QUANTITATIVE LYOTROPY[1]

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Until recently the lyotropic activity of different ions has been expressed only qualitatively. A quantitative investigation of the lyotropic series has now given a deeper insight into the mechanism of ionic action.

It has been shown (7, 8) that, on salting out lyophilic colloids with mixtures of sodium sulfate and other sodium salts, the amounts of both salts that are necessary to bring about flocculation are in linear relationship. Except at very low concentrations, the salt action is perfectly additive. Figures 1 and 2 show this behavior for agar and gelatin. It is remarkable that several ions counteract the salting-out action of the sulfate ion; this "salting-in" effect does not depend on the ion only, but also on the nature of the colloid. It appears that a proper measure for the salting-out action of the ions is expressed by the angle between the lines in the diagram and the axis of the abscissae. If α be this angle for a certain salt in the case of gelatin and β of the same salt in the case of agar, the following relation holds:

$$\cot \alpha = A \cot \beta + B$$

The directions of the lines in both diagrams are in projective relationship to each other, as has been pointed out by Bruins (3). Ascribing to every ion a number, N, fixed by the following relation:

$$N = a \cot \varphi + b$$

where a and b are constants and φ is the angle formed by the salt-line of the ion and the axis of the abscissae in the diagram, the angles are different in the case of different colloids, but the number N is characteristic for every ion. Fixing a scale, we use two arbitrary numbers. Choosing $SO_4^{--} = 2.00$ and $Cl^- = 10.00$, we find from the diagram:

$$N = 4.00 \cot \varphi + 10.00 \text{ (agar)}$$
$$N = -4.78 \cot \varphi + 11.15 \text{ (gelatin)}$$

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The calculated N values are in good agreement (see table 1). Computations give for the other ions the numbers shown in table 2.

This method enables us to predict the salting-out action of different salts in the case of other colloids, provided that the action of two ions is known. This has been proved by experiments carried out on hemoglobin (5). According to this view a linear relationship between the flocculating action

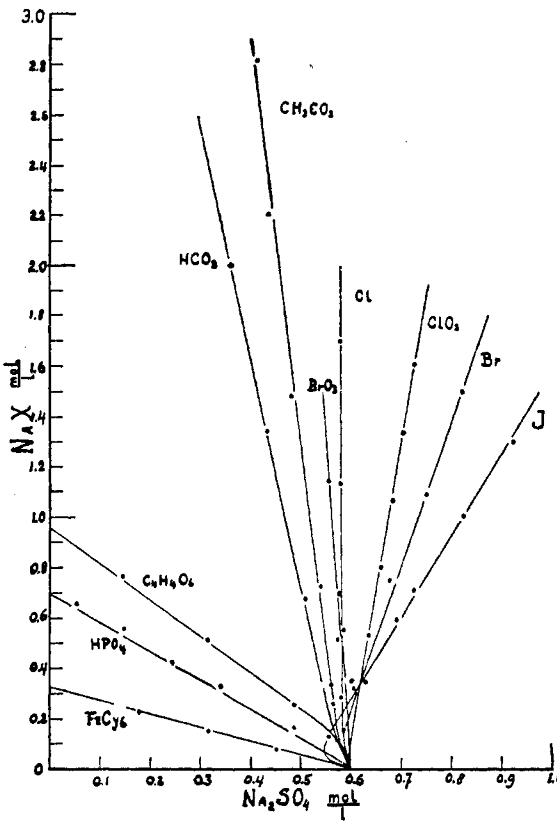

FIG. 1. Concentrations of different sodium salts plotted against concentrations of sodium sulfate, mixtures of which are necessary to bring about flocculation of agar-agar sols.

of the different sodium salts and the lyotropic numbers N is required (figure 3).

It can be shown that the numbers obtained in the case of salting-out experiments with lyophilic colloids play an important part in other lyotropic phenomena.

a. Swelling. Plotting the relative increase in weight of gelatin, swollen

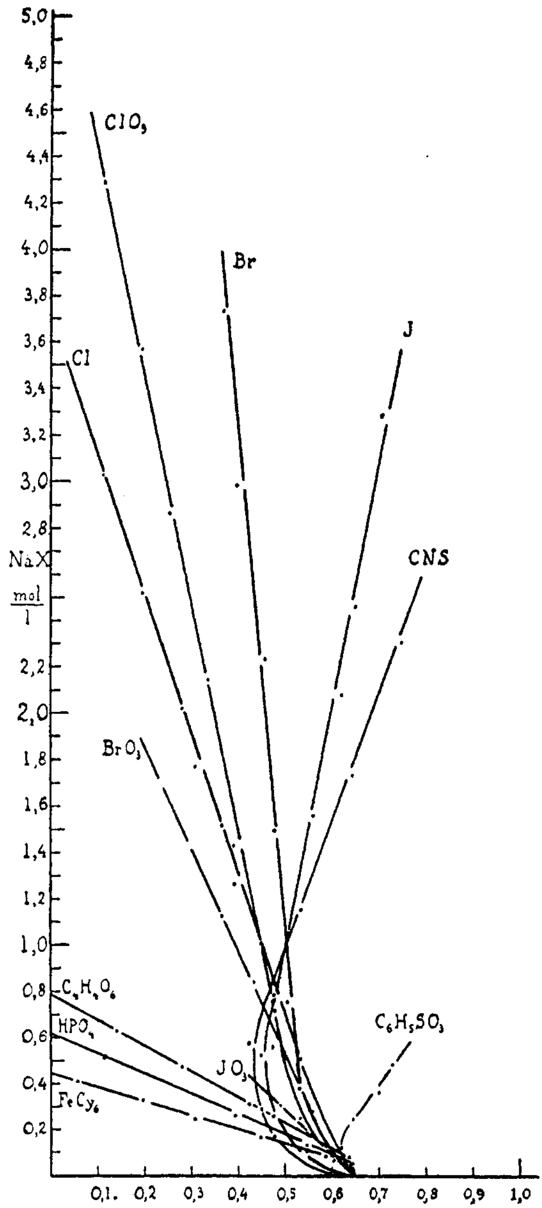

FIG. 2. Concentrations of different sodium salts plotted against concentrations of sodium sulfate, mixtures of which are necessary to bring about flocculation of gelatin sols.

in different solutions of sodium salts of the same concentration against the lyotropic numbers of the respective anions, linear relations occur (9). This is shown in figures 4a and 4b for temperatures of 0°C. and 18°C. Both lines cut the axis at the point $N = 9.8$, this number indicating the

TABLE 1

Calculated values of N

	BrO_3^-	NO_3^-	ClO_3^-	Br^-	I^-
Agar	9.72	10.1	10.74	11.50	12.50
Gelatin	9.38	10.2	10.58	11.14	12.48
Number used	9.55	10.1	10.65	11.30	12.50

TABLE 2

Calculated values of N for other ions

Ion	F^-	IO_3^-	$H_2PO_4^-$	NO_3^-	ClO_4^-	CNS^-
Value of N	4.8	6.25	8.2	11.6	11.8	13.25

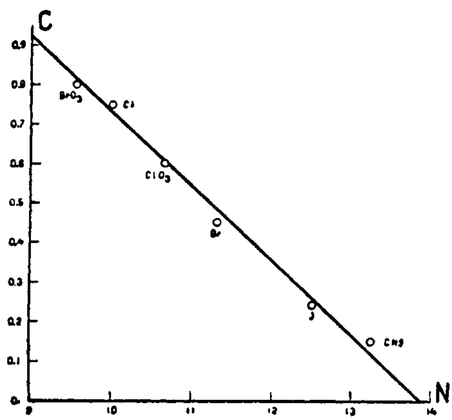

FIG. 3. Concentrations of different sodium salts, necessary to flocculate hemoglobin sols, plotted against the lyotropic numbers.

difference between ions which increase and those which decrease the swelling of gelatin.

b. Gelation and solation of lyophilic colloids. If Pascheles' data about gelation and solation temperatures of gelatin in salt solutions are plotted against the lyotropic numbers of the respective ions for various salt concentrations, linear relations occur (15, 6) (see figure 5).

c. Rate of saponification of esters. Hoeber's data on the rate of saponification of esters (10) as influenced by different salts, as well as Arrhenius' data (1), form straight lines, when plotted against lyotropic numbers (9) (see figure 6).

d. Viscosity of salt solutions. The viscosities of different salt solutions, if taken in the same valency group are, as has been pointed out by Merckel, in linear relationship with the lyotropic numbers, shown in figure 7 for

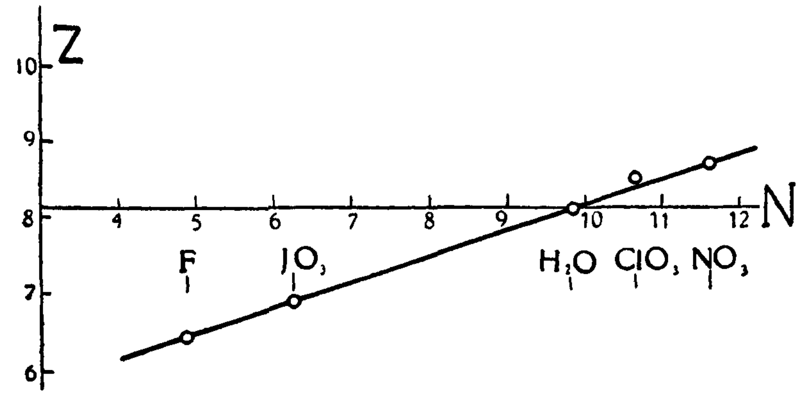

FIG. 4a. Relative weight increase of gelatin, swollen at 0°C., in different solutions of sodium salts of the same concentration, plotted against the lyotropic numbers.

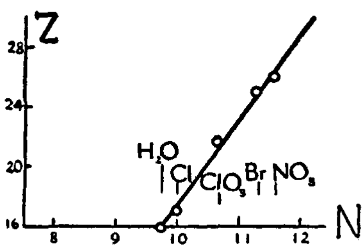

FIG. 4b. Relative weight increase of gelatin, swollen at 18°C. in different solutions of sodium salts of the same concentration, plotted against the lyotropic numbers.

different univalent sodium salts (12). This enables us to calculate the viscosity of salt solutions up to normal concentrations, within a few tenths of a per cent, when only two in the group are known.

The lyotropic numbers of the alkaline earth ions may easily be computed from their viscosity (12). Analogous regularities occur equally for this group as for the alkaline and halide ions.

The lyotropic numbers of cations have been calculated from the flocculating action of different salts on gold sols (9, 19). It appeared that only

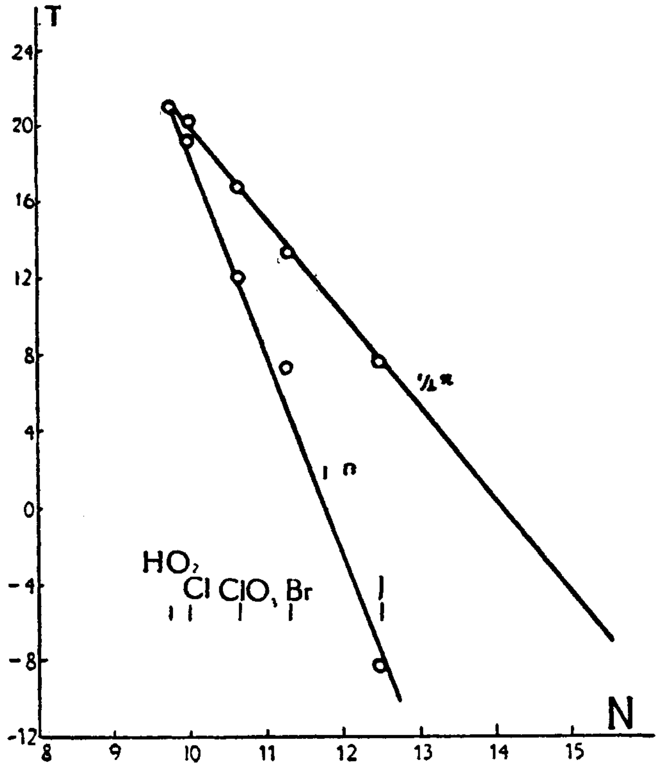

FIG. 5. Gelation temperature of gelatin in different solutions of sodium salts, plotted against the lyotropic numbers.

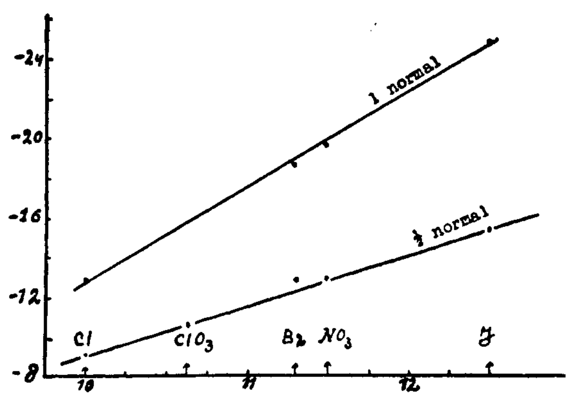

FIG. 6. Rate of saponification of ethyl acetate as influenced by different solutions of sodium salts, plotted against the lyotropic numbers.

those experiments could be used in which the decrease in the number of particles had been counted during the flocculation. From projective

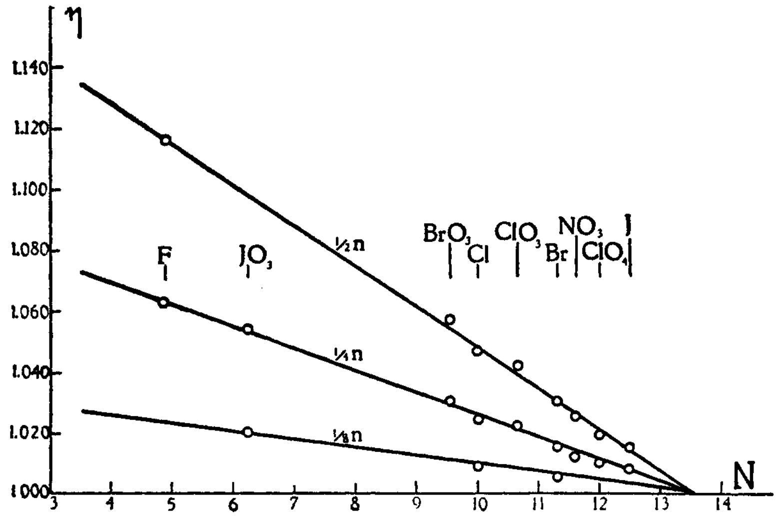

FIG. 7. Viscosity of different solutions of sodium salts with monovalent anions, plotted against the lyotropic numbers.

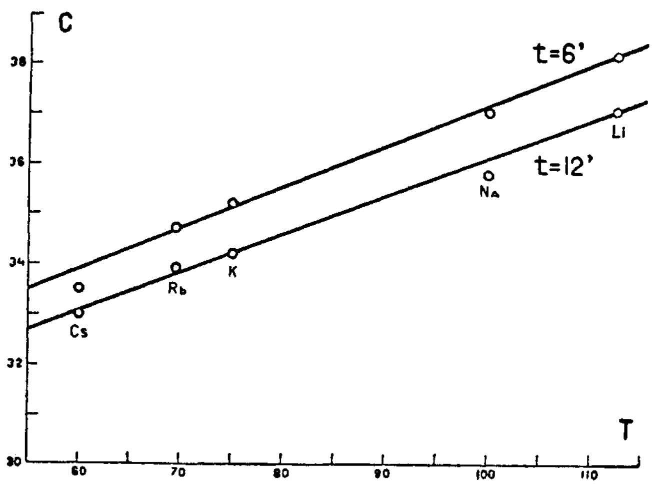

FIG. 8. Concentrations of different alkaline chlorides, causing the same decrease in the number of particles of a gold sol in the same time interval, plotted against the lyotropic numbers.

relations between the time–flocculation curves in the diagram, the numbers in table 3 for the alkaline series were derived from Tuorila's flocculation data (16). In table 3 the numbers for sodium and potassium are arbitrary, to fix the scale. It can be shown that these numbers are in linear relationship with various flocculation data. Figures 8 and 9 show this relation in the case of flocculation of gold and paraffin sols.

As with anions, these cation numbers are important in different lyotropic experiments. Linear relations are found in several data about electro-

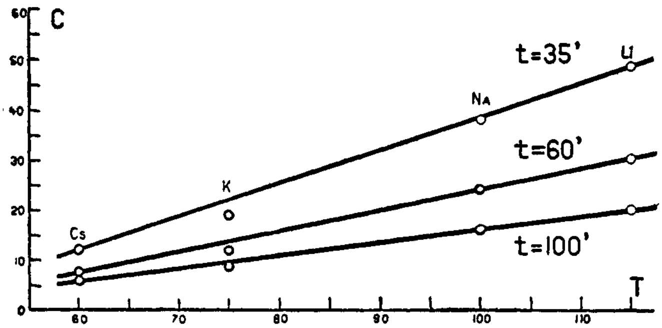

FIG. 9. Concentrations of different alkaline chlorides, causing the same decrease in the number of particles of a paraffin sol in the same time interval, plotted against the lyotropic numbers.

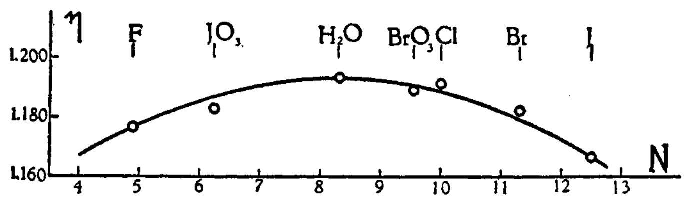

FIG. 10. Viscosity of dextrin in different solutions of sodium salts, plotted against the lyotropic numbers.

TABLE 3

Lyotropic numbers of cations of the alkaline series

Cation	Li^+	Na^+	K^+	Rb^+	Cs^+
T	115	100	75	69.5	60

kinetic potentials. The ionic exchange in artificial permutites (11) follows the same laws.

If the influence of the ions is more complicated, we cannot expect linear relationships. In the case of the viscosity of dextrin dissolved in different salt solutions, a curve was obtained when the data were plotted against the lyotropic numbers (figure 10). The adsorption of electrolytes by starch is still more complicated. Plotting the adsorption data of an experiment on *amylum solani* against the lyotropic numbers, a cubic curve was obtained (13) (see figure 11). The usefulness of the quantitative method is clearly

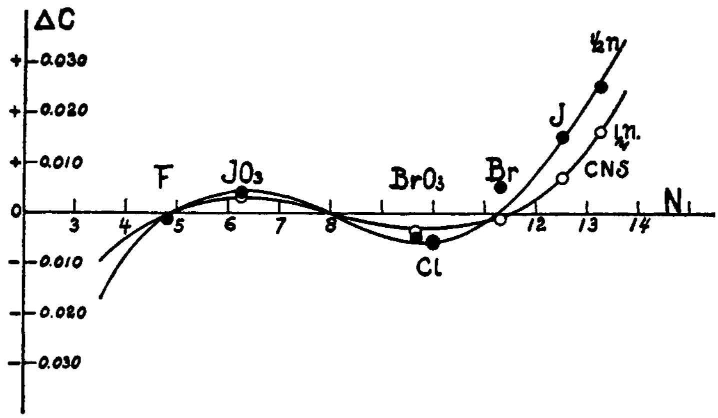

FIG. 11. Adsorption of sodium salts by potato starch, plotted against the lyotropic numbers.

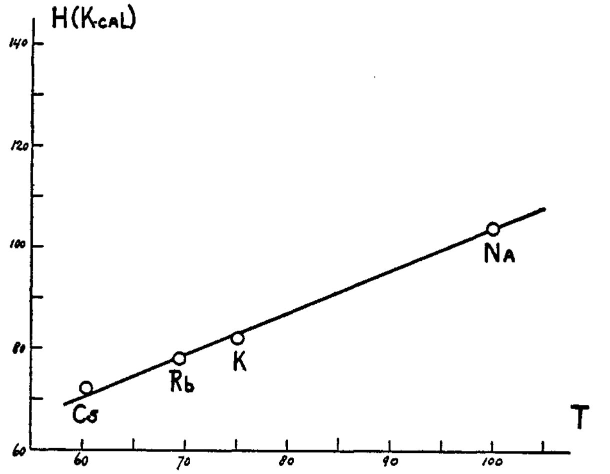

FIG. 12. Heat of hydration of alkaline ions, plotted against the lyotropic numbers

shown in these cases. According to older views, the lyotropic effect would be in complete disorder.

It has been shown that the surface tension of molten salts (14) at 1000°C. is in linear relationship with the lyotropic numbers. This proves clearly that the numbers are independent of the temperature.

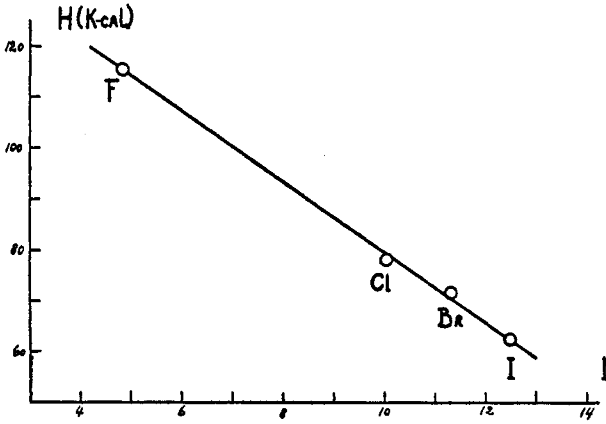

FIG. 13. Heat of hydration of halide ions, plotted against the lyotropic numbers

TABLE 4

Heat of hydration of ions

Ion	IO_3^-	$H_2PO_4^-$	BrO_3^-	NO_2^-	ClO_3^-	NO_3^-	ClO_4^-	CNS^-
H (in kg-cal.)	114	98	89	82	79	71	70	58

Standard values: Cl^- = 85; I^- = 64 kg-cal.

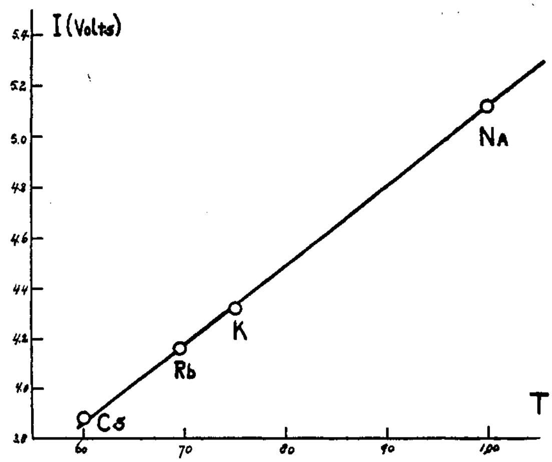

FIG. 14. Potential of ionization of alkaline metals, plotted against the lyotropic numbers.

The meaning of the lyotropic numbers can be understood from the following considerations: Plotting the lyotropic numbers against the heat of hydration of the ions, recalculated according to Fajans' method (17), linear relations are obtained (9) (figures 12 and 13). This leads to a calculation of the heat of hydration of complicated ions, the value of which was hitherto unknown (4) (see table 4). It is now clear that we could in any case have plotted heats of hydration instead of lyotropic numbers against lyotropic effects. As the former are not known in the case of every ion, we preferred to use the lyotropic numbers as a standard.

Since the heat of hydration of ions depends on the electric field which surrounds them, the lyotropic effects are beyond doubt caused by the different electric field strengths of the ions (18). This view is supported by the data on the energy of ionization, which are in perfect linear relationship with the lyotropic numbers (figure 14). A theory dealing only with the influence of ions on the state of polymerization of the H_2O molecules (2) is incorrect, since lyotropic effects occur equally in non-aqueous surroundings.

SUMMARY

1. The lyotropic activity of ions, influencing different phenomena, such as salting out, swelling, gelation and solation of lyophilic colloids, viscosity of salt solutions, rate of reactions, flocculation of lyophobic colloids, ionic exchange, heats of hydration, etc., are expressed quantitatively.

2. The lyotropic series are caused by different ionic field strengths.

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