This work was supported by the National Institutes of Health and by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Potentiometric Measurement of Ion-pair Dissociation Constants. HCl, NaCl and KCl in 70% Dioxane–30% Water[1]

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RECEIVED OCTOBER 12, 1956

In the calculation of ion-pair dissociation constants K from potentiometric data the difficult part is the estimation of the activity coefficients, y', of the free ions. For solvents of intermediate dielectric constant, Marshall and Grunwald derived the equation, $-\log y' = 0.8686\,\{1 - [\log(1 + 2.303\,S\sqrt{\mu})]/S\sqrt{\mu}\}$, (where S is the Debye–Hückel limiting slope and μ the free ion ionic strength). The validity of this equation is now demonstrated by means of accurate potentiometric data for concentrations ranging from 8×10^{-5} M up to 0.0025 M where interionic effects of higher order than pairwise become significant. E.m.f. data accurate to 0.05 mv. even at the lowest concentrations were obtained by the following experimental techniques. The measuring cell was: glass electrode/solution X/AgCl–Ag, it having been shown that the e.m.f. of the cell: Pt–H_2/solution X/glass electrode, is constant for our solutions. The Ag–AgCl electrode was of the silver mirror-electrolytic type, equilibrated in 10–15 minutes and was free from aging effects. The ionic strengths were low enough so that different methods of extrapolation to infinite dilution led to almost identical values for the standard e.m.f. Activity coefficients for HCl were predicted without adjustable constants by means of the equation of Marshall and Grunwald and of a conductometric value of K, and agreed to ±0.06% with the measured values. The same approach led to precise values of 10^3K for NaCl (5.35 ± 0.07) and KCl (2.35 ± 0.11).

In solvents of intermediate dielectric constant where the formation of short-range ion pairs is not negligible, Bjerrum's approach to the problem of ionic activity coefficients[2] is particularly useful. In this approach, the troublesome short-range interionic effects need not be calculated explicitly; they are accounted for by the device of an equilibrium (1), between the short-range ion pairs C^+A^- and the long-range pairs or free ions. Thus, if c is

$$C^+A^- = C^+ + A^- \qquad (1)$$

the formal concentration and y the molar activity coefficient of the electrolyte, and if α is the fraction and y' the activity coefficient of the free ions, y is given by equation 2 and α by equation 3.

$$y = \alpha y' \qquad (2)$$

$$\alpha^2(y')^2c/(1 - \alpha) = K \qquad (3)$$

Since in equation 2, the factor α allows for the short-range interactions, the calculation of y' involves long-range interactions only. K in equation 3 is the ion-pair dissociation constant.

In a recent paper from this Laboratory[3] it was shown that K may be identical with the ion-pair dissociation constant deduced from conductivity data if the equations for the equivalent conductance Λ and for y' are given to a better approximation than that of the limiting laws. For uni-univalent electrolytes equation 4 was derived for y' from a plausible model for the charging process of a free ion in media where the ionic diameter is small compared to the Bjerrum distance $q = \epsilon^2/2DkT$.

$$-\log y' = \frac{\epsilon^2[\kappa q - 2.303\log(1 + \kappa q)]}{2.303\,q^2DkT} \qquad (4)$$

In this equation, ϵ is the unit of ionic charge, D the dielectric constant, k Boltzmann's constant, and T the absolute temperature. $1/\kappa$, the effective thickness of the ionic atmosphere, is defined as usual[2,4] by equation 5, where μ is the ionic strength of the free ions and N is Avogadro's number.

$$\kappa^2 = 8\pi\epsilon^2N\mu/1000DkT \qquad (5)$$

For practical calculations equation 4 reduces to the form 4a, where S, the Debye–Hückel limiting slope, is equal to $1.825 \times 10^6/(DT)^{3/2}$

$$-\log y' = 0.8686\,\{1 - [\log(1 + 2.303\,S\sqrt{\mu})]/S\sqrt{\mu}\} \qquad (4a)$$

We now report potentiometric data, accurate to 0.05 mv., for solutions of HCl and its mixtures with NaCl and KCl in 70.00 wt. % dioxane–30.00 wt. % water at concentrations as low as 0.0001 M. (This concentration is low enough to permit an unambiguous evaluation of the standard potential and hence of y.) In this solvent (D = 19.07 at 25°) the formation of ion pairs is considerable even at low concentrations, and the data furnish a good basis for the testing of equations 2, 3 and 4a. Using the conductometric value of K for hydrochloric acid,[3] the predicted values of y agree with observation within 0.06% up to 0.0025 M and are in error by no more than 2.6% at 0.01 M. For NaCl and KCl, conductometric K values are not available, but application of equations 2, 3 and 4 to the data for HCl–NaCl and HCl–KCl mixtures at ionic strengths below 0.002 M leads to highly precise values of K over several-fold variations in the solute concentrations. One may conclude, therefore, that the potentiometric method, in conjunction with equations 2, 3 and 4a, is well-suited to the precise determination of ion-pair dissociation constants.

E.M.F. Measurements and Electrode Behavior.—The cell used in this work is shown in equation 6,

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[1] This work was supported by the National Science Foundation.

[2] N. Bjerrum, *Kgl. Danske Videnskab. Selskab, Math-fys. Medd.*, **7**, No. 9 (1926).

[3] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

[4] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1950, second edition, p. 32.

and the e.m.f. is related to the activity of hydrochloric acid in the cell solution by equation 7

glass elect./soln. in 70.00 wt. % dioxane/AgCl–Ag (6)

$$E = E^* - (RT/F) \ln a_{\text{HCl}} \qquad (7)$$

where E is the measured e.m.f. (in v.), R the gas constant and F the Faraday constant, a the activity and E^* a constant for a given solvent, temperature and glass electrode. Equation 7 is correct only if the e.m.f. of cell 8 is absolute constant for all solutions used in this work; in other words, if the

Pt–H_2 (g., 1 atm.)/soln. in 70.00 wt. % dioxane/glass electrode (8)

hydrogen ion activity as measured by the glass electrode is equal to that measured by the hydrogen electrode. That this is indeed the case was shown as follows.

Harned and Calmon[5] have measured the e.m.f. of the cell 9, and their measurements overlap ours

Pt–H_2 (g., 1 atm.)/HCl in 70.00 wt. % dioxane/AgCl–Ag (9)

in the range 0.0008 to 0.035 M hydrochloric acid. At concentrations above 0.002 M their e.m.f. values were accurate to ±0.1 mv., but at 0.001 and 0.0008 M the reproducibility of their values was only ±0.5 mv.[5] Since the e.m.f. of cell 8 is equal to the difference between that of cell 9 and that of cell 7, we constructed a large-scale graph of their data for cell 9, and from this graph and our experimental values for cell 7, obtained values of $E(9) - E(7)$ for four different glass electrodes. (The actual data for electrode C are shown in Table III.) At acid concentrations above 0.0014 M, these values were found to be constant for any one glass electrode, as shown in Table I. At concentrations below 0.0014 M, there were systematic drifts in $E(9) - E(7)$; for example, at 0.001 M, in six separate experiments with three glass electrodes, the values of $E(9) - E(7)$ differed from the constant values obtained at the higher concentrations by -0.6 ± 0.1 mv. This difference is of the order of the reproducibility of $E(9)$ at this concentration[5] and may, therefore, be ascribed to errors in $E(9)$ rather than $E(7)$.

TABLE I

COMPARISON OF E.M.F. VALUES OF CELLS 7 AND 9 AT ACID CONCENTRATIONS BETWEEN 0.0014 AND 0.035 M

Glass electrode	$E(9) - E(7)$ (v.)	Av. dev. (mv.)	No. of points	E^* (v.)	E^0 (v.)
A	0.6984	0.1	30	−0.6313	0.0671
B	.6995	.2	15	− .6325	.0670
C	.6988	.1	40	− .6318	.0670
D	.6968	.2	5	− .6298	.0670

In order to verify this inference, the e.m.f. of cell 8 was actually measured for glass electrode D, with the results shown in Table II. Over a range of pH much wider than that used in the experiments with cell 6, $E(8)$ was constant within the standard experimental error of ±0.1 mv. Moreover, the mean value of $E(8)$, 0.6968 v., recorded in these experiments was in excellent agreement with $E(9) - E(7)$ as recorded in Table I. Thus the hydrogen ion activity as measured by the glass electrode is equal to that measured by the hydrogen electrode, and equation 7 is valid whenever the Ag–AgCl electrode is behaving reversibly.

TABLE II

E.M.F. MEASUREMENTS FOR CELL 8; GLASS ELECTRODE D; 25.00°

Solutes	$E(8)$ (v.)[a]
0.316 M HCl	0.6969
.00208 M HCl	.6969
.000150 M HCl	.6967
.0035 M acetic acid and 0.0011 M sodium acetate	.6968

[a] Corrected to p_{H_2} = 1 atm. using the vapor pressure data of A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

There was every indication that this was indeed the case in the present work. The electrode used was of the silver mirror-electrolytic AgCl type which had previously given superior performance in 95% methanol.[6] The e.m.f. values for cell 7 proved to be reproducible to ±0.05 mv. even at concentrations as low as 8×10^{-5} M. This represents a significant improvement over previous measurements in this system at low concentrations. Electrode equilibrium was established in all cases in as little as 10 to 15 minutes. E.m.f.'s with different silver mirror–AgCl electrodes were virtually indistinguishable; the maximum difference noted during a two-year period, in which not less than twelve electrodes were prepared, was 0.05 mv. No aging effects were noted: the e.m.f. of an electrode which had been in use for three months agreed precisely with that of a freshly prepared one, five minutes after preparation. When not in use, the electrodes were stored in distilled water. However, it was found to be permissible to store the electrodes in air if they were first thoroughly rinsed and freed from all contaminants.

Thermal and thermal-electrolytic AgCl electrodes require long periods for equilibration and are often subject to aging effects. These undesirable properties seem to be caused by the great porosity of the electrodes, and by the thickness of the AgCl coating.[6] The long equilibration times are especially troublesome in mixed solvents containing a volatile organic component. In this respect, the silver mirror–AgCl electrode offers a decided advantage.

Regarding the glass electrodes, reproducible e.m.f. values were obtained if the electrodes were first equilibrated for 24 hours in 70% dioxane (see Experimental). The values of E^* for a given glass electrode (obtained as described in the next section) remained constant over a period of several months. For example, electrode C gave constant E^* values for five months, but readings became erratic after accidental exposure to air-drying for 2–3 days.

It seemed important to prove that surface effects were negligible even at very low concentrations. We therefore varied the surface area to which the solutions were exposed in the cell, as well as the volume of the solutions. At the concentrations 1.2×10^{-4}, 2.4×10^{-4} and 6×10^{-4}, sur-

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[5] H. S. Harned and C. Calmon, THIS JOURNAL, **60**, 2130 (1938).

[6] E. L. Purlee and E. Grunwald, *J. Phys. Chem.*, **59**, 1112 (1955).

face to volume ratios were changed by a factor of 7, and at 8 × 10^{-4} by a factor of 20, without causing any significant change in e.m.f.

Evaluation of E^*.—When equation[7] is rewritten in the form 10

$$E + (RT/F)\ln c_{\mathrm{H}}c_{\mathrm{Cl}} = E^* - (RT/F)\ln y_{\mathrm{H}}y_{\mathrm{Cl}} \quad (10)$$

all experimental quantities appear on the left, and it is seen that accurate values of y are obtained only when E^* is known. The usual procedure for evaluating E^* is to obtain approximate values of $y_{\mathrm{H}}y_{\mathrm{Cl}}$ from theory, and then to extrapolate the function 11 to infinite dilution. Unless the experimental data

$$E + (RT/F)\ln c_{\mathrm{H}}c_{\mathrm{Cl}} + (RT/F)\ln (y_{\mathrm{H}}y_{\mathrm{Cl}})_{\mathrm{approx}} \quad (11)$$

extend to sufficiently low concentrations, this extrapolated value may well depend on the theory used for obtaining approximate values for $y_{\mathrm{H}}y_{\mathrm{Cl}}$. In order to establish the accuracy of a given value for E^*, it is *necessary*, but not sufficient, to show that a reasonable number of different theoretical models for the approximation of $y_{\mathrm{H}}y_{\mathrm{Cl}}$ all lead to the same value of E^*. Unfortunately, there is no way of satisfying a *sufficient* condition for accuracy since there is no way of knowing from which concentration it is safe to extrapolate to infinite dilution. Though very improbable, it is not impossible that different extrapolation functions all err to the same extent in the region of extrapolation. Nevertheless, this is the most stringent requirement available for testing the accuracy of E^*, and it is far more stringent than the requirement often imposed: that E^* remain constant over a finite concentration range when calculated on the basis of a single theory for $y_{\mathrm{H}}y_{\mathrm{Cl}}$ through the adjustment of a theoretical parameter.

Owing to the large number of measurements, we shall report in detail only the data for electrode C (see Table III). For purposes of extrapolation, the data were plotted on a large-scale graph, and smoothed e.m.f. values were obtained at rounded concentrations, except for the very lowest concentration where the actual value was used.

Four different methods were used for extrapolation.

(1) $(y_{\mathrm{H}}y_{\mathrm{Cl}})_{\mathrm{approx}} = 1$: the left side of equation 10 was plotted *vs.* $\sqrt{c}$ and the nearly linear variation observed at concentrations less than 6 × 10^{-4} was extrapolated to infinite dilution. The intercept E^* is −0.63195 v. The slope, 0.548, is somewhat greater than the value 0.504 expected from the Debye–Hückel limiting law for a solvent of dielectric constant 19.07.

(2) $(y_{\mathrm{H}}y_{\mathrm{Cl}})_{\mathrm{approx}} = \mathrm{antilog}_{10}\,(-8.514\sqrt{c})$, as predicted by the Debye–Hückel limiting law: the extrapolation function 11 was plotted *vs.* c, as shown in Fig. 1. At concentrations below 3 × 10^{-4} M, the plot becomes linear, and the intercept $E^* = -0.63178$ v.

(3) $(y_{\mathrm{H}}y_{\mathrm{Cl}})_{\mathrm{approx}}$ was estimated from Bjerrum's approach, using equations 2 and 3, and equation 12 for y', where S is the Debye–Hückel limiting slope.

$$\log y' = \frac{\kappa q}{2.303\,(1 + \kappa q)} = \frac{S\sqrt{\alpha c}}{1 + 2.303\,S\sqrt{\alpha c}} \quad (12)$$

Equation 12 is a possible alternative to equation 4[3,7] and is derived from a different model for the charging process. K is 7.37 × 10^{-3} and was computed from the conductivity data of Owen and Waters[8] for hydrochloric acid at 25° by a method employing equation 12.[3] Details of the calculation of y have been described previously.[9] The extrapolation function 11 was plotted *vs.* c, as shown in Fig. 1. There is only slight curvature below 9 × 10^{-4} M, with intercept $E^* = -0.63184$ v.

TABLE III

OBSERVED E.M.F. VALUES FOR HCl IN 70 WT. % DIOXANE WITH CELL (6) AT 25.00°[a]

10^4c_{HCl}	$-E$, v.	10^4c_{HCl}	$-E$, v.
209.6	0.37914	10.178	0.26065
188.2	.37516	10.080	.26040
167.6	.37104	10.032	.26003
151.3	.36753	9.905	.25947
139.70	.36456	9.868	.25922
136.77	.36374	9.157	.25615
134.10	.36291	9.021	.25543
104.78	.35393	8.596	.25342
83.82	.34589	8.144	.25093
55.88	.33046	7.553	.24775
33.53	.31023	7.445	.24707
25.40	.29897	6.693	.24235
21.28	.29174	6.578	.23854
20.36	.28996	6.082	.23804
20.03	.28925	6.047	.23779
19.74	.28866	5.316	.23193
19.22	.28750	5.013	.22938
18.33	.28563	4.934	.22854
16.75	.28181	4.886	.22723
15.12	.27759	4.151	.22073
13.636	.27324	3.510	.21304
13.577	.27313	2.372	.19462
12.836	.27076	1.660	.17786
12.690	.27028	1.0371	.15506
10.633	.26253	0.7542	.13961
10.313	.26137		

[a] Glass electrode C, Table I, was used in these measurements.

(4) $(y_{\mathrm{H}}y_{\mathrm{Cl}})_{\mathrm{approx}}$ was again estimated from Bjerrum's approach, using equations 2 and 3, but equation 4 for y'. The values of y' at several rounded concentrations are listed in Table IV. K is 6.67 × 10^{-3} and was computed from conductivity data of Owen and Waters[8] by a method employing equation 4.[3] y values were calculated as described previously.[9] As shown in Fig. 1, the data fall on a straight line of zero slope; $E^* = -0.63180$ v.

The mean of the four values obtained for E^* is −0.63184 v., which will be rounded off to −0.6318 v. in the subsequent treatment of the data.

It is instructive to consider the effect of increasing the lowest concentration from which the extrapolations are made. If this were as high as 2 × 10^{-4} M, that is, three times as high as the lowest concentration which was actually used, the inter-

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[7] R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1949, section 924. There are minor errors in equations 5, 9 and 10 of this text.

[8] B. B. Owen and G. W. Waters, THIS JOURNAL, **60**, 2371 (1938).

[9] Ref. 3, p. 2147.

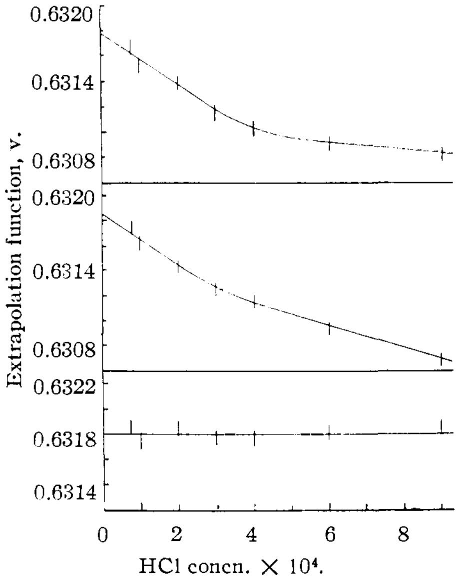

Fig. 1.—Extrapolation plots: top, method (2); middle, method (3); bottom, method (4).

cepts would have been virtually the same. At still higher concentrations, however, the intercepts will diverge. For example, if the extrapolations are made from 0.002 *M*, the plots for methods (3) and (4) will look as shown in Fig. 2. The values of the apparent intercepts are −0.6312 v. for method (4) and −0.6303 v. for method (3). The difference between these two values is many times the experimental error and is highly significant. Furthermore, both values differ significantly from the value, −0.6318 v., obtained by all four methods of extrapolation from the lower concentrations. In fact, since the values of the extrapolation function 11, as estimated by method (3), are nearly constant between 0.004 and 0.02 *M* HCl, one might erroneously conclude that this method predicts activity coefficients correctly and that E^* is equal to the average value of the extrapolation function in this range, or −0.6294 v.

TABLE IV

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS, *y*, FREE-ION ACTIVITY COEFFICIENTS, *y'*

10^4c	*y*		$10^4\mu$	*y'*
	Calcd.	Obsd.		
1	0.9028	0.9029	1	0.9143
3	.8333	.8334	3	.8584
5	.7903	.7899	5	.8259
7	.7583	.7586	7	.8016
10	.7187	.7190	10	.7725
12	.6983	.6985	12	.7576
15	.6720	.6712	15	.7378
18	.6490	.6483	18	.7210
20	.6360	.6356	20	.7107
22	.6227	.6224	22	.7013
25	.6060	.6067	25	.6891
30	.5805	.5839	30	.6708
40	.5425	.5478	40	.6416
50	.5140	.5211	50	.6185
60	.4900	.5084	60	.5993
70	.4695	.4794	70	.5830
80	.4520	.4623	80	.5689
100	.4216	.4330	100	.5455
150	.3725	.3851	150	.5035
200	.3387	.3536	200	.4746

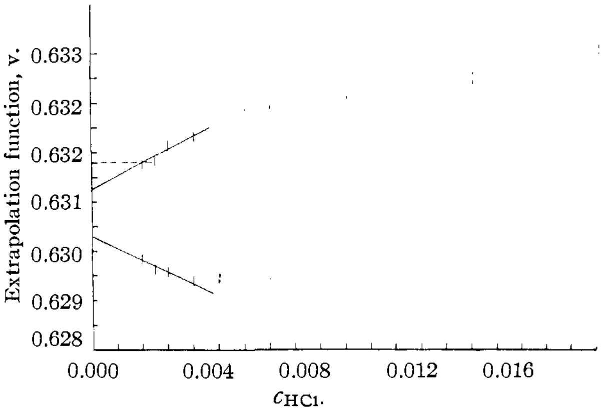

Fig. 2.—Values of the extrapolation function 11 at higher concentrations: bottom, method (3); top, method (4); dotted line, 0.6318 v.

So far we have only considered extrapolation functions in which there are no adjustable parameters. Harned and Calmon[5] in their extrapolations for hydrochloric acid used the Debye–Hückel theory including the extended terms of Gronwall, La Mer and Sandved. They adjusted the ion-size parameter until the values of the extrapolation function, 11, were constant in the concentration range 0.002 to 0.02 *M*. The average value of the function 0.06584 v. (on the *c*-scale), was then identified as E^0 for cell 9 at 25.00°. Using our value, −0.6318 v., for E^* of glass electrode C, and the experimental value of 0.6988 v. for $E(9) - E(7)$ for this electrode (see Table I), we obtain $E^0 = 0.0670$ v. In the same way, the data for the other glass electrodes lead to E^0 values of 0.0671 or 0.0670 v. It appears that the procedure employed by Harned and Calmon resulted in an error of the same type as that illustrated for method (3).

Comparison of Observed and Predicted Activity Coefficients for Hydrochloric Acid.—The accuracy of method (4) for predicting *y*, that is, of equations 2, 3 and 4, will now be tested. It must be pointed out that method (4) is the only one of the methods tested which results in constant values for the extrapolation function 11 at low concentrations. Since this constant value was equal to E^*, it may be concluded that the estimated values of $y_{H}y_{Cl}$ were accurate. This is clearly evident from the data in Table IV. In the concentration range up to 0.0025 *M*, the mean discrepancy between calculated and observed *y* values is only 0.06%, which is accounted for by 0.03 mv. error in e.m.f. The deviations seem to be random. At higher concentrations the predicted activity coefficients become increasingly too small, but even at 0.01 *M* the error is only 2.6%. Accuracy of this order is perfectly acceptable for many applications. As shown in Table V, the activity coefficients begin to deviate from the values predicted by equations 2, 3 and 4 at nearly the same concentration, 0.0025 *M*, where the conductivity data of Owen and Waters[8] fail to fit a theory based on equations 2, 3, 4, and the expression 13 for the equivalent conductivity, Λ.

$$\Lambda/\alpha = \Lambda_0 - [S_\Lambda \sqrt{\alpha c}/(1 + 2.303S\sqrt{\alpha c})] \quad (13)$$

In equation 13, which was proposed by Marshall and Grunwald,[3] S_Λ is the Onsager limiting slope and S the Debye–Hückel limiting slope. In these calculations, K was 6.67×10^{-3} and S_Λ 233.3. It will be noted that in the range above 0.0025 M where the deviations are systematic, the calculated values of y and Λ are both less than the observed ones and deviate by approximately the same percentage. Thus the application of equations 2, 3 and 4 to activity coefficients and to equivalent conductivities leads to consistent results in that the interionic effects are overestimated in both cases at the higher concentrations.

TABLE V

FIT OF EQUATIONS 2, 3, 4 AND 13 TO CONDUCTIVITY DATA[8] FOR HCl IN 70% DIOXANE, 25.00°

10^4c	Equiv. conductance Obsd.	Calcd.
1.346	89.1	88.7
4.149	85.2	85.2
5.856	83.3	83.5
8.340	81.4	81.5
15.36	77.2	77.4
15.82	77.1	77.1
25.80	73.4	73.2
33.91	71.2	70.8
39.46	70.0	69.3
71.59	65.2	64.0

According to theoretical calculations of Fuoss,[10] at 25° triple ion formation begins to be appreciable at concentrations greater than $3 \times 10^{-7}\ D^3$, or 0.0021 M in 70% dioxane. This concentration coincides approximately with the concentration where the extrapolation function 11 actually begins to deviate from E^*, but it must be pointed out that the deviations cannot be accounted for by triple ion formation. Analysis shows that the formation of triple ions would result in a lowering of both y and Λ *below* the values predicted by a theory in which the formation of triple ions is neglected; the actual deviations are in the *opposite* direction.

It is conceivable that the observed deviations might be due to an error in the estimated interionic effects caused by preferential hydration of the ions. This would leave a solvent medium containing effectively more than 70% dioxane. Since E^0 or E^* becomes more negative with increasing dioxane content, the drift of the extrapolation function 11 toward more negative values at the higher concentrations, shown in Fig. 3, could be accounted for. Unfortunately, this explanation does not fit the conductance data since Λ_0 for HCl decreases with increasing dioxane content.[8] The observed values of Λ should therefore be less than the calculated ones if the ionic hydration hypothesis were correct.

Potentiometric Measurement of the Ion-pair Dissociation Constants. HCl–NaCl and HCl–KCl Mixtures.—So far we have been able to show that observed y values for hydrochloric acid agree completely with predicted ones on the basis of equations 2, 3 and 4 at concentrations below 0.0025 M. Since the value of K_{HCl} was obtained from conductivity data and since the value of E^* was independent of the method of extrapolation, the prediction of y was independent of the e.m.f. data and the measurement of y relied in no way upon any particular theory. Having thus established the validity of the method, we may now use it for the potentiometric measurement of ion-pair dissociation constants for other salts. We report e.m.f. measurements for HCl–NaCl and HCl–KCl mixtures which show that ion-pair dissociation constants may indeed be obtained with good precision. In these measurements, cell 6 was used, wherein the total electrolyte concentration was kept below 0.0025 M.

The relevant experimental data are shown in Table VI and VII. It is seen that the individual solute concentrations varied over wide ranges; the ratio $c_{\text{HCl}}/c_{\text{NaCl}}$ ranged from 0.2 to 4.3, and the ratio $c_{\text{HCl}}/c_{\text{KCl}}$ ranged from 0.26 to 3.5. The K values were calculated as follows.

The experimentally determined quantities are the formal concentrations c_{HCl} and c_{NaCl}, and E. From the latter and the known value of E^*, the quantity $a_{\text{H}}a_{\text{Cl}}$ is calculated according to equation 14. Next the concentration of H^+Cl^- ion pairs is

$$a_{\text{H}}a_{\text{Cl}} = \text{antilog}\,[(E^* - E)/0.05915] \quad (14)$$

calculated from the known values of $a_{\text{H}}a_{\text{Cl}}$ and K_{HCl} according to equation 15, and the concentration of free hydrogen ion c_{H^+}, according to equation 16.

$$c_{\text{H}^+\text{Cl}^-} = a_{\text{H}}a_{\text{Cl}}/K_{\text{HCl}} \quad (15)$$

$$c_{\text{H}^+} = c_{\text{HCl}} - c_{\text{H}^+\text{Cl}^-} \quad (16)$$

We may now write equation 17 where the left-hand side is known

$$a_{\text{H}}a_{\text{Cl}}/c_{\text{H}^+} = c_{\text{Cl}^-}(y')^2 \quad (17)$$

and where on the right side c_{Cl^-} is the concentration of free chloride ion. (c_{Cl^-} is equal to the free ion ionic strength μ.) Equation 17 is solved by successive approximations. Various values are assumed for c_{Cl^-}, the corresponding values of y' are obtained, and the right-hand side of 17 is calculated. The value of c_{Cl^-} is then adjusted so that the right-hand side of 17 is exactly equal to the known value of $a_{\text{H}}a_{\text{Cl}}/c_{\text{H}^+}$.

TABLE VI

ION-PAIR DISSOCIATION CONSTANT OF SODIUM CHLORIDE IN 70.00 WT. % DIOXANE, 25.00°

10^4c_{HCl}	10^4c_{NaCl}	$(E^* - E)$, v.	10^3K_{NaCl}
2.395	11.967	−0.4027	5.44
4.697	11.736	− .3832	5.34
9.042	11.302	− .3630	5.22
9.446	16.819	− .3581	5.37
9.784	13.053	− .3592	5.40
10.146	9.009	− .3609	5.34
10.534	4.680	− .3635	5.44
10.739	2.392	− .3654	5.27
13.072	10.899	− .3510	5.34
		Mean ± stand. dev.	5.35 ± 0.07

K_{NaCl} is now calculated simply according to equation 18. As shown in the last column of Tables

$$c_{\text{Na}^+} = c_{\text{Cl}^-} - c_{\text{H}^+} \quad (18a)$$

$$c_{\text{Na}^+\text{Cl}^-} = c_{\text{NaCl}} - c_{\text{Na}^+} \quad (18b)$$

$$K_{\text{NaCl}} = c_{\text{Na}^+}c_{\text{Cl}^-}(y')^2/c_{\text{Na}^+\text{Cl}^-} \quad (18c)$$

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(10) R. M. Fuoss, THIS JOURNAL, **57**, 488, 2604 (1935).

VI and VII, the mean values are $K_{NaCl} = 5.35 \times 10^{-3}$ and $K_{KCl} = 2.35 \times 10^{-3}$. The standard deviations of single K values are estimated as 1.4% for NaCl, and 4.7% for KCl; the standard deviations of the *mean* values are estimated as 0.5% for NaCl and 1.3% for KCl. These deviations can be accounted for by standard errors in the e.m.f. determinations of 0.02–0.03 mv. The maximum errors of the K values are estimated conservatively as 5% for NaCl and 7% for KCl. A more precise estimate of the accuracy can be made when the K values have been checked by the conductometric method. Preparations for making these measurements in this Laboratory are under way.

TABLE VII

ION-PAIR DISSOCIATION CONSTANT OF POTASSIUM CHLORIDE IN 70.00 WT. % DIOXANE, 25.00°

10^4c_{HCl}	10^4c_{KCl}	$(E^* - E)$, v.	10^3K_{KCl}
2.531	9.650	−0.4053	2.42
2.673	10.20_0	− .4028	2.54
4.995	9.522	− .3846	2.32
5.288	10.05_0	− .3821	2.44
7.394	9.398	− .3719	2.26
7.893	9.910	− .3694	2.24
8.962	10.25_1	− .3647	2.35
9.180	7.876	− .3657	2.41
9.180	7.876	− .3657	2.41
9.410	5.382	− .3671	2.49
9.410	5.382	− .3672	2.30
9.651	2.760	− .3692	2.28
9.731	9.268	− .3626	2.24
10.376	9.772	− .3602	2.18
		Mean ± stand. dev.	2.35 ± 0.11

Experimental

Materials.—The best available commercial grade of 1,4-dioxane was slightly acidified with concentrated hydrochloric acid and shaken with an excess of ferrous sulfate. After standing in contact with the ferrous sulfate for 24 hours the solution was filtered and subsequently purified as previously described by Marshall and Grunwald.[11] Water was redistilled from alkaline permanganate in an all-glass apparatus. Constant boiling hydrochloric acid was prepared from reagent grade hydrochloric acid according to the method of Foulk and Hollingsworth.[12] The acid was analyzed by titration with sodium hydroxide which was standardized with National Bureau of Standards samples of benzoic acid and potassium acid phthalate. The analyses agreed to within ±0.05% of the value reported by Foulk and Hollingsworth.

70 wt. % dioxane–water mixtures were prepared gravimetrically with an accuracy in composition of ±0.02%. Sodium and potassium chloride solutions were prepared from reagent grade salts dried at 120° for at least 72 hours. Only *freshly* prepared solutions were utilized in the experiments. All volumetric ware was calibrated.

E.M.F. Measurements.—E.m.f. measurements were made with a Beckman model GS *p*H-meter in conjunction with a Rubicon potentiometer as previously described.[13] Temperature was maintained at 25.00 ± 0.01° in a large water thermostat. Beckman glass electrodes (#1190-42) and silver mirror–AgCl electrodes[6] were employed. When not in use the glass electrodes were stored in 70 wt. % dioxane and the Ag–AgCl electrodes were stored in doubly distilled water.

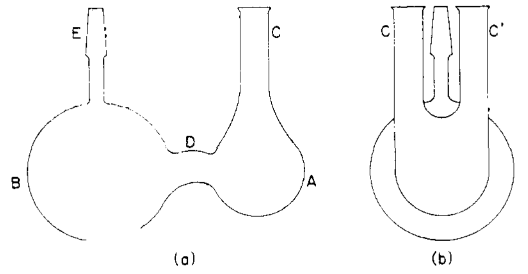

Fig. 3.—Dilution cell.

We have observed that the glass electrode requires a relatively long period of time for equilibration with a given solvent medium. Accurate E^* values are obtained only when the glass electrode has equilibrated in the solvent medium of precisely correct composition. In 70% dioxane the time required for equilibration is *ca.* 24 hr. These effects are illustrated by the following experiment.

Glass electrode "C" was stored in doubly distilled water for 24 hours, then soaked in 70% dioxane for 30 min. prior to e.m.f. measurements of solutions 1, 2 and 3 of Table VIII for HCl in 70% dioxane. The measurements of solutions 1, 2 and 3 were made successively; each solution shown in Table VIII was observed over a period of 45 min. during which there were no drifts in e.m.f. The values of $E(9) - E(7)$ appear to be constant, but are too negative by 1.7 mv. After the electrodes had remained in solution 3 for an additional 6 hr., the e.m.f. had changed significantly. The apparent E^* value was now −0.6306 v., thus confirming a slow drift in the expected direction.

Glass electrode "C" was then equilibrated in 70% dioxane for another 24 hr. and the measurements 4, 5, 6 and 7 of Table VIII were performed. It is clearly evident that equilibration of the glass electrode in the proper solvent has resulted in the correct value for E^*. The quantity $E(9) - E(7)$ is, of course, the same as previously observed (Table I).

During prolonged storage of the glass electrode, the solvent composition may change slowly due to evaporation or peroxide formation. We found it to be important that the electrode be equilibrated in freshly prepared solvent of the correct composition if accurate measurements of e.m.f. were to be obtained.

TABLE VIII

EFFECT OF FAILURE TO EQUILIBRATE THE GLASS ELECTRODE WITH 70% DIOXANE

	10^3c_{HCl}	$E(9) - E(7)$, v.	Apparent E^*, v.
	Measurements before electrode equilibrium		
(1)	15.12	0.6971	......
(2)	6.052	.6971	......
(3)	1.512	.6971	−0.6301
	Measurements after electrode equilibrium		
(4)	13.41	0.6988	......
(5)	1.675	0.6988	− .6318
(6)	1.031	....	− .6318
(7)	0.497	....	− .6318

It is not at all unlikely that analogous phenomena have been operative in measurements performed by other workers in non-aqueous and aqueous organic solvents. For example, Gutbezahl and Grunwald[14] observed systematic e.m.f. drifts in the system 95 vol. % ethanol–water, and Marshall and Grunwald[3] observed slight drifts in 82 wt. % dioxane–water. However, these workers took the precaution of correcting for the drifts in e.m.f.

We, therefore, caution against the practice of standardization of the glass electrode in water when subsequent measurements are to be made in another solvent, and call attention to the slow equilibration of the glass electrode with the solvent medium. Equilibrium e.m.f.'s, *i.e.*, thermodynamically reversible, can be obtained only after equilibrium between the glass membrane and solvent medium has been attained. When glass electrodes are routinely used in the

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(11) H. P. Marshall and E. Grunwald, THIS JOURNAL, **76**, 2000 (1954).

(12) C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).

(13) A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(14) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 559 (1953).

laboratory, we recommend that they be stored in the appropriate solvent medium.

Cell Techniques.—Part of the success of the present work is attributed to the cell design. A special type of dilution cell was constructed and is shown in Fig. 3. The cell consists of a small electrode chamber A, and a larger dilution chamber B. With a clamp attached to the connecting arm D, the cell was mounted in a manner such that a free rocking motion about an axis perpendicular to the plane of (a) in Fig. 3 could be obtained when desired. The electrodes were mounted in C and C′ with the aid of tightly fitted cork stoppers. Dilution of the original sample, placed in compartment A, was accomplished by adding solvent from a buret to compartment B *via* the port E, without removing the cell from the thermostat. After solvent was added, the cell was rocked about its axis until complete mixing was attained. Return of the cell to its horizontal position left a sufficient quantity of solution in the electrode compartment and an e.m.f. reading could be obtained. Electrode equilibration was obtained in 10–15 min. in all experiments and e.m.f. values were found to remain constant for as long as eight hours with solutions 5×10^{-4} *M* in HCl.

The dilution cell techniques eliminate the necessity for pre-rinsing the electrodes carefully between measurements on individually prepared solutions, decrease the possibility of solution contamination and increase appreciably the mechanical efficiency of measurements. Careful checks showed that e.m.f. values obtained by the dilution cell techniques were virtually indistinguishable from those obtained with individually prepared solutions. The reproducibility of measurements was found to be ±0.05 mv. over the entire concentration range studied.

Surface effects were studied by varying the surface area exposed to the solutions in the cell as well as the volume of solution. Three types of cells were employed: (a) the dilution cell, (b) a cell similar to the dilution cell, but consisting of a single compartment, and (c) a beaker cell consisting of a 180-ml. electrolytic beaker equipped with a tightly fitted cork stopper supporting the electrode. E.m.f.'s measured in solutions as dilute as 1.2×10^{-4} *M* HCl at widely varying surface/volume ratios differed at most by 0.1 mv. (see text, E.M.F. Measurements and Electrode Behavior). Surface effects are thus considered to be negligible.

E.m.f. measurements in the HCl–NaCl and HCl–KCl mixtures at varying acid/salt ratios were obtained as follows. Approximately 100 ml. of *ca.* 0.001 *M* HCl was prepared in the dilution cell. Aliquots of *ca.* 0.01 *M* salt solution were successively added to the cell from a semi-micro buret. After the addition of each aliquot of salt solution, the solution was thoroughly mixed and an e.m.f. measurement made. The procedure was then reversed and e.m.f. measurements obtained after successive additions of HCl aliquots to *ca.* 0.001 *M* salt solutions. This method resulted in wide variation of the individual electrolyte concentrations as well as the acid/salt ratios (*cf.* Table VI and VII).

Experiments with Cell 8.—The electrodes were a lightly platinized Beckman No. 1281 platinum electrode and a Beckman No. 1190-42 glass electrode. Matheson reagent grade hydrogen gas was passed first through a cold trap at −78°, then through a Greiner–Friedrichs gas washing bottle filled with 70.00 wt. % dioxane–water, and finally through a sintered glass disk into the solution to be measured. Electrode equilibrium appeared to be established in 2 to 3 hours, but all solutions were observed periodically over a 24-hour period. The hydrogen was allowed to pass over the platinized platinum electrode at a rate of *ca.* 0.2 ml./sec. for 30 minutes before, and during, each measurement, but was turned off between measurements. The e.m.f. values increased rapidly to a maximum, which remained constant for many hours, but eventually decreased slowly. The maximum e.m.f. was therefore accepted as the equilibrium value. All readings were corrected to a hydrogen pressure of 1 atm.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Measurement of Acid Dissociation Constants and Ion-pair Dissociation Constants in Solvents of Intermediate Dielectric Constant. Carboxylic Acids and their Sodium and Potassium Salts in 70% Dioxane–30% Water[1]

BY E. LEE PURLEE AND ERNEST GRUNWALD

RECEIVED OCTOBER 12, 1956

The e.m.f. of cells of the type: glass electrode/MA(c), MCl(c), HA(c_{HA})/AgCl–Ag, has been measured at 25° using 70% dioxane as the solvent and formic acid, acetic acid and propionic acid and their sodium or potassium salts as solutes. The data obtained at ionic strengths below 0.0025 *M* have been extrapolated to infinite dilution according to the equation $K_A' = K_A[1 + 2c(y^*)^2(K_{MA}^{-1} - K_{MCl}^{-1})]$, where K_A is the thermodynamic acid dissociation constant, K_{MA} the ion-pair dissociation constant of the sodium or potassium salt of the acid and K_{MCl} that of NaCl or KCl, and y^* is the known molar activity coefficient of HCl at the concentration $2c$. The validity of the extrapolations has been established by obtaining good agreement between the K_A values based on the data for the sodium salts and those based on the data for the potassium salts. From the slopes of the extrapolation plots, the ion-pair dissociation constants of the sodium and potassium salts of the acids have been deduced.

In solvents of intermediate dielectric constant, the measurement of acid dissociation constants is complicated by the formation of ion pairs.[2–4] In the preceding paper,[5] we described a method for treating ion-pair dissociation, which is based on equations 1 and 2. In these equations, a_i is the activity of a given ionic species, c_i is the actual molar concentration of *free ions* of the type i, and y' is their molar activity coefficient; S is the Debye–Hückel limiting slope, and μ the free-ion ionic strength.

$$a_i = c_i y' \qquad (1)$$

$$-\log y' = 0.8686\left[1 - \frac{\log(1 + 2.303S\sqrt{\mu})}{S\sqrt{\mu}}\right] \qquad (2)$$

This approach will now be applied to the measurement of K_A for formic acid, acetic acid and propionic acid, and to that of the dissociation constants of the sodium and potassium salts of these acids. All measurements were made in 70.00 wt.% dioxane–30.00 wt.% water at 25.00°, at ionic strengths ranging from 0.0004 to 0.002 *M*, under which conditions equations 1 and 2 have been shown to apply.[5]

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[1] This work has been supported by a grant from the National Science Foundation.

[2] I. M. Kolthoff and S. Bruckenstein, THIS JOURNAL, **78**, 1 (1956).

[3] E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

[4] E. J. Corey, THIS JOURNAL, **75**, 1172 (1953).

[5] E. L. Purlee and E. Grunwald, *ibid.*, **79**, 1366 (1957).