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SOME ELECTROMOTIVE FORCE MEASUREMENTS WITH CALCIUM CHLORIDE SOLUTIONS

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The chemical potential, or partial molal free energy, of sodium or potassium chloride in a mixture of ethyl alcohol and water varies with changing solvent as should be expected if the deviation from ideality were due entirely to electrostatic effects. The very different behavior of hydrogen chloride may be explained simply by the existence of the hydrogen ion in solution in the form of the monohydrate.² So it is of interest to study calcium chloride, which has a heavily solvated solid phase in equilibrium with its solution in either solvent. Measurements were made of the electromotive force at 25° of the cell Ag, AgCl, CaCl₂(I), CaHg_x, CaCl₂(II), AgCl, Ag (double cell). Such measurements in aqueous solution have been published by Lucasse³ and, since the presentation of the thesis on which this paper is based, by Fosbinder.⁴ To study more closely the behavior of the amalgam electrodes, measurements were also made on the cell CaHg_x, CaCl₂, AgCl, Ag (single cell). It was expected that the chief difficulty would be due to chemical action at the amalgam electrode and that alcohol would be less reactive than water, so that a technique which proved satisfactory for aqueous solutions would work well in the alcohol mixtures. The expectations were not realized. Successful determinations were made in water, and fairly accurate ones in 46% (25 mole %) alcohol, but the behavior with 72% (50 mole %) alcohol was so different that no determinations could be made and no attempt was made to work at higher alcohol concentrations.

Apparatus and Materials

The double cell was essentially the same as that of MacInnes and Beattie⁵ except that the amalgam droppers were bent into a U shape and were about 5 mm. in diameter. The single cell was half the double cell, with an amalgam dropper having a single outlet. Droppers were used with tips varying from 1 to 11 mm.

Measurements were made in an atmosphere of hydrogen. Tank hydrogen was passed over copper at about 300°. That which was to be used over the solutions was then bubbled through some solution of the same composition; that which was to be used over the amalgam was dried by passing over calcium chloride and phosphorus pentoxide.

The water used for all solutions was twice-distilled "conductivity" water. Com-

¹ From a thesis submitted in May, 1928, by Ralph F. Tefft in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Scatchard, *THIS JOURNAL*, **47**, 2098 (1925).

³ Lucasse, *ibid.*, **47**, 743 (1925).

⁴ Fosbinder, *ibid.*, **51**, 1345 (1929).

⁵ MacInnes and Beattie, *ibid.*, **42**, 1123 (1920).

mercial alcohol was refluxed with lime for several days and then distilled. The middle portion was redistilled from aluminum amalgam, and the water content was determined from the density.

Calcium carbonate was prepared by precipitation from a solution of c. p. calcium chloride with c. p. ammonium carbonate, and was washed until free from chlorides. The stock solution of calcium chloride was prepared by the action of constant-boiling hydrochloric acid on an excess of this calcium carbonate. After the action had subsided, hydrogen was passed through for several hours. The hydrogen-ion concentration of this solution was between the methyl orange and phenolphthalein neutral points; the calcium chloride concentration was determined gravimetrically as silver chloride. The solutions of calcium chloride were prepared by weight dilution of this stock solution with water or with water and alcohol. A stream of hydrogen was passed through the diluted solution for five or ten minutes to remove any air admitted during the handling.

Mercury was purified by being passed eight times through a tower containing dilute nitric acid and mercurous nitrate, and then twice distilled in a current of air under reduced pressure. In recovering mercury from used amalgams, the distillations were omitted. The calcium amalgam, which contained 0.02–0.05% of calcium, was prepared by the electrolysis of the stock solution of calcium chloride with a mercury cathode. It was then rinsed, dried and stored in an evacuated pyrex container.

The silver–silver chloride electrodes were prepared by the method of MacInnes and Beattie,⁵ and chloridized in the solution in which they were to be used except that for solutions more concentrated than 0.3 *M* they were chloridized in 0.1 *M* solution, because electrolysis in the more concentrated solutions gave a compact non-conducting layer. At least 5 electrodes were prepared in each case, and that one used which was nearest the average in electromotive force. No electrode was considered in the average which differed from the others more than 0.05 mv.

The apparatus was placed in a water thermostat maintained at $25.00 \pm 0.01^\circ$. The potentiometer was a Leeds and Northrup Type K with an unsaturated cadmium sulfate reference cell. This cell was frequently checked against a series of saturated cadmium sulfate cells.

Measurements with the Single Cell

The cell $\text{CaHg}_x, \text{CaCl}_2, \text{AgCl}, \text{Ag}$ was used with approximately 0.02% calcium amalgam and 0.1 *M* calcium chloride in water with a series of U-shaped amalgam droppers having tips about 1, 3, 7 and 11 mm. in diameter. The rate of flow was varied from less than one drop per second to a continuous stream, and the electromotive force was also measured after flow was stopped. The electromotive force after stopping the flow was practically independent of the size of the tip. It decreased one or two-tenths of a millivolt per minute.

The 1-mm. dropper showed considerable fluctuation while the amalgam was flowing, and the electromotive force with streaming amalgam was 6 mv. less than with no flow. The 7-mm. dropper was much steadier and decreased only 2.5 mv. The 3-mm. dropper was intermediate in its behavior. The 11-mm. dropper behaved quite similarly to the 7 mm. one except that a bubble of hydrogen which formed on the surface was not carried away even with rapid flow and, presumably for that reason, the results were more erratic.

Measurements were also made on the cell $\text{ZnHg}_x, \text{ZnCl}_2, \text{AgCl}, \text{Ag}$ with about 0.05% zinc amalgam and about 0.1 *M* aqueous ZnCl_2 , and with a 5-mm. dropper. The electromotive force at 10 drops per second (almost continuous flow) was 0.5–0.6 mv. less than that immediately after the flow was stopped.

With the double cells the rate of flow was varied greatly, keeping the two rates as nearly equal as possible. That value was accepted which held over a large range of rates. The changes noted were probably due to small differences in the two rates, for there was no trend of the difference with the rate and visible differences between the two rates did give large changes in electromotive force. This technique was satisfactory with aqueous solutions if the rate was not too great (fast streaming) and the amalgam concentration not too small (less than 0.015%).

The direction of the change in electromotive force with changing rate of flow is surprising. Chemical action at the electrode would decrease the calcium concentration and increase that of calcium ion, and so decrease the electromotive force. The effect would be smaller the more rapid the flow, so that rapid flow should give the largest electromotive force.

The only cause which occurs to the authors which would give an electromotive force decreasing with the rate, and decreasing the more rapidly at high rates, is failure to obtain equilibrium between the surface and the bulk of the amalgam. If the interfacial tension decreases with increasing calcium content of the amalgam, the calcium will be adsorbed at the interface, and calcium will have a smaller chemical potential in a fresh surface than in the bulk liquid from which it is formed. The resulting decrease in electromotive force should be greater the more rapid the flow. This explanation also accounts for the fact that the difficulty is greater the more dilute the amalgam, for the relative unsaturation would be greater, but that it is practically independent of the salt concentration.

No measurements have been made of the interfacial tension between calcium amalgams and solutions of calcium salts. Schmidt⁶ and Oppenheimer⁷ have measured the surface tensions of amalgams *in vacuo*. The first found that lithium and the alkaline earth metals increase the surface tension of mercury greatly and that zinc does a little, while sodium and potassium give large decreases. The second found that lithium decreases the surface tension even more than sodium, and that calcium gives a considerable decrease. Meyer⁸ measured the interfacial tension of zinc and the alkali amalgams against aqueous solutions of their salts. He found that all decrease the interfacial tension, lithium enormously. His results parallel those of Oppenheimer. The effect is in the proper direction to account

⁶ Schmidt, *Ann. Physik*, **39**, 1108 (1912).

⁷ Oppenheimer, *Z. anorg. allgem. Chem.*, **171**, 98 (1928).

⁸ Meyer, *Z. physik. Chem.*, **70**, 315 (1910).

for our observations with zinc amalgam and, if the parallelism to Oppenheimer's results may be extended to calcium amalgam, it should give a much larger effect in the same direction. This is also in accord with our observations.

Our double cell technique gave measurements in 46% alcohol reproducible only to 0.5 mv. instead of 0.1–0.2 mv., but they still seemed fairly satisfactory. With 72% alcohol, however, the discrepancies were so great that measurements were again attempted with the single cell, using a 5-mm. dropper. Two runs were made. In the concentrated run the amalgam concentration was about 0.04% and the salt concentration about 0.2 *M*. In the dilute one the amalgam was about 0.01% and the salt about 0.02 *M*. In both cases a scum, probably calcium hydroxide, formed on the surface of the amalgams. The fluctuations were very large, particularly at the slower rates of flow with the concentrated amalgam. The electromotive force increased with rate of flow, about 35 mv. for the concentrated and about 45 for the dilute. In both cases the increase was large even after the flow was continuous.

Since the effect of the rate of flow is so enormous, there is little chance of maintaining the two rates of flow in the double cell near enough equal to give significant results. Measurements with aqueous solutions on one side and alcoholic solutions on the other are quite out of the question since the electromotive force is changed in opposite directions by changing the rate. For this reason work on alcoholic solutions was discontinued.

Wolfenden and his co-workers⁹ made measurements with a single jet electrode with sodium amalgam and a methyl alcoholic solution of sodium chloride. With 0.04% amalgam they found that the electromotive force increased about 4 mv. when the rate of flow was increased, and that the effect was independent of the salt concentration. They concluded that the cause was not chemical action because the increase persisted with large rates of flow. With 0.003% amalgam they found that increasing the rate of flow sometimes increased the electromotive force somewhat more than with the concentrated amalgam and sometimes gave a decrease of the same order of magnitude.

The argument of these authors against chemical action as the cause of the effect of changing rate applies equally to our results. If adsorption is the cause, it must be adsorption of the metal ion, and it is surprising that they found practically no change for a hundred-fold increase of salt concentration. The difficulties of any explanation are enhanced by the magnitude of the effect which must be explained, for the change in electromotive force with the alcoholic calcium chloride solutions corresponds to a twenty- or thirty-fold increase of calcium ion. That such a change can result from chemical action, adsorption or the combination of the two is scarcely to be expected.

⁹ Wolfenden, Wright, Kane and Buckley, *Trans. Faraday Soc.*, **23**, 491 (1927).

Measurements with the Double Cell

Since the accuracy of measurement decreases for very dilute solutions, a 0.1 *M* solution in water was chosen as comparison standard. Table I gives the results of the measurements with aqueous solutions. The first column gives the exact concentration of the reference solution (in moles per 1000 g. of solvent); the second column, the concentration of the second solution; the third column, the measured electromotive force; and the fourth column gives this value minus the value calculated from the Debye-Hückel equation with the constants given below. In Fig. 1 these deviations are shown graphically together with the corresponding deviations

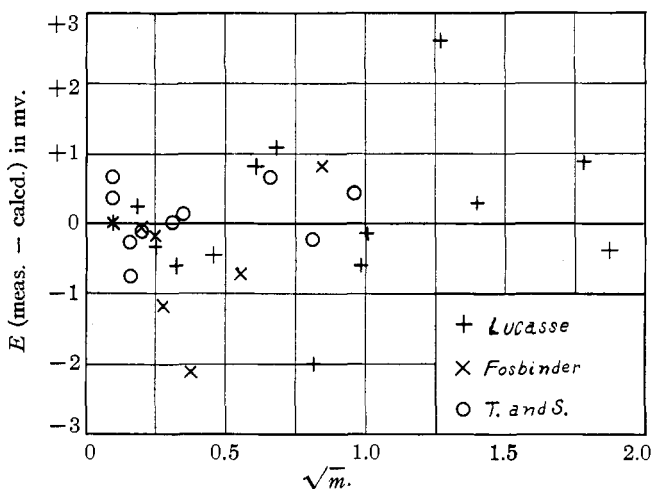


Fig. 1.—Electromotive force of calcium chloride cells.

of the measurements of Lucasse and of Fosbinder, both of whom used a 0.01 *M* solution as reference standard. The measurement of Fosbinder at 0.0897 *M* and all his measurements above 1 *M* are omitted because the deviations are larger than the scale of the figure. The average deviation of our measurements is 0.41 mv.; below 1.0 *M* that of Lucasse is 0.71 mv.,

TABLE I

ELECTROMOTIVE FORCE OF CALCIUM CHLORIDE CONCENTRATION CELLS IN WATER

m_1	m_2	$E(\text{meas.})$	$E(\text{meas.} - \text{calcd.})$
0.09989	0.009921	0.0761	+0.0004
.09978	.010509	.0742	+ .0007
.10041	.02594	.0439	- .0003
.09983	.02758	.0412	- .0007
.09989	.04113	.02892	- .00010
.09993	.12634	-.0078	+ .0001
.10029	.4420	-.0558	+ .0007
.09968	.6589	-.0768	- .0002
.10056	.9301	-.09615	+ .00043

and of Fosbinder 1.45 mv. The agreement between these independent observations gives some assurance that the electromotive force of the calcium chloride concentration cell with aqueous solutions does measure the free energy of transfer of the salt.

A concentration cell such as [Ag, AgCl, CaCl₂(I), CaHg_x], CaCl₂(II), AgCl, Ag in which the composition of solution (I) is kept constant during a series of measurements while solution (II) is varied may be treated as though that portion of the cell in brackets were a single electrode. This treatment is particularly convenient when the variation in solution (II) is a change in the solvent. By the theory of Debye and Hückel, the electromotive force, E , of such a cell is given by

$$E = E_0 - k \log \frac{m}{1 + wm} + \frac{A\sqrt{c}}{1 + \alpha\sqrt{c}} - \beta c - k' \quad (1)$$

m is the number of moles of salt per kilogram of solvent, c the moles per liter of solution (both in solution II), and w is one-thousandth of the average molecular weight of the solvent multiplied by the number of ions in one mole of salt.¹⁰ E_0 depends upon the temperature, the nature of the solvents on the two sides and on the concentration of solution (I). The computation of the numerical constants need not be repeated here, but it is sufficient to say that for a bi-univalent electrolyte at 25° k is 0.088725 volt and k' is 0.01781 volt; if the solvent is water, w is 0.054, A is 0.1550 volt, and $\alpha = 0.568 a$, where a is the diameter of the mean collision sphere of the ions in Ångström units; in 25 mole % alcohol, w is 0.075, A is 0.310 volt, and $\alpha = 0.716 a$. β is a function of the solvent composition and the temperature which must be determined from the data.

If the solvent is the same on the two sides, the constants α and β may be determined from two measurements, and E_0 is given from the fact that E must be zero when the two concentrations are equal. If the solvents are different, three measurements are necessary to determine the three constants. Equation 1 was used to determine the small correction necessary because m_1 was not exactly 0.1 M , and to determine the difference in E_0 between our measurements and those of the other workers, who used different standard concentrations.

For aqueous solutions the volume concentrations were computed by the equation $c/m = 0.99707 - 0.0214 m - 0.0019 m^2$, and the constants used are $\alpha = 2.1$, which corresponds to $a = 3.70$, $\beta = 0.04$ volt, and $E_0 = -0.13217$ volt when $m_1 = 0.1 M$. Values of γ computed with these constants are given in the following paper.¹¹

The results in 25 mole per cent. alcohol, with solution I in water, are given in Table II. The first column gives the concentration of the aqueous solu-

¹⁰ For any one solvent, then, $m/(1 + wm)$ is proportional to the mole fraction of either ion.

¹¹ Scatchard and Tefft, *THIS JOURNAL*, 52, 2272 (1930).

TABLE II

ELECTROMOTIVE FORCE OF CALCIUM CHLORIDE CELLS IN 25 MOLE PER CENT. ALCOHOL

m_1	m_2	ρ_2	E	E_0
0.1102	0.01316	0.91995	-0.0081	-0.2219
.1003	.1192	.92798	-.0785	-.2278
.1003	.9712	.99126	-.16295	-.2244

tion, the second that of the alcoholic solution in moles per kilogram of solvent, and the third column gives the measured density, from which the volume concentrations were calculated. The fourth column gives the measured electromotive force, and the fifth E_0 calculated from Equation 1. Giving a the same value as in water, α is 2.65, and the data are fitted best by taking $\beta = 0.05$ volt. The average E_0 is -0.2247 volt. The average deviation is large, 2 millivolts, but this is not surprising in view of the extreme difficulty with 50 mole per cent. solutions.

According to Debye's theory of salting out, etc.,^{12,2} the change in E_0 with changing solvent should depend upon the molecular weights of the two solvents, their dielectric constants, and the electrical radius of the ions, b , according to the equation (for a bi-univalent electrolyte)

$$E_{01} - E_{02} = 0.088725 \log \frac{M_2}{M_1} + \frac{21.50}{b} \left(\frac{1}{D_2} - \frac{1}{D_1} \right) \quad (2)$$

For water and 25 mole per cent. ethyl alcohol, the first term is 0.01266 volt, leaving 0.0799 volt for the electrical term. The coefficient of $1/b$ is 0.1605 volt. This gives $b = 2.0$ Ångström units, which agrees with the value computed from the salting out of H_2 , O_2 and CO_2 .¹³

Summary

The electromotive force of the cell $Ag, AgCl, CaCl_2 (0.1 M, aq.), CaHg_x, CaCl_2 (m), AgCl, Ag$ has been measured at 25° with m varying from 0.01 to 1.0 in water and in 25 mole per cent. ethyl alcohol, and the Debye theory has been applied to the results.

With aqueous solutions the potential of the calcium amalgam electrode decreases slightly with increasing rate of flow, probably because of adsorption of calcium at the interface.

With water-alcohol mixtures the potential increases rapidly with increasing rate of flow, so that accurate measurements are not possible when the alcohol concentration is large.

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¹² Debye and MacAuley, *Physik. Z.*, **26**, 22 (1925).

¹³ Scatchard, *Trans. Faraday Soc.*, **23**, 454 (1927).