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E. M. F. MEASUREMENTS IN MOLTEN DIVALENT METAL-METAL HALIDE SOLUTIONS¹ ✓

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ABSTRACT

Potentiometric studies on concentration cells of the type C, M(N₁), MX₂(1-N₁) || MX₂(1-N₂), M(N₂), C, where M represents Hg, Cd, Pb and Zn, MX₂ the halide, and N denotes the metal mole fraction, were made at various temperatures. Slopes of plots of the log metal concentration vs. e.m.f. yielded apparent Nernst n values of 2 for Hg-HgCl₂ at 300° and for Cd-CdCl₂ at 580°. For Pb-PbI₂ apparent Nernst n values of about 2.2 - 2.3 were found at 585° and 693°; for Pb-PbCl₂ the low metal solubility made detection of an n value difficult but a value of 2 appeared probable. No constant e.m.f.s were obtained in Zn-ZnCl₂ melts at 658 and 695°. The above n values of 2 indicate a two electron reaction at the electrode and are consistent with the existence of metal atoms M or cation dimers M₂⁺². No evidence for the monomer ion M⁺ was observed.

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INTRODUCTION

Electromotive force measurements of concentration cells with molten bismuth-bismuth halide solutions^{2,3} have yielded information as to the

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- (2) L. E. Topol, S. J. Yosim and R. A. Osteryoung, J. Phys. Chem., 65, 1511 (1961).
(3) L. E. Topol and R. A. Osteryoung, J. Phys. Chem., 66, 1587 (1962).
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species present in these systems. These results have shown that more than one lower-valent metal species exist in these melts. Since a similar study in divalent metal-metal halide melts would be expected to yield information as to the entities present, the potentiometric procedure has been extended to cells with mercury, cadmium and zinc dissolved in their respective molten chlorides and with lead in its fused chloride and iodide.

EXPERIMENTAL

Materials - The chemicals used in this study were all reagent grade. HgCl_2 was dissolved in anhydrous methanol and filtered to remove any Hg_2Cl_2 that might be present. The solution was then evaporated to dryness, washed with distilled water and dried again. The salt was finally sublimed in a chlorine atmosphere at 300° . The system was purged of chlorine by repeatedly flushing it with dry nitrogen at room temperature and then evacuating it. The CdCl_2 , ZnCl_2 and PbCl_2 salts were all melted under an HCl atmosphere; after several hours, the HCl flow through the fused salt was stopped and Cl_2 introduced. The molten salt was finally purged with nitrogen and filtered through a fine fritted disc. The CdCl_2 and ZnCl_2 , after purification, were

handled in a helium-filled dry box. PbI_2 was mixed with iodine and heated overnight in an evacuated, sealed vessel enclosed in an oven at 150° . The iodine was then removed from the mixture by sublimation at 200° and the PbI_2 melted and filtered under nitrogen. AgCl and NaCl were dried under vacuum at 200° . The metals used were melted under helium and filtered to remove oxide impurities. The graphite and tungsten electrodes have been described elsewhere⁴.

(4) L. E. Topol and R. A. Osteryoung, J. Electrochem. Soc., 108, 573 (1961).

Apparatus and Procedure - The cells and coulometric procedure to add metal used in this investigation were similar to those employed in the previous studies^{2,3,4}. In brief, a three compartment cell was used; the outer compartments served as a reference half-cell and as a working anode, respectively. The reference half-cell was joined to the middle compartment by an asbestos fiber, whereas a fritted disc separated the middle compartment from the working anode. Metal was added to the middle compartment by passing a known number of coulombs between this compartment and the working anode. The e.m.f. was then measured between graphite electrodes in the middle and reference half-cells. At the higher temperatures (above 600°) Vycor cells were substituted for Pyrex. In these cells, the fritted quartz discs (manufactured by Thermal American Fused Quartz, Dover, New Jersey) were impregnated⁵ with SiO_2 to decrease their porosity.

(5) F. R. Duke and R. A. Fleming, J. Electrochem. Soc., 106, 130 (1959).

Purified argon was allowed to flow slowly through the cells. However, for the Hg-HgCl_2 and Zn-ZnCl_2 measurements, the half-cells were sealed under a pressure of argon of about 30 cm and completely immersed in a silicon oil and metal bath, respectively, to keep temperatures uniform throughout and thus prevent the distillation of metal. To increase the conductivity of these systems in order to facilitate the coulometric addition of metal, 2 mole % NaCl was added. The working anodes, utilized in the Hg-HgCl_2 and Zn-ZnCl_2 cells in the coulometric generation of metal species, were platinum. Platinum is subject to anodic dissolution in chloride solutions at these temperatures and thus prevents a chlorine pressure buildup in the anode compartment. The reference half-cells in most of the cells investigated were composed of a graphite electrode and weighed amounts of the respective metal and salt to yield a metal mole fraction of 0.005 or if this concentration was above the solubility limit, a saturated solution; in the Cd-CdCl_2 cells, however, a Ag/AgCl (2 mole %) in CdCl_2 reference was employed in addition to Cd (0.5%) in CdCl_2 since cadmium in this system was found to be somewhat volatile at the temperatures of measurement (ca. 600°). In addition, it was found that the use of tungsten anodes usually resulted in the passage of only a limited quantity of current in the coulometric addition of cadmium before a large resistance occurred in the cell. This obstruction to current flow did not occur when gold or platinum anodes were substituted for tungsten. It thus appears that either an insulating film is formed on the tungsten anodes or chlorine gas bubbles congregate on the frit. Although e.m.f.s in the Hg-HgCl_2 system were quite stable, the relative stability decreased in the Cd-CdCl_2 , Pb-PbI_2 , Pb-PbCl_2 and Zn-ZnCl_2 cells in the order listed.

RESULTS

Potentials of cells of the type

where M represents Hg, Cd, Pb and Zn, MX_2 the halide and N the metal mole fraction, were measured at various temperatures. In Figures 1, 2 and 3 are shown some typical plots of log concentration of metal expressed as Q (microequivalents of electricity passed in the coulometric addition of metal) vs. e.m.f. (against a reference electrode) for Hg-HgCl₂ at 287°, Cd-CdCl₂ at 378° and Pb-PbI₂ at 693°, respectively. In all three figures the uncorrected points at low metal concentrations fall below the straight line that can be drawn through the higher metal concentration (or log Q) data. As in the bismuth-bismuth halide solutions it was assumed that these deviations from linearity can be ascribed to the presence of an initial concentration of lower-valent metal species in the molten salt. The concentration of these species can be calculated from the initial e.m.f.s of the cells and the reference concentration. For example, in the case of Hg-HgCl₂ at 287° (Fig. 1): E = 0.0527 v at Q = 10 microequivalents and the concentration of the reference compartment = 600 microequivalents/8.95 gm HgCl₂. From the Nernst relation, assuming n = 2, $E = 0.0527 = \frac{0.112}{2} \log \frac{600}{(Q_0 + 10)}$, and we find Q₀ = 60 microequivalents/20.65 gm HgCl₂. The log Q values are corrected accordingly, and the corrected data are not only linear over the whole composition range studied but also yield apparent Nernst n values much closer to the integer 2 than the uncorrected values. These data along with the calculated

initial metal concentration corrections in microequivalents per weight of salt are summarized in Table I. For Pb-PbCl₂ cells at 580° and 710°, the limited stability of the e.m.f.s, which is presumably related to the low solubility of metal (0.020 and .052 mole % at 600° and 700°, respectively⁶), did not permit the calculation of an accurate value of n.

(6) J. D. Corbett and S. von Winbush, J. Am. Chem. Soc., 77, 3964 (1955).

However, for the few data that were obtained an n of 2 appeared to be most probable. For Zn-ZnCl₂ at 658° and 695° no constant e.m.f.s could be obtained.

DISCUSSION

The electrode reaction to be considered in cell (1) is the following

where x and y are integers and y may also equal zero. For a reversible half-cell the Nernst relation,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M^{+2}]^x}{[M_x^{+y}]} \quad (3)$$

where the brackets denote activities and n = (2x-y) for reaction (2), may be employed. For low concentrations of metal (where N_{MX₂} is essentially unity), if Henry's law holds, it can be shown² that

$$E = \frac{RT}{(2x-y)F} \ln Q + \text{constant} \quad (4)$$

Here Q is the number of equivalents of current passed to generate the

species M_x^{+y} , i.e.,

$$Q = N(MX_2)_0 (2x-y) \quad (5)$$

where N is the mole fraction of M_x^{+y} , and $(MX_2)_0$ is the initial number of moles of MX_2 . Thus, if the cells are reversible and liquid junction potentials and departures from Henry's law are negligible, a plot of $\log Q$ vs. E at constant temperature should yield a straight line, the slope of which depends on $(2x-y)$. Since values of $2 = (2x-y)$ for the apparent Nernst n were found in the $Hg-HgCl_2$, $Cd-CdCl_2$ and $Pb-PbI_2$ systems and appears to be consistent with the results in the $Pb-PbCl_2$ system also, entities of the type M_x^{2x-2} are present. Possible examples of such species are $M^+(x=1)$ and $M_2^{+2}(x=2)$, but, unfortunately, no distinction can be made here between the two. Other evidence tends to favor the formation of subhalide in both $Hg-HgCl_2$ ⁷ and $Cd-CdCl_2$ ⁸ melts.

(7) S. J. Yosim and S. W. Mayer, J. Phys. Chem., 64, 909 (1960).

(8) L. E. Topol and A. L. Landis, J. Am. Chem. Soc., 82, 6291 (1960).

Actually, metal atoms, which would be easily polarized, would presumably exist in these melts as solvated species of the type $M-M^{+2}$. The difference between such a solvate and the chemical entity M_2^{+2} is then mainly due to a difference in the degree of interaction between the metal atom and cation. Values for these energies of interaction in infinitely dilute solution can be calculated⁹ and are found to be

(9) L. E. Topol, "Thermodynamic Considerations on the Interactions in Metal-Metal Salt Solutions," to be published.

appreciable, about -18 kcal, in the Hg, Zn and Cd systems and larger still (-31 kcal) in the lead system at the temperatures of this investigation. The larger interaction energy with lead atoms is presumably related to their greater polarizability as compared to the group II B metal atoms. It is interesting that although the mercury system is the only one above in which a solid subhalide is known to exist, the interaction energy in the Hg-HgCl₂ melt is no larger than that in the cadmium or zinc solutions.

It was thought that if M₂⁺² dimers were present, some noticeable dissociation would result at low metal concentrations. However, at the lowest concentrations measured (N = 0.0003 Hg in HgCl₂, 0.0003 Cd in CdCl₂ and 0.0004 Pb in PbI₂) no sign of monomers, i.e., n = 1, was detected. Thus, if any M⁺ is present in these melts, its concentration must be insignificant above 0.03 mole % metal.

Karpachev and co-workers have conducted similar e.m.f. studies on Cd dissolved in CdCl₂ (50 mole %) - KCl (25%) - NaCl (25%) at 700°¹⁰ and

(10) S. Karpachev and A. Stromberg, Zhur. Fiz. Khim., 13, 397 (1939).

on Pb-PbCl₂¹¹ at 700°. In the cadmium solution these workers found a linear

(11) S. Karpachev, A. Stromberg and E. Jordan, *ibid.*, 18, 43 (1944).

e.m.f. vs. log concentration relation over the entire solubility range investigated and calculated an apparent Nernst n of 2. In the Pb-PbCl₂ melt a similar linear plot was observed and an n of 1 resulted. It is interesting that no departures from linearity were found at low metal

concentrations as in the present investigation, especially in the Pb-PbCl_2 solution. In the cadmium melt the presence of the alkali chlorides would tend to decrease the initial metal concentration, and, more important, the most dilute solution measured was 0.059 g. atom Cd/l. or about 0.3 mole %. This concentration is much greater than the dilute metal concentrations in the present study. In fact, in this investigation solutions containing more than 0.3 mole % Cd (approximately 1,000 micro-equivalents in Fig. 2) also fall on a straight line before corrections are applied. However, in the Pb-PbCl_2 solution where low metal solubility occurs no obvious explanation for the difference in results is apparent. In addition, Karpachev's value of unity for n is not only contrasted to the "probable" n of 2 indicated here but is also in disagreement with a polarographic study¹² the results of which favored the species Pb_2Cl_2 .

(12) J. J. Egan, J. Phys. Chem., 65, 2222 (1961).

i.e., in accord with an $n = 2$.

The solubility of a metal in its salt can also be obtained with cells of the above type from the number of equivalents of current passed to yield a saturated solution. This point is readily detected since no further changes in e.m.f. between this compartment and the reference will be found with passage of current. (If the reference half-cell, itself, consists of a saturated solution of the metal, then the point of attainment of zero e.m.f. will indicate the solubility concentration.) In the mercury and cadmium systems the solubility limit of the metal was not reached, but for the lead-lead halide systems Table II gives a comparison

between the solubilities found by this method and those reported in the literature. Although there is reasonable agreement between the potentiometric and analytical Pb-PbI_2 values, the agreement is much poorer in the chloride. Since the solubility of Pb in its molten chloride is very low, any initial concentration or formation (by reduction) of metal in the salt will result in a relatively large error in the value. It is interesting to note that the potentiometric values for the solubility of Pb in PbI_2 are larger than the analytical values found previously. If these present values are truly high, it may be indicative of the fact that some electronic conduction occurs in this system; i.e., the true concentration of metal formed on electrolysis (see Equation 5) is less than that given by the number of equivalents of current passed. The n value for Pb-PbI_2 being somewhat larger than 2 is also in accord with this possibility.

TABLE I

Apparent Nernst n Values in Divalent Metal-Metal Halide Solutions

System	Temp. (°C)	Calculated Initial Metal Concn. (Microequivalents/gm salt)	n	
			Uncorrected	Corrected
Hg-HgCl ₂	287	60/20.65	2.28	2.08
	297	42/19.25	2.23	2.01
Cd-CdCl ₂	578	105/29.60	2.15	2.00
	581	108/30.71	2.28	2.08
Pb-PbI ₂	585	50/33.75	2.5	2.3
	693	100/59.00	2.4	2.2
Pb-PbCl ₂	580	3/38.50		(2.2)
	710	3/33.50		(2.1)

TABLE II

The Solubility of Pb in Molten PbCl_2 and PbI_2

<u>System</u>	<u>Temp.</u> (°C)	<u>Solubility (mole %)</u>	
		<u>This work</u>	<u>Literature</u> ¹³
Pb-PbCl_2	580	0.012	0.018
	710	.024	.053
Pb-PbI_2	585	.18	.14
	693	.57	.41

(13) J. D. Corbett, S. von Winbush and F. C. Albers, J. Am. Chem. Soc.,
79, 3020 (1957).

Figure 1.

Log Q vs. E results for Hg-HgCl₂ cells at 287°

Figure 2.

Log Q vs. E results for Cd-CdCl₂ cells at 578°

Figure 3.

Log Q vs. E results for Pb-PbI₂ cells at 693°