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

At 0·083 $M$ phthalate: log $A$ = 1·30; log $B$ = 3·0 ± 0·09; log $C$ = 4·30 ± 0·09; and log $D$ = 5·17 ± 0·09.

At 0·16 $M$ phthalate: log $A$ = 1·78; log $B$ = 3·20 ± 0·03; log $C$ = 4·47 ± 0·03; and log $D$ = 5·17 ± 0·08.

The mean value of log $D$ = 5·17 agrees well with the log $\beta_{10} = 5·14$, the stability constant of [Cd(Ox)]$_3^-$.

The values of $A$, $B$, $C$ and $D$ were used in calculating the stability constants of mixed species. The mixed complex species $[\text{Cd(Ox)} (\text{phthalate})]^{2-}$, $[\text{Cd(Ox)}]_2^-$ (phthalate)$^-$ and $[\text{Cd(Ox)} (\text{phthalate})]^{2-}$ were found to have the stability constants log $\beta_{11} = 3·75$, log $\beta_{12} = 5·02$ and log $\beta_{13} = 3·89$ 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 Waters. The calculated values for complexation constants are:

(i) $3 \times 10^{3·36} \times 10^{3·53} = 10^{3·5} \times 10^{3·53} = 10^{3·5} \times 10^{3·53}$ as compared to $10^{0·02}$ observed for $[\text{Cd(Ox)}]_3^-$ (phthalate)$^-$

(ii) $3 \times 10^{3·36} \times 10^{3·53} = 10^{3·5} \times 10^{3·53}$ as compared to $10^{0·02}$ of $[\text{Cd(Ox)} (\text{phthalate})]^{2-}$.

The increase in the values for these species were respectively $10^{0·02}$ and $10^{0·02}$.

The statistical factor favouring the formation of mixed complex $[\text{Cd(Ox)} (\text{phthalate})]^{2-}$ is two. The observed value ($10^{0·02}$) is larger than the calculated ($10^{0·02}$) by $10^{0·02}$. The greatest enhancement is observed for the $[\text{Cd(Ox)}]_3^-$ (phthalate)$^-$ complex.

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

![Scheme 1](image)

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

**References**


**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

Received 13 January 1976; accepted 22 May 1976

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 interaction, while Cu(II) trichloroacetate shows normal magnetic properties of a paramagnetic complex in solid state. Such a typical behaviour of these two alkanotes has also been established in organic solvents 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 alkanotes. Recent polarographic investigations show that Cu(II) monochloroacetate gives double wave

**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

Received 13 January 1976; accepted 22 May 1976

**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. Such a typical behaviour of these two alkanotes has also been established in organic solvents 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 alkanotes. Recent polarographic investigations show that Cu(II) monochloroacetate gives double wave**
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 while copper(II) trichloroacetate shows only a maximum suppressor and soluble in water and organic solvents. Sodium perchlorate (Analar) was used as a supporting electrolyte. Gelatin of high purity was used as aqueous solutions at d.m.e.

The reference rate constant, $K_r$, is a measure of the rate of electron transfer from electrode to increase with rise in temperature, indicating more, the forward rate constants $K_{f1}$, $K_{f2}$, and $K_{f3}$ have been observed to increase. Almost for all cases, the forward rate constants $K_{f1}$ 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

$K_r = \frac{1}{I} \times \frac{1}{D^{1/2}} \times 10^a$ cm sec$^{-1}$ 

$h = 40$ cm; $m = 190$ mg sec$^{-1}$, $t = 422$ sec.

$m^2 I^2 D^{-1/2} = 1950$ mg$^2$ sec$^{-1}$ 

$h = 50$ cm; $m = 250$ mg sec$^{-1}$, $t = 325$ sec

$m^2 I^2 D^{-1/2} = 241$ mg$^2$ sec$^{-1}$

Table 1 — Polarographic Characteristics of Copper(II) Monochloroacetate and Trichloroacetate

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp.</th>
<th>El/2 (V)</th>
<th>$i_0$ (µA)</th>
<th>Reciprocal slope of log plot</th>
<th>$D^{1/2} \times 10^a$</th>
<th>$K_r$ cm sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>15</td>
<td>-0.0059</td>
<td>2.85</td>
<td>2.92</td>
<td>0.027</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-0.0025</td>
<td>3.29</td>
<td>3.29</td>
<td>0.026</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>+0.0012</td>
<td>3.65</td>
<td>3.75</td>
<td>0.026</td>
<td>2.70</td>
</tr>
<tr>
<td>Ethanol (25%)</td>
<td>15</td>
<td>+0.0059</td>
<td>1.70</td>
<td>1.73</td>
<td>0.043</td>
<td>1.30 6.500</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+0.0175</td>
<td>2.35</td>
<td>2.40</td>
<td>0.042</td>
<td>1.40 7.047</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>+0.0200</td>
<td>2.65</td>
<td>2.70</td>
<td>0.038</td>
<td>1.60 7.662</td>
</tr>
<tr>
<td>Acetone (25%)</td>
<td>15</td>
<td>+0.0059</td>
<td>2.55</td>
<td>2.74</td>
<td>0.036</td>
<td>2.00 6.973</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+0.0090</td>
<td>3.20</td>
<td>3.44</td>
<td>0.042</td>
<td>2.50 7.909</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>+0.0110</td>
<td>3.60</td>
<td>3.87</td>
<td>0.042</td>
<td>2.70 7.745</td>
</tr>
<tr>
<td>Ethanol (22%)</td>
<td>15</td>
<td>-0.0070</td>
<td>2.63</td>
<td>2.70</td>
<td>0.036</td>
<td>2.00 6.500</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-0.0005</td>
<td>2.05</td>
<td>2.13</td>
<td>0.040</td>
<td>2.20 6.717</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-0.0030</td>
<td>2.30</td>
<td>2.38</td>
<td>0.040</td>
<td>2.40 7.297</td>
</tr>
<tr>
<td>Ethanol (25%)</td>
<td>15</td>
<td>+0.0125</td>
<td>1.80</td>
<td>1.84</td>
<td>0.040</td>
<td>1.40 7.150</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+0.0190</td>
<td>2.08</td>
<td>2.12</td>
<td>0.040</td>
<td>1.50 7.400</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>+0.0225</td>
<td>2.50</td>
<td>2.38</td>
<td>0.040</td>
<td>1.70 7.745</td>
</tr>
<tr>
<td>Acetone (25%)</td>
<td>15</td>
<td>+0.0000</td>
<td>2.30</td>
<td>2.47</td>
<td>0.038</td>
<td>1.80 6.809</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+0.0005</td>
<td>2.60</td>
<td>2.60</td>
<td>0.038</td>
<td>2.20 7.400</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>+0.0150</td>
<td>2.88</td>
<td>3.09</td>
<td>0.040</td>
<td>2.20 7.662</td>
</tr>
</tbody>
</table>
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 cannot be discussed. In the case of Cu(II) dichloroacetate, it has been noted (Table 1) that at a particular temperature, the reaction rate constant is one pass 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

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

B. Subrahmanyan & M. C. Eshwar

Department of Chemistry, Indian Institute of Technology Bombay 400076

Received 6 October 1975; accepted 24 May 1976

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 \( \lambda_{\text{max}} \) at 500 and 540 respectively, and obey Beer’s law in the concentration ranges 0-01 to 1.2 and 0-24 to 3-4 \( \mu \text{g/ml} \) 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 0-0010 \( \mu \text{g/cm}^2 \) 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. Among pyridylazo dyes, 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo) resorcinol (PAR) have been used as versatile reagents for the spectrophotometric determination of various metal ions. Spectrophotometric methods for the determination of Zr(IV) and Hf(IV) using PAN and PAR 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 micromolar amounts of the two metal ions. The proposed method is simple, rapid, highly sensitive and selective.