the apparatus used in this investigation, consult Publications Nos. 180 and 210 of the Carnegie Institution of Washington.

Discussion of Results.

As can be seen from the tables, measurements have been made of the viscosities of solutions of these salts at 15°, 25°, 35° in mixtures of 25, 50 and 75% of each of the three solvents with water. Caesium salts, with the possible exception of the carbonate, are practically insoluble in the alcohols and in acetone; and in a number of cases it was impossible to obtain solutions more concentrated than one-fourth normal in the 75% mixtures. In fact, caesium nitrate was not more soluble than tenth-normal in 75% methyl alcohol and 75% acetone, while it is impossible to obtain even that concentration in 75% ethyl alcohol. One peculiarity previously noted in the case of rubidium chloride in 75% acetone was also observed with caesium chloride. A one-half normal concentration of this salt could easily be prepared, but with a partial separation of the acetone from the solvent. However, on cooling below 10° a perfectly homogeneous mixture again resulted, which separated again into two layers on warming. The nitrate at this concentration merely remained partially undissolved. The results obtained are tabulated for each salt, under the heads of the different solvent mixtures, the blank spaces indicating that the salt was insoluble at the concentration in question. In general, both of the salts lower the viscosity of water and of the 25% mixture of all the solvents, and increase the viscosity of the 75% mixture. These facts are in perfect accord with the results obtained in earlier work with salts of potassium and rubidium. In the 50% mixtures the two salts manifest somewhat different behavior. The chloride in 50% methyl alcohol shows an increase in viscosity at all temperatures for the most dilute solutions, and a tendency of the more concentrated solutions to pass over into negative viscosity. The nitrate in the same solvent showed a decided negative viscosity effect.

In 50% ethyl alcohol, a decrease in the viscosity of the solutions as compared with that of the solvent was noted at the lower temperature, a transition to positive viscosity taking place at higher temperatures. Again, the nitrate decreases the viscosity of the solvent at all temperatures.

With regard to the 50% acetone-water mixture, an increase in viscosity at all temperatures is to be noted in the case of the chloride, while the nitrate in this solvent shows a tendency to decrease the viscosity of the solvent, although it increases at the higher temperatures. The difference in the effect produced by these salts, in comparison with that effected by the salts of rubidium, lies in the shifting of the transition point from negative to positive viscosity, towards the mixtures containing the larger percentage of acetone. This follows from the different molecular volumes of the cations of rubidium and caesium. When acetone and water are mixed, the principal changes take place in the association of the acetone. Consequently, until considerable water has been introduced the solvent particles are quite large, so that even caesium nitrate, having the largest negative viscosity coefficient in water, increases the viscosity of the 75% mixture and even of the 50% mixture, except at lower temperatures. For rubidium salts, no examples of negative viscosity are to be noted until the 37.5% mixture is reached. No data are available for comparison with rubidium salts in alcohol-water mixtures, but it has been shown that potassium iodide increases the viscosity of these mixtures to that concentration containing 40% alcohol. In this instance, however, caesium nitrate decreases the viscosity of the 50% mixture, positive viscosity manifesting itself only in the 75% mixture.

This shifting of the transition point from negative to positive viscosity towards the more concentrated solvents (regarding water as the diluent) with increase in the molecular volume of the salt, brings out clearly the gradual breaking down of the associated molecules into smaller particles with greater fractional surfaces, the difference in the sizes of the particles at different points on the dilution curve, being clearly brought out by the effect produced by salts of differing molecular volumes.

The apparent transition from negative to positive viscosity with rise in temperature, noted in certain instances, would seem to indicate either a polymerization of the salt or else a solvent envelope which is broken down with rise in temperature. Since these salts are the least solvated, the first assumption is apparently the more plausible.

Measurements are now in progress of the effect of these salts on the viscosity of glycerol and of glycerol-water mixtures.

BALTIMORE, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS. PART III.

BY J. P. BONARDI AND C. JAMES.

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This article describes the continued search for a rapid, efficient and economical method for the separation of yttrium from the yttrium earths. All the methods which are herein given are of a fractional precipitation type.

Precipitation by Means of Ammonium Sebacate.—About 12 g. of the mixed oxides were dissolved in dilute nitric acid, diluted to 1200 cc. and made neutral by the addition of ammonium hydroxide. The solution was then boiled and stirred with steam. In order to keep the volume of the liquid in the flask constant, a bunsen burner was always kept going underneath. When the liquid boiled, a 10% solution of ammonium sebacate was added until a fair-sized precipitate had formed. The precipitated sebacates were granular and filtered readily. The filtrate from Fraction I was similarly treated and this was carried out until five fractions were obtained. The various fractions were dissolved in dilute nitric acid, boiled and precipitated with a hot solution of oxalic acid.