NOTES

A Note on "Acid–Base Properties of Fibers. Part II. A Polyelectrolyte Theory of the Combination of Fibers with Acids and Bases"

In a recent article bearing the above title,[1] Mathieson and Whewell have presented a very interesting analysis of the combination of wool and nylon with simple acids.

There appears, however, to be some doubt as to the consistency of the theoretical analysis and the following comments might perhaps provoke a useful discussion in this respect.

Equation (7) of Mathieson and Whewell[1] is

$$\mathrm{pH} = \mathrm{p}K_0' - \log\left[(1-\alpha)/\alpha\right] - 0.4343/RT)\left[\chi F + \pi \bar{V}_\mathrm{H} + \Delta\mu^\circ_\mathrm{H}\right] \tag{1}$$

and is correct, insofar as it is permissible to separate the affinity of the acid $\Delta\mu^\circ_{\mathrm{HX}}$ into the two independent components $\Delta\mu^\circ_\mathrm{H}$ and $\Delta\mu^\circ_\mathrm{X}$.

However, Mathieson and Whewell appear to take the viewpoint that their measured values for $\Delta\mu^\circ_\mathrm{H}$ are in fact a measure of the *anion* affinities $\Delta\mu^\circ_\mathrm{H}$, which is impossible if $\Delta\mu^\circ_\mathrm{H}$ and $\Delta\mu^\circ_\mathrm{X}$ have been thermodynamically correctly defined.

One may argue that the anion affinity $\Delta\mu^\circ_\mathrm{X}$ can only influence the titration curve, as described by eq. (7) of Mathieson and Whewell, through the quantities π and χ, so that the apparent inconsistency presumably arises in the method used to calculate χ.

Equations (10) and (12) of reference 1 can be put into the forms

$$C_{\mathrm{i},1} = C_{\mathrm{i},2}\left(\frac{\gamma_{\mathrm{i},2}}{\gamma_{\mathrm{i},1}}\right)\exp\left\{-\frac{(\chi F + \pi\bar{V}_\mathrm{i} + \Delta\mu^\circ_\mathrm{i})}{RT}\right\} \tag{2}$$

and

$$C_{\mathrm{j},1} = C_{\mathrm{j},2}\left(\frac{\gamma_{\mathrm{j},2}}{\gamma_{\mathrm{j},1}}\right)\exp\left\{\frac{(\chi F - \pi\bar{V}_\mathrm{j} - \Delta\mu^\circ_\mathrm{j})}{RT}\right\} \tag{3}$$

so that they may be directly compared with equations (19) of Mathieson and Whewell,[1] which were apparently used to calculate χ.

$$C_{\mathrm{i},1} = C_{\mathrm{i},2}\exp\left\{-\epsilon\chi/kT\right\} \tag{4}$$

$$C_{\mathrm{j},1} = C_{\mathrm{j},2}\exp\left\{\epsilon\chi/kT\right\} \tag{5}$$

Equations (4) and (5) are consistent with equations (2) and (3) only when the activity-coefficient ratio is assumed to be unity in each case and when $\Delta\mu^\circ_\mathrm{i}$ and $\Delta\mu^\circ_\mathrm{j}$ are zero, the terms in π also being zero. This is a disguised Donnan-Membrane equilibrium of a very simple form, which nevertheless appears to describe the titration of wool and nylon with hydrochloric acid in a satisfactory manner.[1,2].

If equations (4) and (5) were used to calculate χ in a more general case, this would apparently force a condition of the type

$$(\pi\bar{V}_\mathrm{i} + \Delta\mu^\circ_\mathrm{i}) = -(\pi\bar{V}_\mathrm{j} + \Delta\mu^\circ_\mathrm{j}) \tag{6}$$

upon the analysis, which may explain the apparent assumption of Mathieson and Whewell that $\Delta\mu_i^\circ$ and $\Delta\mu_j^\circ$ are functionally related. There is therefore some doubt about the use of eqs. (19) of Mathieson and Whewell[1] in the general case, and it would be useful to know whether or not this calculation procedure was used by Mathieson and Whewell, e.g., in obtaining the comparison in Table IV of reference 1.

References

1. A. R. Mathieson and C. S. Whewell, *J. Appl. Polymer Sci.*, **8**, 2029 (1964).
2. A. R. Mathieson, C. S. Whewell, and P. E. Williams, *J. Appl. Polymer Sci.*, **8**, 2009 (1964).

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