POTENTIOMETRIC BEHAVIOUR OF HUMIC ACID IN AN AQUEOUS MEDIUM

R. K. Shah, I. M. Bhatt and M. R. Chokshi*

Chemistry Department, University School of Sciences, Gujarat University, Ahmedabad-380009

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Humic acids were extracted from different soils of Gujarat. From potentiometric studies of humic acids in an aqueous medium in absence and in presence of 0.1 M NaCl their polyelectrolytic nature is revealed.

Soil-humic acids are polybasic acids containing functional groups like carboxyl (-COOH), hydroxyl (both phenolic and alcoholic, the former one predominating) enolic, primary amino and imino groups[1].

The behaviour of polymeric electrolytes in a solution is largely determined by the electrostatic free energy arising from the dissolution of ionogenic groups from the polymeric backbone. Conductometric and potentiometric titrations are the two well known methods employed for identification as well as the determination of the amount and under suitable conditions, the relative orientation of these ionogenic groups in a poly-functional macromolecule[2].

The information from potentiometric titration curves can be used to understand the nature of functional groups present in the molecule and its electrochemical behaviour. The titrations can be carried out in presence and absence of a neutral electrolyte such as sodium chloride.

Marshall et al[3] and Sandhoff[4] have given titration curves of natural humic acids in aqueous media.

Humic acids behave as polyelectrolytes and are good ion exchangers.

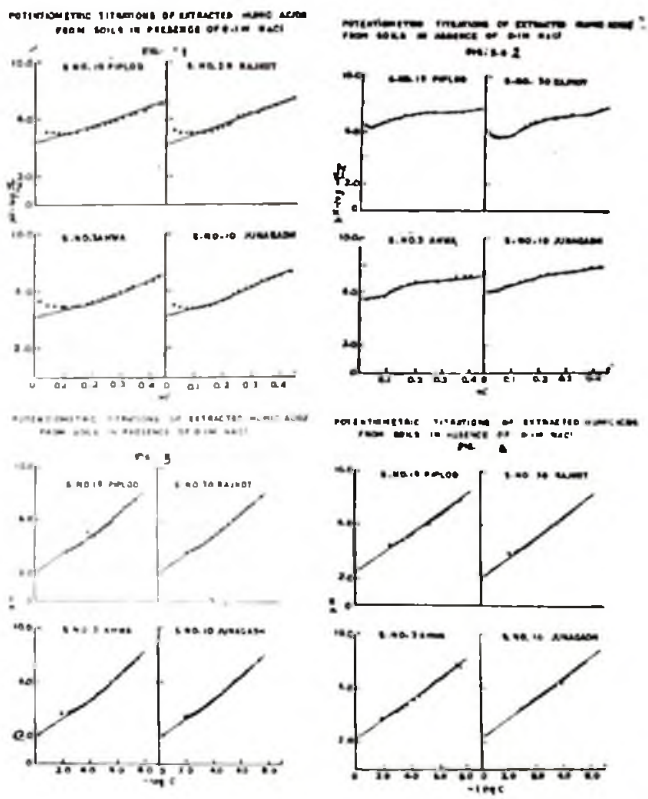
Some investigators tried to determine the amount of -COOH groups by potentiometry. The phenolic -OH groups are titrated above pH 7.0 while the -COOH groups are neutralized up to pH 7.0. Others consider the pH 8.2 as the limit instead of 7.0.

Experimental

Humic acids were extracted from different soils of Gujarat(Ahwa, Junagadh, Piplod and Rajkot) by alkali method and were purified by HCl + HF treatment, dialysis and using ion exchange column (Amberlite IR-120)[5-7]. 0.025 gm of humic acid was taken in 100 ml of water in absence and in presence of 0.1 M NaCl and titrated against 0.01 N NaOH.

In order to locate the inflexion points, more accurately, differential curves were plotted when required. pK_{av} at 50% neutralization, pK_1 and pK_2 corresponding to first -COOH and second phenolic -OH inflexion points respectively were calculated from the graphs, pK_{av} and pK_{int} were also calculated from the graph of pH vs. -logC and $\left(pH - \log \frac{\alpha}{1-\alpha} \right)$ vs α plots.

Table-1 presents dissociation constants and inflexion points data for extracted humic acids by potentiometric method.



Figs. 1-4 present the potentiometric behaviour for extracted humic acids in presence and absence of 0.1 M NaCl.

Discussion

The potentiometric titration curves with 0.01 N NaOH are shown in figs. 1 – 4. The end points have been located from the differential curves.

The apparent pK values at 50 per cent neutralization in absence of electrolytes range from 6.30 to 6.90 and in presence of electrolytes range from 5.00 to 5.55. If these acids are not treated as very weak acids, an approximate pK_{av} can be obtained from the equation : $pH = \frac{1}{2} pK_{av} - \frac{1}{2} \log C$. These values range from 4.0 to

* Chemistry Department, Bhavan's R. A. College of Science, Khanpur, Ahmedabad-380 001.

5.0 in absence of 0.1 M NaCl and 3.8 to 4.2 in presence of 0.1 M NaCl. They agree well with the values from pH titration curves. The addition of salt lowers the pK_{av} value by about 0.2 to 0.8 units. The adddition of salt lowers the pK_{av} for soil humic acids[8] from 6.4 to 5.4, while those of 'Merck' humic acid[9] range from 6.8 to 7.0.

The pK_{int} values can be calculated from the equation[1]

$$\log \frac{\alpha}{1-\alpha} - pH = pK_{int} - 0.868\ \alpha\ \bar{W}\ Z \ldots\ldots (i).$$

where $\alpha = \frac{\bar{r}}{n}$; $\bar{r}$, average number of H^+ ions dissociated per macromolecule, calculated as the ratio of the milliequivalent, of base added to the base exchange capacity or total acidity; n is the average total number of such dissociable protons per molecule,; $\bar{Z}$, net average charge on the molecule; and W, electrostatic interaction factor.

From the graph of $\left(pH - \log \frac{\alpha}{1-\alpha} \right)$ vs α pK_{int} will be found out as the intercept, since $\bar{Z} = 0$, pK_{int} value lies between 5.10 to 5.95 in absence of 0.1 M NaCl and 3.8 to 4.40 in presence of NaCl.

Figures also show that the relevant curves are linear in presence of 0.1 M NaCl, but not linear in absence of 0.1 M NaCl. The non-linear behaviour would mean that they follow Tanford's argument[10] that the electrolyte electrostatic free energy of dissociation and the size of the molecular charge change with ionization. This is in accordance with expectations, since these humic acids are polyelectrolytes in nature as revealed by their viscosity properties, and they obviously do expand with increasing charge.

In presence of 0.1 M NaCl, however, the polyelectrolyte behaviour is suppressed and the linearity of the curve is observed.

The values of pK_{int} in absence of electrolytes are quite high, 5.10 to 5.95, in comparison with 4.7 for side chain –COOH groups in polyacids. This discrepancy may arise from the fact that the assumption of a single type of dissociable group is probably not correct. The participation of, for instance, a large number of phenolic groups will obviously cause a great value in pK_{int}. In a macromolecule having different kinds of titratable groups, the pK_{int} for each kind can be evaluated separately, if each type of group is not known.

When salt is added, the values of pK_{int} are lowered and become closer to 4.40 to the actual value, viz. 4.7 for the –COOH carboxyls. In presence of salts, the polyelectrolyte molecules become coiled and compact and perhaps most of the phenolic groups get buried in the molecule. Moreover, in presence of electrolytes, the exposed phenolic groups get buried in the molecule. Moreover, in presence of electrolytes, the exposed phenolic–OH groups would undergo exchange reactions, viz. $-OH + Na^+ \rightarrow ONa + H^+$ which is corroborated by the observed pH drop in 0.1 M NaCl (initial pH, Table 1). This is equivalent to a lowering of pK_{int} for those phenolic groups.

It is further noted that in some cases the curves in absence of salt are not linear, while in its presence, they are linear. The non-linearity only means that it is not constant since $W = \frac{3e^2}{5DR_e}(1 + 0.6\ KR_e + 0.4\ K^2R_e^2)$ where R_e = radius of equivalent hydrodynamic sphere; it is evident that in absence of salt, R_e is not constant. This conclusion is entirely in accordance with the polyelectrolyte character of humic acids.

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Table - 1 Dissociation Points and other Data

DATA	PLACES							
	Ahwa		Junagadh		Piplod		Rajkot	
	A	B	A	B	A	B	A	B
Initial conc%	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Initial pH	3.55	3.90	3.40	4.40	3.60	4.20	3.65	3.85
pK_1	4.10	4.20	3.95	4.70	4.00	4.60	4.20	4.40
pK_2	6.30	6.45	6.70	7.15	6.10	6.90	6.70	6.75
Inflexion (ml) I	6.2	1.1	6.0	1.4	3.6	0.8	4.6	3.2
II	11.2	10.0	13.0	8.0	10.0	8.5	11.0	11.0
pH at equivalence	7.40	7.60	8.25	8.30	8.00	8.25	7.90	8.00
pK_{cv}	4.20	4.40	4.20	4.40	4.20	5.00	4.40	4.00
pK_{int}	4.20	5.10	4.30	5.80	4.40	5.80	4.30	5.10
B.E.C. per 100 gm (Acidity)	448	400	520	320	400	340	440	440
Basicity	2	2	2	2	2	2	2	2

A - In presence of 0.1M NaCl ; B - In absence of 0.1M NaCl

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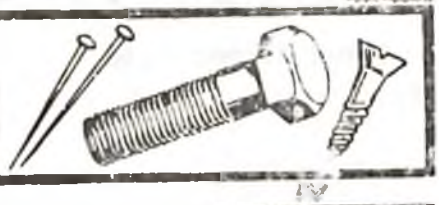
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