# The Determination of the Activity Coefficients of Pb(II), Cd(II), and Zn(II) Chlorides in *N,N'*-Dimethylformamide by Means of Electromotive-force Measurements of the M(Hg)/MCl$_2$(DMF)/AgCl; Cells*

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Electromotive-forces have been measured for the cells of the M(Hg)/MCl$_2$(DMF)/AgCl;Ag type at 25.00± 0.01 °C, where M are Pb, Cd, and Zn metals and were M(Hg) are amalgams saturated with these metals. The standard potentials of the corresponding metals relative to the silver-silver chloride have been determined, and the mean activity coefficients and the standard free-energies of formation have been calculated for the solvated salts of PbCl$_2$, CdCl$_2$, and ZnCl$_2$ from the electromotive-foce data. Experimental works were carried out by using an H-shaped Pyrex glass cell which was coated externally with silicon grease to eliminate electrical leakage from the water bath. The electromotive-force measurements were made with a digital voltmeter, the voltage sensitivity and the input impedance of which were 10 μV and 100 megohms respectively. The standard potentials for the cells of the M/MCl$_2$(DMF)/AgCl;Ag type were 0.327$_1$ V for PbCl$_2$, 0.576$_2$ V for CdCl$_2$, and 0.898$_6$ V for ZnCl$_2$.

In the early measurements of electromotive-force, Ulisch and Spiegel[1)] discussed the reproducibilities of silver silver chloride and calomel electrodes in acetonitril as a solvent containing chloride ions. Pavlopoulos and Strehlow[2)] measured the standard electrode potentials for various first kind electrodes in formamide. Luksha and Criss[3)] determined the standard electromotive-forces for cells of the M(Hg)/MX(NMF)/AgX; Ag type, where M is Li, Na, K, or Cs and where X is either Cl$^-$ or Br$^-$, and determined the activity coefficients of alkali metal ions in anhydrous *N*-methylformamide (NMF). Marple[4)] studied the nonpolarizability of Cd(Hg)/CdCl$_2$ as reference electrode for polarographic studies in anhydrous *N,N'*-dimethylformamide (DMF). Studies of various reversible chloride electrodes which are used in dimethylsulfoxide, DMF, and propylene carbonate were carried out by Synott and Butler.[5)] According to their paper, thallium, lead, and cadmium chloride electrodes were all stable in DMF, but the CdCl$_2$ was apparently the most stable in potential. The initial potential, 1.653 V, varied by less than 1 mV over the next 12 hr. In the present study, the electromotive-forces have been measured for cells of the M(Hg)/MCl$_2$/AgCl; Ag type, where M are Pb, Cd, and Zn metals and where M(Hg) are amalgams saturated with these metals. The standard potentials of the corresponding metals relative to the silver-silver chloride electrode were determined, and the mean activity coefficients and standard free-energies of formation were obtained for the solvated salts of PbCl$_2$, CdCl$_2$, and ZnCl$_2$.

## Experimental

*Solvent.* DMF purified by the method described in a previous paper[6)] was used. The specific conductivity of the DMF used was 7.0～7.5×10$^{-8}$ ohm$^{-1}$ cm$^{-1}$ at 25 °C. Karl-Fisher titrations indicated the water content in the distilled DMF to be less than 0.03%.

*Anhydrous Metal Chlorides.* Anhydrous metal chloride was prepared from hydrated metal chloride by treating it with thionyl chloride according to Tyree's method.[7)]

*Amalgams.* Lead, cadmium, and zinc amalgams were prepared by the method of Kolthoff.[8)] A quantity of metal was gently heated together with mercury and a small amount of diluted sulfuric acid, and then the amalgam thus prepared was carefully washed with diluted sulfuric acid and stocked under diluted sulfuric acid. The amalgam used as a heterogeneous (saturated) one.

All the other reagents used were of an analytical grade.

*Electrodes.* The Ag-AgCl electrode was prepared from Pt wire plated with silver by means of the electrolytic method.[9—10)] The electrode was made up from 0.50 cm-diameter Pt wire sealed in Pyrex glass. Lengths of wire up to 15 cm were left exposed and spiralled, and then it was plated with silver by means of electrolysis from a mixed solution of silver nitrate and potassium cyanide. Eight electrodes were prepared at a time, and those with a bias potential greater than 0.3 mV were discarded. All the electrodes were stored in double-distilled water before use. The dropping analgam electrode used had a flow rate of 1～2 s/drop. No effect of the flow rate on the electromotive force (EMF) of the cells could be observed as had been reported by Walfenden *et al.*[11)] and Scatchard and Tefft.[12)]

*Apparatus.* The H-cell was made of Pyrex glass, and the two electrodes inserted into the cell were fixed with a silicon rubber stopper. The cell, coated externally with silicon grease to eliminate an electrical leakage from the water bath, was thermostatted on the water bath at 25.00±0.01 °C.

All the electromotive-force measurements were made with a Kuwano Electric Instruments, model DM-750, digital voltmeter. The voltage sensitivity and the input impedance of this voltmeter were 10 μV and 100 megohms respectively.

*Experimental Procedures.* About a 0.1 molal metal chloride DMF stock solution was prepared by dissolving a quantity of anhydrous metal chlorides in DMF in an ice bath. The concentration of metal chloride in the stock solution was determined by chelatometric titration[13)] with EDTA before the solution was used in each experiment.

The electromotive-foce measurements were carried out in

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the manner described by Luksha and Criss.[3] Readings were taken approximately every 2 min, for a period of 45 min in general, but in a few cases for as long as 90 min.

## Results and Discussion

The electromotive-force of a cell containing 2—1 electrolytes and with its electrodes in their standard states is given by:

$$E = E^\circ - \frac{3RT}{nF} \ln m\gamma_\pm, \qquad (1)$$

where the symbols have their usual meanings. The expanded Debye Hückel equation gives the mean activity coefficient for the 2—1 electrolyte as:

$$\log \gamma_\pm = -\delta_r\sqrt{m} + \beta m,$$

$$\text{where:} \quad \delta_r = 6.3213\times 10^6 \frac{\rho_0^{1/2}}{(\varepsilon T)^{3/2}}, \qquad (2)$$

$\beta$ is a constant, $m$ is the molality, and $\rho_0$ and $\varepsilon$ are the density and the dielectric constant of the solvent respectively. For DMF at 25 °C, $\varepsilon$ is 36.7 and $\rho_0$ is 0.944 g/cm$^3$, giving a value of 0.1148 kg/mol for $\delta_r$. The substitution of Eq. (2) into Eq. (1) and the rearrangement of the terms give:

$$E + \frac{3RT}{nF}\ln m - \frac{(2.303)3RT\delta_r\sqrt{m}}{nF} = E^\circ - \frac{(2.303)3RT\beta m}{nF}, \qquad (3)$$

The substitution of the appropriate constants into Eq. (3) leads to

$$E + 0.0887\log m - 0.455\sqrt{m} = E^\circ - 0.0887\beta m, \qquad (4)$$

The cell employed in this experiment is written as:

$$\mathrm{M(Hg)/MCl_2(DMF)/AgCl;\ Ag.} \qquad (a)$$

The measured potential of the (a) cell is not the electromotive force represented by $E$ in Eq. (4), but, rather, a potential, $E'$, related to $E$ by:

$$E' = E - E'', \qquad (5)$$

where $E''$ is the potential of a cell of this type:

$$\mathrm{M/MCl_2(soln)/M(Hg).} \qquad (b)$$

To correct the observed potential to that which one would obtain for a pure metallic electrode, the $E''$ value must be added to the observed potential. Making this substitution and setting the left-hand side of Eq. (4) equal to $E'''$ gives:

$$E''' = E^\circ - 0.0887\beta m. \qquad (6)$$

The resultant potentials then refer to a cell employing a pure metallic electrode and may be written as the (c) cell:

$$\mathrm{M/MCl_2(DMF)/AgCl;\ Ag} \qquad (c)$$

The relationships between the electromotive-force and the time of measurements at various concentrations are shown in Fig. 1 for the zinc chloride cell. As may be seen from Fig. 1, the potentials reached an equilibrium within 10 min from the begining of the measurements. The data obtained are summarized in Table 1. The first two columns give the molality of the cell solution and the measured potential respectively. The third column gives the potential required to correct the observed potential to that for a pure metallic electrode that is, the potential corresponding to the electromotive-force for cells of the (b) type cell. The values of the potential are listed from the literature.[13,14] The fourth column gives the values of $E'''$ in Eq. (6), and the fifth column gives the potentials for cells of (c) type cell. The $E'''$ values are plotted against the molality and extrapolated to an infinite dilution by the method of least-squares to obtain $E^\circ$. Some typical results obtained are shown in

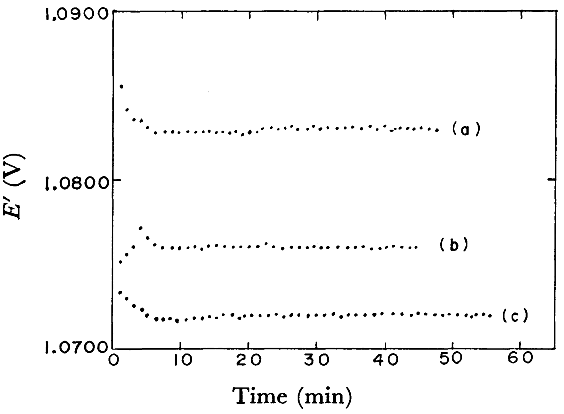

Fig. 1. Stability of electromotive-force for cell of type(a). (a): 0.1117 $m$ ZnCl$_2$, (b): 0.1861 $m$ ZnCl$_2$, (c): 0.2606 $m$ ZnCl$_2$.

Table 1. Electromotive-force data for electrolytes in DMF at 25 °C

| Molality | $E'$ | $E''$ | $E'''$ | $E$ |
|---|---|---|---|---|
| | | PbCl$_2$ | | |
| 0.0053 | 0.5587 | 0.0058 | 0.3311 | 0.5645 |
| 0.0106 | 0.5397 | 0.0058 | 0.3235 | 0.5455 |
| 0.0212 | 0.5208 | 0.0058 | 0.3118 | 0.5266 |
| 0.3018 | 0.5141 | 0.0058 | 0.3055 | 0.5199 |
| 0.0424 | 0.5086 | 0.0058 | 0.2989 | 0.5144 |
| 0.0529 | 0.5041 | 0.0058 | 0.2889 | 0.5099 |
| 0.0635 | 0.5000 | 0.0058 | 0.2848 | 0.5058 |
| 0.0741 | 0.4973 | 0.0058 | 0.2795 | 0.5037 |
| | | CdCl$_2$ | | |
| 0.0065 | 0.7473 | 0.0505 | 0.5719 | 0.7978 |
| 0.0131 | 0.7394 | 0.0505 | 0.5707 | 0.7899 |
| 0.0196 | 0.7328 | 0.0505 | 0.5681 | 0.7833 |
| 0.0261 | 0.7291 | 0.0505 | 0.5656 | 0.7796 |
| 0.0327 | 0.7262 | 0.0505 | 0.5628 | 0.7769 |
| 0.0457 | 0.7239 | 0.0505 | 0.5583 | 0.7744 |
| 0.0537 | 0.7221 | 0.0505 | 0.5510 | 0.7708 |
| 0.0588 | 0.7211 | 0.0505 | 0.5502 | 0.7697 |
| 0.0653 | 0.7111 | 0.0505 | 0.5500 | 0.7616 |
| | | ZnCl$_2$ | | |
| 0.0185 | 1.1060 | 0.0000 | 0.8882 | 1.1060 |
| 0.0372 | 1.0961 | 0.0000 | 0.8815 | 1.0961 |
| 0.0745 | 1.0878 | 0.0000 | 0.8635 | 1.0878 |
| 0.1117 | 1.0828 | 0.0000 | 0.8461 | 1.0828 |
| 0.1489 | 1.0790 | 0.0000 | 0.8299 | 1.0790 |
| 0.1861 | 1.0760 | 0.0000 | 0.8163 | 1.0760 |
| 0.2234 | 1.0736 | 0.0000 | 0.8006 | 1.0736 |
| 0.2606 | 1.0718 | 0.0000 | 0.7875 | 1.0718 |
| 0.2987 | 1.0703 | 0.0000 | 0.7751 | 1.0703 |

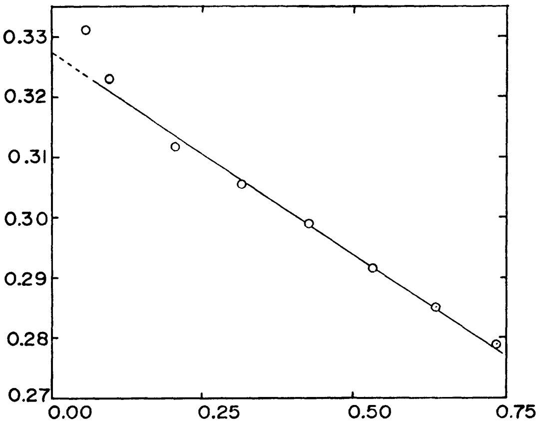

Fig. 2. Relationship between $E'''$ and molality for $PbCl_2$ cell.

Fig. 2. Although the plots in the case of a concentration higher than 0.1 mol of a cell solution are not shown in Fig. 2, the relationship between the electromotive-force and the concentration of metal chloride makes a curve with a gentle slope. It may be considered that the dissociation of metal chloride in DMF becomes difficult in proportion to the increasing concentration of the salt. The standard potentials for the cells of the (c) type as evaluated by the least-squares treatment, are given in Table 2. From the data of the electromotive-force measurements of the (c) type cells and the standard potential, the activity coefficients of the corresponding salts in DMF are obtained. The rearrangement of Eq. (1) gives:

TABLE 2. STANDARD POTENTIALS FOR CELL OF TYPE (C)

| Cell | $E^\circ$ (V) |
|---|---|
| Pb \| $PbCl_2$ (DMF) \| AgCl; Ag | $0.327_1$ |
| Cd \| $CdCl_2$ (DMF) \| AgCl; Ag | $0.576_2$ |
| Zn \| $ZnCl_2$ (DMF) \| AgCl; Ag | $0.988_6$ |

$$\log \gamma_\pm = \frac{E^\circ - E}{0.0887} - \log m \qquad (7)$$

from which $\gamma\pm$ values for various electrolytes have been evaluated. The smoothed values of $E$ and the activity coefficients for a round concentration of metal chloride in cells of the (c) type listed in Table 3. The plots of the activity coefficients against the concentrations of metal chlorides related to this work are shown in Fig. 3.

TABLE 3. SMOOTHED VALUES OF $E$ AND ACTIVITY COEFFICIENTS FOR ROUND CONCENTRATIONS FOR CELL (C)

| Molality | $PbCl_2$ |  | $CdCl_2$ |  | $ZnCl_2$ |  |
|---|---|---|---|---|---|---|
|  | $E$ | $\gamma_\pm$ | $E$ | $\gamma_\pm$ | $E$ | $\gamma_\pm$ |
| 0.01 | 0.5450 | 0.349 | 0.7936 | 0.354 | 1.116 | 0.354 |
| 0.02 | 0.5275 | 0.275 | 0.7837 | 0.229 | 1.105 | 0.236 |
| 0.03 | 0.5205 | 0.220 | 0.7765 | 0.184 | 1.099 | 0.184 |
| 0.04 | 0.5150 | 0.190 | 0.7730 | 0.151 | 1.095 | 0.153 |
| 0.05 | 0.5150 | 0.171 | 0.7708 | 0.128 | 1.092 | 0.133 |
| 0.06 | 0.5070 | 0.156 | 0.7690 | 0.112 | 1.090 | 0.114 |
| 0.07 | 0.5040 | 0.145 | 0.7677 | 0.104 | 1.089 | 0.102 |
| 0.08 | 0.5015 | 0.135 | 0.7667 | 0.103 | 1.0885 | 0.091 |
| 0.09 | 0.5010 | 0.124 | 0.7660 | 0.102 | 1.0882 | 0.081 |
| 0.10 | 0.500 | 0.110 | 0.7655 | 0.101 | 1.0880 | 0.073 |

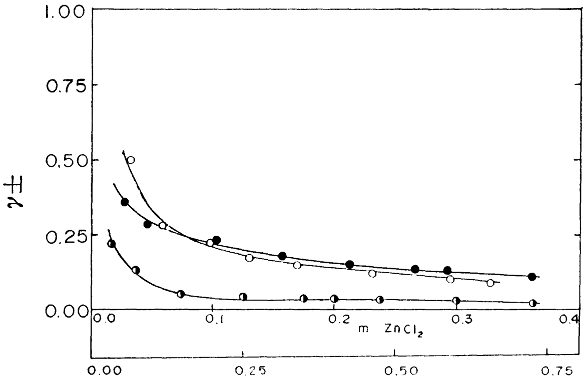

Fig. 3. Relationships between activity coefficients and molalities of metal chlorides in DMF.
—○—: $PbCl_2$, —●—: $CdCl_2$, —◑—: $ZnCl_2$.

*Standard Free-energies of the Solvated Electrolytes.* The general reaction for the (c) cell is:

$$M(s) + 2AgCl(s) = 2Ag(s) + MCl_2(soln),$$

and the corresponding standard free-energy change for this reaction is:

$$\Delta G^\circ = G^\circ_{\mathrm{f}_{\mathrm{MCl_2(soln)}}} + 2G^\circ_{\mathrm{f}_{\mathrm{Ag(s)}}} - G^\circ_{\mathrm{f}_{\mathrm{M(s)}}} - 2G^\circ_{\mathrm{f}_{\mathrm{AgCl(s)}}} = -nFE^\circ \qquad (8)$$

where $G^\circ_{\mathrm{fMCl_2(soln)}}$ is the standard free-energy of the formation of a solvated $MCl_2$. The standard free-energy of the formation of a solvated salt, $MCl_2$, is then given by:

$$G^\circ_{\mathrm{f}_{\mathrm{MCl_2(soln)}}} = 2G^\circ_{\mathrm{f}_{\mathrm{AgCl(s)}}} - nFE^\circ \qquad (9)$$

The values for the standard free-energies of formation have also been calculated for the corresponding solvated salts; they are listed in Table 4.

TABLE 4. STANDARD FREE-ENERGIES OF FORMATION OF SOLVATED METAL CHLORIDES IN DMF

| Salt | $-G_f^\circ$ (kcal/mol) |  |
|---|---|---|
|  | DMF | $H_2O$ |
| $PbCl_2$ | 67.54 | 68.51 |
| $CdCl_2$ | 79.03 | 81.28 |
| $ZnCl_2$ | 93.90 | 97.88 |

The standard free-energy of the formation for silver chloride was obtained from Lange:[16] $G^\circ_{\mathrm{fAgCl(s)}} = -26.22$ kcal/mol. The standard free-energies of the formation of solvated lead, cadmium, and zinc chlorides in aqueous solutions are also listed in Table 4, thus facilitating a comparison of these data. As may be seen from Table 4, the free-energy values in DMF were larger than in the aqueous solution. It may, therefore, be considered that these metal chlorides in DMF have larger solvation energies than in aqueous solutions, for the free-energy of the formation of $MCl_2$ (s) is always the same in these solvents.

## References

1) H. Ulisch and G. Spiegel, *Phys. Chem.*, **177**, 103 (1936).

2) T. Pavlopoulos and H. Strehlow, *Z. Phys. Chem.* (Frankfurt), **2**, 89 (1954).

3) E. Luksha and C. M. Criss, *J. Phys. Chem.*. **70**, 1949 (1966).

4) L. S. Marple, *Anal. Chem.*, **39**, 844 (1967).

5) J. C. Synnott and J. N. Butler, *ibid.*, **41**, 1890 (1969).

6) M. Saito, *ibid.*, **47**, 1784 (1975).

7) S. Y. Tyree, Jr., "Inorganic Syntheses," Vol. 4, McGraw-Hill Inc., N.Y. (1953), p. 104.

8) I. M. Kolthoff, "Volumetric Analysis," Vol. III, Interscience Pub. Inc., N. Y. (1957), p. 19.

9) W. H. Harnibrook, G. J. Janz, and A. B. Gordon, *J. Amer. Chem. Soc.*, **64**, 513 (1942).

10) H. S. Harned, R. W. Ehlers, *ibid.*, **55**, 2179 (1933).

11) J. H. Wolfenden, C. P. Wright, N. L. Ross Kane, and R. I. Buckley, *Trans. Faraday Soc.*, **23**, 491 (1927).

12) G. Scatchard and R. F. Refft, *J. Amer. Chem. Soc.*, **52**, 2265 (1930).

13) W. Biedermann and G. Schwarenbach, *Chimia* (Switz), **2**, 56 (1948); H. Flaschka, *Mikrochim. Acta*, **39**, 38 (1952).

14) W. R. Crmody, *J. Amer. Chem. Soc.*, **51**, 2095 (1929).

15) W. J. Clayton and W. C. Vosburg, *ibid.*, **58**, 2093 (1936).

16) N. D. Lange, "Handbook of Chemistry," 10th Ed., McGraw-Hill, Inc., N. Y. (1961), p. 1576.