chloro-4-quinoline aldehyde was heated at 90–95° for two hours. On cooling the aldimine crystallized. After two recrystallizations from benzene it weighed 2.9 g., and melted at 125–125.5°.

Anal. Calcd. for $C_{12}H_{11}N_2OCl$: C, 61.4; H, 4.73; N, 11.94. Found: C, 61.36; H, 4.96; N, 12.0.

A solution of 2.66 g. of the aldimine in 100 ml. of absolute alcohol containing 0.05 g. of pre-reduced platinum oxide was shaken with hydrogen at 40 lb./sq. in. until absorption ceased (forty minutes). The product crystallized on evaporation of part of the solvent, and melted at 147–150° (dec.).

Anal. Calcd. for $C_{12}H_{13}N_2OCl$: C, 60.9; H, 5.54; Cl, 15.0. Found: C, 60.7; H, 5.23; Cl, 15.2.

6-Chloro-α-(4-diethylamino-1-methylbutylamino)-lepidine.—A mixture of 4.1 g. of pure Noval diamine and 4.8 g. of 6-chloro-4-quinoline aldehyde was warmed at 75–80° for forty minutes. It was then dissolved in 75 ml. of absolute ethanol and shaken with hydrogen in the presence of 0.1 g. of pre-reduced platinum oxide. Absorption was complete in ninety minutes. The alcohol was removed, the residue taken up in dilute hydrochloric acid, and the *p*H adjusted to 6, to precipitate any unreacted aldehyde or its reduction product. The filtrate was made strongly basic, and the amine taken up in ether. Distillation of the extract gave 5.6 g. (67%) of a light yellow oil, b. p. 171–174° (0.04 mm.), $n^{20}D$ 1.5587–1.5593. The oil was dissolved in *n*-propanol and two equivalents of propanolic hydrogen chloride added. On cooling the dihydrochloride separated, m. p. 149–151.5°.

Anal. Calcd. for $C_{19}H_{30}N_3Cl_3 \cdot H_2O$: C, 53.7; H, 7.59; N, 9.89; Cl, 25.0. Found: C, 53.8; H, 7.6; N, 10.3; Cl, 24.6.

7-Chloro-α-(β-hydroxyethylamino)-lepidine, SN-8646.[13]—A mixture of 5.44 g. of 7-chloro-4-quinoline aldehyde and 1.8 g. of ethanolamine was heated at 80–90° for forty minutes, and then hydrogenated in 100 ml. of absolute ethanol in the presence of 0.1 g. of pre-reduced platinum oxide. The solvent was evaporated and the residue washed with a little cold acetone to remove adhering oil. The white crystalline product melted at 123–125° and weighed 3.7 g. (55%). It was soluble in alcohol and hot dioxane, insoluble in acetone.

Anal. Calcd. for $C_{12}H_{13}N_2OCl$: C, 60.9; H, 5.54; Cl, 15.0. Found: C, 61.2; H, 5.4; Cl, 14.9.

The hydrochloride was prepared by evaporating a solution of the base in dilute hydrochloric acid. The hygroscopic hydrochloride melted at 110°.

7-Chloro-α-(4-diethylamino-1-methylbutylamino)-lepidine, SN-11,197.—This was prepared as described for the 6-chloro isomer. The product was a light yellow oil, b. p. 179–184° (0.07 mm.) and was obtained in 67% yield. The dihydrochloride, prepared in propanol, melted at 106–108°.

Anal. Calcd. for $C_{19}H_{30}N_3Cl_3 \cdot 2H_2O$: C, 51.5; H, 7.74; N, 9.5; Cl, 24.0. Found: C, 51.66; H, 7.89; N, 9.1; Cl, 24.3.

6-Ethylaminohexylamine.—6-Bromohexylphthalimide (67 g.) was added to a solution of 45 g. of ethylamine in 100 ml. of dry benzene, at 10°, and the reaction mixture was allowed to stand with occasional cooling, for twenty-four hours. The benzene solution was extracted with dilute hydrochloric acid, and the extract made strongly basic. The dark oil was hydrolyzed with hydrazine hydrate and hydrochloric acid.[14] The amine, obtained in 10–15 g. yield, had b. p. 82–84° (5 mm.), $n^{20}D$ 1.4512, d^{20}_4 0.8431, *MR*D obs. 46.0, *MR*D calcd. 46.2.

Anal. Calcd. for $C_8H_{20}N_2$: N, 19.42. Found; N, 19.61.

The diamine dihydrochloride melted at 200–203°.

7-Chloro-α-(6-ethylaminohexylamino)-lepidine, SN-13,154.—This was prepared from 7.2 g. of 6-ethylaminohexylamine and 9.5 g. of 7-chloro-4-quinoline aldehyde. The product, a light yellow oil, was obtained in 7 g. (44%) yield; it had b. p. 190–195° (0.2 mm.), $n^{20}D$ 1.5563. The dihydrochloride, prepared in propanol, melted at 195–200°.

Anal. Calcd. for $C_{18}H_{28}N_3Cl_3$: C, 55.0; H, 7.16; Cl, 27.1. Found: C, 54.7; H, 7.43; Cl, 27.3.

Summary

1. Several lepidylamines derived from 6-chlorolepidine and 7-chlorolepidine have been prepared.

2. 7-Chlorolepidine, 6-chloro- and 7-chloro-4-quinoline aldehyde and the corresponding carbinols have been synthesized.

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[13] The numbers are those assigned by the Survey of Antimalarial Drugs to identify the drugs in their records. The antimalarial properties of these substances will be tabulated in a forthcoming monograph.

[14] Manske, *J. Chem. Soc.*, 2348 (1926).

NOTRE DAME, INDIANA RECEIVED APRIL 5, 1946

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

Transference Numbers and Activity Coefficients in Zinc Iodide Solutions at 25°

BY R. H. STOKES[1] AND BARBARA J. LEVIEN

A comparison of the activity coefficients of the halides, perchlorates and nitrates of zinc with those of magnesium has shown[2] that the halides of zinc exhibit increasing abnormality in passing from the iodide through the bromide to the chloride. A parallel behavior is found in the transference numbers, for while that of zinc perchlorate is normal up to the highest concentration measured (4 *M*), the cationic transference numbers of the chloride and bromide fall rapidly with increasing concentration, reaching negative values above 2 *M* in zinc chloride solutions[3] and above 2.7 *M* in zinc bromide solutions.[4] The only work on concentrated solutions of the iodide appears to be that of Hittorf,[5] who made only three measurements. The present paper reports activity coefficients and transference numbers of zinc iodide from 0.05 to 10 *M*, derived from isopiestic vapour pressure data and e. m. f. measurements on cells with transference, at 25°.

Experimental.—The technique of isopiestic measurements on zinc iodide solutions has been

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[2] R. H. Stokes and B. J. Levien, THIS JOURNAL, **68**, 333 (1946).

[3] A. C. Harris and H. N. Parton, *Trans. Faraday Soc.*, **36**, 1139 (1940).

[4] H. N. Parton and J. W. Mitchell, *ibid.*, **35**, 758 (1939).

[5] W. Hittorf, *Pogg. Ann.*, **106**, 513 (1859).

described elsewhere.[6] For the more concentrated solutions used here, sodium chloride and sulfuric acid were taken as standard substances, the experimental results being given in Table I. Osmotic and activity coefficients derived therefrom are given in Table II. Recent improvement in our knowledge of the vapor pressures of sodium and potassium chloride[7] solutions has necessitated recalculation of the results for zinc iodide up to 2.5 *M*: consequently the values in Table II differ somewhat from those given earlier.[6] The method of setting up and measuring the cells

$$\text{Zn-Hg(2-phase)} \mid \text{ZnI}_2(m_1) \mid \text{ZnI}_2(m_2) \mid \text{Zn-Hg(2-phase)}$$

was similar to that already described[2] for cells containing zinc perchlorate. In all cases m_1 was 0.3 *M*, whilst m_2 was close to a round molality. A small correction (of the order of 0.1 mv.) was subsequently made to the e. m. f. from a plot of a suitable deviation function, to give the e. m. f. at the exact round value, reported as E_t in Table III. The e. m. f. reached its equilibrium value in less than an hour, and remained constant within 0.03 mv. for at least twenty-four hours.

TABLE I

ISOPIESTIC SOLUTIONS OF ZINC IODIDE AND EITHER SODIUM CHLORIDE OR SULFURIC ACID AT 25°

m_{ZnI_2}	m_{NaCl}	m_{ZnI_2}	m_{NaCl}	m_{ZnI_2}	m_{NaCl}
1.167	2.208	1.253	2.369	1.335	2.519
1.350	2.548	2.234	3.847	2.554	4.263
3.113	4.960				
m_{ZnI_2}	$m_{\text{H}_2\text{SO}_4}$	m_{ZnI_2}	$m_{\text{H}_2\text{SO}_4}$	$m_{\text{H}_2\text{SO}_4}$	m_{ZnI_2}
2.204	2.880	2.737	3.331	3.682	4.079
3.814	4.183	3.825	4.190	4.033	4.354
4.595	4.829	4.950	5.156	5.192	5.364
5.593	5.714	5.848	5.966	5.956	6.070
6.392	6.498	6.542	6.652	6.848	6.965
7.963	8.186	8.454	8.761	9.464	9.934
9.994	10.546	10.960	11.638	11.892	12.638

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF ZINC IODIDE SOLUTIONS AT 25°

m	ϕ	γ	m	ϕ	γ
0.05	0.890	0.619	5.5	1.431	1.613
0.1	0.893	.581	6.0	1.488	1.777
0.3	0.957	.564	6.5	1.553	1.977
0.6	1.083	.645	7.0	1.622	2.212
1.0	1.220	.800	7.5	1.696	2.493
1.3	1.274	.901	8.0	1.775	2.830
1.6	1.291	.972	8.5	1.849	3.201
1.9	1.287	1.018	9.0	1.919	3.610
2.5	1.262	1.070	9.5	1.982	4.047
3.0	1.259	1.119	10.0	2.038	4.510
3.5	1.276	1.185	10.5	2.089	4.997
4.0	1.302	1.264	11.0	2.134	5.504
4.5	1.339	1.362	11.5	2.172	6.018
5.0	1.386	1.483	12.0	2.205	6.543

TABLE III

E_t = E. M. F. OF THE CELL: $\text{Zn-Hg (2)PHASE-} \mid \text{ZnI}_2\ 0.3M \mid \text{ZnI}_2\ m \mid \text{Zn-Hg (2-PHASE)}$.

E = e. m. f. of the corresponding cell without liquid junction (calculated from the activity coefficients)

n_+ = transference number of the zinc ion (all at 25°)

m	E_t, mv.	E, mv.	n_+	δ, mv.
0.05	−41.81	−65.11	0.382	−0.06
.1	−26.89	−41.18	.363	.03
.3	(0.00)	(0.00)	.332	.00
.6	21.39	31.87	.317	.08
1.0	40.90	59.83	.291	.01
1.3	51.53	74.53	.269	− .05
1.6	59.63	85.47	.234	.02
1.9	66.19	93.86	.192	.05
2.5	76.90	106.35	.115	− .09
3.0	84.73	115.09	.056	.02
4.0	100.43	130.90	−.050	.03
5.0	116.81	145.64	−.190	.11
5.75	130.07	156.13	−.300	.00
8.0	174.73	188.63	−.444	.00
10.0	214.49	215.19	−.550	− .01

In the case of zinc iodide it would be possible to measure directly the e. m. f.'s of the cell without transference, as was done by Bates using the zinc amalgam and silver–silver iodide electrodes. Such e. m. f.'s would, however, be subject to large errors arising from the solubility of silver iodide in the electrolyte; Bates[8] noted that this solubility was appreciable even in the region of 0.5 *M*. Hence we have preferred to calculate the e. m. f.'s from the activity coefficients of Table II, using the relation

$$E = 0.08871 \log (m_2\gamma_2/m_1\gamma_1)$$

The relation between E_t and E was too complicated to fit to an equation, so the anion transference number, $n_- = \mathrm{d}E_t/\mathrm{d}E$, was obtained by interpolating E_t to round values of E at 10-mv. intervals, and then differentiating by the method of Rutledge.[9] The differential coefficients were then plotted against E and read off at the values of E corresponding to the round molalities in Table III. These final values were checked by graphical integration of the relation

$$E - E_t = \int_{0.3}^{m} n_+ \, \mathrm{d}E$$

where n_+, the transference number of the zinc ion, is equal to $(1 - \mathrm{d}E_t/\mathrm{d}E)$. The column titled δ in Table III gives the difference between the observed values of E_t and those found by the graphical integration, and shows the check to be quite satisfactory.

Discussion.—The transference numbers of the zinc ion are plotted against $\sqrt{m}$ in Fig. 1. The value of 0.410 for zero concentration was calculated from the accepted limiting mobilities, and is seen to be quite consistent with the results in Table III. The gradual fall up to about 1 *M* is similar to that found with zinc perchlorate, and

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(6) R. H. Stokes, *Trans. Faraday Soc.*, **41**, 12 (1945).

(7) R. A. Robinson, *Trans. Roy. Soc. N. Z.*, **75**, 203 (1945). A summary of Robinson's revised data for NaCl and KCl was given in an appendix to a previous paper, ref. 2.

(8) R. G. Bates, THIS JOURNAL, **60**, 2983 (1938).

(9) G. Rutledge, *Phys. Rev.*, **40**, 262 (1932).

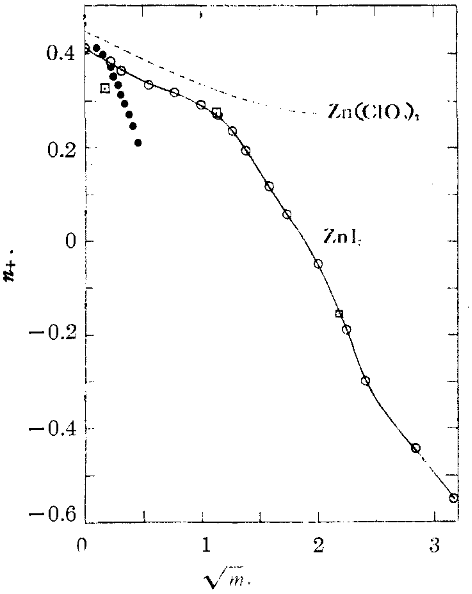

Fig. 1.—Transference numbers in zinc iodide solutions: ⊙, present work; ●, Egan and Partington; ⊡, Hittorf. Hittorf's measurements were at an unspecified temperature, probably about 15°.

does not suggest any significant amount of abnormality in solutions below this concentration. Above 1 *M*, however, the transference number turns sharply downward, becoming negative at 3.53 *M*. In zinc chloride, negative values are reached above 2 *M*, and in zinc bromide above 2.7 *M;* consequently we may conclude that the tendency to form complex ions is greatest in the chloride, and least in the iodide. It is noteworthy that this order is the reverse of that found among the cadmium halides: it is however confirmed by the order of the activity coefficient curves, as was clearly shown in an earlier paper.[2]

The points of Hittorf[5] at 4.73 *M* ($n = -0.157$) and 1.277 *M* ($n = 0.273$) lie very close to our curve, but his dilute solution at 0.0278 *M* ($n = 0.325$) gives a point well below it, and scarcely compatible with the value at zero concentration. It seems possible that the Hittorf method does not work satisfactorily in dilute solutions of zinc iodide, as Egan and Partington,[10] using it in solutions below 0.2 *M*, obtained results widely different from both ours and Hittorf's. They interpreted their results as showing the formation of complex ions even in such dilute solutions, but weakened their case considerably by quoting in support of it the extremely high values of the activity coefficients of zinc iodide found by them[11] in an e. m. f. investigation. In reality complex ion formation must be associated with abnormally low activity coefficients, since it causes a reduction in the total number of ions present. For example, cadmium iodide, a well established case of complex ion formation, has an activity coefficient of only 0.068 at 0.2 *M*, as compared with 0.478 for calcium chloride, a typical normal salt of the same valency type. Furthermore, it has been shown[6] that the work from which they derived the high activity coefficients in question is quite incompatible with the isopiestic data for zinc iodide and with the e. m. f. measurements of Bates.[8] These latter are in satisfactory agreement, and confirm the conclusions of the present paper in indicating normal behaviour below 1 *M*.

We wish to thank Dr. R. A. Robinson for his interest in this work.

Summary

Isopiestic vapor pressure measurements have been made to determine the activity coefficients of zinc iodide in aqueous solutions up to 12 *M* at 25°. These have been combined with e. m. f. measurements of cells with transference to give the transference numbers of the zinc ion from 0.05 up to 10 *M*. The transference number is normal up to about 1 *M*, but thereafter falls rapidly, becoming negative above 3.5 *M*. Thus zinc iodide forms complex anions less readily than the bromide, which in turn does so less readily than the chloride.

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[10] D. M. Egan and J. R. Partington, *J. Chem. Soc.*, 191 (1945).

[11] D. M. Egan and J. R. Partington, *ibid.*, 157 (1943).