

The Dissociation Constant of Cresol Red in Sea Water.

By

Philip H. Mitchell and Ivon R. Taylor,

the Biological Laboratory of Brown University, Providence, R. I.,

and the Woods Hole Oceanographic Institution,

Woods Hole, Mass.

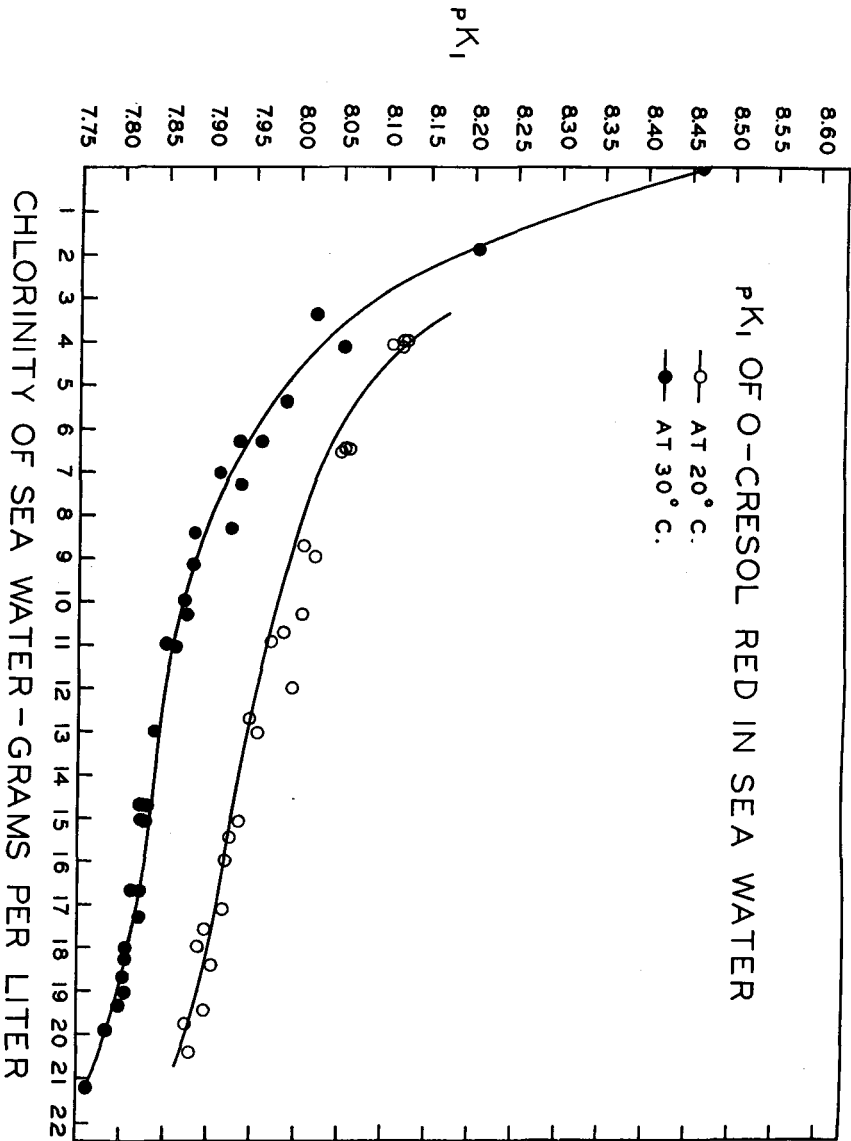
THE technical improvements during recent years in methods for colorimetric estimation of pH permit the attainment of results which exceed in precision and reproducibility the accuracy of available information concerning the behaviour of pH indicators as influenced by the ionic strength, specific ion effects, temperature and other conditions in the solutions to be measured. This discrepancy has been particularly noticeable in our experience with the pH bicolorimeter of the Hastings type. So far as the actual measurements are concerned, results would seem to justify computation of the pH to the third place of decimals. But the formula for computing,

$$\text{pH} = \log \frac{\text{depth of alkaline standard}}{\text{depth of acid standard}} + \text{pK}_i,$$

means that precision is limited by the accuracy of knowledge of the value for pK_i , the logarithm of the reciprocal of the dissociation constant of the indicator in the particular solution measured. This limitation has probably been encountered in many laboratories. We have met it in several instances. One of them is the estimation of the pH of sea water.

It therefore seemed advisable to undertake more accurate measurements of the so-called "salt effect" of sea water upon indicators and also of the temperature effect. The indicator chosen for an initial investigation was o-cresol red because it is now widely used for pH measurements on sea water.

Values already available are those given by Wells (1) and by Ramage and Miller (2). In neither of these investigations was the temperature effect established and in the work of Ramage and Miller, CO_2 was eliminated from the water by prolonged bubbling of hydrogen through it. The effect of removal of CO_2 upon the dissociation constant of the indicator is unknown.



We now have a satisfactory method for obtaining the pH of solutions quickly, accurately, and without any serious difficulties due to CO_2 . This is by means of the glass electrode. Its usefulness in our experience with it was largely influential in our decision to undertake the work here reported. The form used has been described by Taylor and Birnie (3).

The procedure was as follows. Sea water samples were prepared

Table 1.
Dissociation Constant of o-Cresol Red in Sea Water at 30° C. and at 20° C.

| Chlorinity | | pH by the glass electrode | $\log \frac{y-x}{x} (1)$ | pK _I |
|--------------------|------------------|------------------------------|--------------------------|-----------------|
| grams per litre | grams per kg. | | | |
| 21.21 | 20.66 | 8.081 | 0.320 | 7.761 |
| 18.33 | 17.93 | 8.073 | 0.269 | 7.804 |
| 16.71 | 16.37 | 8.060 | 0.238 | 7.822 |
| 14.75 | 14.49 | 8.041 | 0.222 | 7.829 |
| 13.00 | 12.80 | 8.006 | 0.170 | 7.836 |
| 11.04 | 10.89 | 7.977 | 0.116 | 7.861 |
| 9.18 | 9.08 | 7.921 | 0.041 | 7.880 |
| 7.33 | 7.27 | 7.589 | 9.656 — 10 | 7.933 |
| 5.40 | 5.38 | 7.484 | 9.499 — 10 | 7.985 |
| 4.17 | 4.16 | 7.381 | 9.331 — 10 | 8.050 |
| 3.39 | 3.38 | 7.334 | 9.276 — 10 | 8.058 |
| | | | | at 20° C. |
| 20.43 | 19.92 | 7.939 | 0.060 | 7.879 |
| 18.41 | 18.00 | 7.942 | 0.039 | 7.903 |
| 16.00 | 17.69 | 7.924 | 0.005 | 7.919 |
| 13.04 | 12.84 | 7.919 | 9.965 — 10 | 7.954 |
| 10.96 | 10.81 | 7.886 | 9.916 — 10 | 7.970 |
| 8.98 | 8.87 | 7.832 | 9.813 — 10 | 8.019 |
| 6.44 | 6.40 | 7.710 | 9.652 — 10 | 8.058 |
| 4.08 | 4.07 | 7.544 | 9.442 — 10 | 8.102 |

¹⁾ Where y = total depth of standards, x = depth of acid one.

by diluting a given specimen with distilled water so as to have a series of varying salt-content checked at the end of the experiment by titration with silver nitrate. Each dilution was then allowed to come to equilibrium with CO₂ in a thermostat at the temperature to prevail during measurements. The pH values were then taken with the glass electrode and shortly afterward observations were made at the same temperature in the bicolorimeter with cresol red as indicator. The log of the ratio of the depths of the two standard colour solutions was subtracted from the corresponding pH to give the pK_I.

The cresol red employed was previously examined by the spectrophotometric method and found to give maximum absorption at a wavelength of 572 m μ and to exhibit an absorption curve which would characterize it as satisfactorily pure. The two standard colours, in the fully acid and fully alkaline condition, were obtained in (a) a phthalate buffer solution prepared after Clark and Lubs and having a pH 3.90 and (b) a borate buffer solution prepared according to Sørensen and having a pH 11.00.

An isohydric condition of the indicator is of course very important for any high degree of precision with slightly buffered solutions. In these observations, we found that for a chlorinity of the salt water less than about 10 parts per thousand seriously discrepant results were

reached unless the indicator solution was adjusted to approximately the same pH as the unknown, and the lower the chlorinity, the greater the necessity for accuracy of adjustment to an isohydric condition if concordant results were to be obtained. With higher chlorinities a considerable variation in the pH of the indicator solution made no difference in the result beyond the usual observational error. The buffering capacity of water of high salinity is sufficient to overcome that of the indicator itself. For the more dilute waters the E. M. F. of each sample as taken with the glass electrode served as a guide for adjustment of the indicator. A small portion of its solution was titrated with very small amounts of 0.001N HCl, tested in the glass electrode after each addition and finally adjusted until it gave a potential varying by not more than one millivolt from that of the water sample which was to be measured.

The pK_I values obtained are shown in Table 1, and in the accompanying graph (Fig. 1). The results shown in Table 1 are those obtained in two typical series of measurements, one at 30° C. and one at 20° C. The results for both of these series and also those for other similar ones are presented graphically in Fig. 1. The point at 30° C. and zero chlorinity is taken from K o l t h o f f (4).

Our values at 20° C. are higher than those of R a m a g e and Miller who included values given by W e l l s, while our values at 30° C. are lower than earlier reported ones. But as temperature is not stated in the earlier reports, one may assume that it would account for some at least of the discrepancies. In the case of pK_s/pK_I for all chlorinity values below about 9 grams per litre our results are all consistently higher than those of R a m a g e and Miller. This is due, presumably, to the fact that we used indicators isohydrically adjusted, for we found that using the ordinary indicator solution (prepared so as to make the monosodium salt) our results were as low as or even lower than those of R a m a g e and Miller.

As one can see from the graph, the pK_I drops off sharply with increases in the lower range of salinities, decreases only gradually through the medium ranges and again falls off rapidly at salinities in the neighbourhood of those found in mid-Atlantic waters.

Summary.

Values for the pK_I of o-cresol red in sea water at various dilutions were obtained at 30° C. and at 20° C. by the use of the glass electrode and the bicolorimeter. The results are shown graphically.

References.

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