TABLE 1 — SURFACE ACIDIC STRENGTH DISTRIBUTION IN SODIUM MOLYBDATE CATALYST

Sample*	Surface area m²/g	n-Butylamine titre values† for indicators of various pk_a values				
		+6·8	+5·0	+3·3	+2·0	−3·0
SM 230	2·5	0·47	0·12	0·12	0·04	0·04
SM 510	0·7	0·42	0·04	0·04	0·04	0·04
SM 660	0·5	0·69	0·15	0·04	0·04	0·04
SM 700	0·3	0·70	0·16	0·04	0·04	0·04

*The arabic numeral signifies the temperature at which sodium molybdate has been calcined.

†The values are expressed as mmoles/g; accuracy ±0·01.

reported for $Na_2MoO_4.2H_2O$ (ASTM Card No. 1-0113). Diffraction pattern of the sample heated at 230° is slightly different and shows the presence of a few new strong lines having $d = 5{\cdot}405$, 3·263, 2·765, 1·865, 1·756, 1·612 Å, etc., resembling closely those reported for standard patterns of Na_2MoO_4 (ASTM Card No. 12-773). Therefore, the endothermic peak at 150° is clearly due to dehydration of the $Na_2MoO_4.2H_2O$. The structure of the dehydrated sample appears to be more crystalline than that of the hydrated one. XRD pattern does not undergo any significant change when the molybdate is calcined at 510° and above. The last endothermic peak at 689° is, however, due to melting. The two peaks at 470° and 643° may be associated with crystal transformation as these changes are not accompanied by any weight change when heated at 470° and above.

Na_2MoO_4 is known to exist[15] in four modifications. The α-form is stable above about 620°; the β-form between 620° and 580°; γ-form between 510° and 410°; and the δ-form below 410°. Thus, the endothermic transitions at 473° and 643° are due to the following transformation:

$$\delta\text{-}Na_2MoO_4 \xrightarrow{470^\circ} \gamma\text{-}Na_2MoO_4 \xrightarrow{643^\circ} \alpha\text{-}Na_2MoO_4$$

The transition between 620° and 580° could not be observed in the DTA curve and hence it is difficult to show the presence of β-Na_2MoO_4.

Surface acidic strength distribution in sodium molybdate samples is shown in Table 1. It is observed that the medium acid sites ($pk_a = +3{\cdot}3$) are reduced as the molybdate is calcined at 510°. The strong acid sites ($pk_a \leqslant +2{\cdot}0$), however, remain almost unchanged up to melting. It is interesting to note that weak acid sites ($pk_a \geqslant +5{\cdot}0$) increase at 660° and above. The acidic strength of $MoO_3.Fe_2(MoO_4)_3$ at $Ho \leqslant +4{\cdot}0$ has been reported by Pernicone *et al.*[16]. They found this molybdate to exhibit varying acid content as a function of calcination temperature. The maximum acidity, 0·06 mmole/g, was found at 500°. Thereafter, a steady decrease was observed up to 700°. At 400°, acidity value at $Ho \leqslant +4{\cdot}0$ was $<0{\cdot}04$. These acidities were found to have a close correlation with catalytic activity of $MoO_3.Fe_2(MoO_4)_3$ in the oxidation of formaldehyde. Sodium molybdate, being oxidation catalyst for many reactions[3,4], may also be expected to use its acidities in the oxidation.

Surface areas of the heat-treated samples of sodium molybdate are given in Table 1. It is seen that when sodium molybdate dihydrate is heated, there is a consistent decrease in the surface area, which may be due to the fact that on heating, the individual sodium molybdate crystals get dehydrated and shrink, thereby increasing the interparticle pores or more appropriately the micropores (dehydration pores) formed in individual sodium molybdate crystallites may enlarge due to sintering, thereby causing a reduction in surface area.

Magnetic measurements reveal that the pure sodium molybdate dehydrate as well as its thermal transition products are diamagnetic.

References

1. SPITALSKII, E. & FUNCK, A., *Z. phys. Chem.*, **126** (1927), 1.
2. *Netherland Pat.* 413,733 (1965), to Imperial Chemical Industries Ltd.
3. *Belg. Pat.* 669,981 (1966) to E. I. du Pont.
4. YATSIMIRSKII, K. B. & FILIPPOV, A. P., *Zh. neorg. Khim.*, **9** (1964), 2096.
5. *Netherland Pat.* 405,089 (1964), to Pennsalt Chemicals Corporation.
6. WILLIAMSON, J. B., *Brit. Pat.* 1,003,347 (1965).
7. BHATTACHARYYA, S. K., RAMACHANDRAN, V. S. & GHOSH, J. C., *Adv. Catalysis*, **9** (1957), 114.
8. SINHAMAHAPATRA, P. K. & BHATTACHARYYA, S. K., *J. thermal Analysis*, **8** (1975), 45; **9** (1976), 279; *Chem. Era*, **XII (3)** (1976), 79.
9. HIRSCHLER, A. E. & SCHNEIDER, A., *J. chem. engng Data*, **6** (1961), 313.
10. GAMO, I., *Bull. chem. Soc. Japan*, **34** (1961), 760, 765, 1430, 1433.
11. ZECCHINA, A., COLUCCIA, S., GUGLIELMINOTTI, E. & GHIOTTI, G., *J. phys. Chem.*, **75** (1971), 2774.
12. DOUGLAS, R. M., *Acta Cryst.*, **10** (1959), 423.
13. NAKAMOTO, K., *Infrared spectra of inorganic and co-ordination compounds* (John Wiley, New York), 1963, 159.
14. BUSEY, R. H. & KELLER, O. L. (Jr), *J. phys. Chem.*, **41** (1964), 125.
15. MELLOR, J. W., *A comprehensive treatise on inorganic and theoretical chemistry*, Vol. 11 (Longmans, London), 1962, 553.
16. PERNICONE, N., LIBERTI, G. & ERSINI, L., *Proceedings of 4th international congress on catalysis, Moscow*, Reprints of paper No. 21, 1968.

Effect of Triton X-100 on the Kinetics of Irreversible Electrode Processes: Polarographic Behaviour of Ni(II), Co(II), Zn(II) & Mn(II)

SUDHINDRA SWARUP SHARMA, S. K. JHA & MUKHTAR SINGH

Department of Chemistry, Agra College, Agra

Received 30 *November* 1976; *accepted* 21 *February* 1977

Polarographic behaviour of Ni(II), Co(II), Zn(II) and Mn(II) has been studied in 0·1*M* KNO_3 in the presence of increasing concentrations of Triton X-100 (0·0-0·01%). The values of the kinetic parameters $k^{\circ}_{f,h}$ and αn_a) have been calculated by Koutecky's treatment. The well established irreversible electrode processes of Ni(II) and Co(II) become more irreversible with an increase in [Triton X-100]. The quasi-reversible electrode processes of Zn(II) and Mn(II) become totally irreversible with increasing [Triton X-100].

GELATIN has been almost universally used earlier as a maximum suppressor. Since Triton X-100 has several practical advantages over gelatin it has become the most widely used suppressor. Colichman[1] has reported the effect of Triton X-100 concentration on i_d and $E_{1/2}$ values of some inorganic deploarizers. However, the effect of increasing concentration of Triton X-100 on the kinetics of electrode processes has remained untouched. With this aim in view the present study covering totally irreversible and quasi-reversible electrode processes has been undertaken.

$Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $ZnCl_2$, $MnCl_2$ and KNO_3 were of AR (BDH) grade and their solutions ($1{\cdot}0 \times 10^{-3}M$) were prepared in conductivity water.

A manual polarograph (Toshniwal, CLO2) in conjunction with a polyflex galvanometer (Toshniwal, PL50) was used. The d.m.e. had the following characteristics (in 0·1M KNO_3, open circuit): $h_{corr.} = 49{\cdot}7$ cm; $t = 2{\cdot}51$ sec; $m^{2/3}t^{1/6} = 2{\cdot}525$ mg$^{2/3}$ sec$^{-1/2}$. All the measurements were made at 25° ± 0·1°C. Purified hydrogen was used for removing dissolved oxygen.

The number of electrons, 'n', involved in the reduction of cations under study ($n = 2$) being well established, Ilkovic equation was used to calculate the value of the diffusion coefficient (D). Subsequently the kinetic parameters (αn_a and $k^0_{f,h}$) were calculated by Koutecky's treatment[2].

A perusal of the slope values of log plots (Table 1) reveals that the well-established irreversible reduction of Ni(II) and Co(II) becomes more irreversible with the increase in the concentration of Triton X-100. The polarographic behaviour of Zn(II) and Mn(II) at different concentrations of Triton X-100 is rather interesting. The slope values show that up to 0·002% concentration of Triton X-100, the reduction of Mn(II) and that of Zn(II) up to 0·001% concentration of Triton X-100 is neither reversible nor totally irreversible, rather it is quasi-reversible[3-8]. However, as the concentration of Triton X-100 is increased further, the reduction of Zn(II) and Mn(II) becomes totally irreversible[9].

The values of the product 'αn_a' at increasing concentrations of Triton X-100 for Ni(II), Co(II), Zn(II) and Mn(II) are listed in Table 2. It is evident that the product αn_a decreases on increasing the concentration of Triton X-100. The polarographic reduction of Ni(II), Co(II), Zn(II) and Mn(II) is a well-established 2-electron process and therefore 'n_a', the number of electrons involved in the rate determining step, can either be 1 or 2. Since the decrease in 'αn_a' values is indiscrete and at no stage the consecutive values vary by a factor of 2, the possibility of decrease in the value of the product, 'αn_a' due to the change in n_a may be ruled out. Thus, it can be concluded that it is the 'α' which is decreasing[10]. A decrease in the value of α implies[11] that the transfer of electron/electrons is made increasingly difficult. In other words, the electrode reaction is rendered increasingly irreversible with the increase in the concentration of Triton X-100. The shift in $E_{1/2}$ to more negative potentials and increase in slope values of log plots (Table 1) are also in agreement with the above conclusions.

TABLE 1 — EFFECT OF INCREASING CONCENTRATIONS OF TRITON X-100 ON POLAROGRAPHIC CHARACTERISTICS OF Ni(II), Co(II), Zn(II) AND Mn(II)

[Triton X-100] %	i_d μamp	$-E_{1/2}$ (SCE)	Slope V	$D \times 10^6$ cm²/sec
		Ni(II)		
0·001	9·328	1·105	0·1174	6·8150
0·002	9·150	1·126	0·1195	6·5076
0·004	3·520	1·161	0·1208	0·9623
0·006	1·760	1·208	0·1220	0·2385
		Co(II)		
0·001	10·384	1·208	0·1187	8·3752
0·002	9·328	1·226	0·1265	6·7548
0·004	6·600	1·378	0·1354	3·2942
0·006	3·960	1·442	0·1392	1·1772
0·008	3·520	1·518	0·1400	0·8983
		Zn(II)		
0·0	10·030	0·980	0·0466	7·9100
0·001	9·944	1·000	0·0514	7·6784
0·002	9·680	1·058	0·0615	7·1824
0·004	5·720	1·101	0·1050	2·4586
0·006	3·520	1·162	0·1300	0·9314
0·008	1·760	1·163	0·1700	0·2310
		Mn(II)		
0·001	9·680	1·482	0·0415	7·4038
0·002	9·408	1·499	0·0501	6·7808
0·004	8·800	1·527	0·0596	5·9340
0·006	8·536	1·553	0·0618	5·4756
0·008	8·360	1·560	0·0625	5·2349
0·010	7·920	1·565	0·0634	4·6526

TABLE 2 — VALUES OF αn_a AND $k^0_{f,h}$ FOR Ni(II), Co(II), Zn(II) AND Mn(II) AT DIFFERENT CONCENTRATIONS OF TRITON X-100

[Triton X-100] %	αn_a	$k^0_{f,h}$ (cm/sec)
	Ni(II)	
0·001	0·4600	$2{\cdot}2710 \times 10^{-10}$
0·002	0·4520	$1{\cdot}525 \times 10^{-10}$
0·004	0·4470	$6{\cdot}6590 \times 10^{-12}$
0·006	0·4420	$2{\cdot}5950 \times 10^{-13}$
	Co(II)	
0·001	0·4566	$5{\cdot}0590 \times 10^{-11}$
0·002	0·4284	$3{\cdot}2570 \times 10^{-11}$
0·004	0·4029	$1{\cdot}9720 \times 10^{-11}$
0·006	0·3893	$6{\cdot}6220 \times 10^{-12}$
	Zn(II)	
0·001	—	—
0·002	0·9028	$8{\cdot}9160 \times 10^{-10}$
0·004	0·5161	$7{\cdot}1290 \times 10^{-10}$
0·006	0·4169	$2{\cdot}5600 \times 10^{-10}$
0·008	0·3180	$2{\cdot}4800 \times 10^{-10}$
	Mn(II)	
0·001	—	—
0·002	—	—
0·004	0·9961	$7{\cdot}1360 \times 10^{-15}$
0·006	0·9771	$5{\cdot}546 \times 10^{-15}$
0·008	0·9522	$2{\cdot}3580 \times 10^{-15}$
0·010	0·9276	$2{\cdot}0870 \times 10^{-15}$

A perusal of Table 2 reveals that the value of $k^0_{f,h}$ decreases on increasing the concentration of Triton X-100. From this it follows that irreversible electrode processes tend to become more so when Triton X-100 is added in increasing amounts.

The observations on the variation of 'αn_a' and $k^0_{f,h}$ with increasing concentrations of Triton X-100 are in conformity with the views of Meites[12]. According to him the most common effect of non-ionic maximum suppressors (such as Triton X-100) is to decrease the rate constant $k^0_{f,h}$, and the value of αn_a is also decreased.

Triton X-100 with well known surface active properties is likely to be adsorbed on the mercury surface. This is further confirmed by the decrease of the interfacial tension, measured by the drop time method[13], on the solution-mercury interface. The adsorbed molecules displace ions from the Helmholtz layer, thereby altering the charge distribution in the double layer and they may also displace the reaction surface away from the electrode. Both these effects alter the potential at the reaction surface. Thus a bridge that may serve to effect the electron transfer from the electrode to an ion at the reaction surface when the maximum suppressor is absent may become impossible to be constructed when it is present.

Thanks are due to Dr S. N. Dubey, Principal, for providing necessary facilities and to the UGC, New Delhi, for the award of contingency grant to one of them (M.S.).

References

1. Colichman, E., *J. Am. chem. Soc.*, **72** (1950), 4036.
2. Koutecky, J., *Chem. Listy*, **47** (1953), 323; *Colln Czech. chem. Commun.*, **18** (1953), 597.
3. Delahay, P., *J. Am. chem. Soc.*, **75** (1953), 1430.
4. Matsuda, H. & Ayabe, Y., *Z. Elektrochem.*, **63** (1959), 1164.
5. Koryta, J., *Electrochim. Acta*, **6** (1962), 67.
6. Gellings, P. J., *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.*, **66** (1962), 477, 481, 799; **67** (1963), 167.
7. Gaur, J. N. & Jain, D. S., *Rev. Polarogr.*, **14** (1967), 206.
8. Gaur, J. N., Jain, D. S. & Kumar, A., *Indian J. Chem.*, **13** (1975), 165.
9. Goto, R. & Tachi, I., *Proc. intern. Polarogr.*, **1** (1951), 69.
10. Jha, S. K. & Srivastava, S. N., *Z. Naturforsch.*, **30b** (1975), 859.
11. Delahay, P., *New instrumental method in electrochemistry* (Interscience Publishers, New York), 1954, 33.
12. Meites, L., *Polarographic techniques* (Interscience Publishers, New York), 1965, 324.
13. Zuman, P. & Kolthoff, I. M., *Prögress in polarographv*, Vol. I (Interscience Publishers, New York), 1962, 88.

Dimeric Halo Complexes of Cr(IV)

S. Sarkar, R. C. Maurya, S. C. Chaurasia &
S. K. Srivastava

Department of Chemistry, T.D. College, Jaunpur 222002

Received 29 *September* 1976; *accepted* 10 *January* 1977

Stable dimeric complexes of Cr(IV) of the type $[Cr(OH)_2X_2Py]_2$ (X = Cl, Br, I) have been prepared by the alcoholic reduction of halochromate(VI) in the presence of pyridinium hydrohalide in pyridine medium. The complexes have been characterized on the basis of reflectance, IR and magnetic moment data.

Only a few complexes of chromium(IV) are known[1-4]. In the present investigation we have observed that the alcoholic reduction of halochromate(VI) in the presence of pyridinium halide in pyridine medium leads to the formation of stable dimeric complexes $[Cr(OH)_2X_2Py]_2$ (X=Cl, Br, I) of chromium(IV). An intermediate anionic chloro-complex, $K_2[Cr(OH)_2ClPyO]_2$ has also been isolated using less quantity of chloride.

These complexes were prepared by dissolving potassium halochromate(VI) and corresponding pyridinium hydrohalide in excess of pyridine containing a little water. On the addition of excess ethanol or methanol, the product started to separate out as brown insoluble solid within an hour at room temperature. The mixture was kept overnight and then filtered under suction, the precipitate washed with water, alcohol, acetone respectively and dried *in vacuo* [yield 80% on the basis of chromium(VI) used in each case]. The intermediate chloro-complex, $K_2[Cr(OH)_2ClPyO]_2$ was isolated without adding Py.HCl in the reaction mixture. After standing overnight the deep brown solution was treated with excess of acetone to precipitate the compound. It was dissolved in alcohol and reprecipitated by adding acetone. Addition of Py.HCl into the alcoholic solution gave an insoluble product.

The formulation of these complexes is based on satisfactory elemental analysis, isolation of the intermediate anionic complex, their disproportionation reaction with alkali, their inability to form any AgX on trituration with aqueous $AgNO_3$, ready expulsion of pyridine from these compounds by the action of NH_3 to give corresponding amine compounds, no reaction with H_2O_2 (iodo compound shows catalytic decomposition of H_2O_2 and on standing liberates iodine). The compounds are paramagnetic ($\mu_{eff} = 2{\cdot}80$ BM at 24°). Their reflectance and IR spectral data are given in Table 1.

The assignments of the IR bands in 800-920 region for Cr-O-H group is supported by the appearance of only ν(OH) with the absence of any δ(H-O-H). Nevertheless, any oxo-grouping, hydroxo or oxo-bridging is difficult to visualize in these complexes on the basis of other observations. This assignment is consistent with the evidence for such a band in certain Mo(IV) complexes[5].

Table 1 — Reflectance and IR Spectral Data of the Complexes

Complex	λ_{max} (nm)	Important IR bands (cm^{-1})†
$[Cr(OH)_2Cl_2Py]_2$	262, 293, 403, 500, 660	3410(s, br), 905(s), 800(s)
$[Cr(OH)_2Br_2Py]_2$	256, 285, 397, 500, 665	3400(s, br), 920(s), 830(s)
$[Cr(OH)_2I_2Py]_2$	256, 295, 394, 575, 778	3390(s, br), 917(s), 815(s)
$K[Cr(OH)_2ClPyO]_2$*	262, 388, 488, 690*	3420(s, br), 912(s), 825(s), 770(s)

*Reflectance spectrum taken in water.
†Coordinated pyridine bands are excluded.