

Ion Activities and Zinc Electrode Reactions in Aqueous Sulfate Solutions

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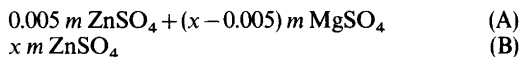
Thermodynamic and kinetic studies have revealed conventional mean-ion and convenient single-ion activity coefficients for zinc(II), magnesium and sulfate ions and standard rate data for the Zn(I)/Zn(II) electron-transfer step (the Zn/Zn(I) step appears inaccessible fast) at solid zinc in $0.005\text{ m ZnSO}_4 + (x - 0.005)\text{ m MgSO}_4$ and partly in $x\text{ m ZnSO}_4$ (for $x = 0.2 - 3.0$) at 25°C . With increasing x , the anion activity coefficient steadily falls, the cation activity coefficients go through a minimum at $x = 0.5$ to 1 , and the standard rate falls. The results show that the main electroactive Zn(I)/Zn(II) couple is one of purely hydrated ions, and they suggest that it may be $\text{Zn}(\text{H}_2\text{O})_6^+/\text{Zn}(\text{H}_2\text{O})_6^{2+}$ of fully hexahydrated ions. Double layer effects are considered and discussed.

After some initial work,¹ a convenient scale for single-ion activities has recently been introduced,^{2,3} and some convenient single-ion activity data have been accumulated.¹⁻⁸ This mostly applies to chloride solutions.¹⁻⁵ The present work backs up and extends the little there is for sulfate solutions.^{6,7} Such activity determinations are important for the evaluation of ionic interactions and reactions in solutions and at electrodes and other interfaces.

From its polarization behaviour^{2,9-12} in comparison with that^{3,13-16} of the Zn(Hg)/Zn(II) electrode, the Zn/Zn(II) electrode appears to react in two consecutive steps with the Zn(I)/Zn(II) electron-transfer step as the rate-determining one. Little is known as to the electroactive Zn(I) and Zn(II) species,^{2,9,15} which in sulfate solution most likely are purely hydrated ions. This is pursued in the present work by studies on kinetic water-activity and double-layer effects. It is hoped that this may assist in elucidating also the double-layer properties of the solid zinc electrode.¹⁷⁻¹⁹

EXPERIMENTAL

The experimental work comprises equilibrium potential measurements on saturated and well-equilibrated Zn(Hg)/Zn(II) and Hg/Hg₂SO₄ electrodes vs. SCE and kinetic polarization measurements on etched (in hot 4 M H₂SO₄) high-purity (99.999%) zinc wire electrodes (exposed surface area near 0.3 cm²) in the two solution series:



with $x = 0.2 - 3.0$ and addition of H₂SO₄ to pH about 3, all at 25°C . The solutions were prepared from *p.a.* quality salts and acid and twice distilled water, deoxygenated with purified and premoistened nitrogen, and kept under nitrogen atmosphere during the measurements.

The kinetic studies mostly are by galvanostatic single-pulse measurements in unstirred solutions and quasi-stationary overvoltage measurements in vigorously stirred (by nitrogen bubbling) solutions. All measurements have been performed with equipment and procedures essentially as previously described.^{1,2} This includes capacity (purity) checking and ohmic drop correction by the slope and the gap of galvanostatic transients on the 10 μs scale.² For "good" zinc wire electrodes, the capacity appeared to be about $55\ \mu\text{F cm}^{-2}$. "Bad" electrodes with lower capacity usually could be improved by strong anodic loads for a few seconds in the test solution. The ohmic drop mostly was well below $1\ \text{V/A cm}^{-2}$.

ACTIVITY DATA

The conventional mean molal activity coefficient (γ_{\pm}) and the convenient single-ion ones (γ'_{2+} and γ'_{2-}) for zinc(II) and sulfate ions in the test solutions should^{2,3} be given by eqns. (1)–(3).

$$\gamma_{\pm} = m^{\circ} m_{2+}^{-\frac{1}{2}} m_{2-}^{-\frac{1}{2}} \exp [f(E'_{2+} - E'_{2-}) - f(E^{\circ}_{2+} - E^{\circ}_{2-})] \quad (1)$$

$$\gamma'_{2+} = m^{\circ} m_{2+}^{-1} \exp [2f(E'_{2+} - (\phi_1 - \phi_r) - E^{\circ}_{2+} + 0.241)] \quad (2)$$

$$\gamma'_{2-} = m^{\circ} m_{2-}^{-1} \exp [-2f(E'_{2-} - (\phi_1 - \phi_r) - E^{\circ}_{2-} + 0.241)] \quad (3)$$

where m° is the standard molality (1 mol kg⁻¹), m_{2+} and m_{2-} respectively, are the zinc(II) and the sulfate molality, f means F/RT , E'_{2+} and E'_{2-} respectively, are the apparent (including liquid junction) reversible Zn/Zn(II) and Hg/Hg₂SO₄ potentials in V(SCE), E°_{2+} and E°_{2-} are the standard potentials of these electrodes in V(SHE), $\phi_1 - \phi_r$ is the liquid-junction potential difference between test and reference (saturated KCl) solution in V, and 0.241 V(SHE) is the recommended value²⁰ for

$E^{\circ}(\text{Hg}/\text{Hg}_2\text{Cl}_2) - f^{-1} \ln(a_{\pm}(\text{sat. KCl})/a^{\circ})$, all at 25 °C. These activity coefficients are bare-ion ones.

Table 1 presents E' values measured, $\phi_1 - \phi_r$ values estimated,⁷ and γ values hence obtained from (1)–(3) for the solution series (A), when use is made of the $E^{\circ}/V(\text{SHE})$ values -0.763 and 0.612 for Zn/Zn(II) and Hg/Hg₂SO₄,^{22,23} respectively. The table moreover reproduces mean ionic and water activity data²¹ for pure magnesium sulfate solutions. These data are presently accepted for the solution series (A), and they partly have been used in determining $\gamma'_{2+}(\text{Mg})$ from its equality to $(\gamma_{\pm}(\text{MgSO}_4))^2/\gamma_{2-}(\text{SO}_4)$. Table 2 presents data correspondingly obtained for the solution series (B), when the $\phi_1 - \phi_r$ values of Table 1 are accepted also for this series. The mean-ion coefficient values of Table 2 check well with previously tabulated ones.²¹

In Fig. 1, a comparison is made of the three ionic activity coefficients of zinc sulfate with those of

Table 1. Data for 0.005 *m* ZnSO₄ + (*x* - 0.005) *m* MgSO₄ + H₂SO₄ (to pH about 3) at 25 °C (see text).

<i>x</i>	0.2	0.5	1.0	1.5	2.0	2.5	3.0
Potential data							
$E'_{2+}(\text{Zn})/V(\text{SCE})$	-1.099	-1.100	-1.100	-1.097	-1.093	-1.088	-1.082
$E'_{2-}(\text{SO}_4)/V(\text{SCE})$	0.419	0.420	0.420	0.422	0.423	0.424	0.424
$(\phi_1 - \phi_r)/V$	-0.001	0.000	0.001	0.001	0.002	0.002	0.003
Activity data							
$\gamma_{\pm}(\text{ZnSO}_4)$	0.12	0.070	0.050	0.042	0.041	0.043	0.050
$\gamma_{\pm}(\text{MgSO}_4)^a$	0.11	0.068	0.049	0.043	0.042	0.044	0.049
$\gamma_{2-}(\text{SO}_4)$	0.11	0.044	0.024	0.014	0.010	0.008	0.007
$\gamma'_{2+}(\text{Zn})$	0.13	0.11	0.10	0.13	0.17	0.25	0.36
$\gamma'_{2+}(\text{Mg})$	0.11	0.10	0.10	0.13	0.17	0.24	0.35
a_w^a	0.996	0.991	0.981	0.969	0.953	0.932	0.905

^a For *x m* MgSO₄.²¹

Table 2. Data for *x m* ZnSO₄ + H₂SO₄ (to pH about 3) at 25 °C (see text).

<i>x</i>	0.2	0.5	1	2	3
Potential data					
$E'_{2+}(\text{Zn})/V(\text{SCE})$	-1.052	-1.042	-1.028	-1.010	-0.992
$E'_{2-}(\text{SO}_4)/V(\text{SCE})$	0.423	0.422	0.428	0.433	0.437
Activity data					
$\gamma_{\pm}(\text{ZnSO}_4)$	0.10	0.062	0.043	0.035	0.041
$\gamma_{2-}(\text{SO}_4)$	0.080	0.038	0.013	0.0047	0.0025
$\gamma'_{2+}(\text{Zn})$	0.12	0.10	0.14	0.27	0.67
a_w^a	0.996	0.991	0.983	0.985	0.911

^a For *x m* ZnSO₄.²¹

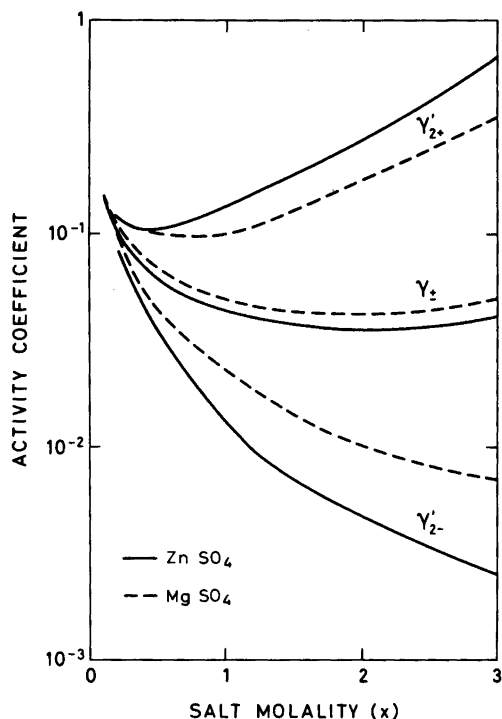


Fig. 1. Molal bare-ion activity coefficients in essentially pure solutions of zinc sulfate (solid curves) or magnesium sulfate (dashed curves) at 25 °C.

magnesium sulfate in essentially pure solutions of these salts. Since the activity coefficient for traces of zinc sulfate in magnesium sulfate solution nearly is the same as for the main salt (Table 1), this comparison essentially also is for the limiting activity coefficients of zinc sulfate in mixed solutions with magnesium sulfate (at zero and infinite zinc/magnesium ratio).

The convenient single-ion activity coefficients are related to absolute ones^{2,3} by $\gamma'_z = \gamma_z r^{-z/2}$ where r is the ratio γ_+/γ_- for potassium chloride in saturated pure solution at the temperature concerned, and z is the charge number (with sign) of the ion concerned. The ratio r is not yet exactly known, but it appears to be near unity at 25 °C.⁴ For any complex species, the activity should be proportional to the mass-action activity product of its constituent bare ions and molecules. This is made use of in the kinetic studies below.

KINETIC DATA

The kinetic data of the present work apply to pre-etched zinc wire electrodes in the solution series (A). A slightly unstable and stirring dependent open-circuit potential, somewhat positive to the reversible Zn/Zn(II) potential (Table 1), was generally obtained. This invalidated any attempt of directly determining the charge-transfer resistance near equilibrium of the electrode, and only Tafel data

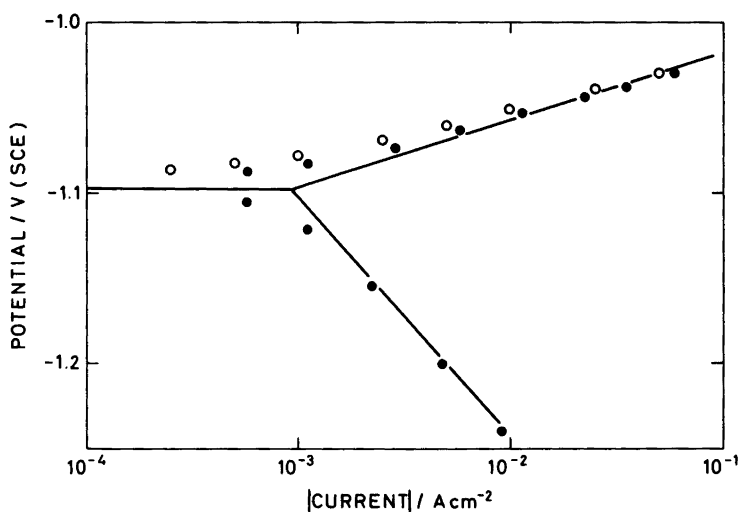


Fig. 2. Charge-transfer data for solid zinc in 0.005 *m* ZnSO₄ + 1.495 *m* MgSO₄ + H₂SO₄ (to pH about 3 at 25 °C from (O) slow measurements in vigorously stirred solution and (●) fast galvanostatic transients in unstirred solution.

Table 3. Exchange data for Zn(I)/Zn(II) at solid zinc in 0.005 m ZnSO₄ + (x - 0.005) m MgSO₄ + H₂SO₄ (to pH about 3) at 25 °C (see text).

x	0.5	1.0	1.5	2.0	2.5	3.0
$i_{o_2}/\text{mA cm}^{-2}$	0.70	0.50	0.50	0.45	0.45	0.40
$I_{o_2}/\text{A cm}^{-2}$	0.20	0.15	0.12	0.09	0.07	0.05

will presently be considered. Examples of such data are given in Fig. 2.

Tafel slopes. In all solutions (A), charge-transfer controlled anodic and cathodic Tafel lines were obtained with $E/\ln i$ slopes of typically $2RT/3F$ and $-2RT/F$, respectively. This agrees with a two-step charge-transfer mechanism in which the Zn(I)/Zn(II) electron-transfer step is rate determining (see Introduction) and essentially symmetric ($\alpha_2 = \frac{1}{2}$). A more exact determination of the slopes was impeded both by the Tafel-linear regions covered being too small and by the reproducibility of the cathodic data being too poor.

Exchange rates. The anodic data of the present work are well reproducible and warrant further treatment. With the reaction mechanism proposed, the anodic Tafel lines should intersect with the reversible potential applying (Table 1) at twice the exchange current of the rate-determining Zn(I)/Zn(II) electron-transfer step.²⁴ Values accordingly obtained for this exchange current (i_{o_2}) are given in Table 3. The exchange current (i_{o_1}) of the Zn/Zn(I) ion-transfer step appears to be inaccessibly high for the present measurements.

From ordinary electrode kinetics,²⁴ i_{o_2} should depend on the bare-ion activity of Zn(II) by (when $\alpha_2 = \frac{1}{2}$):

$$i_{o_2} = I_{o_2} (a'_{2+}/a^0)^{3/4} = I_{o_2} (\gamma'_{2+} m_{2+}/m^0)^{3/4} \quad (4)$$

where I_{o_2} is a bare-zinc-ion standardized exchange rate which still depends on ligand activities and double-layer effects. Also values accordingly obtained for I_{o_2} from i_{o_2} and activity data (Table 1) are given in Table 3.

Double-layer and ligand effects. With increasing concentration of the supporting salt (MgSO₄), I_{o_2} clearly falls (Table 3). This fall is steeper than can be expected solely from activity effects by water or sulfate ions as ligands in the electroactive species, and double-layer effects must be invoked. Since the sulfate-ion activity ($\gamma'_{2-} m_{2-}$) is nearly constant over the solution series concerned (Table 1), this may be illustrated by a log-log plot of I_{o_2} against the water activity applying. Such a plot is given in Fig. 3,

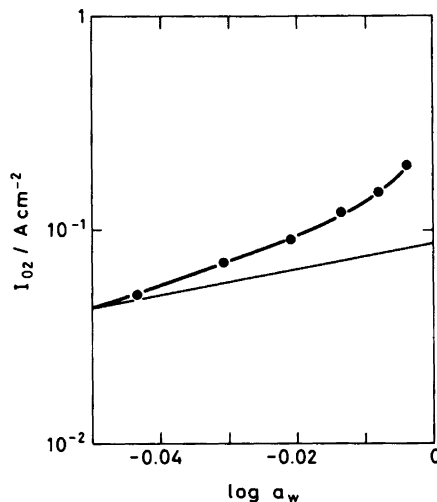


Fig. 3. Log-log plot of I_{o_2} vs. a_w for solid zinc in 0.005 m ZnSO₄ + (x - 0.005) m MgSO₄ + H₂SO₄ (to pH about 3) at 25 °C. The straight line slopes as for sole sixth-order water dependence.

where also comparison is made to a line sloping as for sole sixth-order water dependence.

The double-layer properties of solid zinc is not well-known, but its potential of zero charge may be near -0.9 V(SCE).^{17,18} The present rate data then apply to negatively charged zinc electrodes with little or no ions specifically adsorbed. The double-layer effect accordingly should be mainly by the Frumkin factor:²⁴

$$\exp [f(\frac{1}{2} - z)\phi_2] \quad (5)$$

where ϕ_2 is regarded the pre-electrode potential, z is the net charge number (with sign) of the electroactive Zn(II) species, and use has been made of $\alpha_2 n = \frac{1}{2}$ for the reaction step considered.

Under the electrode conditions noted, ϕ_2 is negative, $|\phi_2|$ decreases with increasing salt concentration, and so consequently does also the Frumkin factor (5) for $z=2$ (but not for $z=0, -2$, etc.). The results in Fig. 3 agree qualitatively with

the expectations from the Frumkin factor for $z=2$ (but not for $z=0, -2$, etc.). The main electroactive Zn(I)/Zn(II) couple hence appears to be one of purely hydrated ions ($z=2$) and not one of sulfato-complexes ($z=0, -2$, etc.).

Further double-layer studies. The results of Fig. 3 are at present difficult to separate genuinely into water-activity and double-layer effects. However, if it be assumed that the electroactive zinc ions are fully hexa-hydrated, and that no unconsidered effect contributes to the changes in I_{O_2} , one should have:

$$\Delta \ln(I_{O_2}/a_w^6) = -3f\Delta\phi_2/2 \quad (6)$$

for connected differences in the parameters noted. This equation enables changes in ϕ_2 to be obtained from those of I_{O_2} and a_w .

Fig. 4 presents the results accordingly obtained for the variation of ϕ_2 with x (from an arbitrary zero at $x=1$) in the solution series (A). A $\Delta\phi/\log x$ presentation is chosen for easy comparison to expectations from the Gouy-Chapman diffuse-layer theory. Such expectations are given by a dashed line in Fig. 4. This line is partly extrapolated (beyond $x=1$) from data in Russel's tables²⁵ for Gouy-

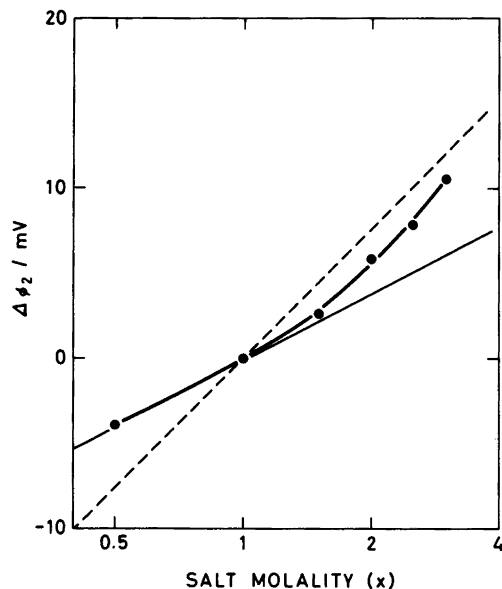


Fig. 4. Values from (6) for $\Delta\phi_2 = \phi_2(x) - \phi_2(x=1)$ vs. $\log x$ for solid zinc around -1.05 V(SCE) in 0.005 m $ZnSO_4 + (x-0.005)$ m $MgSO_4 + H_2SO_4$ (to pH about 3) at $25^\circ C$.

Chapman values of $|z|\phi_2$ at mercury in solutions of an unadsorbed and unassociated $z:z$ electrolyte like NaF, and it applies to electrodes with sufficiently negative charge to make $d\phi_2/d\ln c$ essentially invariant to changes in this charge. The dashed line thus gives the steepest variation allowed by the Gouy-Chapman theory. The variation should be smaller if the electrode charge be less negative than considered.

At low salt concentration (x), the results follow a $\Delta\phi_2/\log x$ line with about half the Gouy-Chapman slope. The increasing deviation from this line at higher salt concentration accompanies an increasing instability of the test electrode (especially in cathodic studies) and an increasing deviation of its open-circuit potential from the reversible Zn/Zn(II) potential (see above). These deviations may be due to some side effect (e.g. precipitation of some compound at the electrode surface) which, with increasing salt concentration, increasingly comes in and makes the observed rates increasingly too low.

The kinetic data underlying the results of Fig. 4 mostly apply to potentials around -1.05 V(SCE). This is only 150 mV negative to the above-noted value for the zero-charge potential of solid zinc. Since also Gouy-Chapman values for $|\phi_2|$ may be too high,^{4,26,27} the ϕ_2 -variation obtained from (6) is not unacceptable. This means that the main electroactive Zn(I)/Zn(II) couple could be one of fully hexahydrated zinc ions as presumed. Due to the Franck-Condon principle, one must expect the two electroactive species of an electron-transfer couple to have one and the same coordination.²⁸

DISCUSSION

The present results are already somewhat discussed in connection with their presentation, and only some closing remarks shall be made on the activities, the kinetics and the double-layer properties revealed.

Activities. Besides being needed and used in the present kinetic evaluations, the convenient single-ion activity data of the present work carry information on the energetics of ion and cosphere interactions in the test solutions, and more so than do the conventional mean-ion data. This includes information on complex formation. The single-ion data partly depend on the validity of the values used for the liquid-junction potential difference $\phi_l - \phi_r$, however.

Some interaction information may be read rather easily from the data collection of Fig. 1. The interpretation and quantitative evaluation of these data, however, require more than can presently be given. The activity data, therefore, are left with previous ones of the same kind¹⁻⁸ for future treatment.

Kinetics. The kinetic results of the present work agree with the two-step mechanism of the Zn/Zn(II) electrode (see Introduction). They further show that the main electroactive Zn(I)/Zn(II) couple in the sulfate solutions used is one of purely hydrated ions, and they suggest that these ions may be fully hexacoordinated solution species. The latter in case agrees with previous kinetic results on zinc in chloride solutions,² and it compares well with corresponding results on manganese,⁴ nickel,¹ and copper.⁸ The kinetic results say nothing about the thermodynamically most stable Zn(I) and Zn(II) species, nor about the electroactive species of the Zn/Zn(I) couple.

Double-layer properties. The present separation of double-layer effects from other effects is not a fool-proof one, but a likely one. It does not yield the pre-electrode potential (ϕ_2) itself, but the sign and changes of this potential. Provided sulfatocomplexes participate negligibly and the electrode charge be sufficiently negative, these changes may seem to be lower than expected from the Gouy-Chapman diffuse-layer theory. This in case adds to similar results on liquid amalgam electrodes^{4,26} in suggesting that Gouy-Chapman values of $|\phi_2|$ may be too high. This agrees qualitatively with more recent double-layer theory.²⁷

It appears that the bare-zinc-ion and water standardized Zn(I)/Zn(II) exchange rate at solid zinc is a little lower (by a factor of about 1.2) in 1 m magnesium sulfate solution (present work) than in 1 M alkali chloride solutions,³ and that the Zn(II) reduction in 0.5 m (or M) magnesium sulfate solution of 0.005 m (or M) Zn(II) is slower (by about half a decade) at solid zinc (present work) than at mercury.¹⁴ These comparisons apply to data obtained at potentials around -1.05 V(SCE) and 25 °C. They support that ϕ_2 be negative at solid zinc (but less so than at mercury) under the conditions applying, and that z be positive (not zero or negative) for the main electroactive Zn(I)/Zn(II) couple. These conclusions partly imply that the electrode material (Zn or Hg) *per se* means little for the rate of electron transfer between a metallic electrode and species in solution.²⁹

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