

(0.005%), the second wave became stretched and ill defined in presence of these surface active substance. Thus the second wave is useful for its determination without surface active substance. The results have been summarised in Table 1.

(iii) *Reduction in presence of selenate ions*: With 0.1M NaOH, chromate ion produces a well developed reduction wave in presence of 0.1 M selenate ions. From the measurements of  $i_d$  vs chromate ion concentration, it is evident that the chromate can be estimated in excess of selenate ions in alkaline solutions. Results are recorded in Table 1.

(iv) *Reduction in presence of bromate ions*: In presence of 0.1M NaOH containing 0.1M bromate ions, chromate ion produces a single well defined reduction wave. The plots of  $i_d$  vs concentration of chromate ions come to linear which shows that the current is limited by diffusion. The results have been incorporated in Table 1.

(v) *Reduction of chromate ions in presence of arsenate ions*: A single well defined wave was occurred for reduction of chromate ions in presence of 0.1M arsenate ions having 0.1M NaOH. From the plots of  $i_d$  vs chromate ions concentration, it is evident that the chromate ions can be estimated in presence of arsenate ions in alkaline medium. The results have been summarised in table 1.

(vi) *Reduction of chromate ions in presence of arsenite ions*: In freshly prepared solution, by mixing arsenite ions & chromate ions in 0.1M NaOH, two reduction waves were obtained. The first wave contained a maximum, whose height increases with increase of chromate ion concentration. This maximum could not be suppressed by addition of large amount of gelatin (0.01%) which deforms the second wave, which is well developed in absence of gelatin. Thus second wave is of analytical use. The results have been summarised in table 1. On keeping the solution it turns bluish-green and the diffusion current decreases with time. Thus chromate ions can be estimated only in freshly prepared arsenite solution in alkaline media.

(vii) *Reduction of chromate ions in presence of tellurate ions*: In alkaline media, chromate ion produces a single reduction wave with a sharp maximum in presence of tellurate ions. The height of the maximum increases with chromate ion concentration. Attempts to suppress this maximum, so that it can be of analytical importance were not successful, even 0.01% of gelatin could not suppress the maximum.

From the above results, it is obvious that small amounts of chromate ions can be determined in excess of molybdate, tungstate, selenate, bromate, arsenate, arsenite & tellurate in alkaline media. However, in presence of arsenite ions, freshly prepared solutions should be used. The attempts to determine chromate ions in presence of tellurate ions was not useful due to non suppression of maximum.

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## Solvent Extraction of Cobalt (II) with a Mixture of Thenoyltri fluoroacetone and Ethylmethylketone in Benzene from acetate Buffers.

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Manuscript received 8 April 1974; revised 4 October 1974;  
accepted 11 December 1974

**E**XTRACTIVE separations of various metal ions from alkaline as well as from acid media using ethylmethylketone (EMK) have been reported<sup>1,2,3</sup>. It has been observed that the solubility of various metal chelates in EMK is greater than in inert solvents, which is due to the higher dielectric constant of the ketone. Its antisnergistic properties have also been observed<sup>4</sup>, but synergism with EMK in combination with thenoyl-trifluoroacetone (HTTA) has not been investigated.

In the present studies, extraction of cobalt (II) from an aqueous acetate medium into a benzene solution of a mixture of thenoyl-trifluoroacetone (HTTA) and ethylmethylketone [EMK] has been studied. The formation of the monoadduct and its conversion into the diadduct have been observed. These studies include the efficiency of the extraction of cobalt (II), the composition of the complexes transferred to the organic phase, and the extraction constant for the synergic reaction.

#### Experimental

Experiments were carried out in a similar manner as described in the previous papers<sup>5,6</sup>.

When experimental conditions are chosen so as to avoid interference from possible side reactions, the synergistic parameters<sup>7,8</sup> are reduced to three: (i) the concentration of the hydrogen ion in the aqueous solution, (ii) that of the chelating acid and (iii) the neutral ligand in the organic phase. Under these conditions, the value of the extraction constant  $K$ , and the composition<sup>9</sup> of the synergistic adduct formed during the extractive transfer of the metal from an aqueous solution, can be calculated with the help of the results of log-log plots of the distribution ratio against one of the three synergistic parameters, keeping the other two constant.

#### Results and Discussion

The plot of  $\log [\text{Co}(\text{TTA})_n \text{EMK}_r]_{org} / [\text{Co}]_{org}$  against  $pH$  for different values of  $[\text{EMK}]_{org}$  are nearly parallel and at any given  $pH$  the distribution coefficient,  $q$ , increases with the concentration of EMK present. Thus the system shows the phenomenon of synergism; in the absence of HTTA the extraction of cobalt by a solution of EMK in benzene is negligible. It has been observed that the number of liberated protons is 2; showing thereby that two molecules of HTTA react with cobalt (II) to release two protons.

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A second series of experiments was carried out in which the concentration of EMK was constant, while that of HTTA was varied over a wide range of concentrations. The plots of the logarithm of the distribution ratio,  $q$ , against  $[\text{HTTA}]_{org}$ , gave a family of straight lines of slope 2.0, indicating that only two HTTA molecules participate in the complexing reaction and free HTTA molecules are not attached to the extracted species since the number of protons liberated is equal to the number of HTTA molecules.

The values of  $\log q$  plotted against  $\log [\text{EMK}]_{org}$  for various fixed values of  $[\text{HTTA}]_{org}$ , resulted a family of curves which could be well represented by lines of integral slope 1 at low EMK concentrations, and of slope 2 at higher concentrations of the ketone. The compositions of the extracted species are thus  $\text{Co}(\text{TTA})_2 \cdot \text{EMK}$  and  $\text{Co}(\text{TTA})_2 \cdot 2\text{EMK}$  respectively.

The dependence of the distribution ratio on the concentrations of the extractant and the hydrogen ion activity indicates that the overall reaction for the extraction process corresponds to  $\text{M}^{2+} + 2\text{HTTA}_{org} + 2\text{EMK}_{org} \rightleftharpoons \text{M}(\text{TTA})_2 \cdot (\text{EMK})_2 + 2\text{H}^+$

The value of (mixed) extraction constant ( $\log K$ ) obtained for the synergic extraction of cobalt (II) by mixtures of HTTA and EMK in benzene was  $-6.8$  at  $30^\circ$ , which is near the values of extraction constants for other oxygen-containing solvent systems reported earlier<sup>5,6</sup>. For comparison among alcohol, ketone and ether systems the corresponding values quoted for butyl glycol (BG) and isopropylether (IPE) are  $-4.0$  and  $-7.4$  respectively. It has been reported by various workers<sup>10</sup> that the solubility of the chelate is affected by the basicity of the solvent, its electron donating ability and the possibility of the metal ion maintaining its coordination number. In the case of alcohols, their particular extractive behaviour is caused by the amphoteric nature of the hydroxyl group, similar to that of water, showing both donor and acceptor properties. This characteristic of alcohol affects their solvating capacity which in turn is the major parameter governing the solubility of cobalt complex in, and their extractability into, them. But in the case of EMK and IPE which lack hydrogen, there is no possibility of hydrogen bond formation, and only available source for coordination is through their basic oxygen. Moreover, the physico-chemical properties of IPE, such as dielectric constant ( $=3.88$ ) and dipole moment, are closer to those of inert solvents than to those of other polar solvents like EMK ( $=18.5$ ) and BG ( $=30.0$ ). Hence the possibility of adduct formation with cobalt-TTA chelate is less favourable in IPE as compared to BG and EMK. Thus the order of increasing extractability of Co-TTA chelate by these solvents can be written as  $\text{BG} > \text{EMK} > \text{IPE}$ . This is in the order expected from the dielectric constants and the donor properties of these solvents.

#### Acknowledgement

The authors are thankful to the Council of Scientific and Industrial Research, New Delhi, for supporting the work.

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#### Spectrophotometric Study of Lanthanum-2-Hydroxy-1,4-Napthoquinone (Lawsone) Complex

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Manuscript received 11 February 1974; revised 5 September 1974; accepted 18 November 1974

**S**PECTROPHOTOMETRIC investigations indicate the formation of 1:3 chelate, wine red in colour, between  $\text{La}^{3+}$  and 2-hydroxy-1, 4-napthoquinone in alcoholic solution.

Survey of literature reveals that 2-Hydroxy-1, 4-napthoquinone (lawsone) has found its application in qualitative and quantitative estimations of various metals. But no interaction of lanthanum with lawsone has been studied. Recently we have studied and established structures of chelate of lawsone with various metals<sup>1</sup>. In the present communication the composition, nature of structure, stability constant of  $\text{La}^{3+}$ . Lawsone chelate is reported.

#### Experimental

Standard solutions of lawsone (K. K. Laboratories, INC., Plainview, New York, A. R.) and lanthanum nitrate (Rare Earth. Ltd. Udog. Mandel, Kerala) were prepared by dissolving the respective compound in double distilled ethyl alcohol (rectified).

Baush and Lomb spectronic-20 spectrophotometer for absorbance measurements and Perkin-Elmer infra cord spectrophotometer for infra red spectra were used.