

boat. Initially the temperature was slowly raised to 300° till the evolution of gases ceased. Then the temperature was raised to 600° in 12 h and to 700° in another 12 h. The sample was kept at 700° for another 12 h with cooling and grinding at the end of every 4 h.

A similar procedure was adopted for the preparation of the EDTA complexes of Sr and V, except that the two metal complexes were prepared in the same solution in view of the high solubility of the vanadium compound.

Usual chemical analysis⁹ was carried out on the prepared samples. The products were also characterised by X-ray diffraction (for powdered samples in a Dron⁻¹ unit with CuK radiation), thermal analysis (in a MOM derivatograph), infrared spectroscopy (in a Perkin-Elmer spectrophotometer using KBr pellet), esr spectroscopy (in a Varian-112 spectrometer and a TCNE marker), optical spectroscopy (for SrTiO₃ only in a Cary-17 D spectrophotometer) and electrical conductivity (for SrTiO₃ only using a two-probe method and sintered pellets). Due to the metallic conduction of SrVO₃, its conductivity could not be measured in the available set-up.

The X-ray diffraction pattern of the SrTiO₃ sample could be indexed to a cubic perovskite lattice with a lattice parameter of 3.9 Å in close agreement with the value quoted in literature¹⁰. No other phase was discernible in the pattern. The endothermic peak corresponding to the melting point of TiO₂ was absent in the derivatogram. This confirms the completion of the reaction. The infrared spectrum of the sample showed a band around 500 cm⁻¹ which has been ascribed to the presence of TiO₆ octahedra¹¹. ESR spectrum at 113 K contained a six-line signal consistent with the hyperfine splitting of the Ti isotopes with nuclear spin 5/2. Occurrence of this sharp signal points to the presence in traces of Ti²⁺ ion. This is further confirmed by the yellow colour of the samples and the broad band at 340 nm in the optical spectrum. Electrical conductivity of the sample measured at room temperature was 2 × 10⁻⁹ Ω⁻¹ cm⁻¹, and the energy of activation in the temperature range of 25-600° was 1.04 eV. This low level of conductivity can only be due to the presence of Ti²⁺ ions in traces.

The X-ray diffraction pattern of the SrVO₃ sample could be indexed to a cubic perovskite sample lattice with a lattice parameter of 3.84 Å in agreement with the value reported in literature¹². The endothermic peak due to the melting of V₂O₅ was absent in the derivatogram of the sample indicating clearly the completion of the reaction. The same inference could be drawn from the absence of the band due to the V=O bond in the infrared spectrum of the sample. ESR spectrum had a signal at a 'g' value of 2.078. The 'g' value larger than the free-spin value denotes the covalent character of the V—O bond in the perovskites. The

broad signal denotes the presence of spin-spin interactions.

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Interaction of Alkali with Zinc Sulphate in Aqueous Media

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PRECIPITATION of basic salts of varying composition had been reported¹⁻⁷ and the phenomenon attributed variously to adsorption of anions⁸, penetration of the anions⁹ into the outer or inner coordination sphere of the metal ion, or formation of polymeric hydrous oxide with hydroxyl bridges between the metal ions¹⁰. The latter postulate was used to explain the relative non-reactivity of hydrous oxides on aging^{4,11}. Weiser and Milligan¹², however, found that gelatinous precipitates of oxides or hydroxides, containing non-stoichiometric amounts of water, became granular on standing (aging). They also concluded from X-ray diffraction data¹³ that water or the residual electrolyte was not bound to the metal ion but was held by adsorption and capillary forces only. Conductance data of Chatterji and Dhar¹⁴ appeared to support this view.

The present work on Zn²⁺ ion, using equilibrium titration technique⁵, has been carried out in view

of the above conflicting results in order to (i) find out whether the anion retention by the precipitate is permanent or not, (ii) calculate the solubility product of $\text{Zn}(\text{OH})_2$ after equilibration of the system, (iii) identify any complex anion formed in the presence of a large excess of alkali by polarographic method and (iv) calculate its thermodynamic and kinetic parameters^{1,4}.

Experimental

All the reagents used were of A.R. grade, excepting Triton X-100 (B.D.H., England). Carbonate-free sodium hydroxide solution (0.9 mol dm^{-3}) was prepared by the standard method^{2,5}. A stock solution (0.25 mol dm^{-3}) was prepared in conductivity water and used directly or diluted as required.

An Elico LI-10 pH-meter was used to measure pH values within ± 0.1 unit. An L & N 4959 electronic conductivity bridge and an Elico CC-03 conductivity cell were used for conductivity measurements. Rodimeter Polarograph, Polariter PO4g and Sargent capillary with characteristics, $m = 1.258 \text{ mgs}^{-1}$ and $t = 5.0 \text{ s}$ for tetraethylammonium bromide (Et_4NBr) solution (0.1 mol dm^{-3}) at 80 cm Hg at zero potential (sce), were used to record the polarograms.

Titrations ($298 \pm 0.5 \text{ K}$) were carried out in a multinecked vessel with a stream of purified nitrogen

playing over the solutions. For equilibrium pH and conductometric studies, the titrant (10 ml) was taken in each of the several stoppered corning bottles, air displaced by purified nitrogen, increasing aliquots of NaOH solution added and the bottles were sealed with molten wax and set aside for 48 h for equilibration, during which time the bottles were shaken frequently. The pH and conductance values were then determined. The bottles were re-sealed and kept aside for one week after which the pH and conductance values were checked again. The results show that 48 h time is sufficient for equilibration.

Polarograms ($298 \pm 0.1 \text{ K}$) of several deaerated ZnSO_4 solutions (1.0 mol dm^{-3}), containing Et_4NOH (concentration varying from 1.0 to 1.0 mol dm^{-3}), Et_4NBr (appropriate amounts to maintain ionic strength at 1.0 mol dm^{-3}) and Triton X-100 (0.001%), were recorded, after allowing the solutions to stand for 48 h .

Results and Discussion

pH-metric and conductometric titrations: Continuous pH-titration of (i) ZnSO_4 solution (0.025 mol m^{-3}) with NaOH solution (0.09 mol dm^{-3}) exhibits a weak inflexion at 0.054 equivalents and the final inflexion at 1.56 equivalents of alkali (Fig. 1, curve 1); that of (ii) ZnSO_4 solution (0.25 mol dm^{-3}) with NaOH solution (0.9 mol

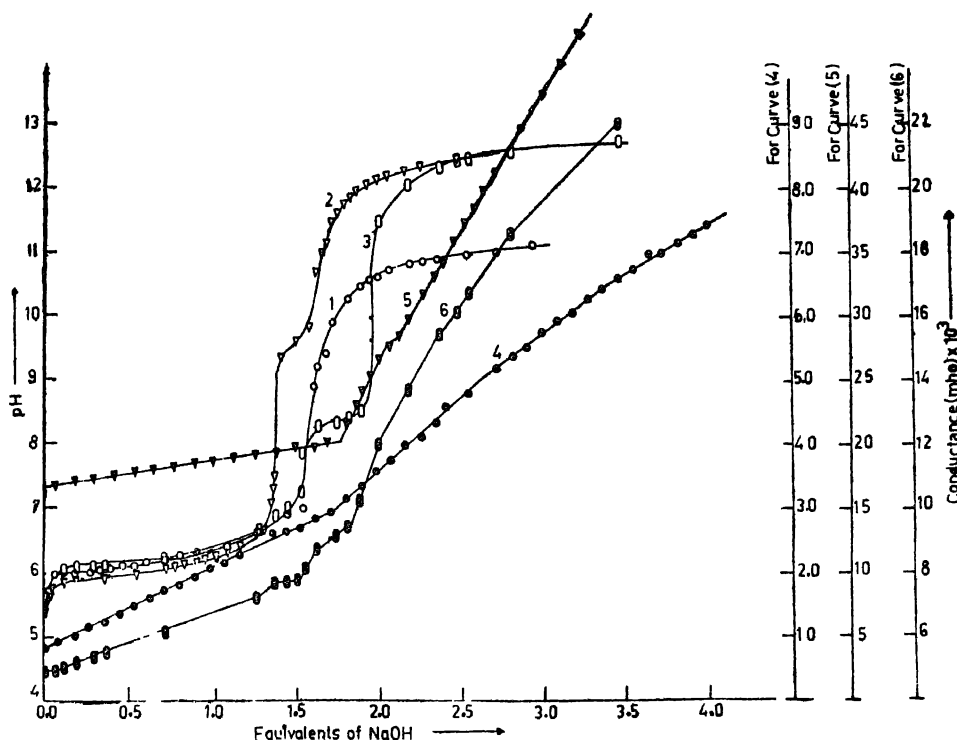


Fig. 1. pH-metric and conductometric titration of ZnSO_4 with NaOH: (1) and (4) ZnSO_4 ($0.025 \text{ mol dm}^{-3}$), NaOH (0.09 mol dm^{-3}) (continuous); (2) and (5) ZnSO_4 (0.25 mol dm^{-3}), NaOH (0.9 mol dm^{-3}) (continuous); (3) and (6) system as in (2) and (5) (equilibrium).

dm^{-3}) also shows a weak inflexion at 0.054 equivalents, but two more inflexions at 1.37 and 1.62 equivalents of alkali are seen (Fig. 1, curve 2).

Continuous conductometric titration curve for the more dilute solution of ZnSO_4 (Fig. 1, curve 4) exhibits a break at 1.73 equivalents of alkali. At 2.66 and 3.33 equivalents, two more breaks seen are due to the partial formation of NaHZnO_2 and Na_2ZnO_2 , respectively. The curve for the stronger ZnSO_4 solution (Fig. 1, curve 5) also indicates a break at 1.73 equivalents of alkali and a short region of constant linear increase in conductance is seen upto 5.5 equivalents of alkali (not shown in the figure).

The equilibrium pH-titration curve of the solution (0.25 mol dm^{-3} ; Fig. 1, curve 3) shows a weak inflexion at 0.11 equivalents and two strong inflexions at 1.54 and 1.95 equivalents of alkali corresponding to stoichiometric compositions, $\text{ZnO} \cdot 0.23 \text{ SO}_3$ and $\text{ZnO} \cdot 0.025 \text{ SO}_3$, respectively. Whereas the first strong inflexion matches closely with that observed by Britton and Robinson³, the second one indicates that the precipitate is nearly free from SO_4^{2-} ions. The calculated value of the solubility product of Zn(OH)_2 at 0.11 equivalents of alkali (weak inflexion) is $2.89 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-6}$ (1×10^{-17} , $1.29 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-6}$)^{16,17}.

Equilibrium conductometric measurements of the stronger solution (0.25 mol dm^{-3} ; Fig. 1, curve 6) exhibits a number of breaks, namely at 0.085, 1.25, 1.50, 1.80 and 2.32 equivalents of alkali. The additional break at 1.25 equivalents (*cf.* above) corresponds to the basic salt composition, $\text{ZnO} \cdot 10.38 \text{ SO}_3$. Beyond the break at 2.32 equivalents, a continuous change of slope upto 3.5 equivalents of added alkali is observed, which indicates gradual dissolution of the precipitated Zn(OH)_2 , forming, presumably, NaHZnO_2 and Na_2ZnO_2 , respectively.

The above results indicate that given adequate time, hydroxyl ions are able to displace sulphate ions from the precipitate almost completely. A new species, $\text{ZnO} \cdot 0.38 \text{ SO}_3 \cdot [2 \text{ Zn(OH)}_2 \cdot \text{ZnSO}_4]$ has been identified from the conductometric 'equilibrium titration' curve. Further, an indication for dissolution of zinc hydroxide is clearly seen in this curve.

Polarographic studies : In order to confirm the formation of the anionic hydroxocomplexes, $[\text{Zn(OH)}_3]^-$ and $[\text{Zn(OH)}_4]^{2-}$ which correspond to the salts, NaHZnO_2 and Na_2ZnO_2 , respectively, and to determine their stability constants and their other thermodynamic and kinetic parameters¹⁴, polarograms of Zn^{2+} ions (1.0 mol dm^{-3}) have been recorded in presence of an excess of hydroxyl ions (Fig. 2). The limiting current vs log [OH] plot

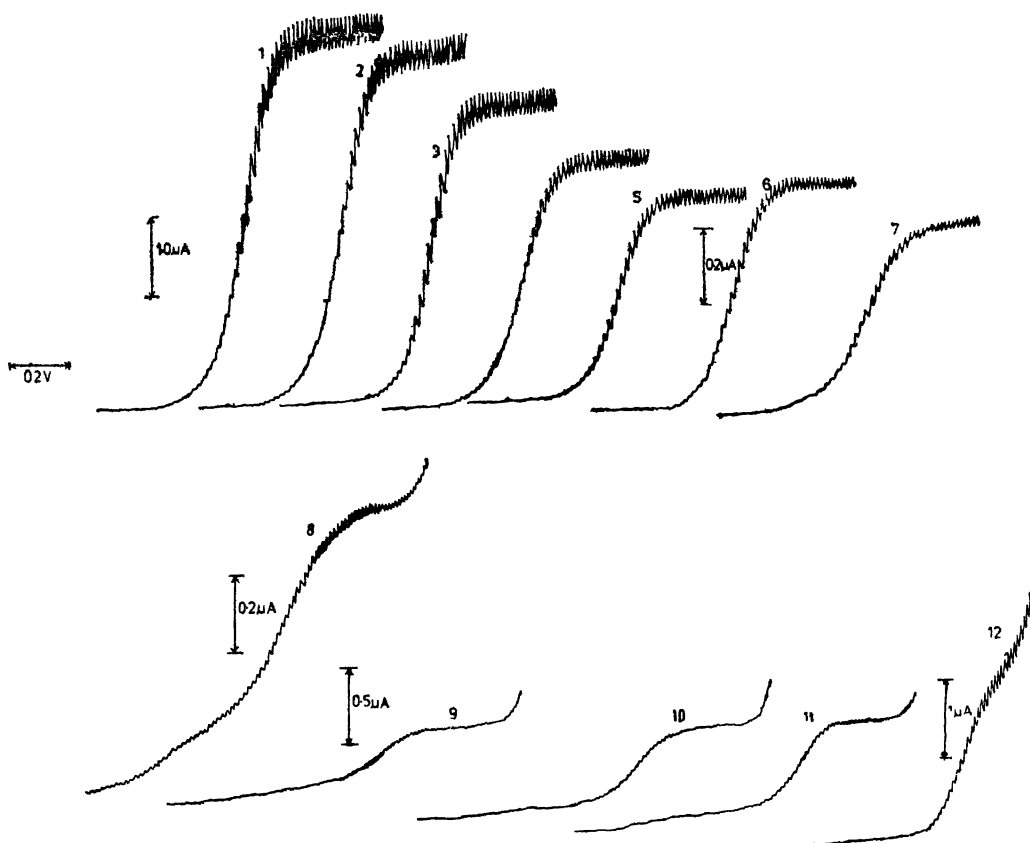


Fig. 2. Polarograms of ZnSO_4 (1.0 mol m^{-3}) in Et_4NOH (Et_4NBr , 1.0 mol dm^{-3}): (1) ZnSO_4 - Et_4NBr ; (2) to (12) Et_4NOH , 0.9, 1.8, 2.7, 4.5, 5.4, 7.2, 25.0, 50.0, 75.0 and 100.0, 1000.0 mol m^{-3} .

TABLE 1—VALUES OF $E_{\frac{1}{2}}^r$ AND $\log k_e^*$ FROM POLAROGRAPHIC DATA FOR Zn^{II} IONS

Sl. no.	$\frac{COH^-}{mol\ dm^{-3}}$	$-\log COH^-$	$-E_{1/11}$	$\frac{-E_{\frac{1}{2}}^r}{V}$	$\frac{-E_{\frac{1}{2}}^r}{V}$	$-\log k_e^*$
1.	0.000	—	0.214	1.205	1.308	0.854
2.	0.025	1.00	0.155	1.402	1.506	0.701
3.	0.050	1.30	0.184	1.392	1.492	0.751
4.	0.075	1.12	0.199	1.436	1.537	0.795
5.	0.100	1.00	0.206	1.446	1.558	0.896
6.	1.000	0.00	0.265	1.474	1.564	0.785

TABLE 2—STABILITY CONSTANTS, STANDARD RATE CONSTANT AND STANDARD POTENTIAL OF $[Zn(OH)_4]^-$

$-E_{\frac{1}{2}}^r$	Slope of $-E_{\frac{1}{2}}^r$ vs $\log COH^-/V$	Slope of $\log k_e^*$ vs $\log COH^-$	n	$\log K$	$\log (k_e^0)^B$	$\frac{(E^0)_B}{V}$
0.0850	0.0850	0.1560	2.87	2.05	10.644	-2.46
						-1.545

(Fig. 3) exhibits clearly the removal of Zn^{II} ions from the solution on increasing the concentration of alkali and the limiting current falls to zero at the mole ratio of 1 : 10. From the mole ratio of 1 : 25, a small gradually increasing current is seen, which grows to about 40% (of the value for free Zn^{II} ions) at the mole ratio of 1 : 1000.

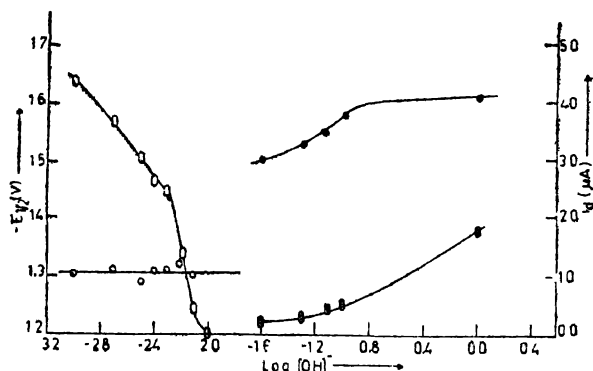


Fig. 3. $E_{1/2}$ vs $\log [OH^-]$ curve for $ZnSO_4$ (1.0 mol m^{-3}) (○, ●); i_a vs $\log [OH^-]$ curve for $ZnSO_4$ (1.0 mol m^{-3}) (○, ●).

The plot of $-E_{\frac{1}{2}}^r$ vs $\log [OH^-]$ is also seen in Fig. 3. A pH-independent linear plot upto 8.0 millimolar alkali, a discontinuity beyond, and at 25.0 millimolar alkali and higher concentration (up to 100 millimolar), a gradual increase of slope is observed as seen for a system of continuous series of complexes. The plot finally attains a constant (nearly zero) slope beyond 100 millimolar alkali concentration, due to the complete formation of the highest complex.

Matsuda and Ayabe's method¹⁴ has been applied to the polarographic data as follows: (i) The semi-log plots (from 25 to 1 millimolar) are drawn and produced backwards to cut the potential axis at $\log i/(i_a - i) = 0$, to obtain $E_{\frac{1}{2}}^r$ and α values; (ii) then the equation,

$$E_{\frac{1}{2}}^r = E_{1/11} - 2.303 \frac{RT}{zF} \left[\log \left\{ 10 - \exp \left(\frac{\alpha zF}{RT} E_{1/11} - E_{\frac{1}{2}}^r \right) \right\} \right]$$

is used to obtain $E_{\frac{1}{2}}^r$ value; (iii) $\log k_e^*$ is then calculated from the equation,

$$\log k_e^* = \frac{\alpha zF}{2.303RT} (E_{\frac{1}{2}}^r - E_{1/11}) - \frac{1}{2} \log t + 0.053,$$

all the relevant data are given in Table 1; (iv) the ligand number of the highest complex, n, is found by using the slope of the plot of $-E_{\frac{1}{2}}^r$ vs $\log COH^-$ (Fig. 4) from the relation,

$$n = \frac{zF}{2.303RT} \frac{\Delta(-E_{\frac{1}{2}}^r)}{\Delta \log COH^-},$$

to be 2.87; (v) the values of the ligand number of the electroactive complex, i, is obtained, using the slope of $\log k_e^*$ vs $\log COH^-$ plot (Fig. 4), from the equation,

$$i = n(1 - \alpha) + \frac{\Delta \log k_e^*}{\Delta \log COH^-}$$

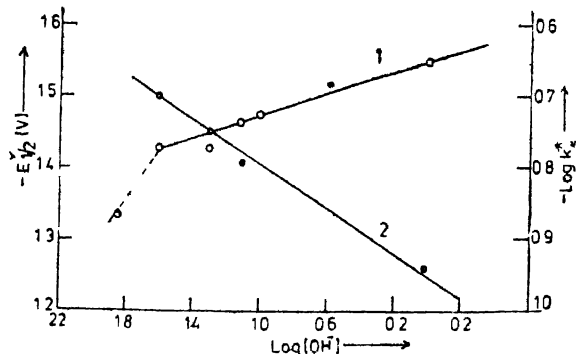


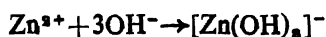
Fig. 4. (1) $E_{1/2}^r$ vs $\log [OH^-]$; (2) $\log k_e^*$ vs $\log [OH^-]$.

and it is found to be 2.05; (vi) stability constant

of the highest complex is then calculated using the reversible relationship,

$$(E_{\frac{1}{3}})_{\text{complex}} - (E_{\frac{1}{3}})_{\text{free}} = \frac{RT}{zF} \ln \left(\frac{D_o}{D_r} \right)^{\frac{1}{2}} - \frac{RT}{zF} \ln K - \frac{RT}{zF} \ln [\text{OH}^-]^3$$

and the value of log K is found to be 10.64. The standard rate constant $(k_o^0)_B$ for the overall reaction,



is then calculated from the relation,

$$k_o^* = (k_o^0)_B \left(\frac{1}{(D_{Mox})^{\frac{1}{2}}} \right)^{1-\alpha} \left(\frac{1}{D_r^{\frac{1}{2}}} \right)^{\alpha} (C_{\text{OH}^-})^{-(1-\alpha)n+1}$$

It is assumed that the diffusion coefficients for the different species are the same and its value, $5.13 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ has been used¹⁴. The value of $(k_o^0)_B$ is $3.47 \times 10^{-9} \text{ cm s}^{-1}$. Finally, the standard potential of the overall reaction, $(E^0)_B$, is calculated from the equation,

$$E_{\frac{1}{3}}^r = (E^0)_B - \frac{2.303RT}{zF} \log \left(\frac{D_{Mox}}{D_r} \right)^{\frac{1}{2}} - \frac{2.303RTn}{zF} \log C_{\text{OH}^-}$$

The value of $(E^0)_B$ is found to be -1.545 V . The final results are given in Table 2.

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Formation Constants of *N*-Benzenesulphonyl-L-(−)-histidine and Related Ligands with Bivalent Cobalt, Nickel, Copper, Zinc and Cadmium

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IN continuation of the work on synthesis¹⁻³, complexation characteristics⁴⁻⁷ and antibacterial properties⁸ of sulphonamides containing benzimidazole or imidazole nucleus, *N*-benzenesulphonyl-L-(−)-histidine (R^bH_2), α -benzenesulphonamido- β -2-benzimidazolyl-L-(−)-*n*-propionic acid (R^pH_2) and α -benzenesulphonamido- γ -2-benzimidazolyl-L-(+)-*n*-butyric acid (R^bH_2) have been taken under study. Recently it has been shown that these three ligands react interestingly with Cu^{2+} in solution⁹ and a number of complexes have been isolated⁷ which show subnormal magnetic moment at room temperature. The present paper describes the determination of formation constants of Co^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} complexes of $R^pH_2^+$ and $R^bH_2^+$ following Irving and Rossotti titration technique¹⁰ in 1:1 water-dioxan at $30 \pm 0.5^\circ$ and $\mu=0.5$ (NaClO_4). The corresponding values for Cu^{2+} have been included for comparison.

Experimental

The ligands R^pH_2 and R^bH_2 were prepared and purified as described in the previous communication³. All other reagents were either A.R. quality or properly purified. The solutions were made in double-distilled CO_2 -free water and purified dioxan⁹.

The pH values of the solution were measured with a Beckman pH meter having a glass electrode (1-13 pH range) in conjunction with SCE connected to the cell by means of an agar-2 M NaNO_3 bridge. The pH meter was calibrated with sodium hydrogen phthalate and borax buffer solution with due temperature correction. Potentiometric titrations of 50 ml solutions in water-dioxan (1:1) of the following compositions were carried out at $30 \pm 0.5^\circ$ and $\mu=0.5$ (NaClO_4) with a 0.150 M NaOH solution in water-dioxan (1:1): (i) 0.01 M HClO_4 , (ii) 0.01 M $\text{HClO}_4 + 0.02 \text{ M } R^pH_2\text{ClO}_4$ or $R^bH_2\text{ClO}_4$, (iii) 0.01 M $\text{HClO}_4 + 0.0075 \text{ M } \text{Co}(\text{ClO}_4)_2$ or $\text{Ni}(\text{ClO}_4)_2$ or $\text{Zn}(\text{ClO}_4)_2$ or $\text{Cd}(\text{ClO}_4)_2 + 0.02 \text{ M}$