

**594.** *Ion-association Constants of Some Acetates by pH  
(Glass Electrode) Measurements.\**

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Ion-pair formation by some alkali, alkaline-earth, transition-metal, and lanthanide acetates in water at 25° has been studied by addition of inorganic salts to sodium acetate-acetic acid solutions. The corresponding pHs were obtained to  $\pm 0.002$  unit by using the  $pK$  of acetic acid to derive the standard potential of the cell before adding the salts. The answers are expressed as dissociation constants at zero ionic strength.

CELLS such as ours,

Glass electrode | NaOH ( $m_1$ ), HA ( $m_2$ ), MY $_n$  ( $m_3$ ) | Sat. KCl, Calomel.

(A = anion, M = cation, Y = chloride, nitrate, or perchlorate), have been used extensively to derive the ion-pair constants of MA, MA $_2$ , etc. The general procedure of using standard buffers to calibrate the pH meter, then measuring the pHs of fixed mixtures of  $m_2$  and  $m_3$  to which varying amounts of  $m_1$  are added, may err in that the electrodes must be washed free from buffer before they are applied to the test solutions. This was avoided by obtaining the potential  $E$  from  $m_1 + m_2$  alone and the pH calculated from (Stockholm conventions<sup>1</sup>)

$$E = E_0 + k' \log [H^+] f_H = E_0 - k' \text{pH} \quad (1)$$

$$\log K(\text{HA}) = -\text{pH} + \log [A^-] + \log f_1 - \log [\text{HA}] \quad (2)$$

\* In this Paper, concentrations denoted  $m$ , and those in the Tables, are molarities. A represents acetate ion.

<sup>1</sup> Ives and Janz, "Reference Electrodes," Academic Press Ltd., London, 1961.

## 3118 Archer and Monk: Ion-association Constants of Some

where  $k' = 59.156$  mv,  $E_0$  = standard cell potential, and  $^2 K(\text{HA}) = 1.751 \times 10^{-5}$ . This means that  $K(\text{HA})$  must be known and the ionic strength  $I$  kept low enough to permit the calculation of activity coefficients  $f$ . In the present case,  $I$  was kept below 0.1 and use made of Davies's equation <sup>3</sup>

$$-\log f_i = 0.5 z_i^2 \{ I^{1/2} / (1 + I^{1/2}) - 0.3I \} \quad (3)$$

Since  $[\text{A}^-] = m_1 + [\text{H}^+]$ ,  $[\text{HA}] = m_2 - m_1 - [\text{H}^+]$ , equations (2) and (3) were first used to give an approximate value of  $[\text{H}^+]$  before calculating the true pH which was then used in (1) to obtain  $E_0$ , whence the pHs of mixtures of  $m_1 + m_2 + m_3$  were found.

This involves our assuming that the liquid junction potential remains constant, that the glass electrode is not affected by the ions M and Y, that equation (3) is valid, and that NaA ion-pairs are absent. Indications that some or all of these factors can be significant arose from measurements when  $\text{MY}_n$  was an alkali-metal salt. The relevant figures are in Table 1 where  $E_0'$  was calculated by the above method,  $Z$  is the initial volume of NaOH of molarity  $m_1' + \text{HA}$  of molarity  $m_2'$ , while  $c$  is the number of mols of stock solution of MY of molarity  $m_3'$  added, *i.e.*,

$$[\text{A}^-]' = Zm_1' / (Z + c) + [\text{H}^+] \quad (4)$$

$$[\text{HA}] = Z(m_2' + m_1') / (Z + c) - [\text{H}^+] \quad (5)$$

$$m_3 = m_3'c / (Z + c) \quad (6)$$

where  $[\text{A}^-]'$  assumes no MA ion-association occurs.

While the  $E_0'$  figures for KCl and CsCl are almost constant, the others show distinct rises as  $m_3$  increases. To get some further information, the potentials of some dilute hydrochloric acid-salt solutions were measured and the  $E_0'$  values calculated (Table 2). Although  $E_0'$  is again almost constant for KCl and CsCl it rises as the molarties of LiCl and NaCl increase up to  $I = 0.1$  (beyond, up to  $I = 0.2$ ,  $E_0'$  is constant for these also). These increases are not so marked as those in Table 1 and we assume that the differences are due to LiA and NaA ion-pair formation. Some figures for magnesium chloride are also included in Table 2 and show that  $E_0'$  is practically independent of this salt. The results in general are akin but in the opposite direction to the voltage departures reported for glass

TABLE 1.  
Potentials and  $E_0'$  values using alkali-metal salts and acetate.  
 $m_1' = 0.02183$ ,  $m_3' = 0.04074$ ,  $E$  and  $E_0' \times 10^4$  v.

Stock solns.	$Z$	$c$	0	1	2	3	4	5	6	7	8
0.920 LiCl	75	$E$ (LiCl)	900	913	923	933	941	947	952	957	961
		$E_0'$	3715	3721	3726	3733	3737	3741	3744	3746	3749
0.906 NaCl	75	$E$ (NaCl)	894	904	912	918	925	930	933	936	940
		$E_0'$	3709	3712	3715	3718	3722	3724	3725	3726	3728
0.933 NaNO <sub>3</sub>	75	$E$ (NaNO <sub>3</sub> )	(880)	894	903	908	913	919	924	928	932
		$E_0'$	(3695)	3702	3706	3707	3709	3712	3714	3717	3719
0.892 KCl	75	$E$ (KCl)	897	905	912	915	919	922	924	926	928
		$E_0'$	3712	3713	3716	3715	3716	3716	3716	3716	3716
1.151 CsCl	100	$E$ (CsCl)	883	890	894	897	899	901	902	902	903
		$E_0'$	3692	3693	3692	3691	3690	3691	3689	3687	3686

electrodes in alkaline solutions. Ives and Janz <sup>1</sup> have reviewed the latter and consider that the departures decrease as the glass cations become smaller and the solution cations become larger. Magnesium, barium, and ammonium have little or no effect on, *e.g.*, Corning 015 glass electrodes. On this basis and from the evidence of Table 2 it is assumed that only with lithium and sodium must  $E_0$  take the salt concentrations into account.

First, an approximate  $E_0''$  was found for the acetates (Table 1) by extrapolating a plot of  $E_0'$  against  $m_2 + m_3$ . To this was added a correction  $\Delta E_0$  obtained from the data of

<sup>2</sup> Cartwright and Monk, *J.*, 1955, 2500.

<sup>3</sup> Davies, "Ion Association," Butterworths Scientific Publns., London, 1962.

TABLE 2.  
Potentials and  $E_0'$  values using metal salts and hydrochloric acids.

HCl = 0.00008412 for LiCl, NaCl, MgCl<sub>2</sub>, 0.0001077 for KCl and CsCl,  $Z = 100$  ml.,  $E \times 10^4$  V

Stock solns.	$c$	0	2	4	6	8	10	12	24
0.831 LiCl	$E$ (LiCl)	—	1344	1333	1325	1316	1311	1304	1270
	$E_0'$	(3787)	3792	3796	3800	3801	3803	3804	3806
1.00 NaCl	$E$ (NaCl)	—	1351	1340	1330	1323	1315	1307	1271
	$E_0'$	(3798)	3802	3806	3808	3810	3811	3810	3810
0.863 KCl	$E$ (KCl)	—	1326	1314	1303	1293	1284	1268	—
	$E_0'$	—	3711	3713	3715	3714	3713	3712	—
0.618 CsCl	$E$ (CsCl)	—	1298	1280	1271	1261	1251	1242	—
	$E_0'$	—	3679	3680	3677	3676	3675	3673	—
0.1056 MgCl <sub>2</sub>	$c$	—	4	8	12	16	20	24	—
	$E$ (MgCl <sub>2</sub> )	—	1349	1333	1319	1308	1296	1285	—
	$\Delta_0'$	—	3798	3801	3802	3804	3804	3804	—

Table 2 by plotting  $E_0'$ (HCl) against  $m_1 + m_3$ . Then  $E_0 = E_0'' + \Delta E_0$  was used in (1) to obtain the pH which in (2) gave  $[A^-]$ . Then, from (4),  $[LiA]$  or  $[NaA] = [A^-]' - [A^-]$ . Values of  $K$ (LiA or NaA) were then calculated, making use of (3). If they showed a drift with  $m_3$ ,  $E_0$  was changed by 0.1mv steps until  $K$  was constant. The effect of doing this is exemplified in Table 3 for LiA.

TABLE 3.  
Dissociation constants of lithium and sodium acetates.

(Data from Table 1;  $K \times 100$ ,  $E \times 10^4$  v)

$c$	0	1	2	3	4	5	6	7	8
LiCl ( $E_0'' = 3709$ )	—	55	60	52	53	58	61	58	58
LiCl ( $E_0'' = 3708$ )	—	44	52	48	48	53	58	57	57
NaCl ( $E_0'' = 3703$ )	170	160	—	—	140	90	140	140	120
NaNO <sub>3</sub> ( $E_0'' = 3692$ )	—	170	120	170	180	140	120	110	105

The dissociation constants of the alkaline earth acetates were calculated along the same lines but  $E_0$  was calculated directly from the potentials of the initial mixture of  $m_1' + m_2'$ , and where needed, making slight adjustments to obtain constant  $K$  values. Since the concentrations of Na<sup>+</sup> and NaA remained virtually constant, while [NaA] was small, errors in  $E_0$  should remain almost constant and thus cancel out when calculating the pHs of the test solutions. The results are summarised in Table 4.

TABLE 4.  
Dissociation constants of the alkaline-earth acetates.

For Mg,  $m_1' = 0.01706$ ,  $m_2' = 0.02715$ ,  $Z = 100$  ml. For Ca and Sr,  $m_1' = 0.01195$ ,  $m_2' = 0.02037$ ,  $Z = 100$  ml. For Ba,  $m_1' = 0.02183$ ,  $m_2' = 0.04074$ ,  $Z = 75$  ml.  $E \times 10^4$  v.

Stock solns.	$c$	0	3	6	9	12	15	18	21	24	27
0.1056 MgCl <sub>2</sub>	$E$ (Mg)	895	915	927	935	943	949	953	957	961	965
$E_0 = 3821$	$10^3K$ (MgA <sup>+</sup> )	—	—	53	53	48	51	48	55	56	56
0.1054 CaCl <sub>2</sub>	$E$ (Ca)	913	925	935	943	948	953	957	961	965	969
$E_0 = 3789$	$10^3K$ (CaA <sup>+</sup> )	—	78	70	68	74	74	87	77	78	75
0.1247 SrCl <sub>2</sub>	$E$ (Sr)	784	798	809	816	823	828	832	837	841	845
$E_0 = 3661$	$10^3K$ (SrA <sup>+</sup> )	—	89	82	77	82	85	87	84	84	82
0.2844 BaCl <sub>2</sub>	$c$	0	1	2	3	4	5	6	7	8	
$E_0 = 3724$	$E$ (Ba)	909	919	927	934	940	945	950	953	958	
	$10^3K$ (BaA <sup>+</sup> )	—	103	107	104	104	104	103	109	103	

Studies of some transition metals (Table 5) indicated that with lead, cadmium, and copper, both MA<sup>+</sup> and MA<sub>2</sub> ion-pairs form. For these systems, values of  $K_2$ (MA<sub>2</sub>) were tried until  $K_1$ (MA<sup>+</sup>) was constant for all the solutions. This meant calculating [MA<sub>2</sub>] from

$$K_2(MA_2) = [MA^+][A^-]f_1^2/[MA_2] \quad (7)$$

and estimating [MA<sup>+</sup>] from

$$[MA^+] = [A^-]' - [A^-] - 2[MA_2] \quad (8)$$

## 3120 Archer and Monk: Ion-association Constants of Some

TABLE 5.

Dissociation constants of some transition-metal acetates.

Zn, Co, Mn, Ni, Pb:  $Z = 100$  ml.,  $m_1' = 0.01195$ ,  $m_2' = 0.02037$ . Cd:  $Z = 75$  ml.,  $m_1' = 0.02625$ ,  $m_2' = 0.05252$ . Cu:  $Z = 50$  ml.,  $m_1' = 0.03237$ ,  $m_2' = 0.05075$ . Selected  $K_2$  values:  $\text{PbA}_2 = 0.040$ ,  $\text{CdA}_2 = 0.060$ ,  $\text{CuA}_2 = 0.040$ .  $E = 10^4$  V.

$m_3'$ and $E_0$	$c$	0	3	6	9	12	15	18	21	24	27
0.0928 Zn(NO <sub>3</sub> ) <sub>2</sub>	$E$ (Zn)	868	885	899	910	919	928	938	946	954	959
$E_0 = 3744$	$10^3K$ (ZnA <sup>+</sup> )	—	27	28	28	28	28	27	26	26	26
0.1245 CoCl <sub>2</sub>	$E$ (Co)	868	890	904	915	925	933	945	951	957	960
$E_0 = 3745$	$10^3K$ (CoA <sup>+</sup> )	—	31	36	37	37	38	33	34	35	36
0.1035 MnCl <sub>2</sub>	$E$ (Mn)	906	923	935	944	953	962	968	974	978	982
$E_0 = 3783$	$10^3K$ (MnA <sup>+</sup> )	—	39	41	43	41	39	39	39	40	41
0.1269 NiCl <sub>2</sub>	$E$ (Ni)	915	935	951	962	972	979	986	992	999	1005
$E_0 = 3791$	$10^3K$ (NiA <sup>+</sup> )	—	35	34	37	37	38	39	38	38	38
0.1000 Pb(NO <sub>3</sub> ) <sub>2</sub>	$E$ (Pb)	903	—	1029	1083	1126	1163	1194	1218	1240	1259
$E_0 = 3780$	$10^3K$ (PbA <sup>+</sup> )	—	—	213	213	214	214	210	211	211	209
0.1002 Cd(NO <sub>3</sub> ) <sub>2</sub>	$E$ (Cd)	983	1013	1041	1064	1083	1089	—	—	—	—
$E_0 = 3758$	$10^4K$ (CdA <sup>+</sup> )	—	122	114	118	117	120	—	—	—	—
0.1226 CuCl <sub>2</sub>	$-E$ (Cu)	1612	1546	1491	1442	1402	1368	1341	—	—	—
$E_0 = 0.1305$	$10^4K_1$ (CuA <sup>+</sup> )	—	58	64	61	59	57	56	—	—	—

Allowance was made for nitrate ion-pairs by use of  ${}^4K(\text{CdNO}_3^+) = 0.4$  and  $K(\text{PbNO}_3^+) = 0.066$ .

The four lanthanides studied (Table 6) were also considered in terms of  $K_1$  and  $K_2$ , and  $K_2$  was selected as above. Kolat and Powell,<sup>5</sup> by a different method of calculation applied to ten lanthanides at  $I = 0.1$ , also considered that only  $\text{LnA}^{2+}$  and  $\text{LnA}_2^+$  form if  $[\text{A}^-]$  is limited, while Sonesson<sup>6</sup> concluded that  $\text{LnA}_3$  can also exist, but he used a much wider Ln : A range.

TABLE 6.

Dissociation constants of some lanthanide acetates.

Series 1.  $m_1' = 0.02625$ ,  $m_2' = 0.05250$ ,  $Z = 75$  ml. Selected  $K_2$  values:  $\text{LaA}_2^+ = 0.027$ ,  $\text{NdA}_2^+ = 0.014$ ,  $\text{SmA}_2^+ = 0.011$ ,  $\text{YbA}_2^+ = 0.015$ .  $E \times 10^4$  v.

$m_3'$ and $E_0$	$c$	0	3	6	9	12	15
0.1195 La(ClO <sub>4</sub> ) <sub>3</sub>	$E$	805	852	898	935	967	993
$E_0 = 3726$	$10^5K_1$ (LaA <sup>2+</sup> )	—	295	310	300	285	290
0.0698 Nd(ClO <sub>4</sub> ) <sub>3</sub>	$E$	968	1008	1046	1081	1113	1144
$E_0 = 3736$	$10^5K_1$ (NdA <sup>2+</sup> )	—	210	200	225	215	195
0.1339 Sm(ClO <sub>4</sub> ) <sub>3</sub>	$E$	971	1056	1135	1202	1257	1301
$E_0 = 3739$	$10^5K_1$ (SmA <sup>2+</sup> )	—	135	150	145	135	135
0.1062 Yb(ClO <sub>4</sub> ) <sub>3</sub>	$E$	963	1021	1071	1112	1147	1175
$E_0 = 3731$	$10^5K_1$ (YbA <sup>2+</sup> )	—	270	285	290	275	270

Series 2.  $m_1' = 0.03412$ ,  $m_2' = 0.05249$ ,  $m_3'$  as in Series 1,  $Z = 75$  ml. Selected  $K_2$  values:  $\text{LaA}_2^+ = 0.027$ ,  $\text{NdA}_2^+ = 0.013$ ,  $\text{SmA}_2^+ = 0.011$ ,  $\text{YbA}_2^+ = 0.017$ .

$m_3'$ and $E_0$	$c$	0	3	6	9	12	15
$E_0 = 3726$	$E$	805	852	898	935	967	993
	$10^5K_1$ (LaA <sup>2+</sup> )	—	275	255	275	275	280
	$E$	789	—	854	886	914	942
$E_0 = 3710$	$10^5K_1$ (NdA <sup>2+</sup> )	—	—	225	210	230	215
	$E$	971	—	1136	1202	1257	1301
$E_0 = 3740$	$10^5K_1$ (SmA <sup>2+</sup> )	—	—	160	150	150	140
	$E$	881	928	971	1009	1045	1072
$E_0 = 3802$	$10^5K_1$ (YbA <sup>2+</sup> )	—	250	280	285	260	265

*Discussion.*—Our average results, together with those of some other workers, with correction to  $I = 0$  were necessary, are in Table 7. There is qualitative indication that lithium and sodium acetates do not completely ionise in that their stoichiometric activity coefficients are a little lower than one would expect by comparison with those of other

<sup>4</sup> Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592.

<sup>5</sup> Kolat and Powell, *J. Inorg. Chem.*, 1962, **1**, 293.

<sup>6</sup> Sonesson, *Acta Chem. Scand.*, 1958, **12**, 165, 1937

TABLE 7.  
Average dissociation constants, with previous results.

	Li	Na	Mg	Ca	Sr	Ba
	0.55	1.5	0.052	0.075	0.084	0.105
	—	—	0.057, <sup>a</sup> 0.1 <sup>b</sup>	0.057, <sup>a</sup> 0.1, <sup>b</sup> 0.16 <sup>c</sup>	0.069, <sup>a</sup> 0.1, <sup>b</sup> 0.36 <sup>c</sup>	0.070, <sup>a</sup> 0.13, <sup>b</sup> 0.39 <sup>c</sup>
	Zn	Co	Mn	Ni	Pb	
(K <sub>1</sub> )	0.027	0.035	0.040	0.037	0.0021	
(K <sub>1</sub> )	0.026, <sup>b</sup> 0.020 <sup>d</sup>	—	—	—	0.0030, <sup>e</sup> 0.0024, <sup>d</sup> 0.0021 <sup>f</sup>	
(K <sub>2</sub> )	—	—	—	—	0.040	
(K <sub>2</sub> )	—	—	—	—	0.025 <sup>g</sup>	
	Cd	Cu	La	Nd	Sm	Yb
(K <sub>1</sub> )	0.0118	0.0059	0.00285	0.00215	0.00145	0.00275
(K <sub>1</sub> )	0.0093 <sup>d</sup>	0.0057, <sup>f</sup> 0.0049, <sup>d</sup> 0.0053 <sup>f</sup>	0.00225 <sup>d</sup>	0.0014 <sup>d</sup>	0.00115 <sup>d</sup>	0.0022 <sup>d</sup>
(K <sub>2</sub> )	0.060	0.040	0.027	0.0135	0.011	0.015
(K <sub>2</sub> )	0.052 <sup>d</sup>	0.040 <sup>d</sup>	0.022 <sup>d</sup>	0.011 <sup>d</sup>	0.010 <sup>d</sup>	0.009 <sup>d</sup>

Refs.: (a) = 8, (b) = 9 (originally at  $I = 0.2$ ), (c) = 10, (d) = 5 (originally at  $I = 0.1$ ), (e) = 7, (f) = 11 (originally at  $I = 0.2$ ), (g) = 12.

uni-univalent salts. For the latter the general trend is an increase from caesium to lithium whereas, at 0.1M, the acetate values are <sup>3</sup> 0.784 (Li), 0.791 (Na), 0.796 (K, Rb), 0.799 (Cs). This feature is also found with the hydroxides and <sup>13</sup> several methods indicate that lithium and sodium hydroxides also undergo ion-association. For the alkaline earths, our figures and those of Nancollas <sup>8</sup> agree well but previous results derived from solubilities <sup>10</sup> appear too high. Our figures fit the observation of Davies <sup>3</sup> for the hydroxides, particularly those of the alkalis and alkaline earths, namely that the pK values are related to  $z_1/z_2(r_M + r_L)$  where  $z$  = ion valence,  $r$  = crystalline radius, and the subscripts M and L refer to metal and ligand. This is also characteristic of other series where L is an organic ligand <sup>3,14</sup> although magnesium is often somewhat out of line. With the acetates, use of <sup>14</sup>  $r_L = 2.24$  Å and known crystalline radii,<sup>15</sup> magnesium fits quite well.

Among the transition metals, the familiar Irving-Williams order <sup>16</sup> of pK (Mn < Co < Ni < Cu > Zn) is almost obeyed but the pKs of the first three are very close, as with the pKs of the sulphates and thiosulphates.<sup>14</sup> This suggests that ion-pairing in these acetates is partly due to Coulomb forces involving the hydrated ions <sup>3</sup> which are of the same size, and only partly due to cation characteristics. These views are supported by the pKs of the lanthanides. The four selected ones are sufficient to confirm Sonesson's more detailed studies <sup>6</sup> of ten lanthanides which show that pK<sub>1</sub> and pK<sub>2</sub> reach minima at samarium (Kolat and Powell <sup>5</sup> also confirm this for pK<sub>1</sub>). With stronger associating ligands such as <sup>1</sup> EDTA, nitriloacetate, and <sup>17</sup> 1,2-diaminocyclohexanetetraacetate, the pK<sub>1</sub> values of the lanthanides are related to the cation crystalline radii. This is similar to what has been mentioned for alkali and alkaline earth ion-pairs. However, as with these, the relationship is not strictly proportional and with the lanthanides there is a small minimum around europium. Further, again recalling a previous comment, the pKs of the lanthanide sulphates <sup>13</sup> are all about the same value, and since their hydrated cation radii are all also about the same, as judged by their limiting conductances,<sup>18</sup> it appears that ionic interaction

<sup>7</sup> Bjerrum, Schwarzenbach, and Sillen, "Stability Constants," Chem. Soc., London, 1958.

<sup>8</sup> Nancollas, *J.*, 1956, 744.

<sup>9</sup> Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314.

<sup>10</sup> Colman-Porter and Monk, *J.*, 1952, 4363.

<sup>11</sup> Tanaka and Kato, *Bull. Chem. Soc., Japan*, 1960, **33**, 417.

<sup>12</sup> Lloyd, Wycherley, and Monk, *J.*, 1951, 1786.

<sup>13</sup> Gimblett and Monk, *Trans. Faraday Soc.*, 1954, **50**, 965.

<sup>14</sup> Monk, "Electrolytic Dissociation," Academic Press Ltd., London, 1961.

<sup>15</sup> Pauling, "Nature of the Chemical Bond," Cornell University Press, New York, 1950.

<sup>16</sup> Irving and Williams, *Nature*, 1948, **162**, 746.

<sup>17</sup> Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 936.

<sup>18</sup> Spedding and Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 882.

in the sulphates involves only the hydrated ions. Thus with these acetates ion-association might be explained as involving hydrated cations at the beginning and end of the series but on this is superimposed increasingly stronger interaction due to cation characteristics associated with the  $4f$  orbitals.

#### EXPERIMENTAL

The potentials were measured with a Radiometer type PHM4c pH-meter that could be read to better than  $\pm 0.2$  mv. The cell was a 150 ml. Polythene bottle, with a hole in the cap for the glass electrode (Radiometer, G202C). Two short plastic tubes were sealed into the neck for a dipping calomel electrode and for pipetting in salt solutions. The metal thermostat bath contained Shell "Diala" oil type B and the metal shelf for the cell and the bath were earthed. In addition a small metal shield was placed around the cell. With this arrangement electrical interference by the bath stirrer and body capacity effects were negligible. Salt solutions were pipetted in after the cell potential had become constant for at least 1 hr. Glass electrodes were stored in buffer in a Polythene bottle in the bath. After salt solution was added and the cell shaken, the potentials became constant within a few minutes.

Most reagents were AnalaR and unless they could be made up by weight, the molarities of the stock salt solutions were found by titrating samples after passing them through a short column of  $H^+$ -ion Zeo-Karb-225 ion exchange resin.

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