Reactions in Mixed Non-aqueous Systems containing Sulphur Dioxide. Part 3.† The Electrolytic Dissolution of Metals

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The metals Mg, Cr, W, Fe, Ni, Cu, Zn, Hg, Al, Sn, and Pb dissolve electrolytically in the mixed non-aqueous solvents sulphur dioxide–dimethyl sulphoxide, –dimethylformamide, –acetonitrile, –acetone, or –nitrobenzene to form solutions containing several sulphur anions. Reactions of the metals Mg, Cr, Fe, Cu, and Zn with dimethyl sulphoxide–sulphur dioxide give pure single products of metal disulphates. The relationship of solvent parameters to metal reactivity is discussed.

It was reported earlier[1-3] that many metals react spontaneously with several binary solvent mixtures containing sulphur dioxide. Criteria were established which enabled a prediction to be made about the ability of this type of binary solvent to dissolve a metal: the binary solvent needs to possess both a high dielectric constant ($\varepsilon > 20$) and a high donor number[4] (>20) before spontaneous metal dissolution can occur. These minimum values of the solvent parameters relate to the two-fold requirement for ionisation of the metal with accompanying formation of the sulphoxylate radical ion, $[SO_2]^-$, and solvation of metal ions with inhibition of recombination of metal ion and $[SO_2]^-$ to form metal and SO_2.

In this paper we describe how several metals can be induced electrolytically into solution in some binary solvents containing sulphur dioxide which are incapable of promoting spontaneous metal dissolution. Several more solvents have been investigated and special attention has been given to those hitherto apparently inert metals (Cr, W, and Hg).

Discussion

The relation of donor number and dielectric constant to metal reactivity is shown in the Figure. Solvents which lie *above* the curve promote spontaneous metal dissolution, whereas those *below* it exhibit no reaction with metals. We have tested the solvents shown in the Figure for spontaneous reactivity with metals, and our conclusions are confirmed.

The principal solvents investigated were dimethyl sulphoxide, dimethylformamide, acetonitrile, acetone, and nitrobenzene. The metals Mg, Cr, W, Fe, Ni, Cu, Zn, Hg, Al, Sn, and Pb were dissolved by using them as sacrificial anodes in a simple electrolytic cell. It is noteworthy that the metals Cr, W, and Hg had previously failed to react spontaneously with any of the binary solvent mixtures, regardless of the position of the co-solvent in the donor number–dielectric constant diagram.

With a few exceptions in the case of the binary solvent dimethyl sulphoxide–sulphur dioxide, electrolytic dissolution of a metal into the binary solvent produces a rather complex mixture, mainly of sulphur oxy-anions such as sulphate, dithionate, and thiosulphate. In a few cases, sulphide was also detected. The disulphate ion is only formed in the binary solvent dimethyl sulphoxide–sulphur dioxide, which is the only binary system capable of oxidising sulphur(IV) to sulphur(VI), in the form of the disulphate ion. The metals Mg, Cr, Fe, Cu, and Zn dissolved electrolytically in dimethyl sulphoxide–sulphur dioxide to form crystalline solvated metal disulphates, which were characterised by elemental analysis, thermogravimetric analysis, and i.r. spectroscopy. The rate of formation of these compounds depends on the potential difference maintained in the electrolytic cell, and on the current. In the case of iron, choice of background electrolyte is important. Use of tetraethylammonium tetrafluoroborate always led to formation of a mixture of sulphate and disulphate, whereas use of tetraethylammonium perchlorate always gave disulphate. In the case of aluminium, a mixture of sulphate and disulphate was obtained, irrespective of the nature of the background electrolyte. Generally, a potential difference of 10 V was applied across the cell, and currents of 40—100 mA were obtained.

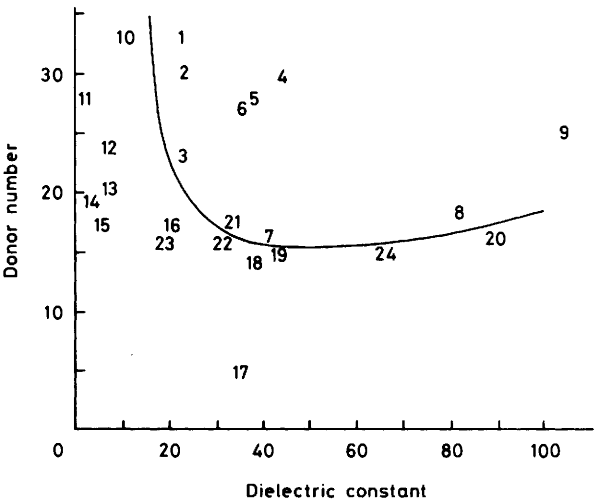

Figure. Plot of dielectric constant *versus* donor number for (1) methanol, (2) ethanol, (3) trimethyl phosphate, (4) dimethyl sulphoxide, (5) dimethylacetamide, (6) dimethylformamide, (7) ethylene sulphite, (8) water, (9) formamide, (10) pyridine, (11) dioxan, (12) tributyl phosphate, (13) tetrahydrofuran, (14) diethyl ether, (15) ethyl acetate, (16) acetone, (17) nitrobenzene, (18) acetonitrile, (19) tetrahydrothiophen 1,1-dioxide, (20) ethylene carbonate, (21) phenylphosphonic dichloride, (22) n-propionitrile, (23) n-butyronitrile, and (24) propylene carbonate

Other factors influencing the rate of formation of the compounds were the metal and the state of passivation of the electrodes. Dithionite ions around platinum electrodes are known to give rise to a significant degree of passivation in mixtures of dimethyl sulphoxide–sulphur dioxide,[5] and it is likely that the various sulphur oxy-anions formed in several binary solvents containing sulphur dioxide also give rise to considerable passivation.

The solvated disulphates of the metals Mg, Cu, and Zn were prepared previously and fully characterised.[2,3] Those of chromium(III) and iron(III) have been prepared for the first

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† Part 2 is ref. 3.

Table. Infrared bands (cm^{-1}) of metal disulphates

$[Cr_2(dmso)_{20}][S_2O_7]_3$	$[Fe_2(dmso)_{10}]$-$[S_2O_7]_3 \cdot SO_2$	Assignment
440w	430m	$[S_2O_7]^{2-}$
570m		
583m	580s	
595m	595s	
690 (sh)	675w	dmso
840s	840s	$[S_2O_7]^{2-}$
	900s	
955s	950s	dmso
1 000s	1 005s	$[S_2O_7]^{2-}$
1 040s	1 030s	
	1 060s	
	1 115s	
	1 125s	
	1 165s	
1 230s	1 235s	dmso
1 330m	1 320m	

time. They are hygroscopic crystalline solids, readily soluble in dimethyl sulphoxide (dmso). The i.r. bands are shown in the Table. The S–O stretching frequency of dmso occurs at 1 053 cm^{-1}. In the complexes, if the bands at 1 000—900 cm^{-1} are assigned to the S–O stretching frequencies, there is a shift of 50—150 cm^{-1} when dmso co-ordinates to the metals. The shift in each case is to a lower frequency compared to the free solvent, and indicates co-ordination to the metal through oxygen. An unusual feature of the products lies in the very large number of co-solvent molecules which appear to form part of the crystals. It is not yet clear how these are disposed in the crystals. Comparisons of the spectra of the disulphates with that of anhydrous potassium disulphate and the reported spectrum of sodium disulphate[6] clearly indicate the presence of the disulphate ion.

The thermal decomposition of the solvated disulphates has been studied up to 1 000 °C. Data for the solvated disulphates of Mg^{II}, Cu^{II}, and Ni^{II} have been reported elsewhere.[2,3] The compound $[Cr_2(dmso)_{20}][S_2O_7]_3$ begins to lose dimethyl sulphoxide at 110 °C and at 400 °C $Cr_2(S_2O_7)_3$ is obtained. Further heating results in loss of SO_3 to give Cr_2O_3 at 700 °C. The compound $[Fe_2(dmso)_{10}][S_2O_7]_3 \cdot SO_2$ begins to lose weight at 110 °C, losing dimethyl sulphoxide stepwise, and SO_2. At 290 °C $Fe_2(S_2O_7)_3$ is obtained. Further heating results in loss of SO_3 to give $Fe_2(SO_4)_3$ at 395 °C, followed by loss of more SO_3 to give Fe_2O_3 at 900 °C.

It may seem surprising that iron is not present as iron(II) in the disulphate, as indicated by the lack of reaction with permanganate ion. However, sulphur dioxide does not show reducing properties in the binary non-aqueous system; indeed, oxidation of sulphur(IV) to sulphur(VI) is permitted.

The steps involved in the oxidation of metal to metal disulphate have already been reviewed in some detail.[2] Much evidence exists to indicate that the $[SO_2]^-$ ion plays an important part in the spontaneous dissolution of metals in several binary solvent systems containing sulphur dioxide.[3] The formation of $[SO_2]^-$ from SO_2 in the presence of metal requires the presence also of a co-solvent, such as dimethyl sulphoxide, which can form a reactive adduct with SO_2. An adduct of 1 : 1 stoicheiometry has been shown to exist in the case of dimethyl sulphoxide–sulphur dioxide.[2]

The co-solvent must possess a high dielectric constant to facilitate joint formation of metal cations and $[SO_2]^-$; it must also possess high donor power to assist formation of solvated metal cations and to prevent recombination of metal cation and $[SO_2]^-$. It has already been shown[3] that $[SO_2]^-$ can be generated electrolytically in binary solvents in the vicinity of an inert anode. It is therefore reasonable to assume that, in a cell containing an inert cathode and a sacrificial metal anode, both metal cations and $[SO_2]^-$ will be generated simultaneously during electrolysis. Indeed u.v.–visible spectra have indicated formation of the brown $[SO_2]^-$ species ($\lambda_{max.} = 395$ nm) near the cathode surface, together with blue metal ion pairs ($\lambda_{max.} = 560$—590 nm), so that the solution in the vicinity of the cathode assumes a green colouration.

In the electrolytic cells, $[SO_2]^-$ undergoes a series of very complex reactions which produce a wide variety of sulphur oxy-anions. This is quite contrary to the simple dimerisation of $[SO_2]^-$ to dithionite, which occurs in those solvent mixtures in which metals dissolve spontaneously. Only in the case of the binary system dimethyl sulphoxide–sulphur dioxide does a straightforward conversion of $[SO_2]^-$ into disulphate occur under electrolytic conditions. In this respect, the oxidation of sulphur(IV) to sulphur(VI) as disulphate, which is unique to the system dimethyl sulphoxide–sulphur dioxide, is the predominant step in the sequence of reactions. In the case of the other binary systems, where this oxidative step cannot occur, several interactions of $[SO_2]^-$ with $[SO_2]^-$, SO_2, and other sulphur oxy-anions are possible on account of the high reactivity of $[SO_2]^-$ towards sulphur and oxygen.

Experimental

All operations were carried out under dry oxygen-free nitrogen. Solvents were dried over molecular sieve 4A, deoxygenated, and redistilled, and then saturated with sulphur dioxide [dried over phosphorus(V) oxide and concentrated sulphuric acid]. An open cell in a dry-box was used. This contained a platinum wire as the cathode, and a background electrolyte of 0.5 mol dm^{-3} tetraethylammonium perchlorate or 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate.

Preparations.—The salts $[Mg(dmso)_6][S_2O_7]$, $[Cu(dmso)_6]$-$[S_2O_7]$, and $[Zn(dmso)_6][S_2O_7]$ were prepared by electrolysing a rod of the metal, used as an anode, into dimethyl sulphoxide–sulphur dioxide until a crystalline precipitate formed at the base of the cell. The precipitate was filtered off and washed with dry diethyl ether. Analyses, i.r. spectra, and thermograms corresponded to those found for the same compounds prepared by spontaneous dissolution of metal in the binary solvent.[2,3]

In the following cases, the method described for the corresponding magnesium compound was followed: $[Cr_2(dmso)_{20}]$-$[S_2O_7]_3$, green crystalline solid (Found: C, 21.8; H, 5.4; Cr, 4.65; S, 37.6. Calc. for $C_{40}H_{120}Cr_2O_{41}S_{26}$: C, 21.9; H, 5.45; Cr, 4.75; S, 37.95%); $[Fe_2(dmso)_{10}][S_2O_7]_3 \cdot SO_2$, yellow crystalline solid (Found: C, 16.1; H, 4.25; Fe, 7.45; S, 36.55. Calc. for $C_{20}H_{60}Fe_2O_{33}S_{17}$: C, 16.15; H, 4.05; Fe, 7.55; S, 36.65%).

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer and on a Pye Unicam SP2000 spectrophotometer as Nujol mulls. Thermogravimetric curves were obtained using a Stanton thermobalance. Carbon, hydrogen, sulphur, chromium, and iron were determined by Mr. A. Hedley of this department.

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