

# Metal Halide and Pseudohalide Complexes in Dimethyl Sulfoxide Solution. VIII. Standard Electrode Potentials in Dimethyl Sulfoxide Solution and Exchange Reactions between Dimethyl Sulfoxide and Water, Involving Metal Ions of Groups 1 B and 2 B

STEN AHRLAND and INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

Standard electrode potentials have been calculated for zinc, cadmium, mercury and copper couples in dimethyl sulfoxide, on the extrathermodynamic assumption that the standard potential of the silver couple is 349 mV more negative in DMSO than in water. All the metals concerned are much less noble in DMSO than in water, *i.e.* the transfer free energies  $\Delta G_{tr}^{\circ} < 0$ . For those ions where they have been determined, the transfer enthalpies  $\Delta H_{tr}^{\circ}$  are even more negative, however, so the transfer entropies  $\Delta S_{tr}^{\circ} < 0$ . These ions are thus more easily solvated by DMSO than by water, and their transfer to DMSO means an increase of the overall order of the system. The preference for DMSO among the ions investigated follows the order  $Zn^{2+} < Cu^{2+} < Cd^{2+} < Hg_2^{2+} < Ag^+ \simeq Hg^{2+} < Cu^+$ . This is, on the whole, their order of softness, with the exception of  $Cu^+$  whose preference to DMSO is stronger than would be expected.

The electrode potentials of redox couples involving metal ions (as always referred to a certain standard electrode) are apt to change considerably between different solvents. For obvious reasons, by far the largest number of potential measurements refer to aqueous solutions. It is, therefore, natural to choose water as a solvent of reference. In the following, the changes of electrode potentials accompanying the transfer of a number of important redox couples from water to the aprotic solvent dimethyl sulfoxide (DMSO) will be discussed.

Any aprotic solvent to be used for such a comparison must evidently be a strongly solvating

one, in order to dissolve the ionic compounds involved. In the present study, DMSO has been chosen, much because measurements referring to zinc, cadmium and copper couples have already been performed in this solvent.<sup>1,2</sup> Moreover, a study of the mercury couples has been a necessary preliminary to an investigation of the mercury(II) halide and thiocyanate complexes formed in DMSO solution.<sup>3</sup>

To relate electrode potentials measured in different solvents, an extrathermodynamic assumption must be introduced.<sup>4,5</sup> The approach nearest to hand is evidently to postulate that the liquid junction potential between two solvents can be suppressed by an appropriate choice of salt bridge.<sup>5,6</sup> The electrode potential differences arrived at in this way also agree fairly well with those resulting from other reasonable approaches.<sup>5</sup> Among these, however, the modified Grunwald assumption that the free transfer energies  $\Delta G_{tr}^{\circ}$  between two solvents are the same for the tetraphenylarsonium ( $Ph_4As^+$ ) and the tetraphenylborate ( $Ph_4B^-$ ) ions, has lately been generally accepted to be closest to the truth.<sup>7-9</sup> This assumption will, therefore, be adopted here. An additional reason for doing so is that the single ion enthalpies of transfer used in the present study have been calculated on this assumption.<sup>9,10</sup>

The electrodes actually used in the present potential measurements in DMSO have been  $Ag/Ag^+$ ,  $Zn(Hg)/Zn^{2+}$ ,  $Cd(Hg)/Cd^{2+}$ ,  $Hg/Hg_2^{2+}$  and  $Hg_2^{2+}/Hg^{2+}$ . The temperature has been 25 °C.

The couple  $Ag/Ag^+$  has been thoroughly studied

in a large variety of solvents, and in the presence of a large variety of anions.<sup>6,7</sup> From the solubility products found, reliable values of  $\Delta G_{tr}^\circ(\text{Ag}^+)$  between numerous pairs of solvents can be calculated, on the assumption that  $\Delta G_{tr}^\circ(\text{Ph}_4\text{As}^+) = \Delta G_{tr}^\circ(\text{Ph}_4\text{B}^-)$ .<sup>7,11</sup> Consequently, the electrode potentials of  $\text{Ag}/\text{Ag}^+$  in any solvent investigated can be related to the reference solvent water. In the following,  $\text{Ag}/\text{Ag}^+$  in water is chosen as the standard electrode, *i.e.*  $E_{\text{Ag}}^\circ(\text{aq}) = 0$ . The value of  $\Delta G_{tr}^\circ(\text{Ag}^+)$  between water and DMSO is <sup>7,11</sup>  $-33.7$  kJ/mol at 25 °C which means that the standard potential in DMSO, referred to  $E^\circ(\text{aq}) = 0$  is  $E^\circ(\text{DMSO}) = \Delta G_{tr}^\circ/nF = -349$  mV. Silver is thus a considerably less noble metal in DMSO than in water.

The other couples investigated in DMSO have been determined relative to  $\text{Ag}/\text{Ag}^+$ . In the case of zinc and cadmium, the two-phase amalgams used attain equilibrium potentials much more quickly and reliably than do the pure metals. As the potential differences between amalgam and metal electrodes are well-known, the standard potentials  $E_{\text{Zn}}^\circ(\text{DMSO})$  and  $E_{\text{Cd}}^\circ(\text{DMSO})$  of the couples  $\text{Zn}/\text{Zn}^{2+}$  and  $\text{Cd}/\text{Cd}^{2+}$  can be immediately calculated from the present measurements. In the case of mercury,  $E_{\text{O}_2}^\circ(\text{DMSO})$  of the couple  $\text{Hg}/\text{Hg}_2^{2+}$  cannot be determined directly, on account of the reproporationation equilibrium  $\text{Hg}(1) + \text{Hg}_2^{2+} \rightleftharpoons \text{Hg}_2^{2+}$  which is situated rather far to the right. Both this potential and also the equilibrium constant  $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$  can be calculated from the standard potentials of the couples  $\text{Hg}/\text{Hg}_2^{2+}$  and  $\text{Hg}_2^{2+}/\text{Hg}^{2+}$ , however, according to  $E_{\text{O}_2}^\circ = (E_{12}^\circ + E_{01}^\circ)/2$  and  $\log K_R = (E_{12}^\circ - E_{01}^\circ)/(RT \ln 10/F)$ . The difference  $E_{12}^\circ - E_{01}^\circ$ , and consequently  $K_R$ , are of course independent of the extrathermodynamic assumption introduced. The value of  $K_R$  can also be checked by direct analysis of solutions in equilibrium (see "Experimental").

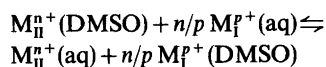
The measurements in DMSO have been performed in two different media, of the ionic strength  $I = 0.15$  and 1 M, in both cases brought about by ammonium perchlorate. The value of  $\Delta G_{tr}^\circ(\text{Ag}^+)$  quoted above does not refer to any of these standard states, but rather to the transfer between the pure solvents.<sup>7</sup> Considering the limited accuracy of  $\Delta G_{tr}^\circ$  and the rather small difference in  $E^\circ$  found for most couples measured between the two DMSO media employed, Table 1, the difference in standard state is of minor importance. For the other metal ions studied, the

values of  $\Delta G_{tr}^\circ$  to be discussed below refer to the DMSO solution of  $I = 1$  M, *i.e.* they have been calculated according to  $\Delta G_{tr}^\circ = nF[E^\circ(\text{DMSO}, I = 1) - E^\circ(\text{aq})]$ .

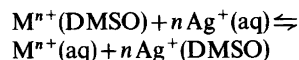
An important reason for the large negative values of  $\Delta G_{tr}^\circ$  found for most ions on transfer from water to DMSO is the large changes in the solvation of the metal ions involved. These changes are reflected in large differences between water and DMSO in the enthalpies of solvation, denoted  $\Delta H_{\text{W}}^\circ$  and  $\Delta H_{\text{D}}^\circ$ , respectively. The enthalpies of transfer,  $\Delta H_{tr}^\circ = \Delta H_{\text{D}}^\circ - \Delta H_{\text{W}}^\circ$  will thus be considerable. They differ appreciably between various ions, however.<sup>12</sup> Among the ions presently discussed, they are well established<sup>10-13</sup> for  $\text{Ag}^+$ , and also for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}_2^{2+}$ .

Due to intermolecular hydrogen bonding, the protic solvent water is much more structured than the aprotic solvent DMSO. Consequently, a transfer of metal ions from water to DMSO is likely to bring about a sizable net increase of order, which tends to make the entropy changes  $\Delta S_{tr}^\circ$  negative. Also other sources of considerable entropy changes are likely to exist. Generally, both  $\Delta H_{tr}^\circ$  and  $\Delta S_{tr}^\circ$  should therefore contribute appreciably to  $\Delta G_{tr}^\circ$ , and hence to the change of  $E^\circ$  between the two solvents. The metal ions so far studied do behave as expected in these respects.<sup>11,13</sup>

Independent of the extrathermodynamic assumption applied, *i.e.* of the values of  $\Delta G_{tr}^\circ$  (*i.e.* of the differences  $E^\circ(\text{aq}) - E^\circ(\text{DMSO})$ ) chosen, the free energy changes  $\Delta G_{ex}^\circ$  of the exchange reactions



can be calculated. Consistent with the present choice of standard electrode,  $\text{Ag}^+$  is chosen as the reference ion  $\text{M}_I^{p+}$  so the reactions considered are



From the values of  $\Delta G_{ex}^\circ$  of these reactions, the values of any other combination of ions can be immediately calculated. The differences  $\Delta E^\circ(\text{aq}) = E_{\text{Ag}}^\circ(\text{aq}) - E_{\text{M}}^\circ(\text{aq})$ ;  $\Delta E^\circ(\text{DMSO}) = E_{\text{Ag}}^\circ(\text{DMSO}) - E_{\text{M}}^\circ(\text{DMSO})$  measured in water and DMSO, respectively, evidently do not depend upon  $\Delta G_{tr}^\circ$ . The emf of a cell with the cell reaction written above is, however,  $\Delta E^\circ = \Delta E^\circ(\text{aq}) - \Delta E^\circ(\text{DMSO})$

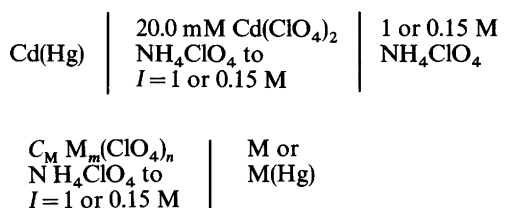
and hence  $\Delta G_{\text{ex}}^{\circ} = -nF\Delta E^{\circ}$ . Also for the calculation of  $\Delta G_{\text{ex}}^{\circ}$ , the standard states chosen are water,  $I=0$ , and DMSO,  $I=1$  M.

In those cases where  $\Delta H_{\text{ir}}^{\circ}$  is known for the ion  $M^{n+}$  participating in the exchange, *i.e.* for  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ , the enthalpy change of the reaction can be calculated according to  $\Delta H_{\text{ex}}^{\circ} = n\Delta H_{\text{ir}}^{\circ}(Ag^{+}) - \Delta H_{\text{ir}}^{\circ}(M^{n+})$ . Provided that  $\Delta H_{\text{ir}}^{\circ}(Ag^{+})$  and  $\Delta H_{\text{ir}}^{\circ}(M^{n+})$  have been calculated on the same extrathermodynamic assumption, as is the case here, the difference in the right membrum, *i.e.*  $\Delta H_{\text{ex}}^{\circ}$  will be independent of this assumption, just as  $\Delta G_{\text{ex}}^{\circ}$ . For those reactions where  $\Delta H_{\text{ex}}^{\circ}$  can be found it is finally also possible to calculate the entropy change  $\Delta S_{\text{ex}}^{\circ} = (\Delta H_{\text{ex}}^{\circ} - \Delta G_{\text{ex}}^{\circ})/T$ .

## EXPERIMENTAL

**Chemicals.** The solvates  $Zn(DMSO)_6(ClO_4)_2$ ,  $Cd(DMSO)_6(ClO_4)_2$  and  $Hg(ClO_4)_2 \cdot 4DMSO$ , used as sources for the respective metal ions, were prepared and analyzed as before.<sup>14,15</sup> Anhydrous  $AgClO_4$  was the source of  $Ag^{+}$ . A mercury(I) DMSO-solvate,  $Hg_2(ClO_4)_2 \cdot 3DMSO$ , was prepared as follows, *cf.* Ref. 16. The hydrate  $Hg_2(ClO_4)_2 \cdot 8H_2O$  (0.05 mol) was dissolved in methanol (30 ml). To prevent hydrolysis, the methanol was acidified with a few drops of concentrated perchloric acid. DMSO (0.10 mol) was added. On cooling to 5 °C, the DMSO solvate precipitated. It was recrystallized from methanol. The mercury content was determined by titration with cerium(IV),<sup>17</sup> found 48.24, calc. 48.08%. Carbon and hydrogen were determined conventionally\*; found 8.77, 2.09; calc. 8.63, 2.17%. Sulfur could not be determined on account of the formation of slightly soluble  $Hg_2SO_4$ . The amalgams were prepared and stored as described previously.<sup>18</sup>

**Procedure.** In practice, a  $Cd(Hg)/Cd^{2+}$  half-cell was always used as a common reference electrode. The cells measured were thus either



\* Analyses performed by the Department of Analytical Chemistry of this Chemical Center.

where  $M=Zn$  (electrode  $Zn(Hg)$ ;  $m=1$ ,  $n=2$ ),  $Hg$  ( $m=n=2$ ) or  $Ag$  ( $m=n=1$ ), or the right hand half-cell was a Pt-electrode in a solution of  $C_M$  M  $Hg_2(ClO_4)_2$  and  $C_N$  M  $Hg(ClO_4)_2$ . For the first type of cells stable emf's, generally reproducible within  $\pm 0.1$  mV, were reached in a few minutes within the range of concentrations used,  $3 \text{ mM} < C_M < 50 \text{ mM}$ . For the mercury(I)–mercury(II) electrode, reproducible equilibrium potentials were rapidly attained only if  $C_N \gtrsim C_M$ , and moreover  $C_N \gtrsim 15 \text{ mM}$ . For all the systems, the emf's measured obey Nernst's law within  $\pm 0.3$  mV.

The difference in potential between the amalgam and the metal electrode is for Cd 50.5 mV while for Zn no difference seems to exist.<sup>19,20</sup>

**Determination of  $K_R$ .** The most precise value of  $K_R$  is obtained from the potentiometric measurements, as described above. A valuable check is possible, however, by analysis of solutions containing  $Hg(II)$  and  $Hg(I)$  in equilibrium with metallic mercury. The equilibrium was approached from both sides, either by shaking the metal with a mercury(II) perchlorate solution, or by dissolving  $Hg_2(ClO_4)_2 \cdot 3DMSO$  in the appropriate ionic medium. When equilibrium had been reached, the metal was filtered off. The total concentration of mercury in this solution,  $C_e$ , was determined by EDTA-titration,<sup>21</sup> after oxidation of the mercury(I) present by boiling with 5 M nitric acid. At equilibrium,  $C_e = [Hg^{2+}]_e + 2[Hg_2^{2+}]_e$ . If  $C_{II}$  and  $C_I$  denote the initial concentration of mercury(II) and mercury(I), respectively, in the two experiments, the following stoichiometric conditions are valid:  $C_{II} = [Hg^{2+}]_e + [Hg_2^{2+}]_e$ ;  $C_I = 2[Hg_2^{2+}]_e + 2[Hg^{2+}]_e$ . Hence the following expressions for  $K_R$  are obtained in the two cases:  $K_R = [Hg_2^{2+}]/[Hg^{2+}] = (C_e - C_{II})/(2C_{II} - C_e)$  and  $K_R = (2C_e - C_I)/(2C_I - C_e)$ .

## MEASUREMENTS AND RESULTS

The standard electrode potentials computed from the present measurements, and referred to  $E_{Ag}^{\circ}(aq)=0$ , are listed in Table 1. Also the potentials of the various copper couples, recalculated on the present scale from values determined previously,<sup>2</sup> have been introduced. For these couples, the medium of lower ionic strength had  $I=0.1$  M, instead of  $I=0.15$  M used presently. This difference should not mean a very great change in  $E^{\circ}(DMSO)$ . For comparison, Table 1 also contains the values<sup>22</sup> of  $E^{\circ}(aq)$  on the same scale. The values of  $E^{\circ}(DMSO)$  referring to  $I=1$  M, and of  $E^{\circ}(aq)$ ,  $I=0$ , have been entered in Fig. 1.

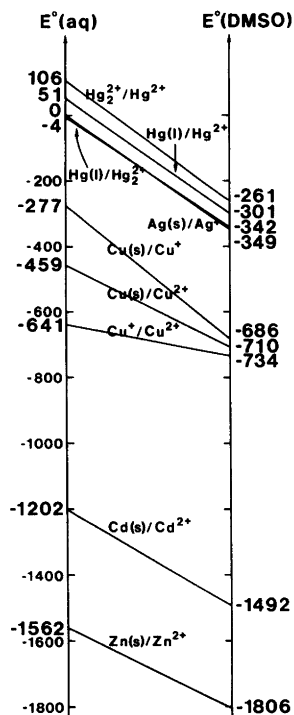


Fig. 1. Standard electrode potentials in aqueous and dimethyl sulfoxide solutions, referred to  $E^\circ(\text{aq}) = 0$  for the  $\text{Ag}(\text{s})/\text{Ag}^+$  electrode.

Table 1. Standard electrode potentials in DMSO and water referred to  $E^\circ(\text{aq}) = 0$  for the silver electrode.

I/M →	$E^\circ(\text{DMSO})$		$E^\circ(\text{aq})$
	1	0.15(0.1)	0
$\text{Ag}(\text{s})/\text{Ag}^+$	-349	-349	0
$\text{Cu}(\text{s})/\text{Cu}^+$	-686	-714	-277
$\text{Cu}(\text{s})/\text{Cu}^{2+}$	-710	-720	-459
$\text{Cu}^+/\text{Cu}^{2+}$	-734	-725	-641
$\text{Zn}(\text{s})/\text{Zn}^{2+}$	-1806	-1811	-1562
$\text{Cd}(\text{s})/\text{Cd}^{2+}$	-1492	-1498	-1202
$\text{Hg}(\text{l})/\text{Hg}^{2+}$	-301	-305	51
$\text{Hg}(\text{l})/\text{Hg}_2^{2+}$	-342	-350	-4
$\text{Hg}_2^{2+}/\text{Hg}^{2+}$	-261	-260	106

The values of  $\Delta G_{\text{tr}}^\circ$  calculated from the standard potentials of Table 1 have been listed in Table 2. In so far as values of the enthalpies of transfer,  $\Delta H_{\text{tr}}^\circ$ , are known,<sup>10,11,13</sup> these have been introduced and hence the entropies of transfer calculated according to  $\Delta S_{\text{tr}}^\circ = (\Delta H_{\text{tr}}^\circ - \Delta G_{\text{tr}}^\circ)/T$ .

Table 2. Standard free energies, enthalpies and entropies of transfer from water to DMSO at 25 °C ( $\Delta G_{\text{tr}}^\circ$ ,  $\Delta H_{\text{tr}}^\circ/\text{kJ mol}^{-1}$ ;  $\Delta S_{\text{tr}}^\circ/\text{JK}^{-1} \text{mol}^{-1}$ ).

$\text{M}^{n+}$	$-\Delta G_{\text{tr}}^\circ$	$-\Delta H_{\text{tr}}^\circ$	$\Delta S_{\text{tr}}^\circ$
$\text{Ag}^+$	34 <sup>a</sup>	55 <sup>b</sup>	-72
$\text{Cu}^+$	40		
$\text{Cu}^{2+}$	48		
$\text{Zn}^{2+}$	47	60 <sup>c</sup>	-44
$\text{Cd}^{2+}$	56	67 <sup>c</sup>	-37
$\text{Hg}^{2+}$	68	76 <sup>c</sup>	-27
$\text{Hg}_2^{2+}$	65		

<sup>a</sup> Refs. 7 and 11. <sup>b</sup> Refs. 11 and 13. <sup>c</sup> Ref. 10.

Table 3. Equilibrium constants,  $K_{\text{ex}}$ , and thermodynamic functions ( $\Delta G_{\text{ex}}^\circ$ ,  $\Delta H_{\text{ex}}^\circ/\text{kJ mol}^{-1}$ ;  $\Delta S_{\text{ex}}^\circ/\text{JK}^{-1} \text{mol}^{-1}$ ) for the reactions  $\text{M}^{n+}(\text{DMSO}, I=1) + n \text{Ag}^+(\text{aq}) = \text{M}^{n+}(\text{aq}) + n \text{Ag}^+(\text{DMSO}, I=1)$ , at 25 °C.

$\text{M}^{n+}$	$K_{\text{ex}}$	$-\Delta G_{\text{ex}}^\circ$	$-\Delta H_{\text{ex}}^\circ$	$\Delta S_{\text{ex}}^\circ$
$\text{Cu}^+$	0.096	-5.8		
$\text{Cu}^{2+}$	2130	19.0		
$\text{Zn}^{2+}$	3750	20.4	50	-99
$\text{Cd}^{2+}$	99	11.4	43	-106
$\text{Hg}^{2+}$	0.75	-0.7	34	-116
$\text{Hg}_2^{2+}$	2.3	2.1		

The values of  $\Delta G_{\text{ex}}^\circ$  for the exchange between water and DMSO of  $\text{Ag}^+$  for other ions  $\text{M}^{n+}$  have been listed in Table 3. As no extrathermodynamic assumption is involved, these values are more precise, and certainly also more accurate, than those determined for  $\Delta G_{\text{tr}}^\circ$ . The corresponding equilibrium constants,  $K_{\text{ex}}$ , have also been calculated, from  $\log K_{\text{ex}} = -\Delta G_{\text{ex}}^\circ/RT \ln 10$ . For the reactions involving  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  it has also, as discussed above, been possible to calculate the enthalpy changes  $\Delta H_{\text{ex}}^\circ$ , and hence also the entropy changes  $\Delta S_{\text{ex}}^\circ$ .

The values of the reproporationation constant  $K_{\text{R}}$  found potentiometrically and by chemical analysis of equilibrium solutions have been entered in Table 4. To ensure a direct comparison with the result of an earlier investigation (see Discussion),  $K_{\text{R}}$  has also been determined in 0.15 M  $\text{Et}_4\text{NClO}_4$  (by shaking mercury(II) with metallic mercury). A value found earlier in a DMSO- $\text{NaClO}_4$  medium is also given.<sup>23</sup> For comparison, values of  $K_{\text{R}}$  determined in water for media of the same ionic strength as used in the present study have also been

Table 4. The reproporationation constant  $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$  in various DMSO and aqueous media, at 25 °C, measured potentiometrically ( $E^\circ$ ) or by analysis of equilibrium solutions, attained from pure mercury(I) solvate  $[\text{Hg}(\text{I})]$  or from pure mercury(II) solutions  $[\text{Hg}(\text{II}) + \text{Hg}(\text{I})]$ . Results from the present measurements, if not otherwise stated.

DMSO $I/M \rightarrow$	$\text{NH}_4\text{ClO}_4$ 1	0.15	$\text{Et}_4\text{NClO}_4$ 0.15	$\text{NaClO}_4^a$ 1
$E^\circ$	$24.0 \pm 2.0$	$33.0 \pm 2.0$		$40 \pm 3$
Hg(I)	$25.0 \pm 2.0$	$27 \pm 5$		
Hg(II) + Hg(I)	$24.5 \pm 2.0$	$36 \pm 5$	$40 \pm 5$	
Mean	$24.5 \pm 1.5$	$34.5 \pm 2.0$		
Water <sup>b</sup> $I/M \rightarrow$	$\text{NaClO}_4$ 1	0.15	$\text{NaNO}_3$ 1 0.15	0
$E^\circ$	172	101	105 89	$88 \pm 4$

<sup>a</sup> Ref. 23. <sup>b</sup> Ref. 24.

entered, as well as the value extrapolated for  $I = 0$ .<sup>24</sup>

Already the low values of  $K_R$  in DMSO are more precisely determined potentiometrically than by chemical analysis; in water the potentiometric method is the best by far.

## DISCUSSION

All the metals concerned are considerably less noble in DMSO than in water, as is evident from Table 1 and Fig. 1. The difference  $E^\circ(\text{aq}) - E^\circ(\text{DMSO})$  is quite large for all the metal electrodes. For ions  $\text{M}^{2+}$  it clearly increases with increasing softness, being 244, 290 and 352 mV for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ , respectively. Also  $\text{Cu}^{2+}$ , with 251 mV, fits fairly well into this order, which would indicate that the solvate bonds are of a more electrostatic character in water than in DMSO.

As stated above, these values are all based on a difference for  $\text{Ag}^+$  of 349 mV. Rather surprisingly, that of  $\text{Cu}^+$  is even higher, 409 mV, though  $\text{Cu}^+$  generally behaves as a less soft acceptor than  $\text{Ag}^+$ .

These differences are immediately connected with  $\Delta G_{\text{tr}}^\circ/n$ , i.e. the free energy of transfer per ionic charge. This quantity is thus exceptionally high for  $\text{Cu}^+$ . As a consequence, the reaction  $\text{Cu}(\text{s}) + \text{Cu}^{2+} \rightarrow 2 \text{Cu}^+$ , where 2  $\text{Cu}^+$  is formed for each  $\text{Cu}^{2+}$  disappearing, is very much favoured in DMSO relative to water.<sup>2</sup> The value of  $K_R = [\text{Cu}^+]^2/[\text{Cu}^{2+}]$  increases by a factor  $10^{5.6}$ , corresponding to a free energy change  $\Delta G^\circ = 2 \Delta G_{\text{tr}}^\circ(\text{Cu}^+) - \Delta G_{\text{tr}}^\circ(\text{Cu}^{2+}) = -32 \text{ kJ mol}^{-1}$  (Table 2). As a consequence,  $\text{Cu}^+$  becomes a fairly stable species in DMSO, the value of  $K_R (= 1/K_D)$  being

0.23 M in 1 M and 0.66 M in 0.1 M  $\text{NH}_4\text{ClO}_4$ , respectively.<sup>2</sup>

On the other hand, the values of  $E^\circ(\text{aq}) - E^\circ(\text{DMSO})$ , or  $\Delta G_{\text{tr}}^\circ$ , are not very different for  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$ , Tables 1 and 2. Consequently,  $K_R$  of the reproporationation  $\text{Hg}(\text{I}) + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$  does not change much between water and DMSO, Table 4. For this system, the transfer to DMSO means a slight stabilization of the divalent state relative to the monovalent one. The difference between the two solvents is so small, however, that a change of medium may bring about effects of the same order of magnitude, Table 4.

These results are throughout compatible with those found earlier<sup>23</sup> for the medium 1 M  $\text{NaClO}_4$  but they differ profoundly from the conclusions arrived at in another investigation.<sup>25</sup> In this study, a large stabilization of  $\text{Hg}_2^{2+}$  relative to  $\text{Hg}^{2+}$  is found on the transfer from water to DMSO. That this in fact does not occur is evident not only from the present measurements, but also from the potentiometric determinations of the equilibrium constants of the mercury(II) halide systems recently performed.<sup>3</sup> These would not have been at all possible had a strong stabilization of  $\text{Hg}_2^{2+}$  relative to  $\text{Hg}^{2+}$  taken place. The reason for the discrepancy may be that the polarographic technique employed does not yield true equilibrium potentials and/or that the indirect determination of  $E_{0.2}^\circ$  via the gold electrode does not work properly.

The contributions of  $\Delta H_{\text{tr}}^\circ$  and  $\Delta S_{\text{tr}}^\circ$  to  $\Delta G_{\text{tr}}^\circ$  also show very interesting trends, Table 2. For the monovalent  $\text{Ag}^+$ ,  $\Delta S_{\text{tr}}^\circ$  is much more negative than for the divalent ions, indicating that the increase of

order accompanying a transfer is by far most marked for  $\text{Ag}^+$ . While  $\text{Ag}^+$  is poorly solvated in water, the solvation in DMSO is very markedly better. This is also reflected in the high value  $\Delta H_{\text{tr}}^{\circ}/n$ , the transfer enthalpy per ionic change. For the divalent ions, both  $\Delta H_{\text{tr}}^{\circ}$  and  $\Delta S_{\text{tr}}^{\circ}$  become more favourable from  $\text{Zn}^{2+}$  to  $\text{Hg}^{2+}$ . As to  $\Delta H_{\text{tr}}^{\circ}$ , the trend is easily rationalized by postulating that the more covalent character of the solvate bonds in DMSO favours the acceptors more, the softer they are. The values of  $\Delta H_{\text{tr}}^{\circ}(\text{Hg}^{2+})$  and  $\Delta H_{\text{tr}}^{\circ}(\text{Ag}^+)$  are thus large for the same reason. The trend in  $\Delta S_{\text{tr}}^{\circ}$  cannot, of course, be interpreted along these lines. The most likely reason might be that the sterical restrictions which must be severe for the DMSO hexasolvates nevertheless are relaxed with increasing radius of the acceptor ion.

The thermodynamics of the exchange reactions reflect the conditions just discussed, Table 3. The transfers of  $\text{Ag}^+$  from water to DMSO, in exchange for the other metal ions concerned, have  $\Delta G_{\text{ex}}^{\circ} < 0$ , except for  $\text{Hg}^{2+}$ , where  $\Delta G_{\text{ex}}^{\circ} \simeq 0$  and for  $\text{Cu}^+$ , where  $\Delta G_{\text{ex}}^{\circ} > 0$ . The values of  $\Delta H_{\text{ex}}^{\circ}$ , known for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ , in all cases strongly favour the exchange. The values of  $\Delta S_{\text{ex}}^{\circ}$  are, on the other hand, all very unfavourable, for  $\text{Hg}^{2+}$  to such a degree that the strongly exothermic  $\Delta H_{\text{ex}}^{\circ}$  is just compensated.

*Acknowledgement.* The support given to this investigation by the Swedish Natural Science Research Council is gratefully acknowledged.

## REFERENCES

- Ahrland, S. and Björk, N.-O. *Acta Chem. Scand. A* 30 (1976) 265.
- Ahrland, S., Bläuenstein, P., Tagesson, B. and Tuhtar, D. *Acta Chem. Scand. A* 34 (1980) 265.
- Ahrland, S., Persson, I. and Portanova, R. *To be published.*
- Strehlow, H. In Lagowski, J. J., Ed., *The Chemistry of Non-aqueous Solvents*, Academic, New York and London 1966, Vol. 1, Chapter 4.
- Parker, A. J. *Chem. Rev.* 69 (1969) 1 and references therein.
- Alexander, R., Parker, A. J., Sharp, J. H. and Waghorne, W. E. *J. Am. Chem. Soc.* 94 (1972) 1148.
- Kolthoff, I. M. and Chantooni, M. K., Jr. *J. Phys. Chem.* 76 (1972) 2024.
- Popovych, O., Gibofsky, A. and Berne, D. H. *Anal. Chem.* 44 (1972) 811.
- Cox, B. G. and Parker, A. J. *J. Am. Chem. Soc.* 95 (1973) 402.
- Ahrland, S., Kullberg, L. and Portanova, R. *Acta Chem. Scand. A* 32 (1978) 251.
- Cox, B. G., Hedwig, G. R., Parker, A. J. and Watts, D. W. *Aust. J. Chem.* 27 (1974) 477.
- Ahrland, S. *Pure Appl. Chem.* 51 (1979) 2019.
- Hedwig, G. R., Owensby, D. A. and Parker, A. J. *J. Am. Chem. Soc.* 97 (1975) 3888.
- Ahrland, S. and Björk, N.-O. *Acta Chem. Scand. A* 28 (1974) 823.
- Sandström, M., Persson, I. and Ahrland, S. *Acta Chem. Scand. A* 32 (1978) 607.
- Potts, R. A. and Allred, A. L. *Inorg. Chem.* 5 (1966) 1066.
- Rao, G. J. and Rao, K. B. *Z. Anal. Chem.* 168 (1959) 81.
- Persson, H. *Acta Chem. Scand.* 24 (1970) 3739.
- Parks, W. G. and LaMer, V. K. *J. Am. Chem. Soc.* 56 (1934) 90.
- Clayton, W. J. and Vosburgh, W. C. *J. Am. Chem. Soc.* 58 (1936) 2093.
- Schwarzenbach, G. and Flaschka, H. *Die komplexometrische Titration*, Enke, Stuttgart 1965, p. 214.
- Handbook of Chemistry and Physics*, 58th Ed., CRC Press, West Palm Beach 1977–1978, D-141.
- Samoilenko, V. M., Lyashenko, V. I. and Polishchuck, N. V. *Russ. J. Inorg. Chem.* 19 (1974) 1632.
- Hietanen, S. and Sillén, L. G. *Ark. Kemi* 10 (1956) 103.
- Foll, A., Le Demezset, M. and Courtot-Coupez, J. *Bull. Soc. Chim. Fr.* (1972) 1207.

Received April 22, 1980.