223. *The Electrolytic Dissociation of Lanthanum Ferricyanide in Mixed Solvents.*

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Conductivity measurements are reported for dilute aqueous solutions of lanthanum ferricyanide in binary mixtures of water with dioxan, acetone, ethylene glycol, and ethanol at 25°. Dissociation constants have been derived, and it is shown that, for the water-rich mixtures studied, the variation of dissociation constant with the dielectric constant of the medium can be accounted for satisfactorily on electrostatic grounds.

The individual deviations of electrolytes from the simple Debye–Hückel and Onsager equations have in many cases been accounted for satisfactorily by the assumption of incomplete dissociation. For a number of salts an adequate explanation is given by the purely electrostatic Bjerrum theory of ion-pair formation; with other salts this treatment gives distances of closest approach of the ions which are considerably less than the corresponding sums of the crystallographic radii, and it is probable that the dissociation is not completely determined by Coulomb forces. The study of variation of dissociation constant with dielectric constant in mixed solvents should provide additional information as to the nature of such association, and may possibly afford a means of distinguishing between the electrostatic and other factors involved. As very few measurements of this nature are available, an investigation has now been made of the dissociation of lanthanum ferricyanide in aqueous dioxan, acetone, ethylene glycol, and ethanol solutions. Lanthanum ferricyanide was chosen as a suitable salt for examination, as it has been shown to behave as a comparatively weak electrolyte in water (Davies and James, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116), and the dissociation constant can be determined with considerable accuracy by a conductivity method.

EXPERIMENTAL.

Materials.—1 : 4-Dioxan (" purissimus " grade) was purified by prolonged refluxing with sodium, and fractional distillation (Kraus and Vingee, *J. Amer. Chem. Soc.*, 1934, **56**, 513). Dielectric constants for aqueous dioxan solutions were obtained from the data of Akerlof and Short (*ibid.*, 1936, **58**, 1241), densities from those of Hovorka (*ibid.*, p. 2264) and of Geddes (*ibid.*, 1933, **55**, 4832), and viscosities from those of Owen and Waters (*ibid.*, 1938, **60**, 2371) and of Geddes (*loc. cit.*).

Acetone (AnalaR) was treated with potassium permanganate, dried (K_2CO_3), and distilled in a stream of dry nitrogen (Schiebe, May, and Fischer, *Ber.*, 1924, **57**, 1330). Dielectric constants for aqueous acetone were obtained from Akerlof's data (*J. Amer. Chem. Soc.*, 1932, **54**, 4132), and densities and viscosities from International Critical Tables.

Ethylene glycol (commercial) was dried (Na_2SO_4), decanted, and distilled twice in an all-glass apparatus under 1 mm. pressure, head and tail fractions being rejected (Smyth and Walls, *J. Amer. Chem. Soc.*, 1931, **53**, 2115). Dielectric constants for aqueous glycol were obtained from Akerlof's data (*loc. cit.*), densities from Knight, Masi, and Roesel's (*J. Amer. Chem. Soc.*, 1946, **68**, 661), and viscosities from Dunstan's (*J.*, 1905, **87**, 11).

Ethanol (" 99% alcohol ") was heated under reflux over freshly fired lime, fractionated, and finally redistilled over aluminium ethoxide (Hartley, *J.*, 1930, 2492). Dielectric constants for aqueous ethanol solutions were obtained from Akerlof's data (*loc. cit.*), and densities and viscosities from International Critical Tables.

The solvents used were stored under nitrogen in sealed glass containers.

Lanthanum ferricyanide, $LaFe(CN)_6,5H_2O$, was prepared and analysed as described by Davies and James (*loc. cit.*).

Procedure.—Conductivity measurements were made at 25° with the apparatus and technique described by Davies (*J.*, 1937, 432). Appropriate quantities of conductivity water and of the organic solvent were weighed into the conductivity cell, and the resistance determined. Small additions of lanthanum ferricyanide stock solution, in mixed solvent of the same composition, were then made from a weight burette, and the resistance measured after each addition. All concentrations were determined by weight, and volume concentrations were calculated from the densities of the mixed solvents, it being assumed that the small amount of salt added did not appreciably alter the density. The results are given in Table I.

DISCUSSION.

Davies and James (*loc. cit.*) have shown that in dilute aqueous solution, lanthanum ferricyanide behaves as a comparatively weak electrolyte, and a value $K = 1{\cdot}82 \times 10^{-4}$ has been derived for its dissociation constant, on the assumption that the limiting Debye–Hückel and Onsager equations are obeyed. A similar treatment has now been applied to the results for this salt in mixed solvents. For each series of measurements, the limiting conductivity Λ_0 has been determined by the method given by Davies (*J.*, 1933, 645) for incompletely dissociated electrolytes; the limitations of such methods have been carefully analysed by Kilpatrick (*J. Chem. Physics*, 1940, **8**, 306), and it would appear that, with electrolytes not weaker than $K \simeq 1 \times 10^{-5}$, only slight errors are liable to occur. In water this extrapolation method gives a value for Λ_0 in good agreement with that obtained independently from the sum of the lanthanum and ferricyanide ionic mobilities (Monk, in the press). Thermodynamic dissociation constants, have been calculated for individual points, are given in Table I, with the mean dissociation constants for each series of measurements in a given mixed solvent. Values of Λ_0 and $\Lambda_0\eta$ are also given, and it may be seen that although Λ_0 varies considerably with change in solvent composition (*e.g.*, in water $\Lambda_0 = 168{\cdot}9$, and in 42·47% w/w glycol, $\Lambda_0 = 57{\cdot}0$) no significant variation in $\Lambda_0\eta$ occurs. Such conformity with Walden's rule is an indication that the effective radii of the solute ions remain almost unchanged. Solvation appears to be predominantly with water molecules, the extent of hydration being almost independent of the absolute concentration of water. This was perhaps to be expected, for in the solvent mixtures studied the molar fraction of water (>80 mols. %) was always much greater than that of the other component of the mixture, and also the tendency for water to form solvated cations is considerably stronger than that of ketones, alcohols, and ethers. Connell, Hamilton, and Butler (*Proc. Roy. Soc.*, 1934, *A*, **157**, 418) have studied the conductivities of lithium chloride and potassium iodide in water–ethanol mixtures, and find that no solvation of the ions by alcohol molecules occurs until about 20 mols. % of alcohol is reached.

TABLE I.

Conductivities of lanthanum ferricyanide solutions in mixed solvents.

(c is given in g.-equivs./litre.)

Dioxan–water mixtures.

9·67% (w/w) Dioxan.
$D = 70·0$, $\Lambda_0 = 138·0$, $\Lambda_0\eta = 1·49$;
mean $K = 7·63 \times 10^{-5}$.

$c \times 10^4$...	2·5421	4·3295	6·5601	9·5877	14·478
Λ	88·34	78·12	70·78	64·19	57·51
$K \times 10^5$	7·66	7·69	7·66	7·62	7·53

18·08% (w/w) Dioxan.
$D = 62·5$, $\Lambda_0 = 124·5$, $\Lambda_0\eta = 1·56$;
mean $K = 2·56 \times 10^{-5}$.

$c \times 10^4$...	2·5888	5·1516	7·1708	10·966	15·574
Λ	58·29	47·69	43·26	37·97	34·10
$K \times 10^5$	2·53	2·57	2·58	2·58	2·56

14·84% (w/w) Dioxan.
$D = 65·4$, $\Lambda_0 = 130·0$, $\Lambda_0\eta = 1·54$;
mean $K = 3·93 \times 10^{-5}$.

$c \times 10^4$...	2·1762	5·0956	7·3913	10·275	14·438
Λ	72·49	58·03	52·26	47·50	43·04
$K \times 10^5$	(3·85)	3·94	3·94	3·94	3·91

24·07% (w/w) Dioxan.
$D = 57·2$, $\Lambda_0 = 110·0$, $\Lambda_0\eta = 1·52$;
mean $K = 1·193 \times 10^{-5}$.

$c \times 10^4$...	2·5664	7·0334	12·463	15·124	19·359
Λ	39·67	28·34	23·35	21·89	20·20
$K \times 10^5$	1·196	1·200	1·195	1·190	1·183

Acetone–water mixtures.

9·00% (w/w) Acetone.
$D = 73·6$, $\Lambda_0 = 131·6$, $\Lambda_0\eta = 1·42$;
mean $K = 12·52 \times 10^{-5}$.

$c \times 10^4$...	1·5749	3·0383	4·7883	7·0618	9·8870
Λ	100·68	90·05	82·17	75·54	69·86
$K \times 10^5$	12·45	12·56	12·53	12·55	12·50

23·57% (w/w) Acetone.
$D = 64·9$, $\Lambda_0 = 103·6$, $\Lambda_0\eta = 1·36$;
mean $K = 4·45 \times 10^{-5}$.

$c \times 10^4$...	1·2617	2·7880	4·9466	7·2372	8·5691
Λ	68·15	56·63	48·62	43·73	41·59
$K \times 10^5$	4·45	4·49	4·47	4·45	4·41

30·49% (w/w) Acetone.
$D = 60·75$, $\Lambda_0 = 100·0$, $\Lambda_0\eta = 1·36$;
mean $K = 2·160 \times 10^{-5}$.

$c \times 10^4$...	2·1864	4·4353	5·9244	8·0335	9·9342
Λ	46·65	37·70	34·42	31·25	29·19
$K \times 10^5$	2·161	2·168	2·164	2·155	2·150

17·83% (w/w) Acetone.
$D = 68·3$, $\Lambda_0 = 110·8$, $\Lambda_0\eta = 1·35$;
mean $K = 7·20 \times 10^{-5}$.

$c \times 10^4$...	1·4492	2·8818	4·7229	6·5979	8·6070
Λ	78·24	68·07	60·57	55·72	51·95
$K \times 10^5$	7·18	7·26	7·20	7·20	7·14

27·32% (w/w) Acetone.
$D = 62·65$, $\Lambda_0 = 102·0$, $\Lambda_0\eta = 1·36$;
mean $K = 2·97 \times 10^{-5}$.

$c \times 10^4$...	2·0594	4·0217	6·4290	7·6875	9·6896
Λ	53·38	44·44	39·05	36·68	34·19
$K \times 10^5$	2·94	2·99	2·99	2·99	2·98

Glycol–water mixtures.

24·25% (w/w) Glycol.
$D = 71·5$, $\Lambda_0 = 87·0$, $\Lambda_0\eta = 1·44$;
mean $K = 9·69 \times 10^{-5}$.

$c \times 10^4$...	2·0037	4·4193	7·1892	9·1217	11·145
Λ	61·23	52·21	46·62	43·92	41·74
$K \times 10^5$	9·67	9·78	9·74	9·67	9·59

37·14% (w/w) Glycol.
$D = 67·5$, $\Lambda_0 = 65·0$, $\Lambda_0\eta = 1·47$;
mean $K = 5·00 \times 10^{-5}$

$c \times 10^4$...	3·3303	7·4270	11·427	14·042	21·502
Λ	34·64	28·22	25·04	23·63	20·97
$K \times 10^5$	4·86	5·02	5·01	5·00	4·95

32·26% (w/w) Glycol.
$D = 69·07$, $\Lambda_0 = 71·0$, $\Lambda_0\eta = 1·42$;
mean $K = 6·97 \times 10^{-5}$.

$c \times 10^4$...	2·1822	4·2806	7·3190	9·0628	11·193
Λ	45·86	39·47	34·48	32·58	30·79
$K \times 10^5$	6·94	7·05	7·02	6·99	6·94

42·47% (w/w) Glycol.
$D = 65·1$, $\Lambda_0 = 57·0$, $\Lambda_0\eta = 1·51$;
mean $K = 3·69 \times 10^{-5}$.

$c \times 10^4$...	4·6609	7·7353	9·9166	13·784	18·463
Λ	25·39	22·12	20·56	18·69	17·18
$K \times 10^5$	3·64	3·72	3·71	3·70	3·68

Ethanol–water mixtures.

14·11% (w/w) Ethanol.
$D = 70·4$, $\Lambda_0 = 103·0$, $\Lambda_0\eta = 1·57$;
mean $K = 7·26 \times 10^{-5}$.

$c \times 10^4$...	1·3924	2·6411	4·3381	6·1564	8·3790
Λ	73·43	64·64	57·65	52·82	48·73
$K \times 10^5$	7·20	7·28	7·29	7·26	7·22

18·89% (w/w) Ethanol.
$D = 67·4$, $\Lambda_0 = 87·0$, $\Lambda_0\eta = 1·52$;
mean $K = 5·04 \times 10^{-5}$.

$c \times 10^4$...	2·6040	4·9131	5·8110	7·2559	8·9311
Λ	49·92	42·47	40·58	38·23	35·99
$K \times 10^5$	5·04	5·05	5·05	5·07	5·02

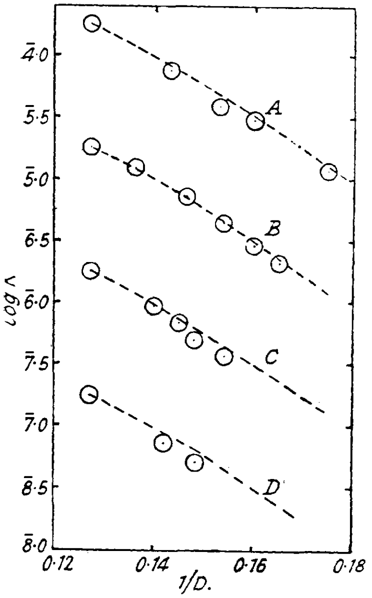
From Bjerrum's theory of ion association (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9) the equilibrium constant K for the formation of an ion pair is given by

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1z_2|}{D\mathbf{k}T}\right)^3 . Q(b)$$

where $Q(b)$ is defined by the integral $Q(b) = \int_2^b e^y y^{-4} dy$, in which $y = |z_1z_2|\varepsilon^2/rD\mathbf{k}T$, $b = |z_1z_2|\varepsilon^2/aD\mathbf{k}T$ and a is the distance of closest approach of the ions. Values of $Q(b)$ and b have been tabulated by Bjerrum (*loc. cit.*) and by Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 1019). Insertion into the above equation of the value $K = 1{\cdot}82 \times 10^{-4}$ for aqueous lanthanum ferricyanide at 25° (Davies and James, *loc. cit.*) gives $a = 7{\cdot}20$ A. This value for the mean ionic diameter being assumed to remain unchanged, values of K have now been calculated for various values of the dielectric constant D, and are represented graphically by the smooth curves in Fig. 1. The observed points are seen to be in good agreement with these curves, the observed decrease in K with decrease in D tending to be slightly greater than the calculated. It appears therefore that in the mixed solvents studied, the variation of K with D can be accounted for on the assumption that Bjerrum ion-pairs formed by stably hydrated lanthanum ions with ferricyanide ions are present, the extent of hydration showing little variation with the water concentration. It has been shown (Davies and James, *loc. cit.*) that the variation of K with temperature over the range 18—30° may also be explained on this assumption. Very few measurements for other salts are available for comparison. Fuoss and Kraus (*loc. cit.*) have shown that ion-pair formation occurs with tetra*iso*amylammonium nitrate in dioxan–water mixtures containing less than about 55% (w/w) of water, the experimentally

FIG. 1.

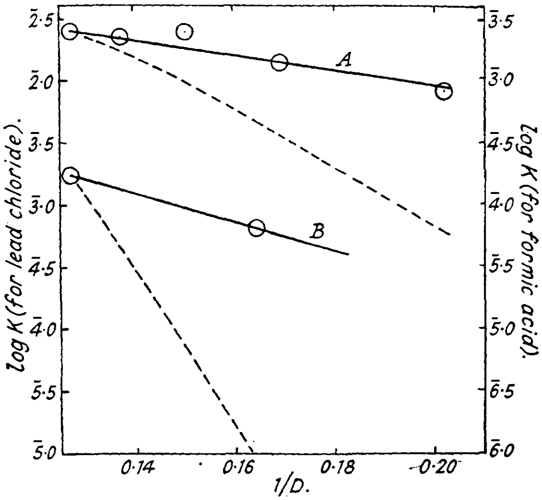
Variation of dissociation constant with dielectric constant for lanthanum ferricyanide in mixed solvents.



A Dioxan–water. B Acetone–water.
C Glycol–water. D Ethanol–water.

The broken curves have been calculated from the Bjerrum equation assuming a = 7·20 A. *for lanthanum ferricyanide in water. Results for acetone, glycol and ethanol–water mixtures have been displaced vertically by* 1, 2, *and* 3pK *units respectively, for clarity.*

FIG. 2.



A Lead chloride in glycol–water mixtures.
B Formic acid in dioxan–water mixtures.
The broken curves have been calculated from the Bjerrum equation.

observed variation of K with D being in excellent agreement with that predicted by the Bjerrum equation.

Lead chloride has been studied in glycol–water mixtures by Norman and Garrett (*J. Amer. Chem. Soc.*, 1947, **69**, 110), and log K values calculated from these measurements (James, *ibid.*, 1949, **71**, 3243) are plotted in Fig. 2, together with values derived from the Bjerrum equation, K being taken as 0·025 for the intermediate ion $PbCl^+$ in water. The observed decrease in K with decrease in D is far smaller than this treatment predicts, although, as Walden's rule is obeyed (water, $\Lambda_0\eta = 1{\cdot}30$; 100% glycol, $\Lambda_0\eta = 1{\cdot}34$), there is no reason to suppose any marked variation in the effective ionic radii. Also, the a value of 1·85 A. derived for aqueous solutions is impossibly small by comparison with the sum of the crystallographic radii, which is 2·75 A. for $PbCl^+$ (Pauling, "Nature of the Chemical Bond," Chap. X). The Bjerrum treatment assumes that ion association is determined purely by Coulomb forces, and its inadequacy in this case indicates that covalent forces are involved in the formation of the $PbCl^+$ ion. The ultra-violet absorption spectra of aqueous solutions have been stated to support this view (Fromherz and Kun-Hou Lih, *Z. physikal. Chem.*, 1931, *A*, **153**, 321).

For silver nitrate, dissociation constants in a number of different solvents are available; values of K, a, and $\Lambda_0\eta$ are given in Table II. Although there is a general tendency for K to decrease with decreasing dielectric constant, other factors are also operative; thus the dielectric constant of ethanol is less than that of benzonitrile, but silver nitrate ionises to a greater extent in ethanol than in benzonitrile. Wide variations in $\Lambda_0\eta$ and a occur, indicating changes in the extent of ionic solvation.

TABLE II.

The dissociation constant and a *parameter of silver nitrate in various solvents.*

Solvent.	D.	$\Lambda_0\eta$.	K.	10^8a, cm.	Reference.
Water	78·5	1·194	1·17	2·42	Robinson and Davies, *J.*, 1937, 574.
Acetonitrile	36	0·640	$1{\cdot}68 \times 10^{-2}$	1·93	Fuoss and Kraus, *loc. cit.*
Methanol	30·3	0·605	$2{\cdot}05 \times 10^{-2}$	3·11	Davies, "The Conductivities of Solutions."
Benzonitrile	26	0·623	$4{\cdot}7 \times 10^{-4}$	1·64	,, ,, ,,
Ethanol	24	0·483	$4{\cdot}4 \times 10^{-3}$	2·79	,, ,, ,,
Ammonia (−33°)	22	0·742	$4{\cdot}85 \times 10^{-3}$	3·45	Fuoss and Kraus, *loc. cit.*
Pyridine	12·4	0·756	$9{\cdot}3 \times 10^{-4}$	6·28	Burgess and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 707.

(The dissociation constants given above refer to 25° unless otherwise stated.)

The data for organic acids in mixed solvents cannot be treated satisfactorily on the basis of simple electrostatic theory. For instance, although formic acid in water has a dissociation constant of $1{\cdot}772 \times 10^{-4}$, almost identical with that for lanthanum ferricyanide, Harned and Done's measurements (*J. Amer. Chem. Soc.*, 1941, **63**, 2579) for formic acid in mixed solvents indicate that the dissociation constant in 20% dioxan is of the order of 100 times greater than the value predicted by the Bjerrum equation (Fig. 2). With weak acids, the binding of ions to form undissociated molecules involves covalent linkage; also, Braude and Stern (*J.*, 1948, 1976) have shown that the state of solvation of hydrogen ions varies markedly with solvent composition in dioxan-water mixtures. Bjerrum's equation cannot therefore be expected to be valid in these circumstances.

It would thus appear that variation of K with D is influenced by changes in the extent of solvation of the solute ions, and also by the nature of the linkage involved in the dissociation process. Where, however, ion-pairs are formed from large spherically symmetrical ions, or large and stably solvated ions, as with tetra*iso*amylammonium nitrate and with lanthanum ferricyanide, variation of K with D is accounted for satisfactorily by the purely electrostatic Bjerrum treatment.

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