

EFFECT OF NON-ELECTROLYTES ON THE ANTAGONISM OF IONS IN COAGULATION OF HYDROPHOBIC SOL

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The effect of the non-electrolytes, viz., methyl alcohol, ethyl alcohol, sucrose, glycerol and glycol, on the antagonism of KCl and BaCl₂ in coagulating arsenious sulphide sols has been studied. It has been found that the non-electrolyte which stabilise the sol increase the antagonism and those which sensitise the sol decrease it.

The coagulating power of ions in mixtures of electrolytes on colloidal solutions is not always additive as observed by different workers (Linder and Picton, *J. Chem. Soc.*, 1895, 87, '67; Weiser, *J. Phys. Chem.*, 1921, 25, 680; Freundlich and Scholz, *Koll.-Chem. Beih.*, 1922, 16, 267; Mukherjee and Ghosh, this *Journal*, 1925, 1, 213, et seq). It has been observed that the total amount of coagulating ions in the case of electrolytic mixtures is sometimes greater than that of the individuals taken separately. Explanation offered for this ionic antagonism (as it is called) is based upon two fundamental assumptions: (i) the inhibiting influence of each coagulating ion on the adsorption of the other, and (ii) the stabilising action of the ions having the same charge as the sol (Fred Hazel, *J. Phys. Chem.*, 1941, 45, 747). Ostwald and Hoffmann (*Kolloid. Z.*, 1937, 80, 186), however, offered an explanation based on the activity coefficients of the coagulating ions, coagulating power being a function of the activity coefficients.

The influence of non-electrolytes on the stability of sols appears to be anomalous. The effect is one of sensitisation in some sols while stabilisation in others. Even the same non-electrolyte, when added to a particular sol, sometimes sensitises the sol towards a certain coagulating electrolyte, but stabilises it against another. The change in dielectric constant consequent upon addition of the non-electrolyte is certainly an influencing factor in such cases, but it alone is not sufficient to explain the facts observed (Lachs and Chwalinski, *Z. physikal. Chem.*, 1932, A159, 172). The influence of the non-electrolyte on the adsorption of both similarly as well as oppositely charged ions should also be taken into consideration.

In the light of the above, non-electrolytes are expected to have some influence also on the antagonism of ions in the phenomenon of coagulation of colloids, and hence, the question of ionic antagonism in presence of non-electrolytes has been reopened.

EXPERIMENTAL

The system studied was the arsenious sulphide sol with the pair of electrolytes, potassium and barium chlorides (the strong antagonistic effect of which is well known). The effects of different non-electrolytes, viz., methyl alcohol, ethyl alcohol, glycol, glycerol and sucrose, in different concentrations have been observed with different concentrations of the coagulating electrolytes.

The arsenious sulphide sol was prepared by mixing equal volumes of a half-saturated solution of arsenious oxide and water, saturated with hydrogen sulphide, and then by passing hydrogen sulphide through the mixture till there was no arsenious oxide left in it. The excess of hydrogen sulphide was driven off with a current of hydrogen gas.

For determining the coagulating concentrations of electrolytes, light from a single-filament lamp was allowed to pass through a layer of definite thickness of the mixture of the sol and electrolytes, placed at a constant distance from the source of light, and the time noted when the sharp outline of the filament just disappeared. The intensity of light was kept constant by passing a constant current through the filament, as shown by a sensitive ammeter. Electrolytes or mixtures of electrolytes are considered to have equi-coagulating concentrations when the time required for reaching the same stage of coalescence is the same in each case. In each case, to 5 c.c. sol was added the mixture of electrolyte solutions, non-electrolytes or water, as the case may be, keeping always the total volume at 10 c.c. The whole mixture was then poured into a glass vessel having rectangular sides and kept at the fixed position at a definite distance from the source of light. The mode of addition of the electrolyte mixture to the sol and mixing was always the same, as any variation affected the results to a considerable extent.

TABLE I

[Coagulating conc. of KCl and BaCl₂ in m. moles/litre]

% Conc. of non-electrolytes.	Methyl alcohol.		Ethyl alcohol.		Sucrose.		Glycerol.		Glycol.	
	KCl	BaCl ₂ .	KCl.	BaCl ₂ .	KCl.	BaCl ₂ .	KCl.	BaCl ₂ .	KCl.	BaCl ₂ .
0	57.5	2.8	60.0	2.8	55.0	3.0	63.5	2.9	6.1	3.0
2.5	54.0	3.0
5	70.0	2.4	65.0	3.4	57.5	3.0
10	92.5	2.0	70.0	4.0	62.5	3.4	62.0	2.4	6.2	2.5
20	95.0	1.8	85.0	4.4	64.0	2.2	6.1	2.2

From Table I we find that in the case of methyl alcohol, the arsenious sulphide sol is stabilised towards coagulation by KCl, but is sensitised towards BaCl₂. Glycerol and glycol have no effect towards coagulation by KCl, but sensitise the sol towards coagulation by BaCl₂. The highest stabilising effect is observed in the case of ethyl alcohol, both towards KCl and BaCl₂. Sucrose appears to have a very small stabilising effect to both the electrolytes.

TABLE II

Antagonism of ions in pure ag. medium

% Coagulating conc. of	KCl.	...	0	30	40	60	80
	BaCl ₂	...	100	119	111	86	57
	Total	...	100	139	151	146	137

TABLE III

% Coagulating conc. of			% Coagulating conc. of		
KCl.	BaCl ₂ .	Total	KCl.	BaCl ₂ .	Total
MeOH (10%).			MeOH (20%).		
0	100	100	0	100	100
27	135	162	26	125	151
54	115	169	53	114	167
81	20	101	79	68	147
EtOH (10%).			EtOH (20%).		
0	100	100	0	100	100
29	140	169	29	164	193
57	110	167	57	136	193
86	35	121	86	55	141
Sucrose (5%).			Sucrose (10%).		
0	100	100	0	100	100
26	131	157	24	135	159
52	107	159	48	118	166
78	53	131	72	71	143
Glycerol (10%).			Glycerol (20%).		
0	100	100	0	100	100
24	108	132	23	102	125
48	98	146	47	91	138
73	62	135	70	63	133
Glycol (10%).			Glycol (20%).		
0	100	100	0	100	100
24	116	140	25	112	137
49	105	154	50	96	146
73	67	140	74	54	128

In Tables II and III the results of observations on ionic antagonism in presence of different non-electrolytes have been shown. Amounts of the electrolytes in the mixture have been shown in percentages of their coagulating concentrations when used separately (as from Table I). The total percentage clearly shows the extent of antagonism. Had there been no antagonism, the total should have come out to be exactly 100. As for example in Table II (2nd row), the mixture of electrolytes containing 20% of the coagulating concentration (0.0550 M) must have 119% of the coagulating concentration of BaCl₂ (0.0028 M) to coagulate the sol.

Two salient points emerge from the above tables (Tables II and III): (1) The antagonism is maximum near about 50% of the coagulating concentration of KCl; at lower or higher KCl-concentration, the coagulating power of BaCl₂ increases and the antagonism decreases. (2) The non-electrolytes, which stabilise the sol, show increased antagonism and those which sensitise the sol decrease the antagonism.

Ethyl alcohol stabilises the sol more than any of the other non-electrolytes, both towards KCl and BaCl₂, and in this case the antagonism is maximum. Sucrose can slightly stabilise the sol towards both the electrolytes and in this case the antagonism

is slightly higher than that in the pure aqueous medium. Although glycerol and glycol have no appreciable effect on the coagulation of the sol by KCl, they sensitise the sol towards coagulation by BaCl₂, and here the antagonism is lower than that in the pure aqueous medium. Methyl alcohol stabilises the sol towards KCl, but sensitises it towards BaCl₂. 20% Methyl alcohol increases the coagulating concentration of KCl by 65% but decreases that of BaCl₂ by 36% only. So it is expected that the antagonism in presence of 20% methyl alcohol will be greater than that in the pure aqueous medium, and this is borne out by the experimental results.

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