532. *The Characterisation of Ions by their Ion-exchange Reactions.*

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The value of an ion-exchange method for the determination of the ratio of nuclear atoms to units of ionic charge, *i.e.*, the " *R* value " or ratio $x:z$, for ions of the type $H_wX_xO_y^{z-}$ present in aqueous solutions has been tested with reference to several systems, particularly those of acids undergoing changes in degree of ionisation or of condensation with changing pH. Possible limitations of the method are discussed.

In a number of studies [1] in these laboratories the identification of ions present in solution has been based on measurements of *R* values.[2] The *R* value, which is defined as the ratio $x:z$ for an ion such as $H_wX_xO_y^{z-}$, is found by the release of chloride or other suitable

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[1] (*a*) Russell and Salmon, *J.*, 1958, 4708; 1961, 3211; (*b*) Cooper and Salmon, *J.*, 1962, 2009.
[2] Everest and Salmon, *J.*, 1954, 2438; 1955, 1444.

reference ion in relation to the uptake of X by an anion-exchanger either in batch equilibrium studies of the reaction

$$\overline{z\text{Cl}^-} + \text{H}_w\text{X}_x\text{O}_y{}^{z-} \rightleftharpoons z\text{Cl}^- + \overline{\text{H}_w\text{X}_x\text{O}_y{}^{z-}} \qquad (1)$$

or in column experiments in which the equilibrium (1) is displaced completely to the right. To meet the point that experimental clarification is required of the implicit assumption that a change in R value of the species sorbed provides a reliable indication of a change in the species present in solution,[3] seven acid systems showing different characteristics have been studied.

Results and Discussion.—The values of R obtained for oxalate, sulphate, selenate, arsenate, phosphate, dichromate–chromate, and periodate systems are shown in Figs. 1—7, respectively. The concentrations indicated in these refer to the total concentrations of the nuclear atom of each acid for S, Se, etc., but to C_2 for oxalate. Where more than one such concentration is indicated the higher ones refer to the most acid solutions only. From these it can be seen that an R value of 0·34 is found close to the pH range where a value of 0·33 would have been expected for the $AsO_4{}^{3-}$ ion (Fig. 4), and that a similar result is obtained with phosphate system (Fig. 5), that R values ranging from 0·50 to 0·51 are found where a value of 0·50 would have been expected for the ions $SO_4{}^{2-}$, $SeO_4{}^{2-}$, $HAsO_4{}^{2-}$, $HPO_4{}^{2-}$, $CrO_4{}^{2-}$, and $H_3IO_6{}^{2-}$ (Figs. 2—7), and that R values between 0·96 and 1·01 are found where a value of 1·00 would have been expected for the ions $HC_2O_4{}^-$, $HSO_4{}^-$, $HSeO_4{}^-$, $H_2AsO_4{}^-$, $H_2PO_4{}^-$, $Cr_2O_7{}^{2-}$, and $IO_4{}^-$ (Figs. 1—7, respectively). In previous studies, which were based on the batch equilibrium method, R values of 2·98 and 3·98 were found for the ions $SiW_{12}O_{40}{}^{4-}$ (ref. 4) and $PMo_{12}O_{40}{}^{3-}$ (ref. 1*b*) where values of 3·00 and 4·00, respectively, would have been expected.

It is thus apparent that there is good correlation between experimental and expected R values for these systems in the regions where there is no rapid change in the nature of the ionic species present in solution and one species is predominant. Under such conditions, which were those applying in the previous work in this field,[1] it appears that the R values are sufficiently reliable to characterise the ions present. The pH range over which such ions predominate is indicated approximately, but not precisely, by the pH range of the plateau in the plot of the R value versus pH (*e.g.*, Figs. 1—7). The correlation between the theoretical and the practical values of R in the region where these are changing with pH is obviously less satisfactory.

The derivation of the theoretical curves is most easily followed with reference to the dibasic acids where the R values change from 1 to 0·5 as the predominant species in solution changes from HA^- to A^{2-}. The equilibria existing in such solutions may be written in terms of the successive dissociation constants and mean (calculated) activity coefficients as follows:

$$[\text{H}_2\text{A}] = [\text{H}^+][\text{HA}^-]f_1{}^2/K_1 \qquad (2)$$

and

$$[\text{A}^{2-}] = K_2[\text{HA}^-]/[\text{H}^+]f_2. \qquad (3)$$

Now $[H_2A] + [HA^-] + [A^{2-}] = J$ (where J is the total concentration of A). (4)

Therefore,

$$[\text{HA}^-] + \frac{[\text{H}^+]f_1{}^2\,[\text{HA}^-]}{K_1} + \frac{K_2[\text{HA}^-]}{[\text{H}^+]f_2} = J, \qquad (5)$$

therefore,

$$[\text{HA}^-] = \frac{J}{1 + \dfrac{[\text{H}^+]f_1{}^2}{K_1} + \dfrac{K_2}{[\text{H}^+]f_2}} = \phi, \qquad (6)$$

and

$$[\text{A}^{2-}] = K_2\phi/[\text{H}^+]f_2. \qquad (7)$$

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[3] Comment of a Referee on paper in ref. 1(*b*).

[4] McPartlin and Salmon, unpublished work.

If it is assumed that the species present are sorbed by the exchanger in the same proportions as those in which they occur in solution, then

$$R([\mathrm{HA}^-] + [\mathrm{A}^{2-}]) = [\mathrm{HA}^-] + \tfrac{1}{2}[\mathrm{A}^{2-}], \tag{8}$$

and it follows that

$$R = (2f_2[\mathrm{H}^+] + K_2)/2(f_2[\mathrm{H}^+] + K_2). \tag{9}$$

Similarly, the expression for R for a simple tribasic acid can be shown to be

$$R = \frac{[\mathrm{H}^+]^2 + \dfrac{K_2[\mathrm{H}^+]}{2f_2} + \dfrac{K_2K_3}{3}\cdot\dfrac{f_2}{f_1f_3}}{[\mathrm{H}^+]^2 + \dfrac{K_2[\mathrm{H}^+]}{f_2} + K_2K_3\cdot\dfrac{f_2}{f_1f_3}}. \tag{10}$$

It can be seen from both these examples that, as would be expected, equilibria which involve non-ionic species have no effect on the expression for R.

When condensation occurs, the final expression becomes more complex. The derivation for the dichromate system for the equilibria:

$$\mathrm{HCr_2O_7^-} \xrightleftharpoons{K_3} \mathrm{Cr_2O_7^{2-}} + \mathrm{H^+} \tag{11}$$

$$\mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O} \xrightleftharpoons{K_2} \mathrm{2HCrO_4^-} \tag{12}$$

or

$$\mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O} \xrightleftharpoons{K_4} \mathrm{2H^+} + \mathrm{2CrO_4^{2-}} \tag{12a}$$

$$\mathrm{HCrO_4^-} \xrightleftharpoons{K_1} \mathrm{CrO_4^{2-}} + \mathrm{H^+} \tag{13}$$

becomes

$$R = 1 + \frac{\dfrac{[\mathrm{H}^+][\mathrm{A}]f_1^2}{K_2K_3} - \dfrac{K_1}{2[\mathrm{H}^+]f_2}}{\dfrac{[\mathrm{H}^+][\mathrm{A}]f_1^2}{K_2K_3} + \dfrac{[\mathrm{A}]f_1^2}{K_2f_2} + 1 + \dfrac{K_1}{[\mathrm{H}^+]f_2}}, \tag{14}$$

where

$$[\mathrm{A}] = \frac{\left[\left(1 + \dfrac{K_1}{[\mathrm{H}^+]f_2}\right)^2 + \dfrac{8Jf_1^2}{K_2}\left(\dfrac{[\mathrm{H}^+]}{K_3} + \dfrac{1}{f_2}\right)\right]^{\frac{1}{2}} - \left(1 + \dfrac{K_1}{f_2[\mathrm{H}^+]}\right)}{\dfrac{4f_1^2}{K_2}\left(\dfrac{[\mathrm{H}^+]}{K_3} + \dfrac{1}{f_2}\right)} \tag{15}$$

Since K_1, K_2, and K_4 are interdependent, similar calculations based on equations (11), (12a), and (13) give identical results when plotted (cf. Sasaki [5]).

For the periodate systems the relevant equilibrium constant is

$$\bar{K}_2 = [\mathrm{H}^+][\mathrm{H_3IO_6^{2-}}]/([\mathrm{H_4IO_6^-}] + [\mathrm{IO_4^-}]). \tag{16}$$

or, since both results reported by Crouthamel *et al.*[6] and our own unpublished work indicate that

$$[\mathrm{IO_4^-}] \gg [\mathrm{H_4IO_6^-}],$$

$$\bar{K}_2 \approx [\mathrm{H}^+][\mathrm{H_3IO_6^{2-}}]/[\mathrm{IO_4^-}]. \tag{17}$$

The system is thus analogous to that of the dibasic acids and the value of R is given by equation (9) with $\bar{K}_2$ in place of K_2.

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[5] Sasaki, *Acta Chem. Scand.*, 1962, **16**, 719.

[6] Crouthamel, Meek, Martin, and Banks, *J. Amer. Chem. Soc.*, 1949, **71**, 3031; Crouthamel, Hayes, and Martin, *ibid.*, 1951, **73**, 82.

Examination of the expression for R in the case of dibasic acids shows that if $[H^+]$ exceeds K_2 by more than one order, R approaches unity, whilst if K_2 exceeds $[H^+]$ by a similar degree, R approaches 0·5. Similarly for tribasic acids it is apparent that when $[H^+] > K_2$, R approaches unity; when $K_2 > [H^+] > K_3$, R approaches 0·5; and, when $K_3 > [H^+]$, R approaches 0·33. The values of K_2 and K_3 must, however, be separated by an order of about 3 in order that a plateau at $R = 0{\cdot}5$ may be formed over any range of pH. With condensation reactions it is more difficult to assess the position. The values of the K's used in deriving the theoretical curves are shown in the Table. For this purpose the most reliable results, or those which are closest to the mean of the values in the literature, have been selected and not those which would have led to the closest agreement with our experimental results.

pK values used in deriving the theoretical R values used in Figs. 1—7.

Acid	Reaction	pK	Ref.	Acid	Reaction	pK	Ref.
$H_2C_2O_4$	$HC_2O_4^- \longrightarrow C_2O_4^{2-}$	4·21	*a*	H_3PO_4	$H_2PO_4^- \longrightarrow HPO_4^{2-}$	7·20	*e*
H_2SO_4	$HSO_4^- \longrightarrow SO_4^{2-}$	2·00	*b*		$HPO_4^{2-} \longrightarrow PO_4^{3-}$	12·36	*f*
H_2SeO_4	$HSeO_4^- \longrightarrow SeO_4^{2-}$	1·99	*c*	H_2CrO_4	$HCrO_4^- \longrightarrow CrO_4^{2-}$	6·50	*g*
H_3AsO_4	$H_2AsO_4^- \longrightarrow HAsO_4^{2-}$	6·77	*d*		$2HCrO_4^- \longrightarrow Cr_2O_7^{2-}$	1·55	*h*
	$HAsO_4^{2-} \longrightarrow AsO_4^{3-}$	11·53	*d*		$HCr_2O_7^- \longrightarrow Cr_2O_7^{2-}$	3·00	*i*
				HIO_4	Equation (17) — $\bar{K}_2$	8·36	6

References: (*a*) Schaap, Laitinen, and Bailar, *J. Amer. Chem. Soc.*, 1954, **76**, 5868. (*b*) Davies, Jones, and Monk, *Trans. Faraday Soc.*, 1962, **48**, 921. (*c*) Gelbach and King, *J. Amer. Chem. Soc.*, 1942, **64**, 1054. (*d*) Britton and Jackson, *J.*, 1934, 1048. (*e*) Bates and Acree, *J. Res. Nat. Bur. Stand.*, 1943, **30**, 129. (*f*) Beukenkamp, Rieman, and Lindenbaum, *Analyt. Chem.*, 1954, **26**, 505. (*g*) Neuss and Rieman, *J. Amer. Chem. Soc.*, 1934, **56**, 2238. (*h*) Tong and King, *ibid.*, 1953, **75**, 6180. (*i*) Beck and Stegmüller, *Arb. Kaiser. Gesundh.*, 1910, **34**, 446; Spitalsky, *Z. anorg. Chem.*, 1907, **54**, 265.

The two theoretical curves plotted in each of Figs. 1—7 have been derived (1) by neglecting activity coefficients, and (2) by using values calculated from Davies's equation [7] for solutions within its range of ionic strength. Comparison of these curves with the experimental ones shows that, although they are similar in shape and coincide at the horizontal portions, there is a general displacement of the experimental curves towards lower pH values. Three reasons for such a displacement are apparent and their consequences are qualitatively predictable. Two of these are the differences in the pH and in the activity coefficients of the ions between the external and the resin phase, and the third is the difference in relative affinities of the various anions for the resin.

Because of the high positive charge carried by the resin network and the consequent exclusion of hydrogen ions from the resin, the measured pH of the solution does not represent the pH value that governs the equilibria in the resin phase. This value may be estimated approximately by application of the Donnan equation.[8] Thus in Fig. 1, for example, at the point on the theoretical (activity-corrected) curve where the pH is 2·5, the solute present is almost exclusively the $HC_2O_4^-$ ion and the concentration product $[HC_2O_4^-][H^+]$ is given approximately by the product $0{\cdot}05 \times 3 \times 10^{-3}$, whilst in the resin phase the corresponding product will, to a first approximation, be equal to $[\overline{HC_2O_4^-}][\overline{H^+}]$; and since by experiment we find $[\overline{HC_2O_4^-}] \approx 1{\cdot}2$, the pH in the resin phase is ~3·9, or ~1·4 units higher than in the external solution; likewise, at pH 5 the pH in the resin is ~5·5, *i.e.*, 0·5 unit higher than in the solution. It can be seen that shifts in the experimental curve of these magnitudes would lead to better agreement with the theoretical curves. Similar arguments may be applied to the other systems.

The second factor causing a displacement of the experimental curve from the theoretical (activity-corrected) curve is the non-equality of activity coefficients in the resin and the solution phases. The differences between the pairs of theoretical curves in each Figure

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[7] Davies, " Ion Association," Butterworths Scientific Publns., London, 1962.

[8] Davies, *Research*, 1950, **3**, 447.

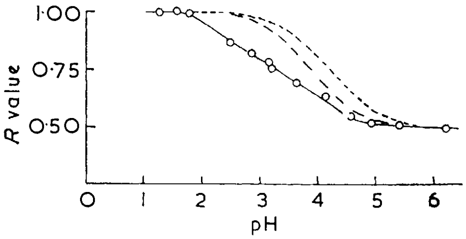

FIG. 1.

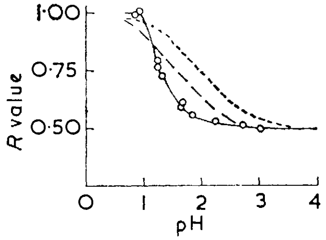

FIG. 2.

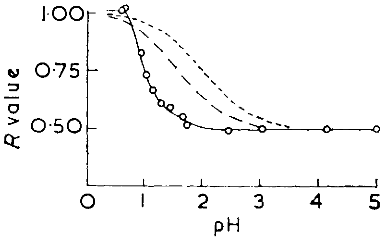

FIG. 3.

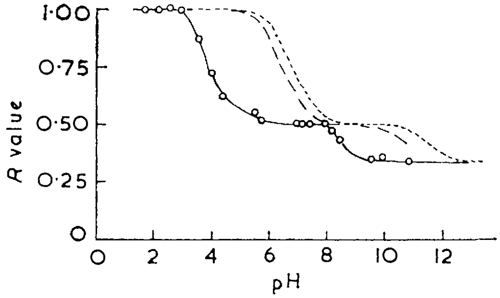

FIG. 4.

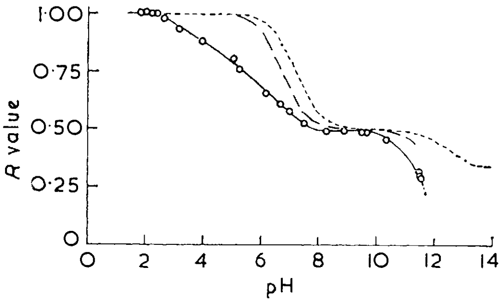

FIG. 5.

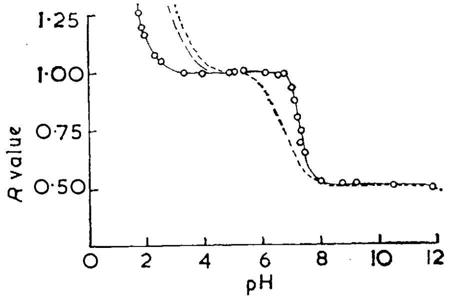

FIG. 6.

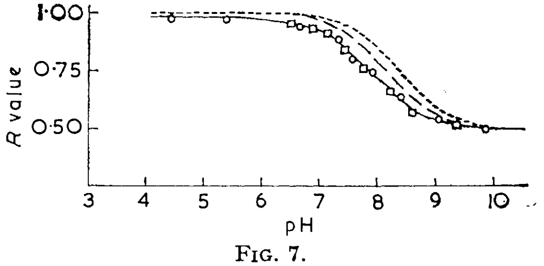

FIG. 7.

FIGS. 1—7. Change of *R* value with pH value; strong-base anion-exchanger of water regain 1·7.

(o) Experimental points at room temperature. (□) Experimental points at 25°.
(– – – –) Theoretical curves. (— — —) Theoretical curves (activity-corrected).

Fig.	System	Concentrations used
1	Oxalate	0·05M (pH 7—1·25)
2	Sulphate	0·019M (pH 4—1·67), 0·077M (to pH 1·23), and 0·1M (to pH 0·85)
3	Selenate	0·05M (pH 5—1·3) and 0·25M (to pH 1·6)
4	Arsenate	0·029M
5	Phosphate	0·05M
6	Dichromate–chromate	0·08M
7	Periodate	0·01M

illustrate the relative importance of activity corrections in the solution. In the resin phase the effect of the higher concentrations will normally be to make the corrections somewhat larger and also more individual. Thus they will vary with the system studied, and, in the present state of knowledge, there is no way of estimating them quantitatively. Such corrections, however, can be expected to be relatively more important for highly charged ions, and this may, in part, account for the larger deviations between experimental and theoretical curves for the arsenate and the phosphate systems in the region of high pH (Figs. 4 and 5).

The neglect of activity corrections for the species present in solution in the earlier studies appears to be justified, insofar as these were concerned primarily with identification of species which predominated under various conditions in dilute solutions, and only the horizontal portions of the curves were considered. It would be unwise to extrapolate too far, and measurement of R values at high concentrations is not considered justified. Indeed, in such conditions the physical sorption of un-ionised species by the resin is possible, as Arden and Giddings's studies of the chromate system [9] have shown.

The third factor causing deviations between the theoretical and the experimental values of R, which applies particularly to the regions where R varies with pH, is the neglect of the relative affinities of the different ions for the resin [assumed to be equal in equation (8), and in deriving equations (10) and (14)] in deriving the theoretical curves. Hence the observed differences are, in part at least, a reflection of the normal resin selectivity. In each case (Figs. 1—7) the deviations are in such a direction that, if at a given pH there is a difference, the experimental R value is generally lower than the theoretical. This implies that the relative affinity of the ions concerned is enhanced by increasing charge (arising, *e.g.*, from loss of protons) and hence will decrease in series such as $AsO_4^{3-} > HAsO_4^{2-} > H_2AsO_4^-$, $CrO_4^{2-} > HCrO_4^-$, or $Cr_2O_7^{2-} > HCr_2O_7^-$. The relative affinity also appears to be enhanced by increased degree of condensation when the charge remains unchanged (*i.e.*, $Cr_2O_7^{2-} > CrO_4^{2-}$).

It can be seen from Fig. 7 that in the periodate system the divergence between experimental and theoretical curves is minimal. This is probably due to the fact that in this system the change from a univalent to a bivalent ion involves more than just the loss of a proton. The work of Crouthamel *et al.*[6] and of ourselves indicates that the univalent species is IO_4^- and that the predominant bivalent species is $H_3IO_6^{2-}$. Thus an increase in size accompanies the increase in charge. It therefore appears that the relative charge densities of the ions should be considered.

A fourth factor which could cause a displacement of the experimental curves from the theoretical ones emerged from the earlier studies.[1] It relates to the porosity of the resins, which should be sufficiently high for all ions present in the solution to gain access to all the resin sites. There will otherwise be changes in the equilibrium in the solution due to the selective sorption of small ions. In the isopoly- and heteropoly-acid systems this will lead, however, as previously indicated (ref. 1*b*), to a change in pH in the solution as it comes to equilibrium with the resin.

A final factor, which needs brief consideration, is the possibility of reaction between the exchanging ions initially in the solution and on the exchanger, respectively (*e.g.*, chloride and periodate; [10] see Experimental section), and side reactions between these and the resin matrix, but such reactions should lead to readily identifiable disturbances of the system.

To summarise: it is not possible, without a knowledge of the relative affinities of the ions for the resin (which are not even constant but are concentration-dependent if the ions are of different valency) and of activities of ions in the resin, to derive the precise relative amounts in which two (or three) ions are present in solution from experimental R values; but it seems reasonable to conclude that the plateaux found in experimental R curves are

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[9] Arden and Giddings, *J. Appl. Chem.*, 1961, **11**, 229.

[10] Ammermüller and Magnus, *Pogg. Annalen*, 1833, **28**, 514.

a reliable indication of the nature of the predominant ionic species in the systems studied; and that, when allowance is made for the several factors discussed, useful conclusions can be drawn concerning the relative stabilities of these species in a changing environment.

EXPERIMENTAL

Solutions.—These were prepared from suitable potassium salts of the acids and either potassium hydroxide or the free acid, which in the case of chromic acid was prepared by ion-exchange from potassium dichromate. Wherever possible, the anion concentrations of the series of solutions in each run were kept constant but with sulphate and selenate the concentration was necessarily increased to obtain the solutions of lowest pH values.

Procedure.—Strong-base anion-exchange resins prepared in the laboratory according to the method of Pepper, Paisley, and Young [11] were used throughout. Air-dried samples (1 g.) of chloride-form resin of known capacity were introduced into small columns (1 × 8 cm.) and swollen in water. A seven-fold excess of each solution of known pH was passed slowly through each of the various columns (in the cases of the oxalate, sulphate, selenate, arsenate, and dichromate). The initial and the final concentrations of the solutions were determined and hence the uptake of anion was calculated; whenever possible, the actual amount of anion sorbed by the exchanger was also checked, and good agreement between the two values was then confirmed. R values were calculated as follows:

$$R = \frac{\text{mg.-equiv. of anion sorbed}}{\text{capacity of resin sample in mg.-equiv.}}.$$

Since periodate reacts with chloride,[10] the resin was initially in the nitrate form for this system.

Slow equilibration was found for the phosphate system, and here the resin was first converted into the phosphate form at pH 7 in a column and washed. The samples were then treated batchwise with a series of phosphate solutions and left to equilibriate for two weeks. The pH of the supernatant solution and the phosphate content of the resin were determined.

For the periodate system, the experiments were repeated with solutions kept at 25°. The difference between the results of these experiments and those at room temperature was negligible, and therefore further systems were examined at room temperature only.

Analysis.—Standard methods were used for all the analyses.

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[11] Pepper, Paisley, and Young, *J.*, 1953, 4097.