STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER). PART VI. INFLUENCE OF NEUTRAL SALTS ON SOME ELECTRO-CHEMICAL AND VISCOUS PROPERTIES

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Influence of neutral salts with cations and anions of different valencies on the p_H, specific conductance and relative viscosity of gum jeol solutions have been examined. Both cations and anions show a tendency towards an increase of p_H at low concentrations followed by a marked depression at higher concentrations. Specific conductance does not show any point of special interest, while relative viscosity shows peculiar variations with ions having different valencies.

Conclusions arrived at from the study of the influence of concentration of the gum jeol solution on the different physical and electrochemical properties thereof (Part V of this series, this *Journal*, 1948, 25, 339) go to show that a gum solution should be treated as composed of particles which are colloidal micelles surrounded by a double layer of counter ions rather than polyvalent ions under the influence of the ionic atmosphere.

The work embodied in the present paper is an extension of the above with a view to further examination of the above conclusions from an altogether different direction, viz , by noting the changes produced in some of the electrochemical and viscous properties under the influence of neutral salts having cations and anions with different valencies. The changes in hydrogen ion activity and specific conductance have been the main targets of attack, as these are expected to show evidences of cation or anion exchange, if any, produced by neutral salts as in many colloidal systems having particles with large surfaces (cf. the extensive works done in this direction by Mukherjee and co-workers,). The changes in the viscous properties have also been examined as they might be of interest to the industrial use of this gum where the viscous properties of the gum solution have been of considerable importance.

For this reason chlorides of Na, K, Ba and Al and the potassium salts of the anionic radicals Cl, NO_3, SO_4, ferri- and ferrocyanides were tried.

EXPERIMENTAL

The methods for the preparation of the solution as well as those for measurements of p_H, specific conductance and relative viscosity have been the same as described in Part V (*loc. cit.*) of this series. Temperature at which these measurements were carried out was the room temperature (30°). The viscometer was of the Ostwald type and showed the time of flow for water to be about 60 seconds. Reproducibility of measurements was the same as mentioned in Part V (*loc. cit.*).

Only freshly prepared gum solutions were used in these investigations. It has been observed that solutions of this gum keep well and do not show any signs of change in their p_H, specific conductance or relative viscosity up to about 40 days after preparation of the aqueous solution, beyond which the solutions have been observed to show signs

of deterioration.*   In the present investigation a gum solution, older than 30 days, was never used.

In the following the effect of neutral salts on the p_H was studied with one preparation (A) and that on conductance and relative viscosity with another (B), both having the identical concentration.   The data on relative viscosity are the mean of five or six determinations of the time of flow which seldom differed from each other by more than 1 to 2 seconds.   The density determination was, however, made only once for each concentration of the neutral salts.

The salts used were of Merck's reagent or B.D.H. 'Analar' quality.   Solutions were always prepared in equilibrium water having specific conductance of 2.0×10^{-6} mho at $30°$.   Results appear below.

Hydrogen-ion Activity.—Cationic influence was studied with the help of NaCl, BaCl₂ and AlCl₃ with a gum solution whose initial p_H was 4.5 (conc., 0.5 g. per 100 c.c. of solution).   Results, represented graphically in Fig. 1, show that with NaCl and AlCl₃ there is an initial rise of p_H followed by a subsequent decrease at high salt concentrations.   The decrease of p_H with NaCl is much smaller than with AlCl₃ where hydrolysis of the salt into HCl is probably responsible for a more marked diminution of p_H.   The initial rise, although small, is significant.   KCl and K₂SO₄ all show this increase (vide Fig. 1), which marks a slight departure from what is commonly observed in those cases where H-ion exchange is known to occur and where p_H tends to diminish right from low concentrations.   The divalent Ba-ion (in BaCl₂) does not, however, show this increase.   The p_H remains almost constant over a certain range of concentrations at the

FIG. 1
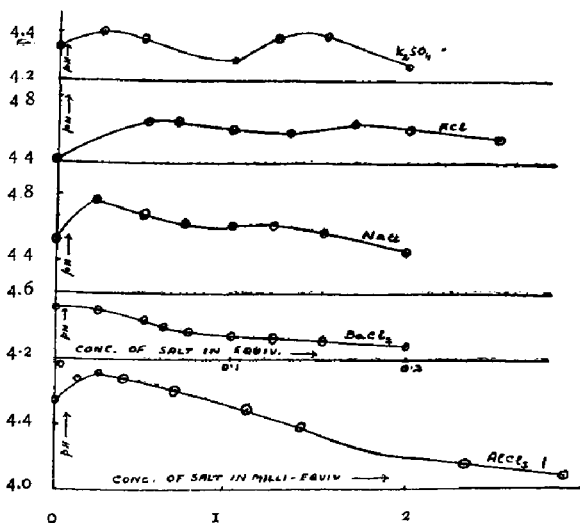
* This aspect will be taken up in a future communication (Part VIII).

beginning beyond which there is a steady downward course. Comparing the depression of p_H at higher concentrations, the cationic order appears to run as Al : > Ba > Na, K. With Al ion, where the hydrolysis of the salt is probably responsible for the more marked changes, as observed herein, the effects occur at much lower concentrations than in Ba, Na and K.

The anionic influence has been observed with KCl and K_2SO_4 (i.e., mono and divalent anions) only. The curves show a second rise of p_H at still higher concentrations with these salts as well as with NaCl. With NaCl and KCl this was small but with K_2SO_4 it was more marked, being of the magnitude of about 0.2 p_H units. $BaCl_2$ and $AlCl_3$ do not show this second rise. With monovalent anion this is small but it increases with increase in the valency of the anion. Possibly with $BaCl_2$ and $AlCl_3$ the effect of the Cl-ion is masked by a stronger effect of cations of higher valencies. Anions of higher valencies could not be examined for practical inconvenience.

The p_H (or H-ion activity) is thus affected in a peculiar manner by cations and anions of different valencies. To understand the nature of these variations (cf. Fig. 1) it appears essential to assess the rôle of two important influencing factors, one of which being the change of ionic strength on addition of neutral salts which tends to diminish the activity of the ions. An initial rise of p_H with Na and Al ions probably owes its origin to this factor. The second influencing factor is the base exchange capacity of the cations which as a rule tends to diminish p_H. The mutual balance of these two opposing factors appears ultimately to determine the nature of the overall change in p_H of the solution in presence of neutral salts. The initial rise of p_H with NaCl and $AlCl_3$ may be the result of the change in ionic strength. It is a common experience that base exchange capacity of divalent ions is higher than that of monovalent ones. The absence of an initial rise of p_H at low concentrations of $BaCl_2$ might thus be due to a stronger base exchange capacity of the Ba ions. The case of Al ions is complicated by partial hydrolysis of the salt.

The rise of p_H at higher concentrations of KCl and K_2SO_4, which has already been referred to as the anionic effect on p_H, appears to find a qualitative explanation if we attribute them to the effect of higher ionic strength at higher salt concentrations. Comparing KCl with K_2SO_4 we find that K_2SO_4 having a divalent anion will increase the ionic strength much more rapidly with concentration and will show the effect thereof earlier than KCl. The occurrence of the maximum at lower concentrations of K_2SO_4 than with KCl thus corroborates these conclusions, at least partially.

Specific Conductance.—Observations have been presented in Table 1 and graphically shown in Figs. 2 and 3. In these measurements the concentration of the gum was kept constant, while that of the salt only varied by taking 5 c.c. of the gum solution and mixing with it exactly 15 c.c. of mixtures of water and the electrolytic solution in different proportions, so that the final volume was 20 c.c. in all. The gum solution thus became exactly 4 times diluted. Readings were taken in ten minutes' time after mixing the salt solution with the solution of the gum.

TABLE I

Sp. conductance of gum solution at 4 times dilution = 1.882×10^{-4} mho.
Initial conc. = 0.489%.   Temp. = 30°.

Salt.	Conc.	Sp. cond. of the salt soln.	Sp. cond. of mix. (calc.)	Sp. cond. (obs.)	Difference
KCl	0.02 N	0.0037	0.0039	0.0036	8.333%
	0.04	0.0054	0.0056	0.0052	7.691
	0.07	0 0084	0.0086	0.0086	0.0
	0.11	0.0135	0.0137	0.0135	1.451
	0.13	0.0168	0.0170	0.0150	13.33
	0.20	0.0235	0.0237	0.0227	4 406
BaCl$_2$	0.025	0.0027	0.0029	0.0025	16.0
	0.038	0.0036	0.0038	0.0036	5.555
	0.062	0.0060	0.0062	0.0056	10.720
	0 10	0.0088	0.0090	0.0087	3.448
	0.11	0.0101	0.0103	0.0097	6.186
	0.13	0.0112	0.0114	0.0101	12.870
	0.16	0.0139	0.0141	0.0135	4 445
	0.19	0.0155	0.0157	0.0144	9.026
AlCl$_3$	1.439×10^{-2}	1.933×10^{-4}	3.815×10^{-4}	3.640×10^{-4}	4.807
	2 158	2.830	4.712	4.298	9.632
	3 597	4.550	6.432	5.772	11.43
	4.6767	5.872	7.754	6.848	13.23
	5.756	7.137	9.019	8.017	12.50
	6.475	7.769	9.651	8.314	16 08
KNO$_3$	0.025	0.0033	0.0034	0.0033	8.031
	0.038	0.0049	0.0051	0.0046	10.86
	0.063	0.0077	0.0079	0.0076	3.948
	0.100	0.0110	0.0112	0.0106	5.661
	0.138	0.0144	0.0146	0.0131	11.45
	0.188	0.0173	0.0174	0.0172	1.162
K$_2$SO$_4$	0.025	0.0037	0.0038	0.0034	14.71
	0.038	0.0055	0 0057	0.0051	11.77
	0 062	0.0086	0.0088	0.0080	10.0
	0.100	0.0127	0.0129	0.0110	17.28
	0 125	0.0157	0 0159	0.0137	16.65
	0.188	0.0219	0.0221	0 0202	9.406
K$_3$Fe(CN)$_6$	0.026	0.0032	0.0034	0.0032	6.25
	0.038	0.0046	0 0048	0.0046	4.347
	0.064	0.0078	0.0079	0.0074	6.325
	0.102	0.0119	0.0121	0.0106	14.16
	0.153	0.0155	0.0157	0.0143	9.790
	0.192	0.0177	0.0179	0.0168	6 548
K$_4$Fe(CN)$_6$	0 025	0 0028	0.0029	0,0023	26.06
	0.038	0.0038	0 0040	0.0032	25.0
	0.063	0.0058	0.0060	0.0048	25.0
	0.100	0 0073	0.0075	0 0071	5.633
	0.150	0.0104	0.0106	0.0101	4.951
	0.1885	0.0128	0.0130	0.0116	12 07

FIG. 2

Conc. of AlCl₃ in N×10³.
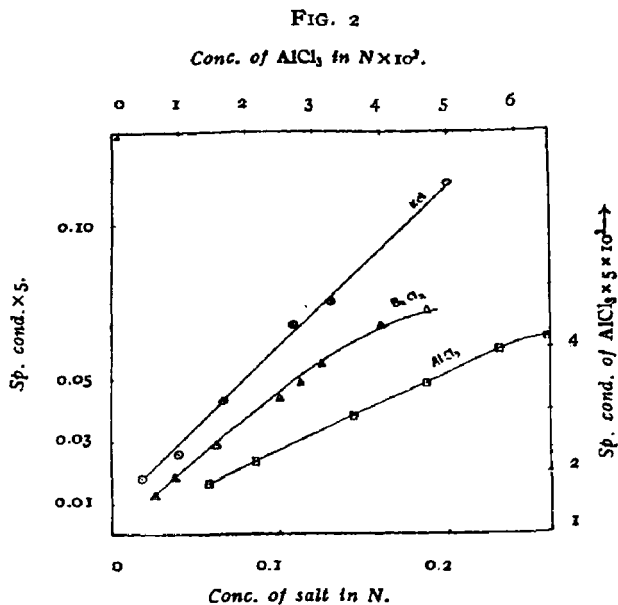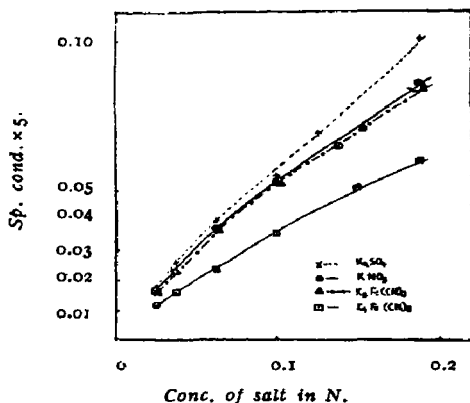

Conc. of salt in N.

FIG. 3

Conc. of salt in N.

The significant fact to be noted in this connection is that the observed specific conductance is never equal to the sum of those of the salt and gum solutions at corresponding concentrations. The observed values are in most cases less than the calculated values obtained by addition of specific conductance values. Both cations and anions behave alike in this respect.

The observations . of Pauli and Ripper (*Kolloid Z.*, 1933, **62**, 162) on specific conductance of mixtures of KCl and arabic acid solutions at different ratios of their concentrations indicate that the observed specific conductance is always higher than the calculated values. This is just the reverse of what has been observed in the present case. The percentage differences, as calculated by them, did not show any regularity with increasing concentrations of the salt which were small in their case as compared to those in the present case, the highest concentration being $2.2 \times 10^{-2}N$. They have explained the higher values of observed specific conductance as the outcome of the liberation of hydrogen ions by the addition of salts (*i.e.*, the base exchange in presence of KCl).* With this gum no such increase in hydrogen ion activity could be observed. On the other hand, both anions and cations, excepting the salt $BaCl_2$, tended to increase the p_H at small concentrations but showed variations of complicated nature at higher concentrations. Over and above this, the fact that this gum possesses some buffering properties (vide Part V) is likely to render its behaviour more complicated. A lowering of specific conductance can thus be understood in the light of the above observations. The irregular manner in which the specific conductance varies with the concentrations of the added salts, however, awaits further clarification.

Relative Viscosity.—The cationic effect on relative viscosity appears in Fig. 4.— With NaCl and $BaCl_2$ there is an initial drop at low salt concentrations, this drop being
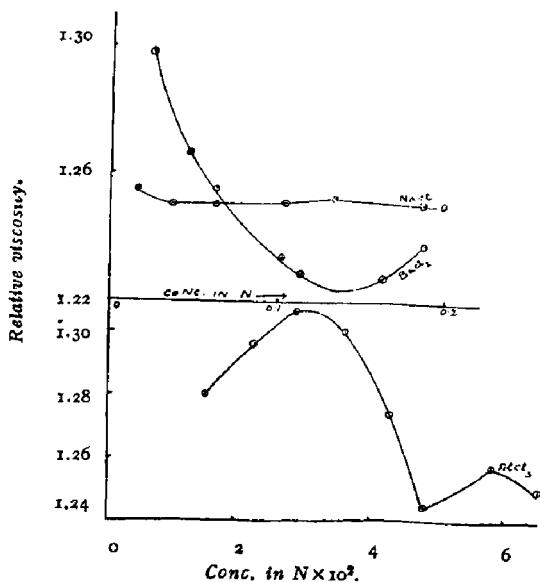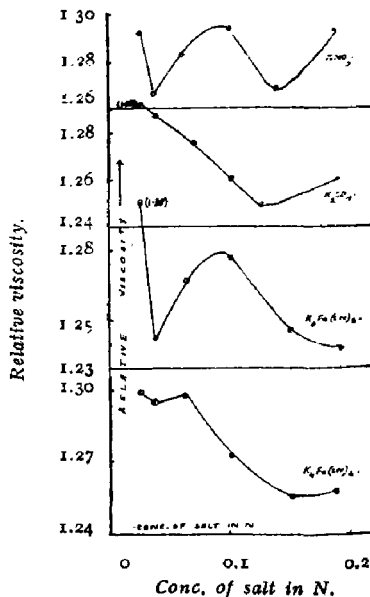
FIG. 4

FIG. 5

Conc. in $N \times 10^2$.

Conc. of salt in N.

* They observed a change of $a_H^{=}$ from 9.16×10^{-4} to 1.22×10^{-3} by addition of $4 \times 10^{-2}N$-KCl to 0.42% arabic acid solution.

less marked with NaCl. With $AlCl_3$, however, there was no initial drop but on the contrary a tendency to rise was evident at low concentrations. The initial decrease of viscosity has been observed by other workers working in different colloidal systems (cf. Bungenberg de Jong in yeast nucleic acid solution, *Rec. trav. chim.*, 1930 **44**, 658 ; Kruyt and Tendeloo in gum arabic solutions, *Koll.-Chem. Beih.*, 1929, **29**, 396).

The increase in viscosity curve (Fig. 4) with Ba and the second increase with Al ions, followed by a decrease at higher concentrations, offer points of interest. $AlCl_3$ has been observed to have a coagulating effect upon the gum solution and at concentrations higher than the coagulating one it has been observed to bring about a reversal of charge. $BaCl_2$ has been observed to possess no such coagulating effect within the concentration range used here as studied by turbidity measurements.

As to the variation of relative viscosity by Al ions (Fig. 4) it appears that the behaviour is rendered complicated by the occurrence of hydrolysis of the salt. With KCl the viscosity practically shows no change. $BaCl_2$ depresses this markedly with concentration. This is, however, quite the reverse of what is usually observed with those ions which show a stronger base exchange capacity. It appears therefore that in the present case, the base exchange capacity is not the only factor in determining the variation of viscosity.

Anionic effect was studied with KNO_3, KCl, K_2SO_4, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ and has been graphically shown in Fig. 5. The curves for monovalent and trivalent ions show a sharp decrease of viscosity at lower concentrations followed by a rise to a maximum at higher concentrations after which there is again a tendency to decrease.

The effect of the anions is also peculiar in that the mono and tri-valent ions show a strong depression at low concentrations which may be attributed to "electroviscous effect" as proposed by Kruyt (cf. Alexander, "Colloid Chemistry", Vol. I, p. 306). The curves for divalent and tetravalent anions show a gradual diminution instead of a sharp one. The monovalent and trivalent ions further show an increase of viscosity at higher concentrations which are altogether absent in the case of bivalent and tetra-valent anions.

The viscous properties thus show peculiarities which cannot be explained from our experience with other colloidal electrolytes. The viscous properties in presence of salts are again the most important ones which have been of interest in the industrial use of this gum. But further work appears necessary before any definite conclusions can be arrived at on this point and such work is in progress.

The authors' best thanks are due to Dr. H. L. Ray, Dr. Ing., the Head of the Chemical Engineering Department for his keen interest and to Dr. T. Sen, Principal for rendering all facilities in connection with this work.

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