[CONTRIBUTION NO. 1246 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Activity Coefficient of Hydrochloric Acid in Concentrated Aqueous Higher Valence Type Chloride Solutions at 25°. I. The System Hydrochloric Acid–Barium Chloride

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From electromotive force measurements of suitable cells, the activity coefficient of hydrochloric acid in barium chloride solutions has been computed in mixtures of 1, 2 and 3 ionic strengths. It is shown that at these concentrations, the logarithm of the activity coefficient of the acid varies linearly with the acid concentration. Following a procedure adopted by Harned which employed the Gibbs–Duhem equation and considerations arising from the application of cross differentiation relations as suggested by Glueckauf, these data are subjected to a critical examination.

From measurements of the electromotive forces of cells of the type

$$H_2 \,|\, HX(m_1),\ MX_n(m_2) \,|\, AgX\text{–}Ag$$

the activity coefficient of the acid may be determined in the presence of the salt at all compositions at a given constant total molality. With cells containing 1–1 chlorides, Harned[1] and Hawkins[2] showed that at constant total molalities varying from 1 to 6 *M*, the logarithm of the activity coefficient of the acid varied linearly with its concentration. Since the use of these cells has not been fully exploited for studying mixtures containing unsymmetrical type electrolytes, measurements of high accuracy of cells containing the systems $HCl\text{–}BaCl_2$, $HCl\text{–}SrCl_2$, $HCl\text{–}AlCl_3$, $HCl\text{–}ThCl_4$, etc., are being carried out in this Laboratory. The principal object of these experiments is to test the limits of validity of the linear relationship.

Thermodynamic Development—Applications of the Gibbs–Duhem Equation

The thermodynamic theory of systems containing two electrolytes and the solvent component has recently been developed by Glueckauf,[3] McKay[4] and their colleagues. These contributions have been largely concerned with the computation of the activity coefficients of the components from measurements of the vapor pressure. Since the electromotive force method leads to the determination of one of the electrolytic components, the method employed by Harned[5] is a suitable one for the present occasion and in the sequel will be extended to systems containing two electrolytes of any valence types in a given solvent.

Since at constant total ionic strength the logarithms of the activity coefficients of many electrolytes appear to vary linearly with their ionic strengths, we shall assume a linear variation of both electrolytic components (1) and (2) as

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \pm \Delta_1 \qquad (1)$$
$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \pm \Delta_2 \qquad (2)$$
$$\mu_1 + \mu_2 = \mu = \text{constant} \qquad (3)$$

In these equations, γ_1 and γ_2 are the activity coefficients of components 1 and 2 in the mixtures, $\gamma_{1(0)}$ and $\gamma_{2(0)}$ their activity coefficients in pure solvent, μ_1 and μ_2 their concentrations expressed as ionic strengths, and α_{12} and α_{21} are the linear constants at a given total ionic strength. The quantities Δ_1 and Δ_2 represent deviations, to be determined by experiment for each individual system. To avoid complicating the subsequent algebraic expressions, we shall omit any speculation as to the nature or magnitude of these deviations since in many cases they are known to be small, even negligible.

Since we consider only that weight of solution containing 1000 g. of water, the Gibbs–Duhem equation may be written in the form

$$\nu_1 m_1 \,\mathrm{d}\ln\gamma_1 + \nu_2 m_2 \,\mathrm{d}\ln\gamma_2 + \nu_1 \mathrm{d}m_1 + \nu_2 \mathrm{d}m_2 = -55.5 \,\mathrm{d}\ln a_w \qquad (4)$$

where a_w is the activity of the water. This equation is subject to the restriction that the pressure and temperature remain constant and that the system be in equilibrium. Although there are no restrictions on composition inherent in equation 4, we impose the condition that all variations in composition occur in such a way that the total ionic strength, μ, remains constant.

The ionic strength is defined by

$$\mu = \Sigma \frac{m_i z_i^2}{2} \qquad (5)$$

where m_i is the molality of the ion and z_i its valence and where the summation is for all the ions in the solution. For any two electrolytes in a mixture, we may relate the ionic strength of each to its respective stoichiometric concentration by

$$\mu_1 = jm_1$$
$$\mu_2 = km_2 \qquad (6)$$

where m_1, m_2 are the molalities and j and k are constants each of which is characteristic of the valence type of electrolyte. By utilizing these relations, equation 4 becomes

$$\frac{\nu_1\mu_1}{j}\,\mathrm{d}\ln\gamma_1 + \frac{\nu_2\mu_2}{k}\,\mathrm{d}\ln\gamma_2 + \frac{\nu_1\mathrm{d}\mu_1}{j} + \frac{\nu_2\mathrm{d}\mu_2}{k} = -55.5\,\mathrm{d}\ln a_w \qquad (7)$$

Consider the hypothetical system in which both linearity rules 1 and 2 are simultaneously valid and introduce a variable $0 \leq x \leq 1$ defined by the equations

$$\mu_1 = x\mu \qquad (8)$$
$$\mu_2 = (1 - x)\mu \qquad (9)$$

so that

$$\mathrm{d}\log\gamma_1 = -\alpha_{12}\mathrm{d}\mu_2 = \alpha_{12}\mu\mathrm{d}x \qquad (10)$$
$$\mathrm{d}\log\gamma_2 = -\alpha_{21}\mathrm{d}\mu_1 = -\alpha_{21}\mu\mathrm{d}x \qquad (11)$$

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[1] H. S. Harned, THIS JOURNAL, **48**, 326 (1926).

[2] J. E. Hawkins, *ibid.*, **54**, 4480 (1932).

[3] E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *J. Chem. Soc.*, S 299 (1949); *Trans. Faraday Soc.*, **47**, 428 (1951).

[4] H. A. C. McKay, *ibid.*, **48**, 1103 (1952); **49**, 237 (1953); H. A. C. McKay and A. R. Mathieson, *ibid.*, **47**, 428 (1951); I. L. Jenkins and H. A. C. McKay, *ibid.*, **50**, 107 (1954).

[5] H. S. Harued, THIS JOURNAL, **57**, 1865 (1935); H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 462.

with the restriction that

$$d\mu_1 = -d\mu_2 \qquad (12)$$

Upon utilization of these relations, equation 7 becomes

$$\left(\frac{\nu_1}{j}\,\alpha_{12} + \frac{\nu_2}{k}\,\alpha_{21}\right) x\mathrm{d}x + \left(\frac{\nu_1}{2.3j\mu} - \frac{\nu_2}{2.3k\mu} - \frac{\nu_2}{k}\,\alpha_{21}\right) \mathrm{d}x = -\frac{55.5}{2.3\mu^2}\,\mathrm{d}\ln a_{\mathrm{w}} \qquad (13)$$

upon suitable rearrangement. Integrating between the limits $x = 0$ and x

$$\left(\frac{\nu_1}{j}\,\alpha_{12} + \frac{\nu_2}{k}\,\alpha_{21}\right) \frac{x^2}{2} + \left(\frac{\nu_1}{2.3j\mu} + \frac{\nu_2}{2.3k\mu} - \frac{\nu_2}{k}\,\alpha_{21}\right) x = -\frac{55.5}{2.3\mu^2}\ln\frac{a_{\mathrm{w(x)}}}{a_{\mathrm{w(0)}}} \qquad (14)$$

This equation expresses the solvent activity in all solutions at constant pressure, temperature at a fixed total ionic strength providing α_{12} and α_{21} which are functions of μ are known. For convenience in the subsequent calculations, it is customary to express the water activity in terms of the practical osmotic coefficient, ϕ.

The practical osmotic coefficient for aqueous solutions is defined by

$$\mu_{\mathrm{w}} = \mu^0_{\mathrm{w}} - \frac{\phi RT}{55.5}\,\Sigma m_{\mathrm{i}} \qquad (15)$$

where μ_{w} is the chemical potential of the solvent, $\mu^{\circ}{}_{\mathrm{w}}$ is its chemical potential in a chosen standard state and the summation is over the molalities of all the ionic species present. Since the solvent activity is defined by the expression

$$\mu_{\mathrm{w}} = \mu^0{}_{\mathrm{w}} + RT\ln a_{\mathrm{w}}$$

it follows that

$$\ln a_{\mathrm{w}} = -\frac{\phi}{55.5}\,\Sigma m_{\mathrm{i}} \qquad (16)$$

$$\ln a_{\mathrm{w}} = -\frac{\phi_1}{55.5}\,\nu_1 m_1 \qquad (17)$$

$$\ln a_{\mathrm{w}} = -\frac{\phi_2}{55.5}\,\nu_2 m_2 \qquad (18)$$

for the single electrolytes 1 and 2, respectively. In a solution containing both electrolytes 1 and 2

$$\mu_1 = x\mu = \frac{m_1}{2}\,(\nu_{1+}z^2_{1+} + \nu_{1-}z^2_{1-}) \qquad (19)$$

$$\mu_2 = (1 - x)\mu = \frac{m_2}{2}\,(\nu_{2+}z^2_{2+} + \nu_{2-}z^2_{2-}) \qquad (20)$$

Electrical neutrality requires the equalities

$$\nu_{1+}z_{1+} = \nu_{1-}z_{1-},\ \nu_{2+}z_{2+} = \nu_{2-}z_{2-}$$

and since $\nu_1 = \nu_{1+} + \nu_{1-}$, $\nu_2 = \nu_{2+} + \nu_{2-}$

$$m_1 = \frac{2x\mu}{\nu_1 z_{1+}z_{1-}} \qquad (21)$$

$$m_2 = \frac{2(1 - x)\mu}{\nu_2 z_{2+}z_{2-}} \qquad (22)$$

Therefore

$$\Sigma m_{\mathrm{i}} = \nu_1 m_1 + \nu_2 m_2 = 2\mu\left[\frac{x}{z_{1+}z_{1-}} + \frac{(1 - x)}{z_{2+}z_{2-}}\right] \qquad (23)$$

In these equations the subscripts 1+, 1−, 2+, 2−, indicate, respectively, the cations and anions of electrolytes 1 and 2. As a consequence of equations 10, 11 and 23

$$-\log a_{\mathrm{w(x)}} = \frac{2\mu\phi_{\mathrm{x}}}{(2.3)(55.5)}\left[\frac{x}{z_{1+}z_{1-}} - \frac{(1 - x)}{z_{2+}z_{2-}}\right] \qquad (24)$$

This equation in combination with (14) yields the expression

$$\left(\frac{\nu_1}{j}\,\alpha_{12} + \frac{\nu_2}{k}\,\alpha_{21}\right) \frac{x^2}{2} + \left(\frac{\nu_1}{2.3j\mu} - \frac{\nu_2}{2.3k\mu} - \frac{\nu_2}{k}\,\alpha_{21}\right)_{\mathrm{x}} = \frac{2}{2.3\mu}\,\frac{\phi_2}{z_{2+}z_{2-}} + \frac{2\phi_{\mathrm{x}}}{2.3\mu}\left[\frac{x}{z_{1+}z_{1-}} - \frac{(1 - x)}{z_{2+}z_{2-}}\right] \qquad (25)$$

which may be used to calculate the osmotic coefficient and, hence, the water activity and vapor pressure for a solution of any composition of two strong electrolytes provided that α_{12} and α_{21} are known at a particular total ionic strength, μ, of the mixture, that the osmotic coefficient ϕ_2 for electrolyte 2 alone is available, and that both linearity rules 1 and 2 are obeyed.

The experiments under consideration determine the activity coefficient of the acid in the salt solution from which α_{12} may be computed. No method is known to evaluate the activity coefficient of the salt in these acid solutions and, subsequently, α_{21}. To obtain this quantity, equation 13 is integrated over the entire range of x, that is, from $x = 0$, corresponding to a solution of electrolyte 1 alone, to $x = 1$, which corresponds to a solution of electrolyte 2. The result is

$$\frac{1}{2}\left(\frac{\nu_1}{j}\,\alpha_{12} + \frac{\nu_2}{k}\,\alpha_{21}\right) + \left(\frac{\nu_1}{2.3j\mu} - \frac{\nu_2}{2.3k\mu} - \frac{\nu_2}{k}\,\alpha_{21}\right) = \frac{2}{2.3\mu}\left(\frac{\phi_1}{z_{1+}z_{1-}} - \frac{\phi_2}{z_{2+}z_{2-}}\right) \qquad (26)$$

which, after replacing j and k by their equivalents μ_1/m_1 and μ_2/m_2 and rearranging, reduces to

$$\frac{\alpha_{21}}{z_{2+}z_{2-}} = \frac{\alpha_{12}}{z_{1+}z_{1-}} - \frac{2}{2.3\mu}\left[\left(\frac{\phi_1}{z_{1+}z_{1-}} - \frac{\phi_2}{z_{2+}z_{2-}}\right) - \left(\frac{1}{z_{1+}z_{1-}} - \frac{1}{z_{2+}z_{2-}}\right)\right] \qquad (27)$$

For mixtures of hydrochloric acid and higher valence type chlorides, $z_{1+} = z_{1-} = z_{2-} = 1$ it follows that

$$\frac{\alpha_{21}}{z_{2+}} = \alpha_{12} - \frac{2}{2.3\mu}\left[\left(\phi_1 - \frac{\phi_2}{z_{2+}}\right) - \left(1 - \frac{1}{z_{2+}}\right)\right] \qquad (28)$$

Further Thermodynamic Developments

Application of the Cross Differentiation Products

A very valuable contribution recently has been made by Glueckauf[3] who has applied the fundamental cross differentiation equations

$$\nu_1\left(\frac{\partial\log\gamma_1}{\partial m_2}\right)_{m_1} = \nu_2\left(\frac{\partial\log\gamma_2}{\partial m_1}\right)_{m_2} \qquad (29)$$

to the problem of mixed electrolytes. Using our notation, $\mu_1 = jm_1$, $\mu_2 = km_2$ under the condition that $\mu = \mu_1 + \mu_2$ is constant, (29) becomes

$$\nu_1 k\left(\frac{\partial\log\gamma_1}{\partial\mu}\right)_{m_1} = \nu_2 j\left(\frac{\partial\log\gamma_2}{\partial\mu}\right)_{m_2} \qquad (30)$$

If both equations 1 and 2 are valid, that is, if

$$\log\gamma_1 = \log\gamma_{1(0)} - \alpha_{12}(\mu - \mu_1)$$

$$\log\gamma_2 = \log\gamma_{2(0)} - \alpha_{21}(\mu - \mu_2)$$

then according to (30)

$$\nu_1 k\left[\frac{\mathrm{d}\log\gamma_{1(0)}}{\mathrm{d}\mu} - \alpha_{12} - (\mu - \mu_1)\frac{\mathrm{d}\alpha_{12}}{\mathrm{d}\mu}\right] = \nu_2 j\left[\frac{\mathrm{d}\log\gamma_{2(0)}}{\mathrm{d}\mu} - \alpha_{21} - \mu_1\frac{\mathrm{d}\alpha_{21}}{\mathrm{d}\mu}\right] \qquad (31)$$

Since $\gamma_{1(0)}$, $\gamma_{2(0)}$, α_{12} and α_{21} are functions of μ only, the coefficient of μ_1 must vanish if the equality is to hold for all values of μ and μ_1. Thus

$$\frac{d(\nu_1 k \alpha_{12} + \nu_2 j \alpha_{21})}{d\mu} = 0 \qquad (32)$$

a result first established by Glueckauf.

This result is most useful as a criterion for deciding whether or not equation 2 is obeyed when equation 1 is known to be valid on the basis of experimental data. To use equation 32, the value of α_{12} must be known for at least two values of μ and α_{21} calculated for each value of μ by equation 27. If

$$\nu_1 k \alpha_{12} + \nu_2 j \alpha_{21} = \text{constant} = S \qquad (33)$$

for the different total ionic strengths, then equation 2 is a valid representation of the behavior of the second electrolyte.

TABLE I

ELECTROMOTIVE FORCES IN ABSOLUTE VOLTS OF THE CELL H_2(1 atm.) | HCl($\mu_1 = m_1$), $BaCl_2$(μ_2) | AgCl–Ag at 25° at 1, 2 and 3 total ionic strengths

	$\mu = 1$		$\mu = 2$		$\mu = 3$
m_1	E	m_1	E	m_1	E
1.0	0.23322	2.0	0.18642	3.0	0.15183
0.9	.23768	1.7	.19418	2.4	.16404
.8	.24220	1.4	.20282	1.8	.17807
.7	.24740	1.1	.21288	1.5	.18619
.6	.25299	0.5	.24095	1.2	.19531
.5	.25954	0.2	.26866	0.9	.20618
.4	.26712			.3	.24151
.3	.27638			.2	.25319
.2	.28866			.1	.27223
.1	.30855				

TABLE II

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS: $\Delta\gamma_1 = \gamma_1(\text{obsd.}) - \gamma_1(\text{calcd.})$

$$\text{Equations used for calculations}\begin{cases}\mu = 1;\ \log \gamma_1 = -0.09086 - 0.0651\ \mu_2\\ \mu = 2;\ \log \gamma_1 = +0.00396 - 0.0653\ \mu_2\\ \mu = 3;\ \log \gamma_1 = +0.12059 - 0.0672\ \mu_2\end{cases}$$

	$\mu = 1$			$\mu = 2$			$\mu = 3$	
m_1	γ_1	$\Delta\gamma_1$	m_1	γ_1	$\Delta\gamma_1$	m_1	γ_1	$\Delta\gamma_1$
1.0	0.8111	−0.0001	2.0	1.008	−0.0010	3.0	1.318	−0.002
0.9	.7972	− .0020	1.7	0.9647	+ .0001	2.4	1.202	− .001
.8	.7881	+ .0009	1.4	.9231	+ .0011	1.8	1.097	+ .001
.7	.7755	.0000	1.1	.8812	− .0002	1.5	1.046	.000
.6	.7640	.0000	0.5	.8058	+ .0006	1.2	.9994	+ .0005
.5	.7529	+ .0003	.2	.7690	− .0007	0.9	.9541	+ .0005
.4	.7413	− .0001				.3	.8696	+ .0006
.3	.7302	+ .0002				.2	.8554	− .0002
.2	.7201	+ .0006				.1	.8419	− .0006
.1	.7077	− .0011						
.01[9]	.6990	.0000						

Experimental Data

The experiments were carried out in cells of the type described in detail by Harned and Morrison.[6] The solutions were made by weighing suitable portions of gravimetrically analyzed hydrochloric acid and barium chloride solutions and diluting with the required amount of water. They were rendered oxygen free by means of nitrogen presaturated with water vapor from solutions of the same composition. All the usual precautions were adopted in manipulating the cells. The silver chloride electrodes were made by heating silver oxide paste and subsequent electrolysis in hydrochloric acid. The cells were run in triplicate and the values recorded in Table I represent their mean. The average deviation from the mean of three measurements was about 0.03 millivolt.

As usual, all cell measurements were corrected to one atmosphere hydrogen pressure. Since the water vapor pressure varies considerably in passing from the pure acid to the pure salt solution, it was necessary to use the actual vapor pressure of each solution in making the correction. The vapor pressure data, computed from the osmotic coefficients given in Table IV, were employed for this purpose.[7]

Table I contains the mean experimental results at the total ionic strengths and acid molalities designated therein. The present values 0.18642 and 0.15183 for the cells containing the acid only at 2 and 3 μ agree with the electromotive forces 0.18640 and 0.15189 obtained by Harned and Ehlers.[8] At 1 μ, however, the latter obtained 0.23336 which is somewhat higher than our values, 0.23322.

The activity coefficients recorded in Table II were computed by the equation

$$E = E^0 - 0.1183 \log \gamma_1^2 m_1(m_1 + 2m_2) \qquad (34)$$

using the value of 0.22246 for E^0 at 25°.[8] At the top of the table are given the numerical equations, corresponding to equation 1, which were derived from these results. The deviations of the observed results, $\Delta\gamma_1$, from those computed by these equations are also tabulated. The smallness of these deviations is excellent proof of the validity of the linear relationship as expressed by equation 1. As may be readily estimated from equation 34 a deviation of 0.1% in γ_1 corresponds to about 0.05 millivolt. A majority of the results lie within this limit.

Further Thermodynamic Calculations

Upon the *assumption* that equation 2 is valid, α_{21} was evaluated by means of equation 28 using the values of the osmotic coefficients obtained from the isopiestic vapor pressure measurements of Stokes[10] and Robinson and Stokes.[11] The values of the osmotic coefficients employed in this computation are given in the second and third columns of Table III and computed values of α_{21} in the next to last column.

TABLE III

DATA EMPLOYED IN EQUATIONS 28 AND 33

	ϕ_1	ϕ_2	α_{12}	α_{21}	S
$\mu = 1$	1.039	0.864	0.0651	−0.0716	0.176
$\mu = 2$	1.188	.996	.0653	− .0824	.145
$\mu = 3$	1.348	.934	.0672	− .0866	.143

In the last column of this table, values of

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(6) H. S. Harned and J. O. Morrison, *Am. J. Soc.*, **33**, 167 (1937).

(7) A very careful analysis of all the errors involved in these measurements is contained in a doctoral dissertation by Robert Gary, Yale University, June, 1954.

(8) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932).

(9) This result was obtained by H. S. Harned and C. G. Geary, *ibid.*, **59**, 2032 (1937).

(10) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

(11) R. A. Robinson and R. H. Stokes, *ibid.*, **45**, 612 (1949).

$S(= 6\alpha_{12} + 3\alpha_{21})$ according to equation 33 are recorded. It is to be observed that S at 1 μ is considerably larger than at the higher ionic strengths and that it is practically the same at 2 and 3 μ. Although the computation of α_{21} is quite sensitive, depending as it does on the accuracy of knowledge of ϕ_1 and ϕ_2, we have reason to believe that the variation in S is real and greater than can be accounted for by experimental error. If this is a true statement, then one would expect that equation 2 is not strictly valid at 1 μ but approaches an exact representation of the facts at the higher concentrations. A similar conclusion has been drawn by Harned[12] from results on HX–MX mixtures. Recent isopiestic vapor pressure measurements by Robinson[13] on the system sodium chloride–cesium chloride also substantiate the conclusion that the rule of linear variation of the logarithm of the activity coefficient becomes valid for both electrolytes in the more concentrated solutions.

TABLE IV

OSMOTIC COEFFICIENTS AND VAPOR PRESSURES AT 25° OF THE SYSTEM $HCl–BaCl_2–H_2O$ ACCORDING TO EQUATION 25

$\mu = 1$			$\mu = 2$			$\mu = 3$		
m_1	ϕ_x	ρ	m_1	ϕ_x	p	m_1	ϕ_x	p
1.0	1.039	22.88	2.0	1.188	21.75	3.0	1.348	20.53
0.9	1.026	22.94	1.7	1.156	21.99	2.7	1.319	20.75
.8	1.012	22.99	1.4	1.121	22.18	2.4	1.287	20.96
.7	0.977	23.04	1.1	1.083	22.36	2.1	1.255	21.17
.6	.981	23.09	0.8	1.040	22.54	1.8	1.220	21.38
.5	.964	23.14	.5	0.990	22.72	1.5	1.183	21.58
.4	.945	23.20	.2	.932	22.89	1.2	1.142	21.79
.3	.924	23.25	.0	.886	23.01	0.9	1.098	21.99
.2	.901	23.29				.6	1.050	22.19
.1	.896	23.35				.3	0.996	22.39
.0	.846	23.40				.0	0.934	22.61

We conclude these thermodynamical considerations by presenting in Table IV the osmotic coefficients, ϕ_x calculated by equation 25 and the water vapor pressures derived from these osmotic coefficients. It is to be noticed that if the logarithms of both activity coefficients in the mixtures obey equations 1 and 2, then ϕ_x must vary quadratically as evidenced by equation 25.

Conclusions

(1) The activity coefficients from electromotive force measurements confirm within narrow limits the validity of equation 1 for the logarithm of the activity coefficient of hydrochloric acid in barium chloride solutions at 1, 2 and 3 μ. The negative deviations at the higher and lower acid concentrations and the positive deviations between these concentrations for log γ_1 at 3 μ may indicate a slight bow convex upward from the linear relationship.

(2) The values of α_{12} are nearly the same at all three ionic strengths. That S is considerably higher at 1 μ than at the higher concentrations is evidence that equation 2 is not strictly valid for the variation of the activity coefficient of barium chloride in hydrochloric acid solutions at an ionic strength of unity.

(3) At the higher ionic strengths, these calculations indicate that both equations 1 and 2 are valid within narrow limits.

(4) In the investigations of these solutions, we believe that considerations of the deviations Δ_1 and Δ_2 in equations 1 and 2 should be explored experimentally for each system.

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[12] H. S. Harned, Table I, *J. Phys. Chem.*, **58**, 683 (1954).

[13] R. A. Robinson, THIS JOURNAL, **74**, 6035 (1952); R. A. Robinson and C. K. Lim, *Trans. Faraday Soc.*, **49**, 1144 (1953); R. A. Robinson, *ibid.*, **49**, 1147, 1411 (1953).

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Polarographic Characteristics of +3 and +5 Arsenic in Hydrochloric Acid Solutions

BY LOUIS MEITES

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Arsenic(V) has been found to be polarographically reducible from concentrated hydrochloric acid solutions, giving a double wave which corresponds to the scheme As(V) → As(0) → AsH_3. New data are presented on the polarographic characteristics of arsenic(III) in hydrochloric acid media.

Introduction

Though the polarography of arsenic in hydrochloric acid solutions has been the subject of several studies, notably those by Kacirkova[1] and Lingane,[2] the published data are not in agreement on several important features.

Kacirkova[1] recorded polarograms of +3 arsenic in 1 N hydrochloric acid. These showed two waves, starting at about −0.3 and −0.6 v. *vs.* S.C.E., which she attributed to a stepwise reduction to elemental arsenic and arsine, respectively. At very low arsenic concentrations the two waves were of equal height, as one would expect, but when the arsenic concentration was increased above about 1mM the height of the well-defined first wave became substantially independent of the arsenic concentration. The height of the second wave, on the other hand, did continue to increase, but more rapidly than the arsenic concentration. Though the shape of the second wave was very poorly defined in the absence of a maximum suppressor, it was materially improved by the addition of, *e.g.*, 5×10^{-4} % methylene blue. Kacirkova explained the peculiar behavior of the first wave height by postulating the formation of a film of adsorbed ar-

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[1] K. Kacirkova, *Collection Czechoslov. Chem. Communs.*, **1**, 477 (1929).

[2] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).