THE INFLUENCE OF MIXTURES OF ELECTROLYTES ON THE VISCOSITY OF SOLS OF GUM ARABIC,

BY

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As is now very well known the determination of the viscosity of lyophilic sols is a method, generally applicable to increase our knowledge of the internal properties of the above mentioned sols.

The study of the influence of electrolytes on their viscosity lead to the conclusion that this influence is of capillary-electric character, as long as the concentrations are small [1]. This means, evidently, that the ions in the first place alter the electric charge of the micelles, which alteration in general corresponds with a diminution of the hydration [2]. According to our knowledge about other facts of capillary-electric character we meet the same phenomena, for example, in measurements of electroendosmosis, kataphoresis and adsorption. We know from these measurements that the higher the valency of the ion, the more they are absorbed, the greater is the effect at comparable concentrations. Further we know from the adsorption of mixtures of capillary-active substances, that the more active component will be more strongly adsorbed, so that the one is replaced by the other [3]. If the solution, therefore, contains equal molar weights of salts with mono- and di- or trivalent ions the concentration of the latter on the absorber will be greater, and even, when present in weaker concentration than the monovalent ion the same may take place [4]. So we can say, that the influence of mixtures of different ions is discarded in favour of the one with the highest valency.

When studying the viscosity of amphoteric colloids, proteins, we have to do in general with mixtures of two electrolytes, the one being an acid or a base, the other being a salt [5]. Really all colloids contain electrolytes and so adding an electrolyte we have, strictly speaking, at least to do with two of them, but this is not the case we were going to mention. Except in the case of proteins no experiments are known on the influence of mixtures of electrolytes on the viscosity of lyophilic sols.

[1] de Jong, Diss. Utrecht 1921. Lier, Diss. Utrecht 1924. Tendeloo, Diss. Utrecht 1926. Bungenberg de Jong, Rec. trav. chim. 42, 1 (1923); 43, 189 (1924).
[2] Tendeloo, l.c.
[3] Rona and Toth, Biochem. Z. 64, 288 (1914).
[4] Rona and Michaelis, Biochem. Z. 94, 250 (1919).
[5] Kruyt and Tendeloo, J. Phys. Chem. 29, 1303 (1925).

During the researches on the colloidal properties of sols of gum arabic, we determined the influence of mixtures of two electrolytes on their viscosity, of which the following gives a short description.

Experimental.·

The measurements have been carried out at 25° C; the solutions were made by adding a certain amount of the solution of electrolytes at 25° to 25 cc of the 2 % sol at 25° and making up the mixture to 50 cc with distilled water at 25°, so as to have the desired concentration of electrolyte in a 1 % sol.

We used a Ostwald-viscosimeter, the velocity of flow of which was small enough to decrease the error in the determinations to 0.1 %, according to the calculations of Grüneisen [6]). We put 10 cc of the mixture into the viscosimeter with a pipette, filled the upper bulb by sucking up the liquid, and determined the time of outflow with a stopwatch, indicating 0.2 sec. The determinations were repeated four times, the first of which was not taken in account.

At the beginning and at the end of each series of determinations a blank one of the sol without electrolyte was made, so as to know the so called irreversible reaction, due to the hydrolysis of the organic substance; usually the difference was so small, that no correction had to been made.

The electrolytes used were KCl, $BaCl_2$ and $Co(NH_3)_6Cl_3$, the concentrations are in milli-equivalents of the kation per liter. First of all we determined the influence of the separate electrolytes, the results of which are tabulated in table I. In the first column are the electrolytes, in the second the concentrations in milli-equivalents per liter, in the third the relative viscosities, in the fourth the values of

$$P = \frac{\eta_s - 1}{\eta_\infty - 1} \times 100$$

where η_∞ is the viscosity of the sol without electrolyte, and η_s the viscosity of the sol with electrolyte.

Table I.

	Conc.	Rel. visc.	P
KCl	1.0	1.389	74.1
	2.0	1.328	62.5
$BaCl_2$	1.0	1.332	63.2
	2.0	1.263	50.1
$Co(NH_3)_6Cl_3$	1.0	1.274	52.2
	2.0	1.201	36.4
Blank	0	1.525	100

The mixtures of the electrolytes have been made up in such a a manner that the total concentration in milli-equivalent per liter was equal to the concentrations of the electrolytes as tabulated in table I, but the ratios of the components were different.

[6]) Wissensch. Abh. Phys. Techn. Reichsanstalt 4, 151 (1905).

The results have been collected in table II; in the first column are the electrolytes, in the second the proportions so as to make up the concentrations mentioned in the third, in the fourth are the relative viscosities, in the fifth the above defined values of P, in the sixth the values of P_{cal}, the meaning of which will be discussed below.

Table II.

	Ratio.	Conc.	Rel. visc.	$P_{det.}$	P_{cal}
Blank	—	—	1.525	100	100
KCl + BaCl₂	1 : 1	1	1.360	68.2	68.4
		2	1.293	55.8	56.3
	1 : 3	1	1.345	65.7	65.9
		2	1.280	53.3	53.4
	4 : 1	1	1.376	71.6	72.0
		2	1.313	59.6	60.0
BaCl₂ + Co(NH₃)₆Cl₃	1 : 1	1	1.304	57.9	57.7
		2	1.232	44.2	44.2
	4 : 1	1	1.321	61.1	61.0
		2	1.250	47.6	47.7
KCl + Co(NH₃)₆Cl₃	1 : 1	1	1.324	61.7	63.2
		2	1.254	48.4	49.4
	1 : 4	1	1.298	56.8	56.6
		2	1.222	42.3	41.6
Blank	--	—	1.525	100	100

By way of example the calculation of P_{cal} for the third one is given here:

From table I one sees

for KCl, conc. 1 milli-eq. per liter   P = 74.1
„ BaCl₂ „   „   „ „   P = 63.2
                    Difference   10.9

Supposing that a mixture KCl + BaCl₂, 1 : 3 will give a figure between the two, at a distance of $^1/_4$ of the difference from the point corresponding with BaCl₂ upwards one obtains $P_{cal} = 63.2 + ^1/_4 \times 10.9 = 65.9$.

Discussion.

It is rather difficult to give an explanation of the results obtained. From the point of view of the capillary-electric behaviour of ions of different valency on the viscosity of lyophilic sols we know that there is always a difference between mono-, di- and trivalent ions at equivalent concentrations which is called a specific influence, the nature of which, however, is unknown. Now the influence of electrolytes on the viscosity of sols is a rather complicated one; the total effect is made up by several other effects as can be seen from the formula given by von Smoluchowski[7]), the viscosity of a sol being a function of the electric charge of the particles, the electrical conductivity

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[7]) Kolloid-Z. **18**, 190 (1916).

of the sol, the dielectric constant of the medium and the radius of the particles. An electrolyte influences all of them.

Now in the case of two electrolytes the only thing we can say from the foregoing, is, that at a given equivalent concentration there is an effect which is probably proportional to the total amount of electrolytes present or that the equivalent amount of ions absorbed by the particles of the lyophilic sol at equal equivalent concentrations is independant of the composition of the electrolyte or electrolyte mixture added; it is however impossible at the moment to discuss the nature of this effect.

Summary.

1. The influence of mixtures of two electrolytes on the viscosity of sols of gum arabic has been determined at 25° C.

2. A comparison of the influence of the separate electrolytes and their mixtures at equivalent concentrations seem to indicate that there is an influence which is proportional to the total amount of the electrolytes present.

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