54. *Activity Coefficients of Zinc Iodide.*

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The electromotive force of the cell ZnHg(2 phases)|ZnI_2(m)|AgI–Ag, in the concentration range 0·007—0·400 molal, at 25° was measured. The standard potential was calculated as 0·61047 v. by an application of the Gronwall, La Mer, and Greiff extended-term equation. The activity coefficients calculated were found to be those of a typical strong electrolyte.

Activity cœfficients of zinc iodide were obtained by Bates (*J. Amer. Chem. Soc.*, 1938, **60**, 2983) from measurements of the e.m.f. of the cell ZnHg(2 phases)|ZnI_2(m)|AgI–Ag, over the concentration range 0·005—0·800 molal, at 5° intervals from 5° to 40° inclusive. The activity cœfficients obtained were those of a typical strong electrolyte, although at molalities above 0·2 they increased slightly with concentration, an effect which was attributed to increasing solubility of silver iodide in zinc iodide solutions. Further measurements were carried out by Baxter (M.Sc. Thesis, London University, 1939), and by Egan and Partington (*J.*, 1943, 157), who employed the cell Zn|ZnI_2 (m), Hg_2I_2(s)|Hg|Hg_2I_2 ZnI_2 (m)|Zn. The results they obtained were consistent with one another, and gave activity cœfficients which, although normal below 0·05 molar (*i.e.*, agreeing with those obtained by Bates), increased rapidly with concentration above this concentration, reaching the abnormally high value of 2·082 at $c = 0·2631$. Stokes and Lieven (*J. Amer. Chem. Soc.*, 1946, **68**, 1582) and Stokes and Stokes (*Trans. Faraday Soc.*, 1945, **41**, 12) obtained activity cœfficients by the isopiestic vapour pressure method, using potassium chloride as reference, over the concentration range 0·01—10 molar, and their activity coefficients were in good agreement with those of Bates. In this research, measurements of the e.m.f. of the cell ZnHg(2 phases)|ZnI_2 (m)|AgI–Ag have been made in the concentration range 0·007—0·400 molal.

EXPERIMENTAL.

Considerable difficulty was experienced in preparing and using the materials for the cells so as to obtain satisfactory results, and the essential experimental details finally adopted are therefore briefly set out below.

Zinc Iodide.—Constant-boiling hydriodic acid, prepared by passing hydrogen sulphide through a suspension of iodine in water, filtering, and distilling in the dark, was partly neutralised with pure zinc (99·996%, from the Imperial Smelting Co., Avonmouth) till the amber colour disappeared. Alternatively, the acid was neutralised with zinc oxide, and the solution decolourised by warming, in small quantities at a time, and with constant shaking, with a little precipitated silver. The colourless solution so obtained usually gave a slight precipitate with hydrochloric acid, but after standing for a week over zinc, this effect disappeared.

The stock solutions so prepared were kept under hydrogen which had been passed over red-hot copper. Weighed quantities of solution were analysed for zinc as pyrophosphate, and the cell solutions were made by diluting weighed quantities of stock solution with weighed quantities of boiled-out water which had been allowed to cool in an atmosphere of purified hydrogen.

Zinc Amalgam.—This was prepared by warming pure zinc (5 parts) and redistilled mercury (95 parts) in an atmosphere of hydrogen and washing with 0·001N-nitric acid and then with water, and was dried by passing dry hydrogen over the surface of the warm amalgam, which was kept under hydrogen.

Cohen (*Z. physikal. Chem.*, 1905, **34**, 612) gave the potential of the zinc amalgam electrode as 0·6 mv. with respect to pure zinc, but Spencer (*Z. Electrochem.*, 1905, **11**, 681) found it to be zero, or practically so, for amalgams more concentrated than 0·65%. Clayton and Vosburgh (*J. Amer. Chem. Soc.*, 1936, **58**, 2093) with the cell $Zn|Zn^{\bullet\bullet}|ZnHg$, in which the solutions were zinc chloride, sulphate, or acetate, concluded that the potential of zinc amalgam was zero with respect to pure zinc. Their cell solutions were free from dissolved oxygen and the cells were filled in complete absence of air. That this is necessary for the reproducibility of this electrode was shown by Horsch (*ibid.*, 1919, **41**, 1787), with the cell $ZnHg(3{\cdot}6\%)|ZnSO_4,Hg_2SO_4|Hg$. Scatchard and Tefft (*ibid.*, 1930, **52**, 2272), with the cell $ZnHg|ZnCl_2,AgCl|Ag$, found a lowering of e.m.f. of 3—5 mv. on passing air over the surface of the amalgam, and this was accompanied by the formation of a dark scum on the surface.

Silver–Silver Iodide Electrodes.—These were made by heating a paste of silver iodide (1 part) and silver oxide (9 parts) on a platinum-wire spiral at 450—475° for 20 minutes in an electric furnace (Bates, *loc. cit.*). The electrodes were prepared shortly before use, and sets of two prepared at the same time and short-circuited in 0·04N-potassium iodide solution, from which oxygen had been removed by alternately evacuating and sweeping out with purified hydrogen, had an asymmetry potential of only 0·03 mv. To attain reproducibility of this order, rigid exclusion of dissolved oxygen from the solutions is necessary (cf. Owen, *J. Amer. Chem. Soc.*, 1935, **57**, 1527; Taylor and Smith, *Nat. Bur. Stand. J. Res.*, 1939, **22**, 307). It was therefore necessary to perform the operation of filling the cell in an atmosphere of hydrogen. The cell vessel, with the zinc amalgam and the silver–silver iodide electrode in place, was alternately evacuated and filled with hydrogen several times, and the air-free solution forced in by hydrogen pressure. The cell was placed in a thermostat at 25° (± 0·02°); the thermostat, and the potentiometer and its accessories stood on an equipotential metal-foil surface (White, *J. Amer. Chem. Soc.*, 1914, **36**, 2011).

Results.—Table I gives the e.m.f. for different solutions. Duplicate cells agreed to within 0·1 mv.; the cells usually reached equilibrium within ½ hour in the thermostat, but solutions below 0·01738*m* required a longer time. The e.m.f.s then remained constant for 6—8 hours, after which most cells showed a gradual increase. The values of *e* for *m* = 0·0080 and 0·0085 were obtained by interpolation from a large-scale plot of *e* against log *m*. Cells containing solutions which had not been decolourised did not come to satisfactory equilibrium.

TABLE I.

Electromotive forces at 25°.

m (molality).	*e* (volts).	*m* (molality).	*e* (volts).	*m* (molality).	*e* (volts).	*m* (molality).	*e* (volts).
0·00695	0·7943	0·00901	0·7852	0·03442	0·7396	0·11475	0·6977
0·00750	0·7916	0·01222	0·7745	0·04620	0·7293	0·16340	0·6843
0·00800	0·7893	0·01738	0·7626	0·06944	0·7154	0·21993	0·6738
0·00850	0·7872	0·02433	0·7515	0·09021	0·7067	0·39060	0·6495

DISCUSSION.

The e.m.f. is given by

$$e = e_0 - 2{\cdot}303 \,.\, 3\boldsymbol{R}T \log (\gamma\, m_{\pm}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the mean stoicheiometric activity coefficient, and $m_{\pm}$ the mean molality:

$$m_{\pm} = m\, ({\nu_+}^{\nu_+} {\nu_-}^{\nu_-})^{1/\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

ν_+ and ν_- being the numbers of positive and negative ions, respectively, formed by the ionisation of one molecule of electrolyte, and $\nu = \nu_+ + \nu_-$. In this case $m_{\pm} = m \times 4^{1/3}$. At 25°, (1) becomes

$$e = e_0 - 0{\cdot}08871 \log \gamma - 0{\cdot}08871 \log m - 0{\cdot}01782 \quad . \quad . \quad . \quad (3)$$

$$e + 0{\cdot}08871 \log m + 0{\cdot}01782 = e_0' = e_0 - 0{\cdot}08871 \log \gamma \quad . \quad . \quad (4)$$

where e_0 is the standard potential. The evaluation of the standard potential e_0 was carried out by Gronwall, La Mer, and Greiff's extended form of the Debye–Hückel equation (*J. Physical Chem.*, 1931, **35**, 2245) which, with numerical constants substituted, is

$$-\log\gamma = 2\left[1{\cdot}5492\frac{1}{(10^8a)}\cdot\frac{x}{1+x} + 0{\cdot}22105\frac{1}{(10^8a)^2}\phi_1 - 0{\cdot}15771\frac{3}{(10^8a)^3}\phi_2 - 0{\cdot}15771\frac{9}{(10^8a)^3}\phi_3\right] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\phi_1 = 10^2[\tfrac{1}{2}X_2(x) - Y_2(x)]$, $\phi_2 = 10^3[\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)]$, $\phi_3 = 10^3[\tfrac{1}{2}X_3(x) - 2Y_3(x)]$, and $x = \kappa a$;

$1/\kappa$ and a are, respectively, the thickness of the ion atmosphere and the mean distance of closest ionic approach in the Debye–Hückel theory. The values of the natural constants used are $\boldsymbol{N} = 6{\cdot}023 \times 10^{22}$ mole^{-1}, $\boldsymbol{k} = 1{\cdot}3804 \times 10^{-16}$ erg-deg.$^{-1}$, $\boldsymbol{e} = 4{\cdot}8025 \times 10^{10}$ e.s.u., $T_0 = 273{\cdot}16°$, and $D_{25} = 78{\cdot}54$, as quoted by Manov, Bates, Hamer, and Acree (*J. Amer. Chem. Soc.*, 1943, **65**, 1765).

The process for evaluating e_0 is similar to that used by Gronwall, La Mer, and Greiff, by La Mer and Cowperthwaite (*ibid.*, 1931, **53**, 4333), La Mer and Parks (*ibid.*, p. 2040), Bates (*ibid.*, 1939, **61**, 308), and Quentin (*Compt. rend.*, 1935, **200**, 1754). A likely value of a is assumed and $\log\gamma$ calculated for a series of molalities, with the values of ϕ_1 and ϕ_3 tabulated by La Mer, Gronwall, and Sandved (*Physikal. Z.*, 1929, **29**, 358), and of ϕ_2 tabulated by Gronwall, La Mer, and Greiff. The value of e_0 is then found from the relation

$$e = e_0 - 0{\cdot}08871\log\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The value of a giving the most constant value of e_0 is taken as the likeliest value, and the corresponding value of e_0 is employed in finding $\log\gamma$ by equation (6).

TABLE II.

m.	$a = 5{\cdot}9$ A.	$a = 6{\cdot}0$ A.	$a = 6{\cdot}1$ A.	$a = 6{\cdot}2$ A.	$a = 6{\cdot}3$ A.
0·00695	0·113253	0·114259	0·114212	0·113249	0·112748
0·00750	0·116862	0·117592	0·117081	0·116538	0·116050
0·00800	0·119740	0·120501	0·119967	0·119399	0·118883
0·00850	0·123364	0·123321	0·122726	0·122139	0·121598

TABLE III.

m.	$a = 5{\cdot}9$ A.	$a = 6{\cdot}0$ A.	$a = 6{\cdot}1$ A.	$a = 6{\cdot}2$ A.	$a = 6{\cdot}3$ A.
0·00695	0·61064	0·61055	0·61055	0·61064	0·61069
0·00750	0·61056	0·61050	0·61047	0·61059	0·61063
0·00800	0·61048	0·61041	0·61046	0·61051	0·61055
0·00850	0·61038	0·61041	0·61038	0·61051	0·61056
Mean	0·61051	0·61047	0·61047	0·61056	0·61061
Total deviation from mean	0·00034	0·00023	0·00018	0·00021	0·00021

Table II gives the values of $-\log\gamma$ for a values of 5·9, 6·0, 6·1, 6·2, and 6·3 A. Table III gives the values of e_0 obtained for these values of a, as well as the total deviations from the mean values of e_0. The final value of a was taken as 6·1 A., this giving $e_0 = 0{\cdot}61047$ v. Stokes and Stokes (*loc. cit.*) repeated Bates's graphical extrapolation of e_0, with the revised constants and $a = 6$ A., and obtained $e_0 = 0{\cdot}61040$ v.

The stoicheiometric activity coefficients were calculated by (6), and in Table IV are compared with those calculated by the Debye–Hückel equations

$$-\log\gamma = \frac{1{\cdot}0184\sqrt{I}}{1 + 0{\cdot}3286a\sqrt{I}} + \log(1 + 0{\cdot}054m) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$-\log\gamma = \frac{1{\cdot}0184\sqrt{I}}{1 + 0{\cdot}3286a\sqrt{I}} + \log(1 + 0{\cdot}054m) - CI \quad . \quad . \quad . \quad . \quad (8)$$

where $I = \tfrac{1}{2}\Sigma m_i z_i^2$, and C is a constant. The most suitable value of C was found to be 0·115.

TABLE IV.

m.	E.m.f.	Eqn. (7).	Eqn. (8).	*m.*	E.m.f.	Eqn. (7).	Eqn. (8).
0·00695	0·767	0·769	—	0·03442	0·641	0·631	0·643
0·00750	0·762	0·763	—	0·04620	0·624	0·607	0·623
0·00800	0·759	0·758	—	0·06944	0·595	0·570	0·594
0·00850	0·752	0·753	—	0·09021	0·574	0·548	0·579
0·00901	0·749	0·748	—	0·11475	0·570	0·528	0·568
0·01222	0·729	0·722	0·726	0·16340	0·567	0·501	0·557
0·01738	0·699	0·692	0·698	0·21993	0·553	0·479	0·555
0·02433	0·666	0·662	0·670	0·39060	0·585	0·440	0·575

To obtain an idea of the magnitude of the second dissociation $ZnI^{\cdot} \rightleftharpoons Zn^{\cdot\cdot} + I'$, the method of Scatchard and Tefft (*J. Amer. Chem. Soc.*, 1930, **52**, 2270) as modified by Harned and Fitzgerald (*ibid.*, 1936, **58**, 2624) was used. On substituting the Debye–Hückel limiting expression with an added linear term, *viz.*, $-\log\gamma = h\sqrt{m} + Bm$, equation (3) gives

$$e_0' = e + 0{\cdot}08871 \log m + 0{\cdot}01782 - 0{\cdot}155\sqrt{m} = e_0 - Bm \quad . \quad . \quad . \quad (9)$$

Scatchard and Tefft showed that e_0' when plotted against $\sqrt{m}$ for various bivalent metal chlorides gave curves with a characteristic maximum, which they attributed to incomplete dissociation of the ion $MX^{\cdot}$. To obtain an estimate of the corresponding equilibrium constant K_2 a plot of $e_0' - e_0$ against $m^{1/2}$ is compared with theoretical plots constructed for different values of K_2. The plot for the zinc iodide data obtained in this research corresponded with a very large value of K_2 in the dilute solutions. By the same method, Bates estimated K_2 as being of the order of 10, and Sillén and Liljeqvist (*Svensk Kem. Tidskr.*, 1944, **56**, 85), by potentiometric titration, obtained a value of about 5. It appears, therefore, that the assumption of complete dissociation of zinc iodide is justified, this salt behaving as a normal strong electrolyte. The activity coefficients obtained are in good agreement with those obtained by Bates, Stokes, and Stokes, and Stokes and Lieven. The value of 6·1 A. obtained for the mean distance of closest ionic approach is smaller than the minimum distance of 7 A. required by Bjerrum's theory (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9) to exclude ion association for a bi-univalent electrolyte, and hence a certain amount of ion association of this kind would have been expected to occur in zinc iodide solutions.

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