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Electrochemical Synthesis of Blue Molybdosulfate Complexes

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Controlled potential electrolysis (CPE) of a Na_2MoO_4/H_2SO_4/40% (v/v) CH_3CN system produced two types of blue molybdosulfate complexes which were isolated as tetramethylammonium-, guanidine-, and choline-salts. The ratios of Mo(VI) : Mo(V) : S(VI) in the complexes were confirmed as 7 : 2 : 1 and 3 : 3 : 4.

Previously, it was reported that the $Na_2MoO_4/H_2SO_4/CH_3CN$ system produced a yellow molybdosulfate complex which had a composition of $[(MoO_3)_9(SO_4)]^{2-}$.[1] The complex was electrochemically reducible to the corresponding blue 9/1-complex. For simplicity, blue complexes here are referred to by their Mo/S ratios.

In this study, CPE was carried out for the $Na_2MoO_4/H_2SO_4/CH_3CN$ system. A three-electrode system was used with a glassy carbon (GC) working electrode (ca. 0.5 g GC-20 fibers, Tokai Carbon), a platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Unless otherwise stated, a 100 ml portion of a given solution was electrolyzed at -0.10 V with a constant stirring by means of a magnetic stirrer. The changes of the electrolysis current with time, i. e., I-t curves were recorded during the electrolysis. The curves were well reproduced provided that the electrolysis parameters were kept unchanged. All the experiments were made at 25 °C. As the results, a blue 3/2-molybdosulfate complex was newly found in addition to the blue 9/1-complex. These complexes were characterized by elemental analysis, and IR- and visible-spectral measurements.

Curve A in Fig. 1 shows a typical I-t curve measured for a 0.1 M (M = mol dm^{-3}) Na_2MoO_4/1.5 M H_2SO_4 system; the current becomes maximum after a 6 h-electrolysis and decreases slowly toward the baseline level. It takes ca. 12 h for the completion of the electrolysis. As is anticipated from the unusual convex curve, the reduction of Mo(VI) may involve rather complicated processes. Nevertheless, the coulometric analysis clearly shows that whole of the Mo(VI) in the solution was converted to Mo(V) in accordance with the overall electrochemical stoichiometry expressed as $Mo(VI) + e^- = Mo(V)$. After the electrolysis, in fact, the solution exhibited an orange-red color characteristic of Mo(V). In contrast, the electrolysis of a 0.1 M Na_2MoO_4/1.5 M H_2SO_4/40% (v/v) CH_3CN system produced a strongly blue-colored solution. The I-t curve is shown in curve B of Fig. 1. It

is noteworthy to point out the fact that the electrolysis was accelerated to terminate within 5 h by the presence of CH_3CN. Moreover, the coulometric analysis indicated that only 90% of Mo(VI) was reduced to Mo(V); therefore, the rest 10% still remained unreduced. Further, the systems consisting of HCl or $HClO_4$ in place of H_2SO_4 did not produce blue solutions. These facts suggest the formation of blue molybdosulfate complexes containing Mo(VI), Mo(V), and S(VI).

The formation of the blue complexes was monitored by measuring the absorption spectra during the electrolysis. The representative spectra are given in Fig. 2. In the early stage of the electrolysis (within 0.75 h), a broad absorption band grew in the 600-800 nm range (curves A-C). At the middle stage where the electrolysis current became maximum, the band started to split into two narrower bands (curves C-E). The spectral change resembled that observed for the electrolysis of the yellow 9/1-complex.[2] As described below, indeed, the blue solution obtained by 0.75 h-electrolysis gave the blue 9/1-complex. Toward the final stage of the electrolysis (3-5 h), the spectrum converges to curve H. A blue 3/2-complex was isolated from the solution. From these observations, the

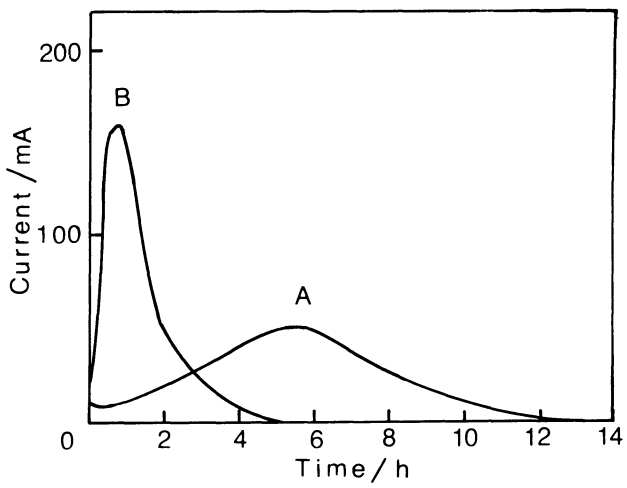

Fig. 1. I-t curves for (A) 0.1 M Mo(VI)/ 1.5 M H_2SO_4 system and (B) 0.1 M Mo(VI)/ 1.5 M H_2SO_4/40% (v/v) CH_3CN system.

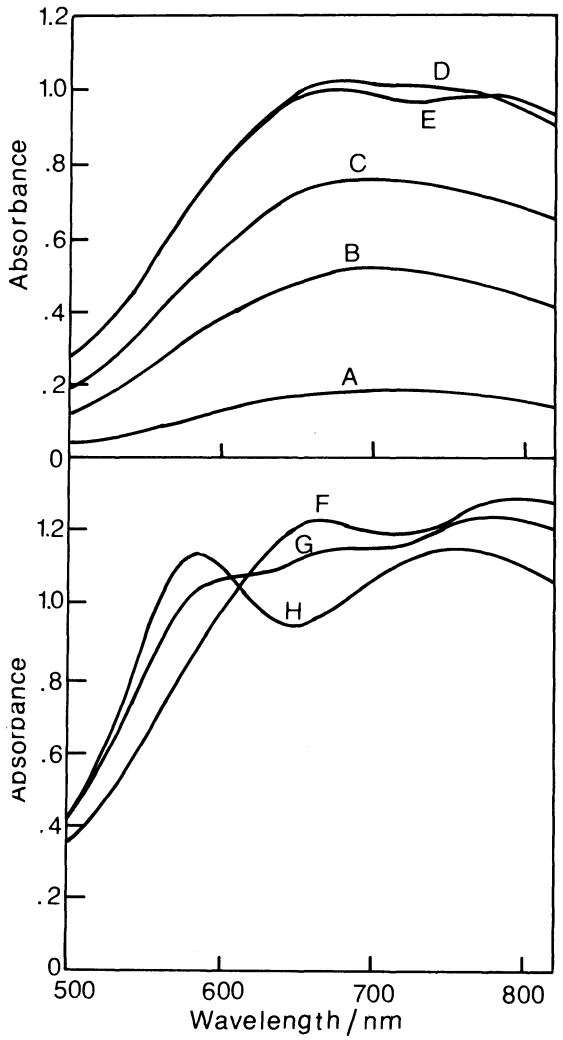

Fig. 2. Absorption spectral change during the electrolysis of 0.1 M Mo(VI)/1.5 M H_2SO_4/40% (v/v) at the time of (A) 0.25, (B) 0.5, (C) 0.75, (D) 1.0, (E) 2.0, (F) 3.0, (G) 4.0, and (H) 5.0 h.

Path length; 0.1 mm.

following synthetic method was established.

The blue 9/1 (18/2)-complex: Electrolyze the 0.1 M Na_2MoO_4/1.5 M H_2SO_4/40% (v/v) CH_3CN system for ca. 0.75 h. Filter the resulting blue solution to remove shag of the GC fibers. Add 3 g of tetramethylammonium chloride or 5 g of choline chloride to the filtrate, and precipitate the respective salts; the guanidine salt did not precipitate. Collect the salts by centrifugation and wash with water several times. Dry the salts in vacuum over Drierite at 40 °C. The yield was ca. 700 mg. The elemental analysis data are summarized in Table 1. The water of hydration can be removed by heating them at 70 °C although the anhydrous salts are slightly hygroscopic. As can be seen, both salts include a complex formulated as $[(Mo^{VI}O_3)_{14}(Mo^{V}O_3)_4(SO_4)_2]^{8-}$, i. e., the 4-electron reduction product of the yellow $[(MoO_3)_{18}(SO_4)_2]^{4-}$.

The blue 3/2 (6/4)-complex: Electrolyze the same solution as above for more than 5 h and treat similarly the resulting solution to precipitate the blue complex. By the addition of 5 g of guanidine hydrochloride, in this case, the guanidine salt was obtained; the salt grew to needle-like crystals in 2 mm length when the mother solution was carefully cooled down to 10 °C. Collect the salts by filtration and wash with 75% ethanolic water. Dry in vacuum over Drierite at 40 °C. The yield was ca. 600 mg. As listed in the lower part of Table 1, the compositions of the salts substantiate a blue molybdosulfate which can be formulated as $[(Mo^{VI}O_3)_3(Mo^{V}O_3)_3(SO_4)_4]^{11-}$

The Mo(V) contents in Table 1 were determined coulometrically by oxidizing the

Table 1. Elemental analysis data on the salts of the blue 9/1- and 3/2-molybdosulfate complexes

Compounds	Composition (%): Calcd[a] / Found						Mo(V)/Mo[b]
	H	C	N	Na	S	Mo	
Blue 9/1(18/2)-molybdosulfates							
$[(CH_3)_4N]_5H_3S_2Mo^{VI}_{14}Mo^{V}_4O_{62}\cdot 4H_2O$	2.11	7.43	2.17		1.99	53.49	0.222
	2.04	7.37	2.02		2.01	53.07	0.234
$[(CH_3)_3NC_2H_4OH]_5H_3S_2Mo^{VI}_{14}Mo^{V}_4O_{62}\cdot 4H_2O$	2.40	8.88	2.07		1.90	51.13	0.222
	2.25	9.03	2.14		1.97	50.39	0.265
Blue 3/2(6/4)-molybdosulfates							
$[(CH_3)_4N]_2Na_4H_5S_4Mo^{VI}_3Mo^{V}_3O_{34}$	1.94	6.43	1.88	6.16	8.59	38.56	0.500
	1.92	6.76	1.67	5.92	8.66	39.45	0.485
$[(CH_3)_3NC_2H_4OH]_2Na_3H_3S_4Mo^{VI}_3Mo^{V}_3O_{34}$	2.22	7.84	1.83	4.51	8.38	37.61	0.500
	2.38	8.27	1.97	4.90	8.28	38.28	0.467
$[NH_2C(NH)NH_3]_3Na_2H_3S_4Mo^{VI}_3Mo^{V}_3O_{34}$	1.62	2.43	8.52	3.11	8.67	38.90	0.500
	1.64	2.56	8.56	3.83	8.79	39.18	0.538

a) The arithmetic mean of the analytical results on six samples of each salt.

b) The ratio of Mo(V) to the total molybdenum in the salts.

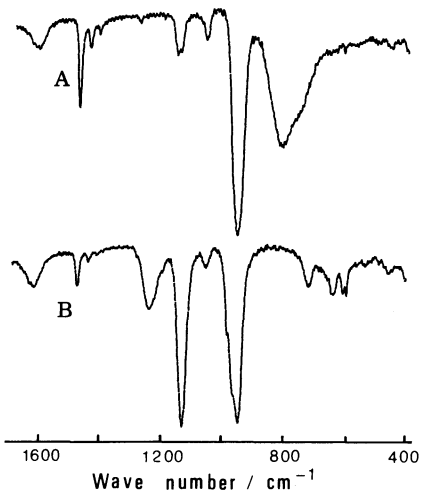

Fig. 3. IR spectra of tetramethylammonium salts of the blue 9/1- (A) and 3/2- (B) complexes in the KBr disk.

blue salts at +1.0 V in 0.1 M $HClO_4$ solutions. The total Mo was determined by both gravimetry[3] and spectrophotometry[4] after the electrochemical oxidation of the blue salts. The ratios of Mo(V)/Mo thus found are given in the last column of Table 1. Besides the definite difference in their compositions, the blue 9/1- and 3/2-complexes are also distinguishable by their solubilities in water; the former dissolves sparingly whereas the latter does easily. The complexes are also well characterized by the IR spectra shown in Fig. 3. The 9/1-complex shows absorption bands at 1160 and 1064 cm^{-1} assigned to the asymmetric and symmetric stretching of the S-O bond.[1] The 3/2-complex shows the corresponding bands at 1135 and 1058 cm^{-1}, and an additional band at 1250 cm^{-1} which can be assigned to the $S{=}O_{terminal}$ bond.

In addition to the yellow 9/1-complex, we have recently isolated a colorless 5/2-complex from the Mo(VI)/H_2SO_4/C_2H_5OH system,[5] although the 5/2-complex was not reduced to the blue species. However, the H_2SO_4 concentration used in the present study is too strong for the yellow and colorless complexes to form.

The 9/1-complex has been isolated as both oxidized (yellow) and reduced (blue) species, whereas attempts to prepare the oxidized form of the blue 3/2-complex have been unsuccessful so far. Preliminary experiments suggest that the conditions for the formation of the molybdosulfates depend on the concentrations of Mo(VI), H_2SO_4, and organic solvents, temperature of the solutions, and the kind of organic solvents. Studies to systematize the formation conditions are now in progress.

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