904. *Precise Measurements with the Glass Electrode. Part IV.*[1] *The Activity-coefficient of Hydrochloric Acid in Mixtures with Calcium or Manganous Chloride at 25°*

By A. K. Covington

Low-resistance glass electrodes have been used to study the variation in the activity-coefficient of hydrochloric acid in mixed solution with calcium or manganous chloride at constant total ionic strength of 0·1 molal. The variation is in quite good accordance with Guggenheim's theory of mixed electrolyte solutions.

In previous Papers in this Series[1] it was shown that, provided that changes in asymmetry potential with time were taken into account by a simple extrapolation procedure, low-resistance glass electrodes could be used to give results of precision comparable to that obtainable with the hydrogen electrode. The technique was tested on cells with,[1b] and without,[1a,c] transport containing hydrochloric acid solutions, and has been extended to studies of nitric and perchloric acids[2a] and some weaker acids.[2b,c]

Almost all e.m.f. studies of mixed electrolyte solutions, with the notable exception of the remarkable work of Güntelberg,[3,4] have been confined[5] to hydrochloric acid solutions of high molality, where the effects of added electrolytes on the activity-coefficient of hydrochloric acid are easily measurable within readily attainable experimental precision

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[1] (*a*) Part I, A. K. Covington and J. E. Prue, *J.*, 1955, 3696; (*b*) Part II, A. K. Covington and J. E. Prue, *J.*, 1955, 3701; (*c*) Part III, A. K. Covington, *J.*, 1960, 4441.

[2] (*a*) A. K. Covington and J. E. Prue, *J.*, 1957, 1567; (*b*) E. J. King and J. E. Prue, *J.*, 1961, 275; (*c*) A. K. Covington, J. V. Dobson, and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1965, **61**, in the press.

[3] E. Güntelberg, *Z. phys. Chem.*, 1926, **123**, 199.

[4] E. Güntelberg, " Studier over Elektrolyter Activiteter," G.E.C. Gads Forlag, Copenhagen, 1939.

[5] H. S. Harned and B. B. Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold, 3rd edn., 1958, ch. 14.

($\pm 0{\cdot}2$ mv). Two methods of working have been used: (*a*) at constant ionic strength with varied proportions of the two electrolytes, and (*b*) at a constant low molality (usually 0·1) of hydrochloric acid and various (higher) molalities of added electrolyte. The experimental studies by method (*a*) of Harned and his collaborators and others led to the establishment of the empirical rules of Harned and of Akerlöf and Thomas.[5] Most of these studies have been confined to mixtures containing three different ions only, usually singly charged. Stokes and Stokes [6] have recently made the first study by the e.m.f. method of a mixture of two electrolytes without a common ion and of different charge type (hydrochloric acid and calcium perchlorate). A most elegant and refined weight-titration procedure was used to obviate the necessity for the careful preparation of a large number of cell-electrolyte mixtures of known concentration. Their experiments were confined to the use of method (*b*) and high molalities.

It is easy to see why studies by method (*a*) at low molality (0·1) are few; preparation of solutions is tedious and results with a precision of $\pm 0{\cdot}01$ mv are desirable, because the effect of the added electrolyte on the activity-coefficient of hydrochloric acid is small. Harned [7] made one such study by using the classical calomel electrode and lithium, sodium, or potassium chloride as added electrolyte. The same year, Güntelberg [3] published the results of a similar study with the silver–silver chloride electrode, but at 20°. He was troubled [4] by contamination of his salts with bromide impurity, and found difficulty in reproducing a constant standard potential for his silver–silver chloride electrodes. Subsequently, he repeated [4] the study at 25°, obtaining results of unsurpassed precision on the hydrogen–silver–silver chloride cell. No similar study of this cell by method (*a*) has previously been reported for mixtures of electrolytes of different charge types. Güntelberg's results support Brönsted's principle of specific interaction of ions and Guggenheim's incorporation of this in his theory [8,9] of mixed electrolyte solutions. It was of interest to test the application of the latter to mixtures of electrolytes of different charge-types in view of Guggenheim's later conclusions [10] that his formulæ were unlikely to be accurate for such mixtures. Manganous chloride was chosen as one added electrolyte because of interest in its use with hydrochloric acid as electrolyte in other cells.[11] Calcium chloride was chosen as the other added salt to be studied, since activity-coefficients have been obtained at low molalities from cells with transport.[12,13]

The hydrogen electrode could have been used for these studies, because neither the calcium nor the manganous ion affects its potential. The use of the glass electrode has, however, the advantage that by transferring it between 0·1m-hydrochloric acid solution and the mixed electrolyte solution, the quantity of interest, namely the *ratio* of the activity-coefficient of hydrochloric acid in the two solutions is obtained directly from the difference in e.m.f. of the two cells

$$\text{glass} \mid \text{HCl (m)} \mid \text{AgCl} \mid \text{Ag} \qquad \text{(A)}$$

$$\text{glass} \mid \text{HCl (m}_1\text{), MCl}_2\text{ (m}_2\text{)} \mid \text{AgCl} \mid \text{Ag} \qquad \text{(B)}$$

at the instant of transfer of the glass electrode between them.

EXPERIMENTAL

All experimental details about the technique of using low-resistance glass electrodes for precise e.m.f. measurements have already been adequately described.[1a,c]

A stock solution of calcium chloride prepared from twice-recrystallised AnalaR material

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[6] J. M. Stokes and R. H. Stokes, *J. Phys. Chem.*, 1963, **67**, 2442.

[7] H. S. Harned, *J. Amer. Chem. Soc.*, 1926, **48**, 326.

[8] (*a*) E. A. Guggenheim, *Phil. Mag.*, 1935, **19**, 588; (*b*) E. A. Guggenheim and L. A. Wiseman, *ibid.*, 1938, **25**, 45.

[9] E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, 1955, **51**, 747.

[10] E. A. Guggenheim, *Kgl. danske Videnskab. Selskab, Mat-fys. Medd.*, 1955, **30**, no. 14.

[11] T. Cressey, A. K. Covington, B. G. Lever, and H. R. Thirsk, *Trans. Faraday Soc.*, 1962, **58**, 1975.

[12] T. Shedlovsky and D. A. MacInnes, *J. Amer. Chem. Soc.*, 1937, **59**, 503.

[13] H. C. McLeod and A. R. Gordon, *J. Amer. Chem. Soc.*, 1946, **68**, 58.

was estimated by differential potentiometric titration [14] with silver nitrate solution that had been standardised by the same method against hydrochloric acid prepared from constant boiling distillate.[15] Electrolytic silver–silver chloride electrodes on platinum gauze were used in preference to the thermal-electrolytic type employed in the e.m.f. studies. The stock solution was weight-diluted to obtain a solution of molality exactly 0·3333. Mixtures of hydrochloric acid and calcium chloride were prepared by direct weighing of the required proportions of this solution and 0·1m-hydrochloric acid.

A stock solution of manganous chloride was prepared from thrice-recrystallised manganous chloride, $MnCl_2,4H_2O$, and estimated by titration against standardised potassium permanganate by the electrometric method of Lingane and Karplus.[16] Solutions were then prepared as for calcium chloride mixtures.

Theory

The e.m.f. of the equivalent cell,

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}\ (\mathrm{m}) \mid \mathrm{H_2} \ldots\ldots\ldots\ldots \mathrm{H_2} \mid \mathrm{HCl}\ (\mathrm{m_1}),\ \mathrm{MCl_2}\ (\mathrm{m_2}) \mid \mathrm{AgCl} \mid \mathrm{Ag},$$

obtained by subtracting the e.m.f. of cell (A) from that of cell (B) at the instant of transfer of the glass electrode, is given by

$$E = \frac{-\boldsymbol{R}T}{F} \ln \mathrm{m_1}(\mathrm{m_1} + 2\mathrm{m_2})\, \gamma^2_{\mathrm{HCl(MCl_2)}} + \frac{2\boldsymbol{R}T}{F} \ln \mathrm{m}\gamma_{\mathrm{HCl(0)}} \qquad (1)$$

where the nomenclature $\gamma_{\mathrm{HCl(MCl_2)}}$ indicates the activity coefficient of hydrochloric acid in the presence of MCl_2 and $\gamma_{\mathrm{HCl(0)}}$ the activity coefficient in absence of added salt (pure hydrochloric acid solution). Later, we shall use $\gamma_{(0)\mathrm{HCl}}$, which is the activity-coefficient of hydrochloric acid present as a trace in the presence of the added electrolyte (at $I = 0{\cdot}1$).

Rearranging equation (1) and introducing $\mathrm{m_1} = xI$ and $\mathrm{m_2} = (1 - x)I/3$, so that the total ionic strength I will be constant, we have

$$\begin{aligned}\log \gamma_{\mathrm{HCl(MCl_2)}} - \log \gamma_{\mathrm{HCl(0)}} &= \frac{-E}{2k} - \tfrac{1}{2} \log xI\,[xI + \tfrac{2}{3}\,(1 - x)\,I] + \log \mathrm{m} \\ &= \frac{-E}{2k} - \tfrac{1}{2} \log \frac{x}{3}(x + 2)\end{aligned}$$

since $\mathrm{m} = I = 0{\cdot}1$ and where $k = (\boldsymbol{R}T \ln 10)/F = 59{\cdot}159$ mv at 25°.

Application of Guggenheim's theory [9] to a mixture of 2 : 1 and 1 : 1 electrolytes gives

$$\ln \gamma_{\mathrm{HCl(MCl_2)}} = \ln \gamma^{\mathrm{st}} + \beta_{\mathrm{H,Cl}}\mathrm{m}_{\mathrm{Cl^-}} + \beta_{\mathrm{H,Cl}}\mathrm{m}_{\mathrm{H^+}} + \beta_{\mathrm{M,Cl}}\mathrm{m}_{\mathrm{Ca^{2+}}}$$

where the β's are specific interaction coefficients based on natural logarithms and $\ln \gamma^{\mathrm{st}} = -\alpha I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ in which $\alpha \equiv A \ln 10$, A being the Debye–Hückel limiting-law constant.

Introducing $\mathrm{m}_{\mathrm{M^+}} = xI$, $\mathrm{m}_{\mathrm{Ca^{2+}}} = \tfrac{1}{3}(1 - x)I$, and noting that

$$\ln \gamma_{\mathrm{HCl(0)}} = \ln \gamma^{\mathrm{st}} + 2\beta_{\mathrm{H,Cl}}$$

$$\ln \gamma_{\mathrm{HCl(MCl_2)}} - \ln \gamma_{\mathrm{HCl(0)}} = (\beta_{\mathrm{H,Cl}} - \tfrac{1}{3}\beta_{\mathrm{M,Cl}})xI + \tfrac{1}{3}\beta_{\mathrm{M,Cl}}I - \beta_{\mathrm{H,Cl}}I \qquad (3)$$

However, $B_{\mathrm{H,Cl}} \ln 10 = 2\beta_{\mathrm{H,Cl}}$ and $B_{\mathrm{M,Cl}} \ln 10 = \tfrac{8}{3}\beta_{\mathrm{M,Cl}}$ where the B's are specific interaction coefficients in terms of decadic logarithms. Thus, a plot of $\log \gamma_{\mathrm{HCl(MCl_2)}} - \log \gamma_{\mathrm{HCl(0)}}$ against x should give a straight line of slope $\tfrac{1}{2}(B_{\mathrm{H,Cl}} - \tfrac{1}{4}B_{\mathrm{M,Cl}})$, if Guggenheim's theory is obeyed by the mixture,[8,9] and the separate specific interaction coefficients can be evaluated from measurements on the pure components.

Results and Discussion

The results of the measurements are given in Table 1. Each e.m.f.-value is the mean of at least six determinations made with more than one glass electrode. With manganous chloride the results calculated by using equation (2) were corrected for the fact that $\mathrm{m_2} = 0{\cdot}3328$ instead of $0{\cdot}3333$ as intended.

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[14] D. A. MacInnes and M. Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 1119.

[15] C. W. Foulk and M. Hollingsworth, *J. Amer. Chem. Soc.*, 1923, **45**, 1220.

[16] J. J. Lingane and R. Karplus, *Ind. Eng. Chem. Analyt. Edn.*, 1946, **18**, 191.

TABLE 1

Added electrolyte	Calcium chloride		Manganous chloride	
x	E (mv)	$\log \gamma_{\mathrm{HCl(CaCl_2)}} - \log \gamma_{\mathrm{HCl(0)}}$	E (mv)	$\log \gamma_{\mathrm{HCl(MnCl_2)}} - \log \gamma_{\mathrm{HCl(0)}}$
1	0	0	0	0
0·75	9·71	$0\cdot0007_1$	9·78	$0\cdot0012_4$
0·5	22·72	$0\cdot0019_2$	22·74	$0\cdot0019_4$
0·25	$43\cdot42_5$	$0\cdot0035_2$	43·43	$0\cdot0033_3$
0·1	68·85	$0\cdot0044_6$	68·89	$0\cdot0044_9$
0·05	—	—	87·31	$0\cdot0044_1$
0	—	0·0046 ($\log \gamma_{\mathrm{(0)HCl}}$)	—	0·0046 ($\log \gamma_{\mathrm{(0)HCl}}$)

The results are plotted in Figure 1. Although these may lie on a curve, it is clear that, within 0·03 mv in the e.m.f., they may be represented by a straight line, and moreover, that both added electrolytes have the same effect on the activity coefficient of hydrochloric acid. From the slope of Figure 1, $B_{\mathrm{Ca,Cl}} = B_{\mathrm{Mn,Cl}} = 0\cdot55$ mole^{-1} kg. taking [1a,b] $B_{\mathrm{H,Cl}} = 0\cdot22$ mole^{-1} kg. The value of $\log \gamma_{\mathrm{(0)HCl}}$ obtained by extrapolation is included in Table 1.

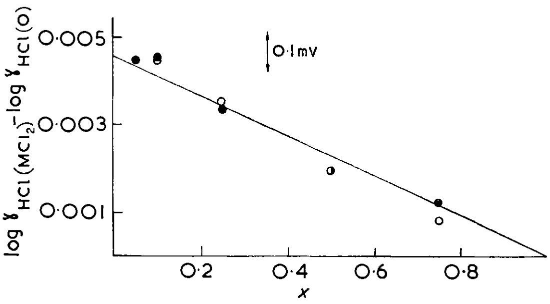

FIGURE 1. Calcium chloride ○; manganous chloride ●

In order to obtain a value of $B_{\mathrm{Ca,Cl}}$ for comparison, the results of Shedlovsky and MacInnes [12] and of McLeod and Gordon [13] on cells with transport have been re-analysed by using the transport-number data of Keenan, McLeod, and Gordon,[17] which differ uniformly by 0·001 from the earlier data of Longsworth [18] for a reason not yet elucidated.

The method of analysis was identical with that used previously for hydrochloric acid concentration cells, with the exception that Robinson and Stokes's method,[19] involving only one graphical integration was employed, and the experimental e.m.f. is divided by a factor of $\frac{3}{2}k$ instead of by k. Shedlovsky and MacInnes's data [12] were converted to the molality scale by using the equation [12] for the density (d)

$$d = 0\cdot99707 + 0\cdot0924c - 0\cdot0042c^{3/2}$$

where c is the molar concentration. The data were also corrected to absolute volts. In order to facilitate direct comparison of the two sets of e.m.f. data, those of Shedlovsky and MacInnes [12] were adjusted from values for a constant molality of 0·0502 to that of 0·02425, which is sufficiently close to the almost constant value of about 0·0249 employed by McLeod and Gordon.[13]

A plot [1b] of $\Delta \log \gamma - \Delta \log \gamma^{\mathrm{st}}$ is shown in Figure 2. Here $\log \gamma^{\mathrm{st}} = -2AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$. The two sets of values are clearly consistent to within less than 0·1 mv, and yield a straight line from which $B_{\mathrm{Ca,Cl}} = 0\cdot63$ mole^{-1} kg. may be derived. The agreement with the value from the mixed electrolyte cell is surprisingly good. The value $\lambda = \frac{3}{4}B = 0\cdot75$ derived by Guggenheim and Wiseman [8b] was based on Longsworth's transport numbers.[18] The same data [13] have been analysed by Stokes and Guggenheim,[20] who preferred a distance of

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[17] A. G. Keenan, H. C. McLeod, and A. R. Gordon, *J. Chem. Phys.*, 1945, **13**, 466.

[18] L. G. Longsworth, *J. Amer. Chem. Soc.*, 1935, **57**, 1185.

[19] R. A. Robinson and R. H. Stokes, " Electrolyte Solutions," 2nd edn., Butterworths, London, 1959, p. 203.

[20] E. A. Guggenheim and R. H. Stokes, *Trans. Faraday Soc.*, 1958, **54**, 1646.

closest approach greater than the value of 3·08 Å taken by Guggenheim;[8] the analysis may then be extended to higher ionic strengths. A fundamental dilemma arises here: the analysis of the mixed-electrolyte cell does not involve an assumption about the value of the ion-size term, but the analysis of the concentration cell does. The choice of 3·08 Å by Guggenheim[8,9] is of course entirely arbitrary. By using 4·7 Å, Stokes and Guggenheim[20] found $B = 0{\cdot}203$ mole^{-1} kg.

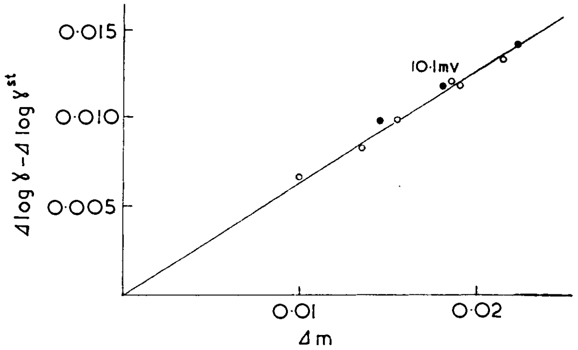
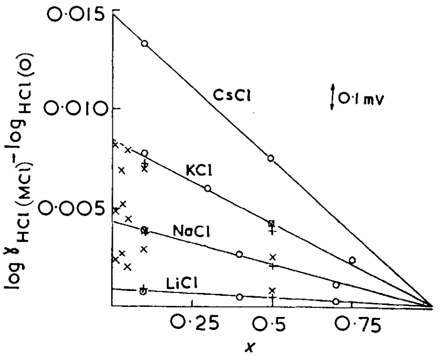


FIGURE 2. Shedlovsky and MacInnes[12] ●; McLeod and Gordon[13] ○

Guggenheim and Turgeon[9] in their survey did not repeat Guggenheim's analysis[8] of Güntelberg's results;[4] for comparison purposes, it is worth including here. Figure 3 shows $\log \gamma_{HCl(MCl)} - \log \gamma_{HCl(0)}$ plotted against x for Güntelberg's early work[3] at 20° and the later work[4] at 25°. The slope of the plot is $\frac{1}{2}$ $(B_{H,Cl} - B_{M,Cl})$ (cf. equation 3). The experiment with cæsium chloride as added electrolyte was not repeated. In the earlier work,[3] Güntelberg found difficulty in obtaining reproducible values for the e.m.f. of the cell containing hydrochloric acid at m = 0·1, because of the presence of bromide impurity.

FIGURE 3. Güntelberg[3] (20°) ○; Harned[7] (25°) ×; Güntelberg[4] (25°) +



The presence of bromide must affect only the standard potential of the silver–silver chloride electrode and not the activity coefficient, since the *changes* in activity coefficient found in the later work, when bromide was excluded, are consistent with the results of the earlier study. Harned's results[7] are also included in Figure 3. There is reasonable agreement between them and Güntelberg's except for lithium chloride, but Harned's results are of lower precision. The point at $x = 0{\cdot}3$, which is systematically in error for all three added electrolytes, has been omitted for clarity. In Table 2 the values of the specific interaction coefficients obtained from Güntelberg's results, assuming $B_{HCl} = 0{\cdot}23$ mole^{-1} kg., are compared with those calculated from measurements on the added electrolytes alone.[9]

TABLE 2

		LiCl	NaCl	KCl	CsCl
B_{MCl} (mole^{-1} kg.)	(Güntelberg[3,4])	0·21	0·15	0·07	−0·06 (at 20°)
	(Concentration cells)	—	0·13	0·09	—
	(Isopiestic v.p.)	0·19	—	0·09	0·00

In a refinement[10] of his treatment[8,21] prompted by an analysis of the problem by Scatchard,[22] Guggenheim has pointed out that the essential underlying approximation is that the contribution to the total free energy of the solution arising from short-range interactions between the species should take a form analogous to that for a regular solution of non-electrolytes. Short-range interactions between ions and water molecules are included as well as ion–ion interactions considered previously.[8,21] The simple formulæ[8a,9] for mixtures are obtained[10] only if the mixture is composed of electrolytes of the same charge type, unless it is additionally assumed that, not only are ions (in Brönsted's words[23]) " uniformly influenced by ions of their own sign," but also that both anions and cations, whatever the magnitude of their change, are " uniformly influenced " by the solvent molecules. As Guggenheim concluded,[10] there is no reason *a priori* why this should be so, but that it is a reasonable approximation is shown by the linearity of Figure 1. The requirement[8a] that the slopes of Figures 1 and 3 should be independent of I for $I < 0{\cdot}1$ has not yet been put to experimental test.

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[*Received, February* 12*th*, 1965.

[21] E. A. Guggenheim, Rep. 18th Scand. Sci. Congress, Copenhagen, 1929, p. 298.

[22] G. Scatchard, *J. Phys. Chem.*, 1954, **58**, 600.

[23] J. Brönsted, *J. Amer. Chem. Soc.*, 1922, **44**, 877.