Conductivity and Solubility Studies of Some Glycollates and Lactates.

By W. P. Evans and C. B. Monk.

Conductivity measurements for a number of glycollates and lactates in aqueous solution at 25°, and the dissociation constants of the ion-pairs MR^+, are reported. The cupric salts have been studied by a solubility method, and the dissociation constants of CuR^+ and CuR_2 calculated. The results are discussed in terms of ionisation potentials and cation radii.

As a continuation to previous systematic studies of salts of monocarboxylic acids (Lloyd, Wycherley, and Monk, *J.*, 1951, 1786; Colman-Porter and Monk, *J.*, 1952, 4363), a number of glycollates and lactates have been examined in order to gain further information on the factors which influence ionisation in these systems. These two anions were chosen since the available evidence (*loc. cit.*) indicates that they are ligands with a moderate capacity for complex formation; they are not so powerful for instance as the aminoacetate (*loc. cit.*) or ethylenediaminetetra-acetate (Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1947, **30**, 1798), but are considerably stronger than others such as the propionate and acetate (Colman-Porter and Monk, *loc. cit.*). A comparison of the dissociation constants of the ion pairs or complexes formed does not, however, point to any one physical factor whereby one can correlate the values obtained between a particular anion and a series of cations. The alkaline earths are an example of this. With the anions from glycine and alanine (Colman-Porter and Monk, *loc. cit.*) and some other strong ligands such as those listed by Williams (*J.*, 1952, 3770), the p*K* values decrease in the order Mg, Ca, Sr, Ba. The glycollate and lactate order is Ca, Mg, Sr, Ba, and this order also occurs with such weak ligands as acetates and propionates. This distinction is not clear-cut, however, for we also find magnesium out of position with some of the strong ligands (Williams, *loc. cit.*), and this feature has been discussed by Williams in a survey covering both organic and inorganic salts of the alkaline earths. It is evident that various factors such as ion size, ionisation potentials, cation hydration, anion ring size, and heat and energy changes all need consideration in attempting to explain the p*K* orders.

A survey including a large number of cations might be helpful in clarifying the position, and this has been the main object of the present work. Both of the anions considered, given cations of relatively strong bases, form salts which can be studied by conductivity methods. The acids, having p*K* values of about 4, do not give rise to serious hydrolytic effects, and the slight amount of hydrolysis which would occur is easily suppressed by adding a trace of free acid. This precaution was taken, the pH being kept near 6, and since these solutions were thereby buffered, small corrections for the mobile hydrogen ion had to be made.

EXPERIMENTAL

The conductivity apparatus and general technique have already been described (Davies, *J.*, 1937, 432; Davies and Monk, *J.*, 1949, 413). The cell constants were determined by using a conductivity equation for dilute solutions of potassium chloride (Jenkins and Monk, *J. Amer. Chem. Soc.*, 1950, **72**, 2695). Conductivity water was prepared by passing distilled water through a mixed bed of ion-exchange resins (Dowex C211 and A244). All measurements were made at 25° $\pm$ 0·01°, and a purified nitrogen stream was maintained over the cell solutions throughout each run.

Zinc lactate was precipitated by mixing solutions of " AnalaR " lactic acid and zinc sulphate, and adding ammonium hydroxide. It was recrystallised from aqueous ethanol till free from sulphate, and finally from conductivity water. Cadmium lactate was similarly prepared, but the first precipitation was slow, complete crystallisation taking about 2 weeks. Manganese lactate was made by warming an excess of the carbonate with lactic acid for some hours beyond the time when carbon dioxide evolution had finished, filtering, cooling, and recrystallising as in the case of the zinc salt. Sodium lactate solutions were prepared by neutralisation with

carbonate-free sodium hydroxide of lactic acid formed by the passage of zinc lactate solutions through a bed of " Amberlite " I.R.100 resin in the hydrogen form. Nickel lactate was too soluble to be prepared by precipitation methods, so lactic acid formed as above was passed through a bed of " Amberlite " A.R.400 resin in the hydroxyl form. Nickel chloride was then passed on to this and the pH of the resulting nickel lactate solution adjusted with a trace of lactic acid.

Calcium glycollate was formed by refluxing an excess of " AnalaR " calcium carbonate and chloroacetic acid for some hours beyond the point where carbon dioxide evolution had ceased to ensure that all the acid had been converted into the glycollate form. The hot solution was filtered and cooled, and the product recrystallised until chloride-free, first from aqueous ethanol and then from conductivity water. This salt was used to make sodium glycollate by the ion-exchange method just described. Nickel glycollate solutions were also made by the ion-exchange method used for the lactate. Zinc and manganese glycollates were made by the method used for the calcium salt, zinc oxide and manganese carbonate being used. This method was also used for cadmium glycollate, but the solution required filtering through asbestos to remove colloidal matter. These last three salts were recrystallised from aqueous ethanol, and finally from conductivity water.

Considerable care was taken to ensure that the concentrations of the stock solutions were known accurately, and at least two independent solutions were used. Zinc concentrations were found by the gravimetric pyrophosphate method ($\pm 0\cdot 02\%$), nickel was estimated by dimethyl-glyoxime ($\pm 0\cdot 05\%$), and the cadmium and manganese solutions were made up by weight after dehydrating the crystals at 80° in a vacuum oven. Attempts were made to dry the manganese salt at 100°, but it turned slightly brown and was slightly heavier than when dried to constant weight at 80°. A check by the pyrophosphate method indicated that drying at 80° was complete to within $\pm 0\cdot 1\%$. Cadmium salts dried at 100° had the same weight as if dried at 80°. Sodium hydroxide solutions were standardised under carbon dioxide-free conditions against potassium hydrogen phthalate ($\pm 0\cdot 1\%$). In the case of the cobalt and lead salts where a mixture method was used, gravimetric determinations of chloride were made ($\pm 0\cdot 02\%$ and $\pm 0\cdot 05\%$ respectively).

The solubility method used for the copper salts was that described by Lloyd, Wycherley, and Monk (*loc. cit.*).

Results.—The limiting anion mobilities were required when interpreting the conductivity measurements, and these were obtained from the sodium salts. Martin and Tartar (*J. Amer. Chem. Soc.*, 1937, **59**, 2672) measured the conductivities of sodium and potassium lactates and derived 38·75 for the lactate ion. Application of Onsager's method of extrapolation (*Physikal. Z.*, 1927, **28**, 277) puts this slightly higher (38·9) and shows at the same time that these salts are completely ionised. Our sodium lactate figures give 35·5, and this considerably lower value can perhaps be attributed to the difference between the methods of preparing the acid, for Martin and Tartar distilled their samples three times under vacuum, whereas we prepared solutions by the hydrogen ion-exchange method described above. The distillation of lactic acid causes condensation polymerisation (see Montgomery, *J. Amer. Chem. Soc.*, 1952, **74**, 1466). Even in dilute solution lactyl-lactic acid is present, and according to Watson (*Ind. Eng. Chem.*, 1940, **32**, 399) it takes several weeks for this to change into lactic acid at room temperature. These factors may account for the differences between Martin and Tartar's figures and ours. By precipitating lactates and converting them into the acid by the resin method, the solutions should be quite free from condensation products. Our figures for sodium glycollate (Table 2), which was also prepared by the resin method, give 40·8 for the limiting mobility of the glycollate ion. No comparable figures have been found, but 390 is quoted for the acid (I.C.T., Vol. VI, p. 262), which, since the value for hydrogen is 349·8 (Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, 1950, p. 172), gives the similar figure of 40·2.

The conductivities of the various salts MR_2, where M^{++} is a bivalent cation and R^- represents glycollate or lactate, can be quantitatively discussed by the method of Davies and Righellato (*Trans. Faraday Soc.*, 1930, **26**, 592). The equilibrium concerned is $MR^+ \rightleftharpoons M^{++} + R^-$, and if α represents the fraction of cations which form MR^+ ion-pairs, then since

$$\mu m = \Sigma \mu_i m_i$$

(μ = molecular conductivity of a solution of molarity m, and subscript " i " signifies ions) we have

$$\Lambda = \lambda_M(1 - \alpha) + \lambda_R(2 - \alpha)/2 + \lambda_{MR}\alpha/2$$

(Λ = equivalent conductivity, λ = ion-equivalent conductivity).   Rearranging, we have

$$\Lambda = \Lambda_1(1 - \alpha) + \Lambda_2\alpha/2$$

where $\Lambda_1 = \lambda_M + \lambda_R$, and $\Lambda_2 = \lambda_{MR} + \lambda_R$.   Both Λ_1 and Λ_2 can be calculated from the corresponding Onsager equations,

$$\Lambda_1 = \Lambda^0_1 - b_1 I^{\frac{1}{2}} \quad \text{and} \quad \Lambda_2 = \Lambda^0_2 - b_2 I^{\frac{1}{2}}$$

and thus α obtained.   In these expressions, b_1 and b_2 are the theoretical Onsager values, and the ionic strength is given by $I = c(1 \cdot 5 - \alpha)$, where c = equivalents per litre.   As a charged ion-pair is involved, an assumption has to be made, and we have taken $\lambda^0_{MR} = 0 \cdot 5\lambda^0_M$.   Some evidence that such a ratio is of the right order can be obtained by comparing the mobilities of the anions of some bivalent acids A^{2-} with those of the corresponding HA^- ions.   Thus Davies *J..*, 1939, 1850) calculated for three organic acids that the ratio is 0·6, 0·59, and 0·52.   Sherrill and Noyes's data for the conductivity of the HSO_4^- ion (*J. Amer. Chem. Soc.*, 1926, **48**, 1861) extrapolate to 51·5, whence, taking the value for SO_4^{2-} as 80·0 (Jenkins and Monk, *loc. cit.*), we

TABLE 1.   *Limiting mobilities and Onsager slopes.*

	Glycollates				Lactates			
	Zn	Ni	Cd	Mn	Zn	Ni	Cd	Mn
Λ^0_1	93·6 [b]	94·5 [a]	93·5 [b]	93·85 [a]	88·3 [b]	89·2 [a]	88·2 [b]	88·55 [a]
Λ^0_2	67·2	67·6	67·1	67·3	61·9	62·3	61·8	62·0
b_1	130·6	131·1	130·6	130·7	129·1	129·5	129·2	129·2
b_2	75·5	75·6	75·5	75·5	74·3	74·4	74·3	74·4

[a] Ni = 53·7, Mn = 53·05 (Jones, Monk, and Davies, *loc. cit.*).   [b] Zn = 52·8, Cd = 52·7 by adjusting Λ^0 until the K values showed no significant drifts with concentration; cf. Zn = 53·0 (Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074).

TABLE 2.   *Conductivities of glycollates.*

Run	10^4c	Λ	10^4I	$10^2\alpha$	10^3K	Run	10^4c	Λ	10^4I	$10^2\alpha$	10^3K
		Nickel						Zinc			
2	15·326	79·02	20·39	16·94	5·57	1	6·196	82·50	9·52	12·37	3·98
1	20·191	75·85	25·88	21·41	5·20	2	6·944	82·47	9·55	12·42	3·97
2	22·145	75·35	28·39	21·84	5·50	2	9·856	80·07	13·26	15·50	4·18
1	24·944	74·09	31·52	23·53	5·50	2	13·858	77·20	18·11	19·34	4·27
1	28·957	72·76	36·04	25·19	5·65	1	13·946	77·21	18·23	19·31	4·31
2	29·028	72·32	36·19	25·33	5·64	2	20·250	73·53	25·45	24·37	4·36
2	34·165	70·50	41·59	28·44	5·45	1	24·101	71·63	29·64	27·04	4·35
2	42·114	67·75	49·52	32·40	5·30	1	31·953	68·19	37·71	32·03	4·27
		Cadmium						Manganese			
2	19·750	81·25	27·68	9·74	13·6	2	7·067	88·24	10·43	2·45	23·9
1	21·804	80·50	30·40	10·58	13·5	1	10·409	86·86	15·28	3·35	24·6
2	24·810	79·50	34·34	11·65	13·5	1	12·769	86·06	18·66	3·84	25·7
1	25·848	79·25	35·70	11·85	13·7	2	14·042	85·67	20·48	4·07	26·2
2	29·388	78·20	40·25	12·98	13·7	1	17·285	84·70	25·15	4·70	27·1
1	31·743	77·50	43·23	13·80	13·6	2	19·342	84·10	28·03	5·14	27·1
1	40·139	75·38	53·70	16·11	13·6	1	20·026	83·88	28·96	5·34	26·9
2	40·566	75·22	54·25	16·32	13·5	2	30·725	81·38	43·83	7·27	27·7
1	55·039	72·37	71·78	19·30	14·0						
		Sodium									
2	8·409	88·57	—	—	—	3	15·44	87·71	—	—	—
1	8·672	88·51	—	—	—	1	19·03	87·32	—	—	—
3	10·483	88·28	—	—	—	3	21·955	87·17	—	—	—
1	13·41	87·89	—	—	—	2	25·53	86·85	—	—	—
2	13·45	87·91	—	—	—	3	49·355	85·43	—	—	—

obtain a ratio of 0·64.   The limiting mobilities of the HCO_3^- and CO_3^{2-} ions are 44·4 (Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, 1935, **57**, 1705) and 69·6 (Monk, *J.*, 1949, 429), respectively, giving a ratio of 0·64.   The available evidence therefore points to an upper limit of $\lambda^0_{MR} = 0 \cdot 65\lambda^0_M$, and calculation with, *e.g.*, our data for manganese and nickel lactates over a concentration range using this ratio lowers the dissociation constants by about 7% from those given in Table 3.   It is therefore reasonable to suggest that our assumption does not result in more than about 5% uncertainty in the derived dissociation constants.

Several approximations are needed to get constant α values, whence the dissociation constants can be calculated :

$$K = [M^{++}][R^-]f_1f_2/[MR^+]f_3 = (1 - \alpha)(2 - \alpha)cf_1f_2/2\alpha f_3$$

the simple Debye–Hückel activity coefficient expression, $-\log f_i = 0.509z_i{}^2I^{\frac{1}{2}}$ in which z_i is the ion valency, being used. The values of Λ^0 and b are given in Table 1. Tables 2 and 3 give the conductivities and the values of α and K for the glycollates and lactates, respectively.

TABLE 3. *Conductivities of lactates.*

Run	10^4c	Λ	10^4I	$10^2\alpha$	10^3K	Run	10^4c	Λ	10^4I	$10^2\alpha$	10^3K
		Nickel						Zinc			
2	13·461	75·65	18·18	14·84	5·86	1	6·126	80·01	8·69	8·22	5·72
1	13·852	75·52	18·70	14·95	5·96	1	8·537	78·14	11·90	10·54	5·84
2	20·067	72·48	26·39	18·88	6·15	2	9·200	77·64	12·78	11·19	5·83
1	26·833	69·80	34·52	22·48	6·24	2	10·647	76·66	14·64	12·46	5·86
2	27·764	69·33	35·21	23·19	6·15	1	12·927	75·08	17·50	14·62	5·75
3	30·658	68·36	38·48	24·49	6·20	2	13·494	74·87	18·24	14·83	5·87
2	36·056	66·46	44·24	27·21	6·10	1	19·288	71·43	25·13	19·72	5·60
1	38·737	65·75	47·27	28·16	6·15	2	20·089	71·28	26·16	19·78	5·78
3	54·666	61·44	63·21	34·43	5·94	2	26·494	68·37	33·39	23·98	5·64
		Cadmium						Manganese			
1	10·445	81·01	15·26	3·99	20·5	2	10·759	82·23	15·92	2·18	39·4
2	11·178	80·69	16·29	4·29	20·2	1	12·277	81·65	18·11	2·68	36·0
2	15·412	79·16	22·27	5·56	20·4	2	15·504	80·76	22·77	3·08	38·4
1	15·523	79·04	22·38	5·76	19·8	1	15·995	80·55	23·48	3·30	36·7
1	19·321	77·86	27·68	6·76	20·1	2	18·444	79·94	27·02	3·62	37·8
2	21·919	77·05	31·20	7·54	19·9	1	22·358	78·88	32·54	4·42	36·2
1	28·076	75·50	39·65	8·87	20·5	2	26·076	78·09	37·85	4·88	37·2
2	34·484	73·93	48·11	10·43	20·3	1	29·550	77·32	42·70	5·43	36·8
1	36·078	73·63	50·26	10·66	20·3						
					Sodium						
2	5·308	83·81	—	—	—	2	24·65	81·81	—	—	—
2	11·688	83·00	—	—	—	1	27·62	81·62	—	—	—
1	12·633	82·83	—	—	—	2	37·58	80·96	—	—	—
1	17·55	82·37	—	—	—	1	40·81	80·85	—	—	—
2	18·73	82·27	—	—	—	3	71·86	79·39	—	—	—

The cobalt salts could not be conveniently investigated by direct measurements since they are too soluble to provide crystals for weighing, and the precise determination of cobalt is somewhat difficult. Instead, the specific conductivities of mixtures of cobalt chloride and sodium glycollate or lactate were measured, and the differences between the observed measurements and those calculated on the assumption that dissociation is complete were used to estimate the concentrations of CoR^+. This method has been applied to some inorganic salts (Jones, Monk, and Davies, *loc. cit.*). If c_1 is the equivalent concentration of sodium salt, c_2 is that of the cobalt chloride, and β that of CoR^+, then since

$$10^3\kappa \text{ (obs.)} = 10^3\Sigma\kappa_i = \Sigma\lambda_ic_i$$

where κ represents specific conductivity, then

$$10^3\kappa \text{ (obs.)} = \lambda_{Na}c_1 + 2\lambda_{Co}(c_2/2 - \beta) + \lambda_{Cl}c_2 + \lambda_R(c_1 - \beta) + \lambda_{CoR}(\beta)$$

and if ionisation were complete,

$$10^3\kappa \text{ (theor.)} = \Sigma(\lambda^0{}_I - b_iI^{\frac{1}{2}}) = \lambda_{Na}c_1 + 2\lambda_{Co}c_2/2 + \lambda_{Cl}c_2 + \lambda_Rc_1$$

whence, by assuming $\lambda^0{}_{CoR} = 0.5\lambda^0{}_{Co}$,

$$\beta = 10^3\{\kappa \text{ (theor.)} - \kappa \text{ (obs.)}\}/\{\lambda_R + 1.5\lambda_{Co}\}$$

β is obtained by approximations, by using $I = (c_1 + 1.5c_2 - 2\beta)$. In the calculation of b_i in the Onsager equations, the valency product terms have been based on the sodium salt and on cobalt chloride. Table 4 contains the measurements and calculations, $\Lambda^0 = 129.6$ being used for cobalt chloride (unpublished work—the data indicate complete ionisation).

Lead lactate has been similarly treated by the mixture method since this salt could not be crystallised. Sodium lactate and lead chloride were used. The latter has a dissociation constant of 0·03 (Righellato and Davies, *loc. cit.*), so that a correction for $PbCl^+$ was necessary. This practically cancels out in the observed and theoretical expressions for κ, and its main

TABLE 4. *Conductivities of cobalt chloride and sodium glycollate or lactate.*

10^4c_1	10^4c_2	$10^4\kappa$ (obs.)	$10^4\kappa$ (theor.)	$10^5\beta$	10^3I	10^3K	10^4c_1	10^4c_2	$10^4\kappa$ (obs.)	$10^4\kappa$ (theor.)	$10^5\beta$	10^3I	10^3K
		Glycollate							Lactate				
18·810	12·651	3·0642	3·1499	7·72	3·624	9·8	26·430	4·706	2·6794	2·7132	3·18	3·286	12·7
18·728	17·324	3·5811	3·6879	9·70	4·278	10·4	26·308	9·637	3·2144	3·2838	6·58	3·945	12·1
18·611	24·105	4·3254	4·4598	12·3	5·229	10·9	26·080	18·974	4·2212	4·3467	11·7	5·219	12·6
10·376	15·516	2·7257	2·7801	4·90	3·255	11·2	25·883	26·978	5·0820	5·2438	15·8	6·321	12·6
24·749	14·859	3·7864	3·9001	10·3	4·498	10·8	7·256	16·784	2·5965	2·6296	3·10	3·180	13·9
							19·560	16·154	3·4325	3·5178	8·12	4·217	12·4
							46·451	14·776	5·2745	5·4205	14·3	6·577	12·8

influence is in correcting the lead-ion concentration in the expression for K, and in the value of I. Table 5 contains the data, where γ represents the $PbCl^+$ concentrations. For lead chloride, $\Lambda^0 = 147·0$ was used (Norman and Garrett, *J. Amer. Chem. Soc.*, 1947, **69**, 110).

TABLE 5. *Conductivity of lead chloride and sodium lactate solutions.*

10^4c_1	10^4c_2	$10^5\beta$	$10^5\gamma$	$10^4\kappa$ (obs.)	$10^4\kappa$ (theor.)	10^4I	10^3K
3·919	2·889	1·42	2·44	0·7093	0·7429	5·569	1·59
5·894	2·874	1·37	3·18	0·8593	0·9028	7·386	1·71
8·333	2·854	1·35	3·99	1·0451	1·0995	9·652	1·74
8·277	7·432	8·67	9·76	1·6053	1·7407	11·73	1·74
5·764	3·651	2·21	3·79	0·9507	1·0026	7·748	1·77
5·746	5·798	5·47	6·05	1·2237	1·3200	8·778	1·65
5·722	8·598	11·7	9·18	1·5764	1·7014	10·10	1·47

The cupric salts had been studied by using the solubility of cupric iodate in solutions of NaR (Lloyd, Wycherley, and Monk, *loc. cit.*). The results suggested that both CuR^+ and CuR_2 are formed, so some fresh measurements were made, and this was confirmed. To calculate both K_1 and K_2 the same method of approximations was used, except that in deriving the amounts of CuR_2, values of K_1 were tried until K_2 remained constant over a concentration range, *i.e.*, the concentrations of CuR^+ were calculated from

$$\log [CuR^+] = \log [Cu^{++}][R^-] - \log K_1 - 2\phi(I)$$

The results are given in Table 6, the solubility in water being taken as $3·26 \times 10^{-3}$ M at 25°. Keefer (*J. Amer. Chem. Soc.*, 1948, **70**, 476) reports the very close figure of $3·245 \times 10^{-3}$, but in

TABLE 6. *Solubility of cupric iodate in sodium glycollate and lactate.*
(Concentrations $\times 10^3$.)

	Glycollate ($10^3K_1 = 1·28$)			Lactate ($10^3K_1 = 0·95$)		
Solubility	6·45	7·36	8·99	6·34	7·70	8·83
Sodium salt	15·12	20·16	30·17	12·69	19·04	25·38
$[Cu^{++}]$	1·07	0·88$_5$	0·67	1·06	0·79	0·65
$[R^-]$	8·41	11·58	18·36	6·26	9·67	14·03
$[CuR^+]$	3·95	4·28	4·75	4·03	4·37	4·93
$[CuR_2]$	1·38	2·15	3·53	1·20	2·50	3·21
10^3I	22·29	27·07	36·85	19·91	25·74	32·20
10^2K_2	1·80	1·69	1·73	1·60	1·24	1·54

previous work (Lloyd, Wycherley, and Monk, *loc. cit.*) $3·33 \times 10^{-3}$ was constantly obtained. The crystals used in obtaining this higher figure were freshly prepared, whereas those used for the present work had been aged for some months, which may explain the difference.

DISCUSSION

A summary of the average pK values obtained in the present work together with some from other sources is given in Table 7. Except for copper and possibly magnesium, the pK's of the glycollates are larger than those of the lactates. The pK order of many copper

salts has been previously explained in terms of induction effects (Lloyd, Wycherley, and Monk, *loc. cit.*), and the electron-displacing ability of the methyl group which accounts for the pK of lactic acid being greater than that of glycollic acid (3·862 and 3·831 at 25° respectively; Harned and Owen, *op. cit.*, p. 580) similarly explains the order of their copper salts. With metals of lower ionisation potential, the overall anion size is generally more important than induction effects (Colman-Porter and Monk, *loc. cit.*) so the pK order of the magnesium salts should be glycollate > lactate. It is noticeable that the pK's of magnesium acetate and propionate are also in the reverse order to the anion size (Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314). The smallness of the magnesium ion may be the reason for this behaviour as it may limit the distance of anion approach; this is referred to on p. 550. Although this does not in itself explain why the larger lactate ion seems to bind slightly more than does the glycollate, yet it may explain why the pK's of this salt are smaller than one would expect from the values of the other alkaline earths, and taken in conjunction with this, the methyl group, in displacing the electrical centre of the

Fig. 1.

Fig. 2.
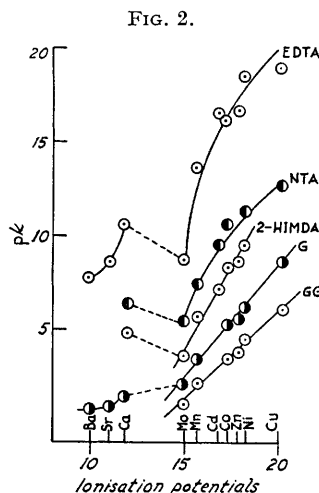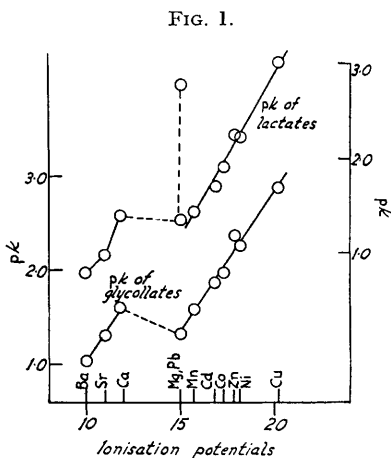
See Table 8 for legends.

carboxylate group nearer to the anion surface, reduces the effective distance of closest approach.

The variations found in any one series on changing the cation have been discussed in several papers. Irving and Williams (*Nature*, 1948, **162**, 746) and Calvin and Melchior

TABLE 7. *Average pK's, ionisation potentials, and cation radii.*

	Ca	Sr	Ba	Mg	Mn	Cd	Co	Zn	Pb	Ni	Cu
pK (Glycollates)	1·59[a]	1·31[b]	1·04[b]	1·33[b]	1·582	1·866	1·975	2·376	—	2·261	2·89 (K_1), 1·77 (K_2)
pK (Lactates)	1·47[a]	0·96[b]	0·77[b]	1·34[b]	1·428	1·695	1·896	2·239	2·777	2·216	3·02 (K_1), 1·82 (K_2)
2nd Ionisation potls. (ev) [c]	11·82	10·98	9·95	14·96	15·70	16·84	17·3	17·89	14·96	18·2	20·2
Cryst. cation radii (Å) [d]	0·99	1·13	1·35	0·65	0·80	0·97	0·72	0·74	1·21	0·70	0·72[e]
λ^0 (cations)	59·50[f]	59·46[f]	63·64[f]	53·06[f]	53·05[g]	52·7[g]	53·5[h]	52·8[g]	70·7[i]	53·7[g]	53·9[j]
Hydrated cation radii (Å)	3·08	3·08	2·88	3·45	3·45	3·48	3·43	3·47	2·59	3·41	3·40

[a] Davies, J., 1938, 277. [b] Colman-Porter and Monk, *loc. cit.* [c] Latimer, " Oxidation Potentials," Prentice-Hall, 1938, p. 14. [d] Pauling, " Nature of the Chemical Bond," Cornell, 1939, p. 346. [e] Ahrens, *Nature*, 1952, **169**, 463. [f] Harned and Owen, *op. cit.*, p. 172. [g] See Table 1. [h] Unpublished work. [i] Norman and Garrett, *loc. cit.* [j] Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074.

(*J. Amer. Chem. Soc.*, 1948, **70**, 3270) suggested that the pK values of several complexes appear to be related to the ionisation potentials of the metals. Previous limited data pointed to magnesium's being an exception to this (Colman-Porter and Monk, *loc. cit.*), and

Williams (*loc. cit.*), considering the Group IIA metals, suggested reasons for the low stability of many magnesium salts (see p. 550). Van Eck (*Rec. Trav. chim.*, 1953, **72**, 50) examined the complexes formed between numerous ligands and up to nine cations. Many of these obey a linear relationship when pK is plotted against the second ionisation potential of the metals, and magnesium does not appear to be anomalous in this scheme. On the other hand, lead and sometimes zinc do not conform. In Fig. 1, the pK data from Table 7 for the lactates and glycollates are plotted against the second ionisation potentials. Again, lead is well out of position, but magnesium fits in fairly well. The plots are not strictly linear, and the other three alkaline earths lie on a separate curve. To compare these salts with some others, further complexes (Table 8) are plotted in Fig. 2. A fairly smooth curve can be drawn from magnesium to copper in all cases, but once more calcium, strontium, and barium have their separate curve, and again lead (not plotted) is unique. The features therefore appear to be general, and as a useful working rule, if the pK values of, say, magnesium and copper are known, those of manganese, cadmium, cobalt, zinc, and nickel can be predicted with reasonable accuracy. Ferrous complexes (iron = 16·15 ev)
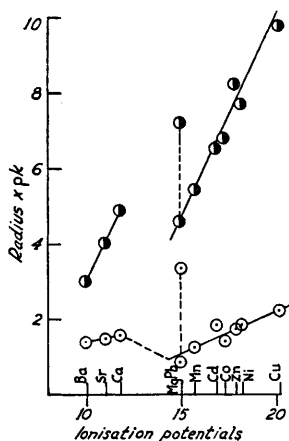

FIG. 3.

⊙ = Crystal radii, ◐ = radii of hydrated ions (Å).
Plots of lactates.

should also fit into this scheme, and for the two cases examined, this seems to be so. These are ethylenediaminetetra-acetic acid (see Table 8) and acetylacetone (Vitert, Fernelius, and Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 2741). The latter data show some scatter, but this may be due to neglect of the incomplete dissociation of the inorganic salts used. The general method of determining the pK's of complexes is to make pH titrations with sodium

TABLE 8. pK *Values of some complexes.* *

	Ca	Sr	Ba	Mg	Mn	Cd	Co	Zn	Pb	Ni	Cu
NTA	6·4	—	—	5·4	7·4	9·5	10·6	10·4	11·8	11·3	12·7
2-HIMDA	4·8	—	—	3·5	5·6	7·1	8·3	8·6	9·5	9·5	—
EDTA	10·6	8·6	7·8	8·7	13·5	16·5	16·1	16·6	18·2	18·5	18·4
G	1·43	0·91	0·77	2·07	3·44	—	5·23	5·52	5·27	6·18	8·62
GG	1·24	—	—	1·06	2·15	—	3·49	3·80	3·23	4·49	6·04

* NTA = Nitrilotriacetic acid (Schwarzenbach, Ackermann, and Ruckstuhl, *Helv. Chim. Acta*, 1949, **32**, 1175; Schwarzenbach and Freitag, *ibid.*, 1951, **34**, 1492). 2-HIMDA = 2-Hydroxyethylimino-diacetic acid (Chaberek, Courtney, and Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5057). EDTA = Ethylenediaminetetra-acetic acid (Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1947, **30**, 1798; Schwarzenbach and Freitag, *ibid.*, 1951, **34**, 576; Schwarzenbach and Heller, *ibid.*, p. 576). G = Glycine, GG = glycylglycine (Monk, *Trans. Faraday Soc.*, 1951, **47**, 297; Colman-Porter and Monk, *loc. cit.*).

hydroxide of inorganic salt-chelating agent mixtures, and sometimes, to overcome solubility difficulties, mixed solvents are used. The ion-association of the inorganic salts is not taken into account, and this may be considerable, especially in mixed solvents. Vitert *et al.* (*loc. cit.*), for instance, obtained different pK's when using chlorides, nitrates, and

perchlorates in mixed solvents, and recognised that the incomplete dissociation of these salts was the probable reason. These authors incidentally (*loc. cit.*, p. 2736) tried plotting pK's against the metal-ion negativities : there is fairly good correspondence, but beryllium, cadmium, and copper are out of line.

The four ions that do not fit in with the main curves of the pK plots of Fig. 1 are relatively large when unhydrated, but are smaller than the others in their hydrated forms. To get some idea of the sizes of the hydrated cations, values (Table 7) have been calculated by means of Stokes's law from the limiting cation mobilities (see Jenkins and Monk, *loc. cit.*). This is admittedly not very accurate, but it serves to give some comparative figures. In general, one would expect pK values to be related to the ion sizes, as well as to the other factors, and to examine this the products of the pK's and both hydrated and unhydrated cation radii are plotted in Fig. 3 against the ionisation potentials (the lactate series has been taken for this). Use of the unhydrated radii seems to show the more promise, but it still does not bring lead into line. Apart from this exception, the inference that interaction involves the bare cations would also seem to receive further support from the hydroxides. Davies (*J.*, 1951, 1256) has shown that the pK's of many hydroxides are related to the bare cation sizes, and Van Eck (*loc. cit.*) has shown that numerous hydroxides fit into the ionisation potential scheme. A fairly regular curve is produced if one plots the product of the pK's and the bare radii against the potentials, thallium and silver being exceptions.

However, one is still forced to recognise that even with this method the lower plot of Fig. 3 for the lactates is in two main parts as in Fig. 1. If magnesium and manganese had larger radii a fairly general curve could be drawn (omitting lead), which brings us back to Williams's suggestion (*loc. cit.*) that the cation size can limit the extent to which anions can approach the small magnesium ion owing to the anion repulsion forces that are set up when the anions are brought into close proximity in the cation neighbourhood. If this is so, the effective radius of the magnesium ion is somewhat greater than the crystallographic value. The same would have to apply, though to a smaller extent, to manganese. On the other hand, the manganese ion is in fact slightly larger than those of zinc and nickel, for instance, so one is by no means certain that this is correct.

The present picture is therefore not entirely satisfactory. Although general features are apparent, the number of exceptions to the various relationships that have been tried indicates that more fundamental principles are involved than those so far considered. A more detailed analysis of the nature of the valency forces may improve the position.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
    UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

U