# Strongly Basic Media

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$H_-$ SCALES for aqueous NaOH and KOH have been set up[1,2] as also for LiOH.[3] As a result of Bell and Bascombe's[4] attempt to theoretically predict $H_0$ values in concentrated acid media a number of workers[2,5] have adopted parallel procedures for basic media and claim good agreement between theory and experiment.

The object of the present work is threefold:

(1) To show that for solutions of equal concentration that the observed trend in basicity [$H_-$(LiOH) < $H_-$(NaOH) < $H_-$(KOH)] is only apparent and not real.

(2) To show that the agreement between theoretical and experimental $H_-$ values is fortuitous.

(3) To point out the dangers in correlating the rates of reaction with such values.

Bell and Prue[6] showed that reaction kinetics can be used to determine the dissociation constants of a number of hydroxides and an approximate value of 5 for $K_{\mathrm{d}}$(NaOH) was obtained. Subsequently[7] a $K_{\mathrm{d}}$ value of 3·4 was determined, as well as 5·1(KOH), and 1·5(LiOH) which compared with a previous value of 1·2.[8] These values, 3·4(NaOH), 5·1(KOH), and 1·5(LiOH) were obtained by a procedure which entailed using small concentrations of hydroxide ion in the presence of large quantities of salts such as NaBr, KBr, and LiBr. We have then assumed that in the equation:

$$K_{\mathrm{d}}.x = ([M]_{\mathrm{T}} - x)([\mathrm{OH}]_{\mathrm{T}} - x)\, f_{\pm}^{2}$$

where $T$ refers to the total concentration, and $x$ is the concentration of ion-pair, that $f_{\pm}^{2}$ may be put equal to $\gamma_{\pm}^{2}$ for the salt at the appropriate concentration. The activity coefficient of the ion-pair is neglected. Therefore in a concentrated

TABLE

$H_-$ *values for aqueous base solutions and concentrations of ion-pair*

| Base | $K_d$[7] | Concentration Molarity | Concentration Molality | $\gamma_\pm$[9] | $K_d/\gamma_\pm^2$ | $x$ | $M^+$ | $H_-$ | $H_-$ Reference |
|---|---|---|---|---|---|---|---|---|---|
| KOH | 5·1 | 1 | 1·04 | 0·62 | 13·3 | 0·07 | 0·97 | 14·0 | |
| | | 2 | 2·16 | 0·59 | 14·6 | 0·25 | 1·91 | 14·49 | |
| | | 3 | 3·36 | 0·60 | 14·2 | 0·55 | 2·81 | 14·81 | 1 |
| | | 4 | 4·70 | 0·62 | 13·3 | 1·0 | 3·7 | 15·12 | |
| | | 5 | 5·90 | 0·63 | 12·9 | 1·5 | 4·2 | 15·45 | |
| NaOH | 3·4 | 1 | 1·04 | 0·69 | 7·14 | 0·12 | 0·92 | 14·17 | |
| | | 2 | 2·14 | 0·74 | 6·21 | 0·45 | 1·69 | 14·47 | |
| | | 3 | 3·30 | 0·84 | 4·82 | 1·05 | 2·25 | 14·65 | |
| | | 4 | 4·56 | 0·98 | 3·54 | 1·94 | 2·62 | 14·77 | 2 |
| | | 5 | 5·90 | 1·15 | 2·57 | 3·00 | 2·9 | 14·87 | |
| | | 6 | 7·10 | 1·3 | 2·01 | 4·20 | 2·9 | 14·95 | |
| LiOH | 1·5 | 1 | 1·04 | 0·80 | 2·34 | 0·26 | 0·78 | 13·43 | |
| | | 2 | 2·15 | 1·06 | 1·33 | 1·0 | 1·15 | 13·53 | |
| | | 3 | 3·30 | 1·50 | 0·67 | 1·87 | 1·43 | 13·93 | 3 |
| | | 4 | 4·60 | 2·40 | 0·26 | 3·63 | 1·10 | 14·04 | |
| | | 5 | 6·00 | 3·90 | 0·10 | — | — | 14·31 | |

solution of base one can calculate the concentration of ion pair by solving the quadratic equation. The results are summarised in the Table.

It can thus be seen that the concentration of ion-pair in the more concentrated media is a substantial fraction of the base concentration and in the case of lithium hydroxide at the higher concentrations is sufficiently high to make an accurate calculation of the free $OH^-$ concentration difficult. As a result of the correction for ion association the potassium and sodium results up to 5M fall on the same line (Figure) and in this respect may suggest an inaccuracy in the lithium results. As a consequence of the correction the $H_-$ of the medium increases more rapidly than indicated by the original data. The increase at the higher concentrations must to some extent reflect the contribution which is made to the basicity of the medium by the ion pair. Such an interpretation is consistent with the results of some recent kinetic measurements.[10]

It follows from the above that any theoretical attempt at postulating the $H_-$ of a particular medium should initially take into account the

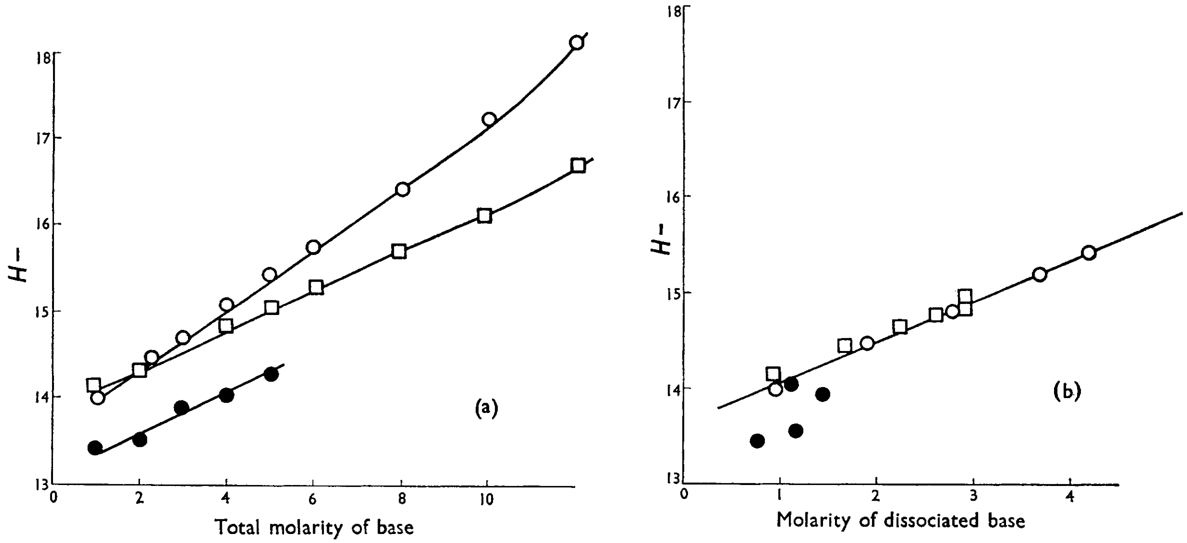

FIGURE. *Plot of* (a) $H_-$ *against total molarity of base;* (b) $H_-$ *against molarity of dissociated base.* ○ *refers to* KOH, □ *to* NaOH, *and* ● *to* LiOH.

various species present in that medium as well as the individual concentrations.

$H_-$ scales[11,12] for methanolic potassium and lithium methoxide solutions show that $H_-$(LiOMe) < $H_-$(KOMe) for a given concentration. The most probable reason for the difference is again ion association and in this instance it is expected to be appreciable at lower concentrations of base than was the case for the hydroxides, in view of the much lower dielectric constant of methanol. No values of $K_d$ have been reported for either NaOMe or KOMe, but if our interpretation of the aqueous base media is correct it does suggest that any correlation between rates of reaction and $H_-$ of methanol–methoxide media as was done[13] for the methanolysis of chloroform, phenethyl chloride, and 1-chloro-3,3-dimethylbutane should take the problem of ion pairing into account before discussing differences in solvation between reactants and transition states.

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