

STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER), PART VIII. INTERACTION OF JEOLIC ACID WITH ACIDS AND BASES

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The jeolic acid behaves like arabic acid (already reported) in its interaction with bases, acids and neutral salts, the difference being essentially in the degree in which the effects appear. It is a monobasic acid, having an equivalent weight of 1200, and dissociation constant of the order of 10^{-4} i.e., of weak character, although its potentiometric titration curve is like that of HCl. Total acidity varies with the nature of the cation used for titration. It shows reverse acidity in its interaction with acids and the existence of base-exchange when treated with neutral salts.

As pointed out towards the end of Part VII of this series (this *Journal*, 1953, 30, 201), interaction of jeolic acid with acids, bases and neutral salts is worth investigation to clarify the behaviour of this acid, forming a colloidal solution in water. The present study comprises the determination of total acidity, basicity, the dissociation constant and the equivalent weight of the jeolic acid both by potentiometric and conductometric titrations with bases and also the estimation of the changes in the hydrogen-ion activity of the solution by the addition of acids and neutral salts.

The object of this investigation is to examine how the nature of the cation influences such properties and also to detect the existence and magnitude of the base-exchange occurring in this system.

EXPERIMENTAL

Two different specimens of jeolic acid were selected for this investigation: (1) A solution of jeolic acid obtained by electro dialysis in absence of acids and (2) a solution obtained by electro dialysis in presence of acids (for procedure of electro dialysis vide this series, Part IV, this *Journal*, 1948, 25, 333). The concentration of these acids was always 1% (10 g./litre of solution).

All measurements were carried out at a temperature of $35^{\circ} \pm 0.1$. Equilibrium water having specific conductance of 1.3×10^{-6} mhos was used throughout.

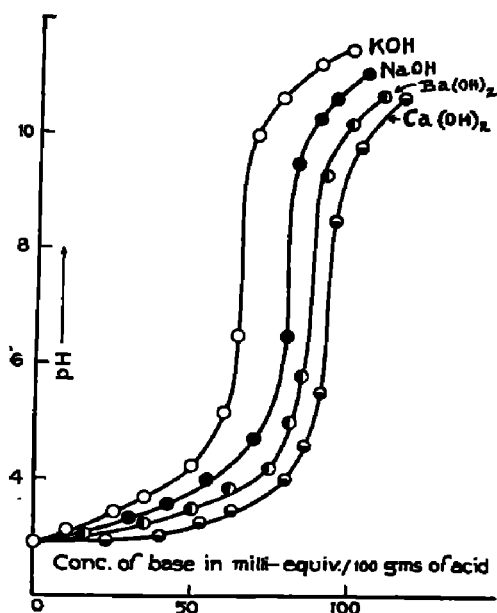
Potentiometric measurements were carried out with the help of hydrogen electrodes with necessary precautions mentioned by Mukherjee and Sarkar (this *Journal*, 1947, 24, 65). Conductometric measurements were carried out as usual at a frequency of 440 cycles.

Four different bases viz., KOH, NaOH, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ were studied and solutions of these bases were always prepared in carbon dioxide-free water.

Potentiometric Study with Bases

Titration curves with the different bases mentioned above for specimen (1) have been given in Fig. 1. These curves are very much similar to those of the arabic acid (cf. Mukherjee and Ghosh, this *Journal*, 1949, 26, 277). They present the nature and shape of a strong monobasic acid with only one inflexion and the p_H of neutralisation is about 7.2. The acid of specimen (2) behaved exactly similarly, and the titration curves have not therefore been shown.

FIG. 1



The total acidity expressed in terms of milliequivalents of the base per 100 g. of the acid was not a constant quantity but varied with the nature of the base used for titration in the same manner as in arabic acid solutions, the only difference being in the relative cationic order: $\text{Ca}(\text{OH})_2 > \text{Ba}(\text{OH})_2 > \text{NaOH} > \text{KOH}$, the last one giving an abnormally low total acidity (vide Mukherjee and Ghosh, *loc. cit.*). The actual figures are shown in Table I. The cationic order in arabic acid was $\text{Ca}(\text{OH})_2 > \text{Ba}(\text{OH})_2 > \text{KOH} > \text{NaOH}$.

TABLE I

Sols.	Total acidity in m.e. of base/100 g. of acid.			
	KOH.	NaOH.	Ba(OH) ₂ .	Ca(OH) ₂ .
Specimen 1	.. 59	79	88.5	96
Specimen 2	.. 62	81	90.0	95.0

It may be mentioned here that although the total acidity changes with the nature of the cation of the base used for titration, the differences are moderate and that it is independent of concentration of the acid as observed by titration with the above bases at different concentrations of the jeolic acid*.

Conductometric Study with Bases

Conductometric titration curves of specimen (1) have been shown in Fig. 2. These curves show two inflexion points, the first inflexion occurs at almost the same amount of base in all the cases and corresponds approximately to the neutralisation of the free acidity (for arabic acid vide Mukherjee and Ghosh, *loc. cit.*). A summary of the observations has been presented in Table II of jeolic acid solution, specimen (1).

TABLE II

Bases.	a_H from p_H $\times 10^4 N.$	m. equiv. of base corresponding to 1st inflexion.	Total acidity in m. equiv. base per 100 g. of acid from 2nd inflexion.
KOH	10.72	11.51	80
NaOH	"	11.72	80
Ba(OH) ₂	"	15.05	89
Ca(OH) ₂	"	15.71	96

* These data have not been presented here as they are exactly of the type shown in the case of arabic acid by Mukherjee and Ghosh (*this Journal*, 1949, 26, 81).

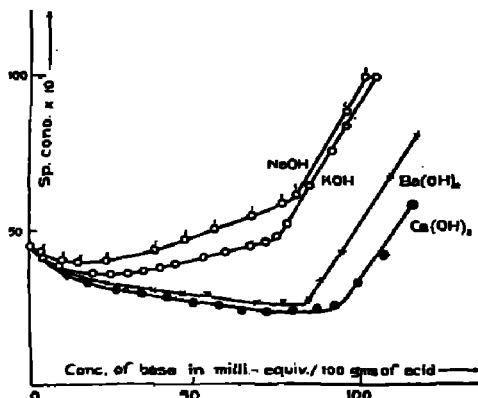
The second inflexion obviously yields the total acidity. Evidently, total acidities obtained from potentiometric and conductometric titrations agree with each other. The base corresponding to the first inflexion point tallies fairly well with the hydrogen-ion activity of the solution at least in the case of KOH. With $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ there has been a slight increase which will be understood in the light of the discussions brought forth in connection with the effect of neutral salts.

The nature of the titration curves simulates that of a weak acid, specially beyond the first inflexion point. The dissociation constant of the acid, as calculated in 1% solution by the formula

$$K = \frac{(a_{\text{H}})^2}{C_{\text{H}} - a_{\text{H}}}$$

comes up to 3.4×10^{-4} where a_{H} corresponds to the hydrogen-ion activity and C_{H} to the total acidity. These are obtained from the first and second inflexion points of the conductometric titration curves. The equivalent weight of the acid calculated from titration with NaOH is about 1200 which is practically equal to that of arabic acid calculated on the same basis. The order of the dissociation constant reveals the acid to be of weak nature although the potentiometric titration curve is like that of a strong acid.

FIG. 2

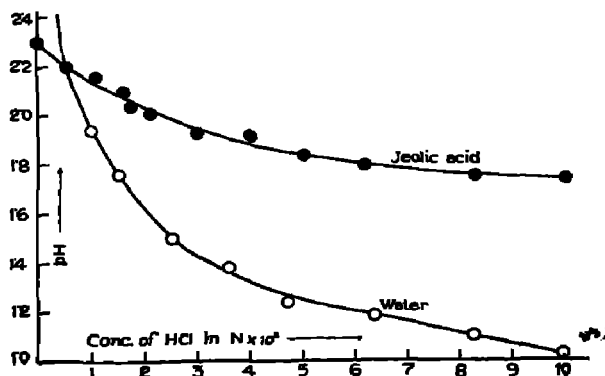


Interaction with Acids

The next point investigated was to examine how these systems interact with acids. For this reason the jeolic acid was titrated with a standard HCl solution and the variation of p_{H} with increasing concentration of HCl was carefully noted by the potentiometric method and compared with such variation in the case of water.

The result of this has been graphically shown in Fig. 3. The behaviour of the jeolic acid is very much like that of arabic acid (cf. Mukherjee and Ghosh, *loc. cit.*). The difference lies only in the degree of buffering in the two cases. The jeolic acid appears to have greater buffering properties, p_{H} remaining very little altered even with the addition of a considerable quantity of the acid. This in a way supports the view that the acid probably remains in part in the non-dissociated state which by suitable adjustment serves as a reserve.

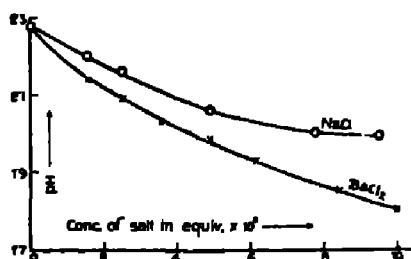
FIG. 3



Interaction with Neutral Salts

The total acidity of the jeolic acid, as observed by titration with bases having different cations, have been found to be different as already stated (vide Table I). These observations first indicated that most probably there might be some base-exchange phenomenon connected with these systems and different cations possessed different base-exchange capacities. This point has been directly put to test by examining the interaction of this jeolic acid with different salts having cations of different valencies. The scope of the investigation comprises, in this case, the variation of hydrogen-ion activity with the addition of increasing amounts of the salts : NaCl and BaCl₂.

FIG. 4



Results represented in Fig. 4 indicate that BaCl₂ depresses the p_H more than NaCl which perfectly fits in with our observation that Ba(OH)₂ shows a higher total acidity than NaOH in both potentiometric and conductometric titrations. Ba(OH)₂ thus liberates greater amount of hydrogen ions and thus exhibits a higher base-exchange capacity. The magnitude of this base-exchange capacity is, however, of a very small order. The anomaly viz., a slightly higher amount of the base is necessary at the first inflexion point with Ba(OH)₂ than what corresponds to the free acidity (a_H) is also understood in the light of these observations, because it appears that there is a slight base-exchange with this acid which is influenced differently by the different cations.

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