Scheme 1

The method of Schaap and McMasters[1] was applied to evaluate the coefficients A, B, C and D in both the sets. The values of these coefficients are given below:

At $0.08M$ phthalate: log $A = 1.30$; log $B = 3.0 \pm 0.09$; log $C = 4.30 \pm 0.09$; and log $D = 5.17 \pm 0.06$

At $0.16M$ phthalate: log $A = 1.78$; log $B = 3.20 \pm 0.03$; log $C = 4.47 \pm 0.03$; and log $D = 5.17 \pm 0.08$

The mean value of log $D = 5.17$ agrees well with the log $\beta_{30} = 5.14$, the stability constant of $[Cd(Ox)_3]^{4-}$.

The values of A, B, C and D were used in calculating the stability constants of mixed species. The mixed complex species $[Cd(Ox)(phthalate)]^{2-}$, $[Cd(Ox)_2(phthalate)]^{4-}$ and $[Cd(Ox)(phthalate)_2]^{4-}$ were found to have the stability constants log $\beta_{11} = 3.75$, log $\beta_{21} = 5.02$ and log $\beta_{12} = 3.89$ respectively.

The observed stability constants of the mixed complexes have been compared with calculated from those of the simple complexes following the procedure suggested by Watters[6]. The calculated values for complexation constants are: (i) $3 \times \beta_{2,0}^{2/3} \times \beta_{0,3}^{1/3} = 10^{4.35}$ as compared to $10^{5.02}$ observed for $[Cd(Ox)_2(phthalate)]^{4-}$ and (ii) $3 \times \beta_{3,0}^{1/3} \times \beta_{0,2}^{2/3} = 10^{3.69}$ as compared to $10^{3.89}$ of $[Cd(Ox)(phthalate)_2]^{4-}$. The increase in the values for these species were respectively $10^{+0.67}$ and $10^{+0.20}$.

The statistical factor favouring the formation of mixed complex $[Cd(Ox)(phthalate)]^{2-}$ is two. The observed value ($10^{3.75}$) is larger than the calculated ($10^{3.46}$) by $10^{+0.29}$. The greatest enhancement is observed for the $[Cd(Ox)_2(phthalate)]^{4-}$ complex.

The various complexation reactions along with their log stepwise stability constants are shown in Scheme 1.

log K value for $[Cd(Ox)]$ to $[Cd(Ox)_2]^{2-}$ is 1.40 while the value for Cd(phthalate) to $[Cd(Ox)(phthalate)]^{2-}$ is 1.85. The larger value of log K for the later reaction shows that the formation of mixed species is favoured. A similar argument holds good for the mixed complex $[Cd(Ox)(phthalate)]^{2-}$ when formed from $[Cd(Ox)]$. It is seen that log K value in the formation of $[Cd(Ox)(phthalate)^{2-}$ from $[Cd(Ox)]$ is much higher than in the formation

of $[Cd(phthalate)_2]^{2-}$ from $[Cd(phthalate)]$ being 1.05 in the former and 0.35 in the latter case.

One of the modes in which mixed ligand complex $[Cd(Ox)(phthalate)]^{2-}$ can disproportionate is:

$$2[Cd(Ox)(phthalate)]^{2-} \rightleftharpoons [Cd(Ox)_2]^{2-} + [Cd(phthalate)_2]^{2-}$$
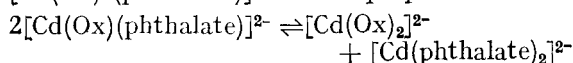
and reaction has the log $K = -1.18$ in the direction written which clearly shows that the formation of the mixed complex is preferred.

That the saturated mixed complexes $[Cd(Ox)_2(phthalate)]^{4-}$ and $[Cd(Ox)(phthalate)_2]^{4-}$ are favoured can be seen by comparing the formation constants for the addition of oxalate anion as a third ligand to $[Cd(Ox)_2]^{2-}$, $[Cd(Ox)(phthalate)]^{2-}$ and $[Cd(phthalate)_2]^{2-}$. Log K values are respectively 1.07, 1.25 and 1.65.

The authors wish to express their deep sense of gratitude to Prof. D. D. Khanolkar for his keen interest and encouragement.

References

1. SCHAAP, W. B. & McMASTERS, D. L., J. Am. chem. Soc., 83 (1961), 4699.
2. DHULEY, D. G., JAHAGIRDAR, D. V. & KHANOLKAR, D. D., J. inorg. nucl. Chem., 37 (1975), 2135.
3. JAIN, D. S., ANAND KUMAR & GAUR, J. N., J. Polarogr. Soc., 13 (1967), 120.
4. DEFORD, D. D. & HUME, D. N., J. Am. chem. Soc., 73 (1951), 5321.
5. KANEMURA, Y. & WATTERS, J. I., J. inorg. nucl. Chem., 29 (1967), 1701.
6. WATERS, J. I. & DEWITT, R., J. Am. chem. Soc., 82 (1960), 1333.

A Study of Cu(II) Monochloroacetate & Trichloroacetate at d.m.e.

H. S. SHARMA, S. S. SINGH & H. L. NIGAM

Department of Chemistry, University of Allahabad
Allahabad 211002

Copper(II) mono- and trichloroacetates have been observed to undergo diffusion-controlled, irreversible reduction at d.m.e. in 25% ethanol and 25% acetone. But in aqueous medium copper(II) monochloroacetate undergoes diffusion-controlled reversible single-electron electroreduction while the other shows irreversible electroreduction. Kinetic parameters of all irreversible electrode processes have been evaluated along with other polarographic characteristics.

COPPER(II) monochloroacetate exhibits metal-metal exchange interaction, while Cu(II) trichloroacetate shows normal magnetic properties of a paramagnetic complex in solid state[1]. Such a typical behaviour of these two alkanoates has also been established in organic solvents[2] of low dielectric constant and having less coordinating ability than water. In aqueous solution, the dimerization reaction appears to be destroyed. These conclusions have been arrived at on the basis of spectral and magnetic properties of these alkanoates. Recent polarographic investigations[3] show that Cu(II) monochloroacetate gives double wave

TABLE 1 — POLAROGRAPHIC CHARACTERISTICS OF COPPER(II) MONOCHLOROACETATE AND TRICHLOROACETATE

(Supporting electrolyte, $0.1M$ NaClO$_4$; maximum suppressor, 0.0025% gelatin)

Solvent	Temp. °C	$E_{1/2}$ (V)	i_D (μA)	I	Reciprocal slope of log plot	$D^{1/2} \times 10^3$ cm² sec	α	K_r cm sec⁻¹
MONOCHLOROACETATE								
Water	15	−0·0050	2·85	2·92	0·027	2·20	—	—
	25	−0·0025	3·2	3·29	0·026	2·40	—	—
	30	+0·0012	3·65	3·75	0·026	2·70	—	—
Ethanol (25%)	15	+0·0050	1·70	1·73	0·043	1·30	0·6500	2·848×10²
	25	+0·0175	2·35	2·40	0·042	1·70	0·7047	1·366×10³
	30	+0·0200	2·65	2·70	0·038	2·00	0·7662	3·767×10³
Acetone (25%)	15	+0·0050	2·55	2·74	0·036	2·00	0·6975	1·165×10³
	25	+0·0090	3·20	3·44	0·042	2·50	0·7097	1·305×10³
	30	+0·0110	3·60	3·87	0·042	2·70	0·7475	2·199×10³
TRICHLOROACETATE								
Water	15	−0·0070	2·63	2·70	0·036	2·0	0·6500	2·316×10²
	25	+0·0000	3·05	3·13	0·040	2·20	0·6727	3·674×10²
	30	+0·0050	3·20	3·28	0·050	2·40	0·7297	9·618×10²
Ethanol (25%)	15	+0·0125	1·80	1·84	0·036	1·40	0·7150	1·714×10³
	25	+0·0190	2·08	2·12	0·040	1·50	0·7400	2·668×10³
	30	+0·0225	2·30	2·35	0·046	1·70	0·7475	2·555×10³
Acetone (25%)	15	0·0000	2·30	2·47	0·038	1·80	0·6809	5·736×10²
	25	+0·0100	2·80	3·00	0·038	2·20	0·7400	2·415×10³
	30	+0·0150	2·88	3·09	0·040	2·20	0·7662	3·221×10³

electroreduction in different organo-aqueous solutions (50% ethanol, 50% acetone or 25% dioxane), while copper(II) trichloroacetate shows only a single step electroreduction in these solvents. Double-wave electroreduction has been attributed to a monomer-dimer equilibrium and the single wave one to a monomer electroreduction. It was, therefore, of interest, to study quantitative aspects of the behaviour of these two alkanoates in various organo-aqueous solutions at d.m.e.

Copper(II) monochloroacetate and trichloroacetate were prepared by standard methods[4,5] and the purity checked by estimating the percentage of copper in each salt. Both these salts are highly soluble in water and organic solvents. Sodium perchlorate (Analar) was used as a supporting electrolyte. Gelatin of high purity was used as maximum suppressor and 20 ml of reaction mixture was always taken in the polarographic cell, care being taken to keep the supporting electrolyte concentration constant.

Polarographic measurements were made with a manual polarographic circuit recommended by Kolthoff and Lingane[6]. All potentials were measured against a Hume and Harris saturated calomel electrode (SCE). Oxygen was removed from the solution with a stream of oxygen free nitrogen, purified by bubbling through vanadous sulphate solution. An atmosphere of nitrogen was maintained over the cell during the recording of polarograms. The characteristics of the dropping mercury electrodes in aqueous medium (open circuit) were as follows:

$h = 30$ cm; $m = 1.45$ mg sec⁻¹, $t = 5.4$ sec, $m^{2/3}.t^{1/6} = 1.696$ mg²/³ sec⁻¹/²

$h = 40$ cm; $m = 1.90$ mg sec⁻¹, $t = 4.22$ sec, $m^{2/3}.t^{1/6} = 1.950$ mg²/³ sec⁻¹/²

$h = 50$ cm; $m = 2.50$ mg sec⁻¹, $t = 3.25$ sec $m^{2/3}.t^{1/6} = 2.41$ mg²/³ sec⁻¹/²

In $0.1M$ sodium perchlorate and gelatin (0·0025%) both the alkanoates of Cu(II) undergo two-electron transfer, diffusion-controlled electroreductions in aqueous, 25% ethanol or 25% acetone. The reversibility of the electrode processes in different solvent media was checked following the method of Oldham and Parry as described in our previous publications[7,8]. The log plot values thus obtained in each case (see Table 1) indicate that both the alkanoates undergo irreversible electroreductions in 25% ethanol or 25% acetone. Similar observation has been recorded for Cu(II) for trichloroacetate in aqueous medium but the Cu(II) monochloroacetate has been observed to undergo reversible electroreduction in aqueous medium.

Kinetic parameters of all the irreversible electrode processes have been evaluated at different temperatures, following the methods of Oldham and Parry[8]. These kinetic parameters (K and α), for the two alkanoates are given in Table 1, along with their other electrode behaviour characteristics (e.g. $E_{1/2}$, i_D, I, $D^{1/2}$, etc.). Halfwave potential in each case have been observed to shift towards more positive values with the rise of temperature and the diffusion current, i_D, have also been observed to increase. Almost for all cases, the forward rate constants $K_{f,h}$ have been observed to increase with rise in temperature, indicating more facile electron transfer.

The reference rate constant, K_r, is a measure of the rate of electron transfer from electrode to

depolarizer and hence, as a matter of fact, provides information about the reversibility of the electrode process under consideration. Because the mono-chloroacetate undergoes reversible electrode process in aqueous medium, the reference rate constant has not been calculated and hence, in this case, the reversibility variations can not be discussed. In the case of Cu(II) trichloroacetate, it has been noted (Table 1) that at a particular temperature, the rate constant increases as one passes from aqueous to organo-aqueous media (25% ethanol or 25% acetone). Consequently, it may be inferred that under the conditions of the experiment, reversibility of the electrode reaction proper increases in organo-aqueous media as compared to that in aqueous medium. However, reference rate constant data do not allow this comparison for the two organo-aqueous solutions.

References

1. KATO, M., JONASSEN, H. B. & FANNING, J. C., Chem. Rev., 64 (1964), 99.
2. MARTIN, R. L. & WHITLEY, A., J. chem. Soc., (1958), 1394.
3. SHARMA, H. S., D. Phil. thesis, University of Allahabad, 1975.
4. BATEMAN, W. G. & HOEL, A. B., J. Am. chem. Soc., 36 (1914), 2517.
5. BATEMAN, W. G. & CONRAD, D. B., J. Am. chem. Soc., 37 (1915), 2553.
6. KOLTHOFF, I. M. & LINGANE, J. J., cited in Polarography (Interscience, New York), 1952, 300.
7. SHARMA, H. S. & NIGAM, H. L., Indian J. Chem., 6 (1975), 690.
8. SHARMA, H. S. & NIGAM, H. L., Indian J. Chem., 14A (1976), 410.
9. OLDHAM, K. B. & PARRY, E. P., Analyt. Chem., 40 (1968), 65.

Spectrophotometric Studies & Analytical Applications of Zr(IV) & Hf(IV) Chelates with 4-(2-Thiazolylazo)resorcinol

B. SUBRAHMANYAM & M. C. ESHWAR

Department of Chemistry, Indian Institute of Technology Bombay 400076

4-(2-Thiazolylazo)resorcinol (TAR) has been suggested as a spectrophotometric reagent for the determination of Zr(IV) and Hf(IV). Both the metals react with TAR in acid media to give red coloured 1 : 4 (metal-to-ligand) chelates, soluble in methanol (20%). The Zr(IV)-TAR and Hf(IV)-TAR complexes exhibit λ_{max} at 550 and 540 respectively, and obey Beer's law in the concentration ranges 0·01-1·2 and 0·24-3·4 µg/ml of Zr(IV) and Hf(IV) respectively. The molar absorptivities of complexes are $6·4 \times 10^4$ (Zr) and $5·8 \times 10^4$ (Hf), and Sandell sensitivity indices are 0·0014 and 0·0030 µg cm⁻² for Zr(IV) and Hf(IV) respectively. It is a highly sensitive and selective method which is simple and permits rapid determination of the traces of Zr(IV) and Hf(IV).

THOUGH a large number of reagents are available for spectrophotometric determination of zirconium, very few reagents are available for the determination of hafnium[1]. Among pyridylazo dye-stuffs, 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo) resorcinol (PAR) have been used as versatile reagents[2] for the absorptiometric determination of various metal ions. Spectrophotometric methods for the determination of Zr(IV) and Hf(IV) using PAN[3,4] and PAR[5,6] as chromogenic reagents have been reported earlier. In the present study it has been found that 4-(2-thiazolylazo)resorcinol (TAR) reacts with Zr(IV) and Hf(IV) in acid range, and the resultant coloured complexes permit spectrophotometric determination of microgram amounts of the two metal ions. The proposed method is simple, rapid, highly sensitive and selective.

pH of the reaction mixture containing 20 µg of Zr(IV) or 40 µg of Hf(IV) was varied from 0·6 to 5·0. Maximum absorbance for zirconium complex at 540 nm was observed in the pH range 1·4 to 1·9 and for hafnium complex at 550 nm in the pH range 1·8 to 3·2. The pH values 1·6 and 2·5 were selected for further studies of Zr(IV) and Hf(IV) respectively, and were maintained by KCl-HCl buffer (pH 1·6) and sodium acetate-HCl buffer (pH 2·5) respectively.

Maximum absorbance was attained after keeping the Zr(IV)-TAR complex for 25 min while in the case of Hf(IV), full colour development took place instantaneously. In both the cases, a minimum of 1·3 ml of the reagent solution (0·1%) was required for complete colour development for solutions containing 25 µg Zr(IV) and 80 µg Hf(IV). Hence, 2 ml of reagent was added in all further studies.

As the complexes of Zr(IV) and Hf(IV) with TAR are sparingly soluble in water, methanol was added to dissolve them. 5 ml of methanol was found to be sufficient for their dissolution in 25 ml of the final solution.

Composition — The metal-ligand ratio in Zr(IV)-TAR and Hf(IV)-TAR complexes was determined by Job's method of continuous variation and was found to be 1 : 4. It was further verified by mole ratio method for both the complexes.

Beer's law was obeyed in the concentration ranges 0·01 to 1·2 µg of Zr(IV) per ml and 0·24 to 3·4 µg of Hf(IV) per ml. Molar absorptivity and Sandell sensitivity of Zr(IV) chelate are $6·40 \times 10^4$ and 0·0014 µg cm⁻² respectively, whereas those for Hf(IV) chelate are $5·80 \times 10^4$ and 0·003 µg cm⁻² respectively.

Effect of added ions — Various ions were tested for possible interference in the determination of Zr(IV) and Hf(IV). The tolerance limit was determined as the amount of ions which caused an error of ±2%. Many cations did not interfere in the determination and their limits are presented in Table 1. However, Cu(II), Co(II), Fe(III), V(V) and Bi(III) interfered in determination of Zr(IV) and Hf(IV). The interference of these ions was overcome by extracting their 1-(2'-pyridylazo)-2-naphthol complexes[8] into chloroform leaving Zr(IV) and Hf(IV) in the aq. phase. Anions such as citrate, tartrate, EDTA, fluoride, oxalate and cyanide must be absent in the determination, as they compete with TAR for metal ions.

Determination of Zr(IV) and Hf(IV) in their binary mixtures has not been possible, since absorption maxima for both complexes are too close and