291. *The Colorimetric Measurement of* pH, *and the Dissociation Constants of the Malonates of Some Bivalent Metals.*

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A colorimetric method is described of measuring the pH of an aqueous solution with an accuracy of 0·01 pH unit. It is emphasised that the apparent " pH " measured with sulphonephthalein indicators is not the same quantity as that obtained electrometrically: the relationship between the quantities measured in these two ways is illustrated.

The dissociation constants of the malonates of a number of bivalent metals, in aqueous solution, are reported and discussed.

The development of the glass electrode, and of pH meters incorporating it, has undoubtedly made the electrometric method the most general method of pH measurement, since it can be applied in the presence of colloids, and in coloured and highly dilute solutions where indicators are inapplicable or inconvenient. Apart from these special cases, however, indicators offer certain advantages, and it seems to us a mistake to regard the electrometric method as the standard, and as always the most accurate, method. A simple comparator being used, indicators readily give a reproducibility of 0·01 pH unit, and although the potentiometric technique can be refined to yield results which are reproducible to a third decimal place, this advantage is offset by the difficulties in interpreting the results, owing to uncertainties in the magnitude of liquid-junction potentials and activity corrections.

Bromophenol-blue was the indicator used in the present work, and our object was to establish its accuracy in measuring true hydrogen-ion concentrations, and then to apply it to the study of ion association in malonate solutions. The usual buffer standards could not be employed, because, although their pH values are known with great accuracy, the interpretation of these is attended by the uncertainties already mentioned. Instead, we used as standards partly neutralised solutions of weak acids, the hydrogen-ion concentrations of which could be calculated with a high degree of accuracy from known dissociation constants.

The Measurement of Hydrogen-ion Concentration with Bromophenol-blue.—The main colour change of the sulphonephthalein indicators is known to be associated with the ionisation of a phenolic hydrogen in the singly-charged yellow carboxylate ion (cf. Kolthoff, *J. Physical Chem.*, 1931, **35**, 1433). For bromophenol-blue, therefore, the indicator equilibrium will be controlled by the equation $f_H \cdot f_{B''}[H^{\cdot}][B'']/f_{HB'}[HB'] = K_I$, and the colour of the indicator will be governed by the ratio $[B'']/[HB']$. Consequently, when we compare two solutions in which the concentration and colour of the indicator are identical, the quantity $f_H \cdot f_{B''}[H^{\cdot}]/f_{HB'}$ is the same in each. At sufficiently low ionic strengths, the ion-activity coefficients may be evaluated by means of the Debye–Hückel limiting equation, or by an empirical extension of this; for instance, at ionic strengths not exceeding 0·05, there are good grounds for believing that departures (at 25°) from the equation $\log f_i = -0{\cdot}5z_i^2\{\sqrt{I}/(1+\sqrt{I}) - 0{\cdot}2I\}$ (Davies, *J.*, 1938, 2093) will be well within the accuracy of 2% at which we were aiming. The activity coefficient of the univalent ions being taken as equal, and that of the bivalent ion B'', *i.e.*, $f_{B''}$, being written as f_2, equality of colour in two solutions will indicate identity of the quantity $pf_2[H^{\cdot}] = -\log f_2[H^{\cdot}]$, or, after introduction of the equation above, of the quantity

$$pf_2[H^{\cdot}] = -\log [H^{\cdot}] + 2\{\sqrt{I}/(1+\sqrt{I}) - 0{\cdot}2\,I\}.$$

We have confirmed this conclusion by preparing two buffer solutions of known ionic composition and widely differing ionic strengths, which gave identical colours with the standard concentration of indicator. The first solution was 0·004931M with respect to sodium hydrogen malonate and 0·03304M with respect to potassium chloride. By using German and Vogel's values for the dissociation constants of malonic acid ($K_1 = 1{\cdot}4 \times 10^{-3}$; $K_2 = 2{\cdot}2 \times 10^{-6}$; *J. Amer. Chem. Soc.*, 1936, **58**, 1546), the hydrogen-ion concentration can be calculated to be $7{\cdot}86 \times 10^{-5}$ mol./l., the ionic strength is 0·03831, and $pf_2[H^{\cdot}] = 4{\cdot}42$. The second solution was 0·005850M with respect to sodium benzoate and 0·004012M with respect to benzoic acid, and for this, $[H^{\cdot}] = 5{\cdot}09 \times 10^{-5}$, $I = 0{\cdot}005850$, and $pf_2[H^{\cdot}] = 4{\cdot}43$. It will be seen that the agreement between the calculated $pf_2[H^{\cdot}]$ values is satisfactory, although the hydrogen-ion concentration of the first solution is more than 50% greater than that of the second. If we use what is perhaps the most usual definition of pH, *viz.*, $pH = -\log f_1[H^{\cdot}]$, where f_1 is a mean value for univalent ions, then the pH of the first solution is 4·18 and that of the second is 4·33, a difference of 0·15 pH unit. This illustrates the errors that may be involved in basing colorimetric measurements on electrometric standards. It may be noted that similar, though smaller, discrepancies arise when monobasic acids, such as phenolphthalein are used as indicators. From the equation $f_H \cdot f_{P'}[H^{\cdot}][P']/[HP] = K_I$, it will be clear that in this case the colour of the indicator is a measure of the quantity $f_1^2[H^{\cdot}]$. Though the correct interpretation of colorimetric pH measurements has been established before (see, for instance, Guggenheim and Schindler, *J. Physical Chem.*, 1934, **38**, 543), it is still frequently found that equality of indicator colour is either taken to imply pH equality (whereas with no type of indicator does the quantity studied correspond to the electrometrically measured pH), or else that the error involved in ignoring activity corrections is negligible. As the example quoted demonstrates, this error may well be large, and now that some reliance can be placed on the calculation of activity coefficients in dilute solutions it seems unfortunate that these differences in scale should often be ignored, or disguised as part of a " salt error."

Ion Association in Malonate Solutions.—Malonic acid, sodium hydroxide, and metal chloride solutions were mixed to give the final concentrations : NaHMal 0·004931M, MCl_2 0·01233M, the standard amount of indicator being added. The colour of the solution was then matched by a standard benzoate or mandelate buffer, thus determining the value of $pf_2[H^{\cdot}]$. The results obtained are shown in Table I, col. 1 showing the cation added to the malonate buffer, and col. 2 giving the $pf_2[H^{\cdot}]$ value. The effect of adding the bivalent chloride is invariably to increase the hydrogen-ion concentration of the " buffer "—by more than 20-fold in the case of copper—a result which is primarily due to the reaction $M^{\cdot\cdot} + HMal' = MMal + H^{\cdot}$. The amount of undissociated metal malonate is calculated as follows. The solution contains, besides water and indicator, the following species : $Na^{\cdot}$, Cl', $M^{\cdot\cdot}$, MMal, Mal'', $HMal'$, H_2Mal, $H^{\cdot}$, OH', and possibly $MHMal^{\cdot}$ (sodium malonate and the metal chlorides are known to be highly dissociated). Of the ions specified, the concentrations of $Na^{\cdot}$ and Cl' are known, that of OH' is negligible in these acid solutions, and that of $MHMal^{\cdot}$, though unknown, is unlikely to be large enough to affect the relative concentrations of the other species. We are left with six unknowns, which can be evaluated by successive approximations from (i) the p$f_2[\mathrm{H}^{\cdot}]$ value, (ii) the equation for electroneutrality, (iii) the known total concentration of malonate radical, (iv) the known total concentration of bivalent metal, and (v) and (vi) the K_1 and K_2 values of malonic acid. The results of the calculations are given in cols. 3—8 of Table I, in millimols./l., and col. 9 shows the ionic strength. Col. 10 gives the dissociation constant of the metal malonate, calculated from the equation $K = f_2^{\,2}[\mathrm{M}^{\cdot\cdot}][\mathrm{Mal}'']/[\mathrm{MMal}]$, and col. 11 gives values previously derived from conductivity measurements (Riley and Fisher, *J.*, 1929, 2006; Ives and Riley, *J.*, 1931, 1998; Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609).

TABLE I.

Cation.	pf_2 $[\mathrm{H}^{\cdot}]$.	$[\mathrm{H}^{\cdot}]$.	$[\mathrm{HMal}']$.	$[\mathrm{Mal}'']$.	$[\mathrm{H_2Mal}]$.	[MMal].	$[\mathrm{M}^{\cdot\cdot}]$.	*I*.	$K\,.\,10^4$.	$K.\,10^4$ (cond.).
$\mathrm{Ba}^{\cdot\cdot}$......	4·39	0·086	4·47	0·241	0·189	0·034	12·3	0·0421	196	—
$\mathrm{Ca}^{\cdot\cdot}$......	4·28	0·109	4·36	0·184	0·235	0·157	12·2	0·0417	32	—
$\mathrm{Mg}^{\cdot\cdot}$ ...	4·19	0·137	4·23	0·143	0·284	0·277	12·1	0·0413	14	16
$\mathrm{Cd}^{\cdot\cdot}$......	4·04	0·191	3·99	0·0962	0·376	0·470	11·9	0·0408	5·6	5·1
$\mathrm{Mn}^{\cdot\cdot}$ ...	$4{\cdot}02_5$	0·197	3·96	0·0923	0·386	0·493	11·8	0·0407	5·1	—
$\mathrm{Co}^{\cdot\cdot}$ ...	3·84	0·299	3·57	0·0546	0·530	0·773	11·6	0·0399	1·9	—
$\mathrm{Ni}^{\cdot\cdot}$ ...	3·72	0·395	3·26	0·0375	0·640	0·997	11·3	0·0394	0·99	0·73
$\mathrm{Cu}^{\cdot\cdot}$......	$3{\cdot}07_5$	1·69	1·20	0·0031	1·021	2·71	9·62	0·0348	0·028	0·025

The results obtained by the two methods are in satisfactory agreement, and show a strong variation in the dissociation constants of the malonates, from the barium salt where ion association is less important than in the sulphates so far studied (Davies, *Trans. Faraday Soc.*, 1927, **23**, 351; Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074), to the weak copper salt which will be only 1% dissociated at 0·025M.

As a first step in interpreting these results we may consider them in the light of Bjerrum's theory of ion association (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9). On the assumption that ion association is wholly due to the Coulomb attraction between oppositely charged ions, this theory gives a relation between the dissociation constant and the sum (*a*) of the radii of the associating ions, which must be assumed spherical and with the charge located at the centre. Table II shows the *a* values derived in this way from our dissociation constants, and also the cationic radii (*r*) given by Pauling (" Nature of the Chemical Bond," Chap. X). There is a rough parallelism between the two, but clearly, other factors are also operative, such as variations, not directly related to radius, in the free energy of hydration of the ions. The large mean ionic diameter found for barium malonate may be explained by the fact that the assumption of spherical symmetry and a central charge is far from the truth for the malonate ion; the *a* values for some of the other salts then become, by comparison, impossibly small, and indicate that for these cations also the assumptions are inadequate.

TABLE II.

Cation.	$\mathrm{Ba}^{\cdot\cdot}$.	$\mathrm{Ca}^{\cdot\cdot}$.	$\mathrm{Mg}^{\cdot\cdot}$.	$\mathrm{Cd}^{\cdot\cdot}$.	$\mathrm{Mn}^{\cdot\cdot}$.	$\mathrm{Co}^{\cdot\cdot}$.	$\mathrm{Ni}^{\cdot\cdot}$.	$\mathrm{Cu}^{\cdot\cdot}$.
a (A.)	10·0	3·74	2·9	2·5	2·4	2·2	2·0	1·5
r (A.)	1·35	0·99	0·65	0·97	0·80	0·72	0·70	—

It is also noteworthy that the order of stability of the undissociated complexes between the bivalent cations and the malonate radical found in this work, as well as in an earlier study of metal exalates (*Trans. Faraday Soc.*, 1932, **28**, 613), is substantially the same (with one exception) as that discussed by Mellor and Maley (*Nature*, 1948, **161**, 436) and Irving and Williams (*ibid.*, 1948, **162**, 746) : the complexes referred to by these workers were chelate in character, and it is stated that for such complexes of bivalent metal ions the stability follows the order given, irrespective of the nature of the ligands involved. That the oxalates and malonates also conform to this order may perhaps be a further indication that the linkage here is also largely covalent, and not merely due to (Coulomb) ion association.

EXPERIMENTAL.

Colour comparisons were made visually in a north light, using a Hellige comparator. The acids were pure specimens, recrystallised three times from conductivity water. The salts were of " AnalaR " grade, used without further purification. Sodium hydroxide was prepared from clean pieces of sodium, which were allowed to react in a platinum dish standing over carbon dioxide-free conductivity water in a vacuum desiccator; the resulting solution was transferred, diluted, and stored with the necessary precautions in a nickel bottle, and was standardised, through hydrochloric acid, against " AnalaR " sodium carbonate. Bromophenol-blue was used as received from B.D.H. Ltd. at a concentration of 1·38 ml. of 0·04% solution in 100 ml. of solution.

The colour standards consisted of 0·01N-mandelic or benzoic acid, partly neutralised by sodium hydroxide or sodium carbonate; that carbonic acid does not interfere at the pH values studied was proved both experimentally and by calculation. Mandelic and benzoic acids were chosen because their dissociation constants are known with high accuracy from conductivity investigations which have also shown ion association to be negligible in dilute solutions of the sodium salts. In making a colour comparison, the standard amount of indicator was added to the solution under test, and 25 ml. of a 0·02N-solution of mandelic or benzoic acid, plus indicator, were then titrated with alkali, with simultaneous additions of conductivity water, to give 50 ml. of a solution of identical colour. This was repeated three times, and the results always agreed to within 0·01 pH unit, one drop of alkali producing a perceptible colour change. The $pf_2[H^\cdot]$ value of the solutions was then interpolated from a graph connecting $pf_2[H^\cdot]$ with the amount of alkali added. This graph was constructed from the activity equation already quoted and the dissociation constant of the acid (mandelic, $K = 3{\cdot}88 \times 10^{-4}$, Banks and Davies, *J.*, 1938, 73; benzoic, $K = 6{\cdot}320 \times 10^{-5}$, Brockman and Kilpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 1485).

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