Ionic Strength Effects on the Activity Coefficient of Methylene Blue and Its Self-Association[1]

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Abstract: The "isoextraction" method has been used to investigate the variation in the activity coefficients of dilute methylene blue perchlorate solutions in sodium fluoride and sodium sulfate solutions. The dye salt behaves like typical inorganic 1:1 electrolytes with moderate ion-size parameters. At low ionic strengths, the activity coefficients tend toward the Debye-Hückel limiting law predictions. Isoextraction studies at a high dye concentration and various concentrations of sodium fluoride have also been performed to investigate the effect of ionic strength on the self-association of methylene blue. The dimerization constant K_2 increases by about 33% as the ionic strength increases by a factor of 40 from 0.0025 to 0.102. The variation in K_2 is in rough accord with that expected from changes in activity coefficients. The results support the previous assumption of negligible counterion participation in association equilibria at low ionic strengths.

The analysis of the self-association behavior of methylene blue (MB) in the previous two papers[4,5] has been based on some assumptions about the effects of activity coefficients at low ionic strengths on the extractability of $MBClO_4$ and the self-association of MB, as well as the negligibility of counterion participation in self-association of MB when the ionic strength, μ, is low. The present paper deals with the use of the "isoextraction" method[4] to study the effect of substantial changes in μ on the extractability of $MBClO_4$, the activity coefficient of monomeric MB salts, and the self-association of MB. Our study is also relevant with respect to some recent suggestions about the importance of counterion association in dye association and metachromatic interactions.[6-9]

The symbols K_A, $K_{A(0)}$, K_2, $K_{2,t}$, B, and b are used as defined in the previous papers.[4,5] The apparatus and the chemicals used have been described previously.[4]

Results and Discussion

Activity Coefficients of Monomeric $MBClO_4$. The variation of the mean ionic activity coefficient, $f_{\pm}$, of monomeric $MBClO_4$ was studied by the isoextraction technique,[4,10] using chloroform as the organic phase. The equilibrium concentration of MB in water was kept within the range of $1-3 \times 10^{-5}$ *M*. All solutions contained 0.001 *M* HCl, for reasons discussed before.[4] The ionic strength of the medium was varied by adding NaF and Na_2SO_4 up to a maximum value of about 0.1. NaF and Na_2SO_4 act as inert electrolytes, since the extractability of MB as the fluoride or the sulfate was ascertained to be negligible. Small corrections, 5–8%, due to the self-association of MB were applied to K_A to obtain $K_{A(0)}$. Sample B[4] of MBCl was used for this work. Later work[4] showed this to be less pure than the sample A used in all self-association studies reported. However, since only the *relative* change in $K_{A(0)}$ with μ is the object of this study, the small amounts of impurities suspected are unlikely to affect the general conclusions.

In Figure 1, $K_{A(0)}$ is plotted on a log scale against $\sqrt{\mu}$. The total variation in $K_{A(0)}$ observed was about 50%. $K_{A(0)}$ can be expressed as

$$K_{A(0)\infty} = K_{A(0)}f_{\pm}^2 \qquad (1)$$

where $K_{A(0)\infty}$ is the value of $K_{A(0)}$ when $\mu = 0$. Thus

$$\log K_{A(0)} = \log K_{A(0)\infty} - 2 \log f_{\pm} \qquad (2)$$

Figure 1 shows the behavior expected of ordinary electrolytes. Although our range of μ, 0.00113–0.098, falls somewhat outside the range of validity of the limiting law of the Debye–Hückel (D–H) theory,[11] the data extrapolate quite well to the initial straight line in Figure 1, representing the limiting D–H slope at 35°. The curved line drawn through the data was calculated from the $f_{\pm}$ data for a typical inorganic electrolyte, NaCl, from standard compilations.[11] The NaCl line gives a fair representation of the data, the agreement being somewhat better with the data obtained in NaF solutions. The deviations from this line suggest a somewhat larger ion-size parameter for $MBClO_4$ than for NaCl in the extensions of the D–H theory to moderate ionic strengths. This seems to be reasonable for the large dye ion. The $K_{A(0)}$ data can be used to estimate an ion-size parameter for $MBClO_4$ if needed.

The following conclusions can be drawn from the above study. The ability of the "isoextraction" technique to provide data in reasonable agreement with the theories of activity coefficients is an important argument for its validity. It also suggests the general usefulness of the method in determining activity coefficients, particularly of the "tracer" variety, where

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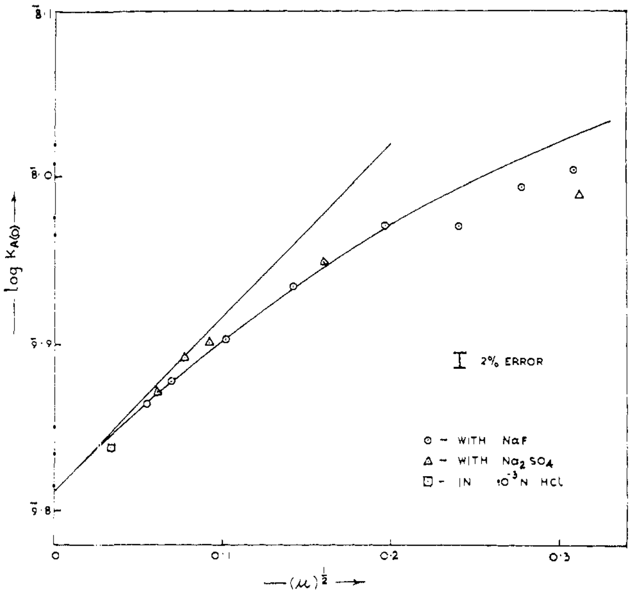

Figure 1. Effect of ionic strength on $K_{A(0)}$ [(equiv/l.)^2] at 34.9°. The initial straight line represents the Debye–Hückel limiting law. The curved line is calculated from the activity coefficients of NaCl.

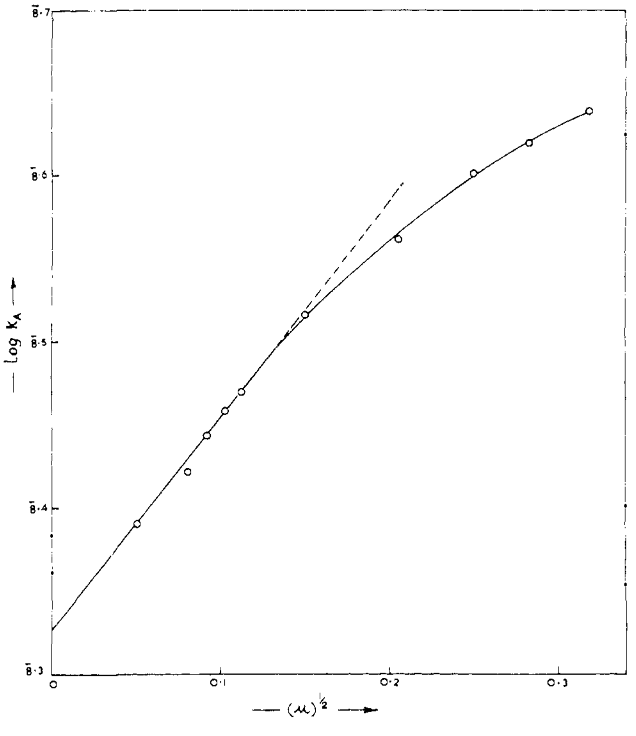

Figure 2. Variation of K_A [(equiv/l.)^2] with ionic strength for an MBCl concentration of 9.5×10^{-4} equiv/l. at 34.9°.

activity coefficients of some extractable electrolyte at low concentrations is determined in the presence of an arbitrary concentration of a nonextractable electrolyte. The $f_{\pm}$ values of $MBClO_4$ are as might be expected for an ordinary electrolyte composed of fairly large ions: dyes thus do not behave very unusually, as is sometimes claimed.[12] As NaF and Na_2SO_4 give rise to about the same changes, the principle of ionic strength applies, and the ion pairing of monomeric MB, even with the bivalent SO_4^{2-}, is probably unimportant in aqueous solutions.

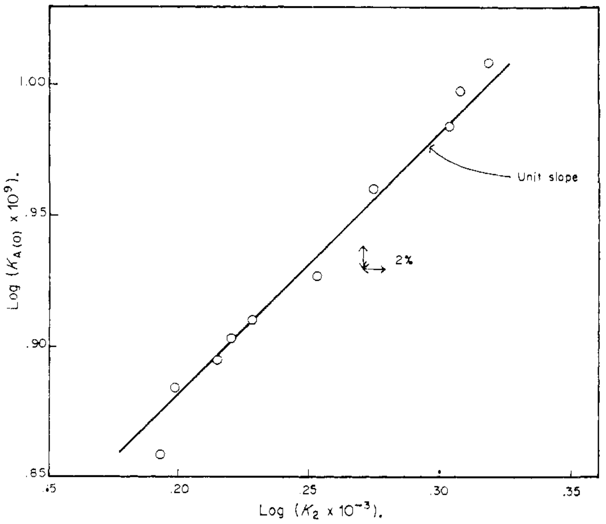

Figure 3. Correlation of $K_{A(0)}$ [(equiv/l.)^2] and K_2 (l./mol) at various ionic strengths in NaF solutions.

Effect of Ionic Strength Variation on the Self-Association of MB. To study the effect of μ on the association of MB, experiments similar to the above were performed with a moderately high dye concentration, 9.5×10^{-4} M, in the presence of 0.001 M HCl, μ being varied by the addition of NaF. Dye association was taken into account in calculating μ. On the addition of NaF, K_A increases somewhat more steeply with μ (Figure 2) than $K_{A(0)}$ (Figure 1). A part of this variation is due to the effect of μ on $K_{A(0)}$. The remaining part, therefore, must be due to an increase in self-association with μ.

To investigate this effect quantitatively, we have used the self-association model Y of the previous paper[5] to calculate K_2 from the relation $K_A/K_{A(0)} = 1 + 2K_2B$ at each value of μ. At 35° this model holds for the dilute solution data in water up to the concentration investigated.[13] As only the *relative* variation in K_2 with μ is of interest, the use of any other model does not change the conclusions appreciably. The sample B of MBCl[4] used to study the variations of $K_{A(0)}$ with μ gave somewhat higher values of $K_{A(0)}$ than the recrystallized sample A, used in the present study, presumably because of the presence of some less hydrophobic and, therefore, less extractable demethylated products.[14] To compare the present data with sample A, the $K_{A(0)}$ values have been scaled down by the appropriate factor of 0.86. Since a constant factor is used, the *relative* change in K_2 with μ is affected only very slightly.

The activity coefficients of reactants and products cancel to a great extent in stepwise association.[5] For dimerization, in the D–H limiting law region, the thermodynamic value $K_{2,t}$ is related to K_2 by the following equation

$$\log K_2 = \log K_{2,t} - 2 \log f_{\pm} \qquad (3)$$

where $f_{\pm}$ is the value for a 1:1 electrolyte. At high μ the limiting law does not apply and the extensions

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of the D–H theories are of very limited use, since ion-size parameters and short-range interactions for dye ions cannot be estimated with any precision. However, the activity coefficients of the dimer and the monomers should continue to cancel to a great extent in K_2. We have, therefore, attempted to extend eq 3 to our higher ionic strength data. This can be done conveniently since essentially the same $f_\pm$ is involved in the dependence of $K_{A(0)}$ on μ (eq 2) and K_2 on μ (eq 3), both in NaF solutions. The two equations together predict a linear variation in log K_2 with log $K_{A(0)}$, when both are evaluated at the same μ, with a slope of unity. Figure 3 shows that this predicted relationship, expected to be valid in dilute solutions, is actually obeyed over the whole concentration range, with an average deviation of about 1% in K_2.

The above correlation may be fortuitous. However, the experimental fact that K_2 increases by only 33% as μ increases by a factor of 40 from 0.0025 to 0.102, suggests strongly that the self-association of MB, at least for the smaller multimers, is controlled mainly by changes in $f_\pm$ when μ is varied, and that counterion participation in the association equilibria is small, at least for the fluoride ion. Otherwise, an increase in counterion concentration by a factor of 40 would have resulted in considerably greater association at 9.5×10^{-4} *M* MB, where the fraction of total dye in the associated form is 75–80%. The previous assumption of no counterion participation[4,5] in the self-association of MB is thus justified.

The present conclusions are in agreement with some recent findings of Padday,[9] published after the present work was completed. Padday[9] has shown by electrometric measurements that counterion association does not play a very important part in dye association and metachromatic interactions, contrary to some recent suggestions.[6–8]

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Study of the Self-Association of Methylene Blue from Protonation Equilibria[1]

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Abstract: The self-association of methylene blue (MB^+) has been investigated by a new method based on the study of the protonation equilibrium of MB^+. The concentration of MBH^{2+} can be estimated by spectrophotometry at 745 mμ. The experiments have been performed in 0.200 *M* HCl. The apparent proton dissociation constant, $K_{pd(A)}$, of the species MBH^{2+}, defined as $B[H^+]/[MBH^{2+}]$, where *B* is the total equivalent concentration of all nonprotonated dye species, varies by a factor of 9 as *B* varies from 2.26×10^{-5} to 1.27×10^{-3} *M*. The extrapolated value of $K_{pd(A)}$ at $B = 0$ gives the true proton dissociation constant, $K_{pd(0)}$, defined as $b[H^+]/[MBH^{2+}]$, where *b* is the concentration of dye monomers. The ratio $K_{pd(A)}/k_{pd(0)}$ thus equals *B*/*b*, and *b* can be obtained as a function of *B*. The estimated association of MB^+ with MBH^{2+} leads to a small correction. The *B*(*b*) data are qualitatively very similar to those obtained by using the "isoextraction" method and are described well by the association model previously found satisfactory for methylene blue at low ionic strengths. The present method thus provides independent confirmation of previous conclusions about the self-association of MB^+. The dimerization constant, K_2, is somewhat higher than expected on the basis of a long extrapolation from our previous study of its ionic strength dependence. If the difference is attributed to ion pairing of the dimer with Cl^-, the derived equilibrium constant for ion pairing is low enough to provide strong support for the assumption of negligible counterion participation in our low-ionic-strength studies.

In previous papers[3–5] we have reported on our study of the self-association of methylene blue (MB^+) by the new "isoextraction" technique. Although the experimental method and the data and their interpretations are felt to be reliable,[3–5] an independent study of the self-association of MB^+ using an entirely different equilibrium method appeared to be highly desirable. The present paper outlines the principles of such a method, based on the protonation reaction of MB at high acid concentrations, and the results obtained therefrom. This new method is also expected to be useful for other systems.

In a broad sense, the principle of the present method is similar to that of the isoextraction method[3] and the solubility method[4] in that an equilibrium reaction involving the monomers is studied as a function of the total concentration so that the competitive equilibrium reactions in the self-association of the monomer can be disentangled.

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