Ion-exchange Evidence for the Polynuclear Ion Tris[hydroxoberyllium(II)]

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The original ion-exchange distribution method for measuring ionic charge, limited to species present at low concentration relative to a reference ion, has been modified for use with high concentrations of the unknown ion. Limitations of this ' inverse ' method have been assessed by measuring the charges of a number of well known ions. A beryllium hydrolysis polymer has been characterized in dilute perchlorate solutions effectively free from other electrolytes. In these slightly acid solutions (pH 5·5) the predominant polymeric species has a charge of +3 and a ' metal atom-to-charge ratio ' of one. This identifies the ion as the trimer $[Be_3(OH)_3]^{3+}$, originally proposed by Kakihana and Sillén on the basis of potentiometric evidence.

THE isothermal ion-exchange equilibrium (1) (barred

$$qB^z + z\bar{A}^q \rightleftharpoons q\bar{B}^z + zA^q \qquad (1)$$

symbols represent resin-phase species and charge values q and z are of the same sign) can be expressed in the form (2),[1] where D_B is the isothermal-equilibrium

$$\log D_B = -(z/q) \log a_A + \text{constant} \qquad (2)$$

distribution coefficient of the species B^z and a_A represents the activity of A^q in the aqueous phase. If B^z is an ion of unknown charge, measurement of its equilibrium distribution coefficient at different solution activities of a second counter-ion A^q (of known charge) can be used to determine the value of z. For this purpose it is essential that B^z should be present as a microcomponent relative to a macroconcentration of A^q.

Under the ' inverse ' condition, that is when the macrocomponent A^q is the ion of unknown charge, equation (1) may still be applied but with two important advantages, (i) the ion of unknown charge can be present at high concentrations and therefore the method is applicable to a polymeric species and (ii) concentrations of the reference ion B^z can be minute (*e.g.* carrier-free radioactive tracer), and therefore measurements can be made in the virtual absence of other electrolytes (*e.g.* supporting electrolyte). The method is limited to systems containing only two counter-ions in solution, the unknown and a reference ion, and this condition must apply throughout the range of concentrations needed to give accurate distribution values.

We have tested the ' inverse ' method on some representative ions (simple, complex, and large and polymeric) whose charge values are well established. From these tests ideal experimental conditions have been determined and applied to characterization of the predominant hydrolytic species in slightly acid beryllium solutions.[2] The method is well suited to a study of this system where interference from supporting electrolyte has been questioned.[3]

EXPERIMENTAL

Analytical grade reagents were used throughout except for beryllium carbonate and chromium trioxide (Laboratory grade). Sodium-22 as aqueous sodium chloride, sulphur-35 as aqueous sodium sulphate, calcium-45 as aqueous calcium chloride, cobalt-60 as aqueous tripotassium hexacyanocobaltate(III), and cerium-144 as cerium(III) chloride in hydrochloric acid (1M) were obtained from the Radiochemical Centre, Amersham.

Chromate solutions of the required concentrations and pH were prepared by mixing aqueous solutions of chromium trioxide with potassium or ammonium dichromate. Beryllium perchlorate solutions were prepared by dilution of stock solutions which were made by dissolving powdered beryllium metal or carbonate in a slight excess of perchloric acid. The test solutions were adjusted to the required pH by cautious addition of hydroxide-form anion-exchange resin, the perchlorate form of which was subsequently removed by filtration. Beryllium concentrations were determined spectrophotometrically [4] with Chrome Azurol S.

The ion-exchange resins Dowex 50 WX1, X8 (50—100 mesh), Amberlite CG-120 [8% divinylbenzene (dvb)] (100—200 mesh), Dowex 1X1, and X8 (50—100 mesh) were conditioned [5a] and equilibrated in columns with appropriate solutions until the eluant and eluate were identical. The capacity of each resin was determined by a standard method [6] and the equivalent volume [5b] of the resins was estimated at various concentrations of external electrolyte by measuring the volume occupied by a known (dry) mass of swollen resin after centrifugation at 2 000 rev. min^{-1}. The weight of dry resin (K^+ or Cl^- form) was determined by bringing moist resin samples to constant weight at 65 °C.

Batch Equilibrium Method.—Distribution measurements were made by weighing ion-exchange resin in the appropriate form (macrocomponent ion) directly into polystyrene equilibration vessels. After addition of a measured quantity of solution containing both macro- and microcomponent ions the vessels were sealed and kept at 20 ± 1 °C. 7 Days were allowed for equilibrium to be established between simple ions and 14 days for complex and polymeric species. Monitoring of the radioactivity of the supernatant solution showed these times to be more than adequate. The distribution coefficient of the microcomponent (D_B) was determined [7] by radioactive counting of original and equilibrium solutions.

Peak Elution Volume (*p.e.v.*) *Method.*—Hydrogen-form resin (*ca.* 1·5 g) was weighed directly into a semi-micro

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[1] K. A. Kraus and F. Nelson, ' The Structure of Electrolytic Solutions,' ed. W. J. Hamer, John Wiley, New York, 1959, pp. 340 *et seq.*

[2] H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, 1956, **10**, 985.

[3] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 1959, **13**, 533.

[4] P. Palkans, ' The Spectrophotometric Determination of Beryllium with Chrome Azurol S,' Australian Atomic Energy Commission/TM175, 1963.

[5] F. Helfferich, ' Ion Exchange,' McGraw–Hill, New York, 1962 (*a*) p. 230, (*b*) p. 118.

[6] J. E. Salmon and K. D. Hale, ' Ion Exchange, a Laboratory Manual,' Butterworths, London, 1959, pp. 85 and 86.

[7] J. Schubert, E. R. Russell, and L. S. Myers, jun., *J. Biol. Chem.*, 1950, **185**, 387.

column and equilibrated with the appropriate beryllium solution. A narrow band of the ion $^{22}_{11}\mathrm{Na}^+$ was loaded on top of the resin bed and this was eluted at room temperature with the same beryllium solution. The effluent history was monitored by radioactive counting using both a flow cell with event marker and a fraction collector. The p.e.v. was accepted only after three consecutive elutions agreed to within one drop ($\pm 0{\cdot}033$ cm^3). Equilibrium conditions were verified by measuring the p.e.v. over a range of flow rates from $1{\cdot}1 \times 10^{-1}$ to $3{\cdot}0 \times 10^{-2}$ cm min^{-1}. The voids volume of the column system was found by elution of the non-sorbable indicator Blue Dextran 2 000. The corrected p.e.v. (V_c) is related [8] to the distribution coefficient (D_B) by the equation $D_B = V_c/m$, where m is the mass of dry resin and V_c the volume required to displace the maximum concentration of the microcomponent counter-ion from the column minus the voids volume of the system.

Calculation of Results.—Least-squares analysis of experimental points was used to find the gradient of equation (2) and from this the observed charge was calculated. Experimental conditions under which equation (2) is no longer applicable are identified [1,9] by non-linearity of the log–log relation or non-integral charge values. The latter effect was used to specify optimum operating conditions since the small concentration ranges employed gave linear correlation coefficients better than 0·97 in all cases.

*'Metal atom-to-charge ratio' of solution species.** These were determined for the various chromate and beryllium solutions by pH titration with standard alkali or acid solutions. The ' metal atom-to-charge ratio ' at a given pH is the ratio of the total number of moles of metal atoms to the number of moles of hydroxide or hydrogen ions required to convert all the metal to its unprotonated mononuclear ionic form.

Metal atom-to-charge ratio of resin-phase species. The Cr$^{\mathrm{VI}}$ content of chromate-form resins was estimated by reacting the resin with excess of iron(II) in dilute sulphuric acid, followed by filtration and back-titration of the aqueous phase with standard potassium dichromate solution. The metal atom-to-charge ratio [10] is the ratio of the number of moles of chromium(VI) to the molar capacity of the resin.

RESULTS AND DISCUSSION

Hitherto techniques based on the change in distribution of an unknown ionic species between an ion-exchange resin and solution on varying either the resin structure [11] or the supporting electrolyte concentration [12] have been limited to low concentrations of the ion under investigation. This restriction has hampered the application of these methods to studies of ionic polymer systems where in many cases unequivocal determination of the charge of a predominant polymeric ion and its ' metal atom-to-charge ratio ' would provide an independent assessment of the species suggested by other physical and chemical studies. Attempts to overcome this problem by examining the absorbed (resin) species [13a,b] have been criticized [13c] because of a lack of evidence to support the assumption that the resin and solution species are identical.

The experimental conditions which must be observed in using equation (2) to measure ionic charge by the method of Kraus and Nelson [1] are: (*i*) the species B^z should be present at much lower concentrations than A^q; (*ii*) the variation of a_A, the independent variable, should be as small as possible; (*iii*) z and q should be of the same sign and represent single ionic species; and (*iv*) there should be no significant change in the specific volume of the resin on variation of a_A. Apart from the work of Whitney and Diamond,[9] which is relevant to condition (*ii*), experimental assessment of these conditions is not available. We have therefore attempted such an assessment for the application of our modified method. Concentrations were used in place of activities, assuming that activity-coefficient ratios remain effectively constant over the concentrations (<1M) employed, an assumption supported by the observations of Whitney and Diamond.[9] Invalidation of this or the other assumptions must lead to disagreement between the measured and known charge values of the test ions. A

TABLE 1

Variation of the observed charge of the macrocomponent ion with changes in microcomponent concentration

Concentration range of macrocomponent ion $[A^q]$/M *	No. of concns. of A^q	Initial concentration of microcomponent ion $[B^z]$/M	Gradient †	Observed charge q
(*a*) ‡ K^+ as KCl		Na^+ as NaCl		
$4{\cdot}0 \times 10^{-3}$—	11	*ca.* 10^{-10}	$0{\cdot}97 \pm 0{\cdot}02$	$+1{\cdot}03 \pm 0{\cdot}02$
$4{\cdot}00 \times 10^{-1}$	7	$1{\cdot}0 \times 10^{-4}$	$0{\cdot}98 \pm 0{\cdot}03$	$+1{\cdot}02 \pm 0{\cdot}04$
	7	$1{\cdot}0 \times 10^{-3}$	$0{\cdot}95 \pm 0{\cdot}02$	$+1{\cdot}06 \pm 0{\cdot}03$
	7	$5{\cdot}0 \times 10^{-3}$	$0{\cdot}77 \pm 0{\cdot}04$	$+1{\cdot}30 \pm 0{\cdot}07$
	7	$1{\cdot}0 \times 10^{-2}$	$0{\cdot}67 \pm 0{\cdot}04$	$+1{\cdot}49 \pm 0{\cdot}09$
(*b*) § Cl^- as NaCl		SO_4^{2-} as Na_2SO_4		
$1{\cdot}67 \times 10^{-2}$—	12	*ca.* 10^{-10}	$2{\cdot}03 \pm 0{\cdot}03$	$-0{\cdot}96 \pm 0{\cdot}02$
$7{\cdot}14 \times 10^{-1}$	9	$3{\cdot}0 \times 10^{-5}$	$2{\cdot}09 \pm 0{\cdot}05$	$-0{\cdot}96 \pm 0{\cdot}02$
	9	$3{\cdot}0 \times 10^{-4}$	$2{\cdot}09 \pm 0{\cdot}08$	$-0{\cdot}96 \pm 0{\cdot}04$
	9	$3{\cdot}0 \times 10^{-3}$	$1{\cdot}5 \pm 0{\cdot}2$	$-1{\cdot}3 \pm 0{\cdot}1$
	10	$3{\cdot}0 \times 10^{-2}$	$0{\cdot}95 \pm 0{\cdot}09$	$-2{\cdot}1 \pm 0{\cdot}2$
(*c*) ‡ K^+ as KCl		Ce^{III} as chloride		
$2{\cdot}40 \times 10^{-3}$— $3{\cdot}6 \times 10^{-1}$	9	*ca.* 10^{-10}	$0{\cdot}52 \pm 0{\cdot}07$	$+5{\cdot}8 \pm 0{\cdot}8$

* The range of concentrations of the species A^q applies to each concentration of B^z. † z/q, Equation (2). ‡ Cation-exchange resin: Dowex 50WX8. § Anion-exchange resin: Dowex 1X8.

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* Here the definition of ' metal atom-to-charge ratio ' of solution species is restricted to hydrolysed, protonated, or polymeric ions.

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[9] D. C. Whitney and R. M. Diamond, *Inorg. Chem.*, 1963, **2**, 1284.

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[11] L. N. Stepanova and A. M. Trofimov, *Radiokhimiya*, 1959, **1**, 403; *Zhur. fiz. Khim.*, 1960, **34**, 1837; *Svensk kem. Tidskr.*, 1961, **73**, 72; A. A. Grinberg, L. N. Stepanova, and A. M. Trofimov, *Radiokhimiya*, 1960, **2**, 78; A. A. Grinberg, G. I. Petzhak, and L. N. Stepanova, *ibid.*, 1968, **10**, 96; L. V. Karago, G. I. Petzhak, and L. N. Stepanova, *ibid.*, 1970, **12**, 266.

[12] J. D. H. Strickland, *Nature*, 1952, **169**, 620; G. A. Welch, *ibid.*, 1953, **172**, 458; M. K. Cooper and D. M. Foster, *J. Chem. Soc.* (*A*), 1968, 2968.

[13] (*a*) M. K. Cooper and J. E. Salmon, *J. Chem. Soc.*, 1962, 2009; (*b*) J. F. Harvey, J. P. Redfern, and J. E. Salmon, *ibid.*, 1963, 2861; (*c*) *ibid.*, ref. 3 therein.

maximum error of ±5% of the correct value has been regarded as acceptable.

The effect of varying the micro- to macro-component concentration ratio [condition (*i*)] is shown in Tables **1**(*a*) and (*b*), where it can be seen that for both cation- and anion-exchangers of normal crosslinkage a ratio of less than *ca.* $10^2:1$ leads to significant deviations from the known charge values. Higher ratios are obviously desirable and can be readily obtained by use of carrier-free radioactive tracers. When condition (*i*) was satisfied (*ii*) was not infringed for macrocomponent concentrations up to 0·7M [Tables **1**(*a*) and (*b*)]. This is in agreement with the findings of Whitney and Diamond.[9]

TABLE 2

Variation of the observed charge of the macrocomponent ion with changes in resin volume

	Cation-exchange resins			
$[A^q]$/M	Dowex 50WX8		Dowex 50WX1	
K^+ as KCl	Equivalent volume (cm^3 $equiv.^{-1}$)			
$3{\cdot}0 \times 10^{-2}$	470		1 210	
$9{\cdot}0 \times 10^{-2}$	470		1 140	
$5{\cdot}0 \times 10^{-1}$	470		940	
$9{\cdot}0 \times 10^{-1}$	470		800	
	q	No. of concns. of A^q	*q*	No. of concns. of A^q
(*a*) * $4{\cdot}00 \times 10^{-3}$—$6{\cdot}00 \times 10^{-1}$	$+1{\cdot}03 \pm 0{\cdot}02$	11	$+1{\cdot}09 \pm 1{\cdot}07$	10
(*b*) * $4{\cdot}00 \times 10^{-3}$—$1{\cdot}00 \times 10^{-1}$			$+1{\cdot}00 \pm 0{\cdot}02$	7
	Anion-exchange resins			
$[A^q]$/M	Dowex 1X8		Dowex 1X1	
Cl^- as KCl	Equivalent volume (cm^3 $equiv.^{-1}$)			
$5{\cdot}00 \times 10^{-2}$	700		2 660	
$1{\cdot}00 \times 10^{-1}$	700		2 360	
$5{\cdot}00 \times 10^{-1}$	700		1 720	
1·00	700		1 570	
	q	No. of concns. of A^q	*q*	No. of concns. of A^q
(*c*) † $1{\cdot}67 \times 10^{-2}$—$7{\cdot}14 \times 10^{-1}$	$-0{\cdot}96 \pm 0{\cdot}02$	12	$-1{\cdot}25 \pm 0{\cdot}08$	11
(*d*) † $1{\cdot}67 \times 10^{-2}$—$1{\cdot}67 \times 10^{-1}$			$-1{\cdot}02 \pm 0{\cdot}02$	7

* $[B^z]$ *ca.* 10^{-10}M-Na^+ as NaCl. † $[B^z]$ *ca.* 10^{-10}M-SO_4^{2-} as Na_2SO_4.

Measurement of the charge on the potassium ion using cerium(III) as reference [Table **1**(*c*)] gave the erroneous value of 5·8 ± 0·8. We believe this to be the result of infringing condition (*iii*). It is known[14] that, in the presence of excess of chloride ion, cerium(III) forms chloro-complexes and therefore the use of cerium(III) as reference ion implies the simultaneous presence in solution of not only positive, but also neutral and perhaps anionic cerium species.

At a given concentration of external electrolyte the equivalent volume of an ion-exchange resin is a function of the degree of crosslinkage in the resin structure. This is usually designated by the nominal percentage of the cross-linking agent, in this case divinylbenzene (%dvb). Variation of the volume of the resin with crosslinkage and external electrolyte concentration [condition (*iv*)] is shown in Table 2. Standard 8% dvb ion-exchange resin exhibited no significant change in equivalent volume over the relatively wide concentration ranges shown in Table 2 and is therefore suitable with respect to condition (*iv*). For ions whose size might impede their access to this resin it is necessary to use resins of lower crosslinkage. For such resins large variations in the concentration of the species A^q can cause gross changes in equivalent volume and lead to unacceptable charge values [Table 2, charge determinations (*a*) and (*c*)]. Meaningful results can then be obtained only if there is some restriction of the higher concentrations of A^q [Table 2, charge determinations (*b*) and (*d*)].

The results summarized in Tables 1 and 2 set approximate limits to conditions (*i*)—(*iv*) for simple ions (K^+ and Cl^-). As a more rigorous test of the 'inverse' method we measured charge values of typical large (I^-), complex {$[Ni(en)_3]^{2+}$ (en = ethylenediamine)}, and polymeric ($[Cr_2O_7]^{2-}$) ions. Experimental conditions were chosen to fall within the limits already discussed. Table 3 shows that the method gives good agreement between measured and known charges of this group of diverse ions. In the case of complex ions it is possible that the resin may contain an ion different from that in solution. Of the three ions in Table 3 this possibility is important only for the dichromate anion. There is evidence[13b,15] for the existence of higher polymers of this anion in the resin phase. Under the experimental conditions of this work, measured metal-to-charge ratios in solution and on the resin suggest that $[Cr_2O_7]^{2-}$ is the only chromium(VI) species in both phases.

The hydrolysis of beryllium in aqueous solution has been extensively investigated and mononuclear and polymeric ions with charge values ranging from one to four have been proposed. The meticulous potentio-

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[14] R. E. Connick and S. W. Mayer, *J. Amer. Chem. Soc.*, 1951, **73**, 1176; G. R. Choppin and P. J. Unrein, *J. Inorg. Nuclear Chem.*, 1963, **25**, 387.

[15] T. V. Arden and M. Giddings, *J. Appl. Chem.*, 1961, **11**, 229.

metric work of Kakihana and Sillén[2] suggested that in 10—100mM-beryllium solutions the most important aqueous species was a trinuclear ion $[\mathrm{Be_3(OH)_3}]^{3+}$. Although other workers[16,17] have extended the work of Kakihana and Sillén, the latter have expressed concern[3] as to the effect of high concentrations of supporting electrolyte (3M-$\mathrm{NaClO_4}$) on formation of polymeric hydrolysis products. Evidence for the existence of an ion corresponding to $[\mathrm{Be_3(OH)_3}]^{3+}$ has also been found by Matijević[17] using the critical-micelle-concentration technique, but so far no direct evidence for the presence of this ion in solutions free from other cations has been reported.

TABLE 3

Charge determination for typical large, complex, and polymeric ions

	$[\mathrm{A}^q]$/M		No. of concns. of A^q	$[\mathrm{B}^z]$/M	Gradient *	q
	I^- as NaI			$\mathrm{SO_4}^{2-}$ as $\mathrm{Na_2SO_4}$		
(*a*)	† $1{\cdot}95 \times 10^{-2}$—$5{\cdot}81 \times 10^{-1}$		7	*ca.* 10^{-10}	$2{\cdot}02 \pm 0{\cdot}05$	$-0{\cdot}99 \pm 0{\cdot}02$
	$[\mathrm{Ni(en)_3}]^{2+}$ as $[\mathrm{Ni(en)_3}]\mathrm{Cl_2}$			Ca^{2+} as $\mathrm{CaCl_2}$		
(*b*)	‡ $9{\cdot}54 \times 10^{-4}$—$9{\cdot}54 \times 10^{-2}$		10	*ca.* 10^{-10}	$1{\cdot}00 \pm 0{\cdot}05$	$+2{\cdot}0 \pm 0{\cdot}1$
	$[\mathrm{Cr_2O_7}]^{2-}$ as $\mathrm{K_2[Cr_2O_7]}$			$[\mathrm{Co(CN)_6}]^{3-}$ as $\mathrm{K_3[Co(CN)_6]}$		
(*c*)	† $1{\cdot}10 \times 10^{-1}$—$3{\cdot}80 \times 10^{-1}$	pH 1·55	6	$1{\cdot}0 \times 10^{-3}$	$1{\cdot}43 \pm 0{\cdot}04$	$-2{\cdot}10 \pm 0{\cdot}06$
(*d*)	§ $1{\cdot}00 \times 10^{-3}$—$2{\cdot}53 \times 10^{-2}$	pH 4·00	6	$1{\cdot}0 \times 10^{-6}$	$1{\cdot}56 \pm 0{\cdot}07$	$-1{\cdot}92 \pm 0{\cdot}09$

* z/q, Equation (2). † Anion-exchange resin Dowex 1X8. ‡ Cation-exchange resin Amberlite CG120. § Metal-to-charge ratios for solution and resin $0{\cdot}94 \pm 0{\cdot}05$ and $0{\cdot}97 \pm 0{\cdot}05$ respectively (defined in the Experimental section).

According to Kakihana and Sillén[2] the trimeric ion exists almost exclusively (>95%) in 10—100mM-beryllium perchlorate solutions 3M in $\mathrm{NaClO_4}$ at pH 5·5. To investigate the existence of this ion in almost complete absence of foreign electrolyte we carried out charge determinations under the conditions shown in Table 4 using $^{45}\mathrm{Ca}^{2+}$ and $^{22}\mathrm{Na}^+$ reference ions at carrier-free radioactive tracer concentration levels. For greater certainty, distribution values were obtained by both static [batch equilibrium, Table 4(*a*)] and dynamic [p.e.v., Table 4(*b*)] methods. During preliminary conversion of columns of cation-exchange resin to the beryllium form there was an initial fall in pH of the eluate beryllium solutions to *ca.* 2 followed by a slow rise back to the eluant value of 5·5. We attribute this behaviour to further hydrolysis of beryllium in the resin phase, an observation consistent with the findings of other investigators who have reported[18] the existence of higher beryllium polymers on the resin.

Under these conditions the simple ion-exchange equilibrium (1) must be restated [equation (3)] to allow for the existence of other counter-ions in the solid phase.

$$xq\mathrm{B}^z + qz\bar{\mathrm{C}}^x \rightleftharpoons xq\bar{\mathrm{B}}^z + xz\mathrm{A}^q \qquad (3)$$

(Here A^q is the macrocomponent solution species of unknown charge, B^z and $\bar{\mathrm{B}}^z$ refer to the microcomponent reference ion in solution and on the resin respectively, and $\bar{\mathrm{C}}^x$ represents one or more ions in the resin phase at equilibrium with A^q.) Provided that the species B^z is at very low concentration with respect to A^q, and that the resin-phase composition ($\bar{\mathrm{C}}^x$) is effectively constant over the concentration range of A^q, equation (3) can still be expressed[19] in the form (2), the only difference being in the constant term. That $\bar{\mathrm{C}}^x$ is constant over the range of $[\mathrm{A}^q]$ used was evident from the linearity of the plots and the integral charge values obtained.

At the metal ion concentrations and pH values shown in Table 4, it is clear that beryllium perchlorate solutions free from other electrolytes contain a single tripositive ion with a 'metal-to-charge ratio' of unity. The only ion to fulfill this specification is $[\mathrm{Be_3(OH)_3}]^{3+}$.

TABLE 4

Charge determinations for the beryllium(II) ion at pH 5·5

$10^3[\mathrm{A}^q]$/M *	$[\mathrm{B}^z]$/M	$\log_{10}D_\mathrm{B}$	Gradient †	q ‡
(*a*) Batch-equilibrium method				
	Ca^{2+} as $\mathrm{CaCl_2}$			
22·4		$0{\cdot}934 \pm 0{\cdot}009$		
31·6		$0{\cdot}84 \pm 0{\cdot}02$		
46·1	*ca.* 10^{-10}	$0{\cdot}73 \pm 0{\cdot}03$	$0{\cdot}666 \pm 0{\cdot}006$	$+3{\cdot}00 \pm 0{\cdot}02$
64·0		$0{\cdot}62 \pm 0{\cdot}02$		
80·2		$0{\cdot}58 \pm 0{\cdot}01$		
119		$0{\cdot}45 \pm 0{\cdot}01$		
(*b*) p.e.v. Method §				
	Na^+ as NaCl			
19·6		$0{\cdot}39 \pm 0{\cdot}01$		
22·7		$0{\cdot}313 \pm 0{\cdot}007$		
30·2	*ca.* 10^{-13} (max.)	$0{\cdot}294 \pm 0{\cdot}007$	$0{\cdot}338 \pm 0{\cdot}002$	$+2{\cdot}96 \pm 0{\cdot}02$
51·1		$0{\cdot}213 \pm 0{\cdot}007$		
86·1		$0{\cdot}15 \pm 0{\cdot}01$		
102		$0{\cdot}12 \pm 0{\cdot}01$		

Resin: Amberlite CG 120 (100—200 mesh).

* Be as beryllium perchlorate at pH 5·5. † z/q, Equation (2). ‡ 'Beryllium atom-to-charge ratio' for solution, 1·06 (defined in the Experimental section). § Flow rate $1{\cdot}1 \times 10^{-1}$ cm min^{-1}.

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