

value of nickel to steric hindrance which prevents the formation of a square planar structure.

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1. Irving, H. M. and Rossotti, H. S., *J. Chem. Soc.*, 1954, p. 2904.
2. Vogel, A. I., *A Text Book of Practical Organic Chemistry*, III Edition, Longmans, p. 177.
3. Irving, H. and Williams, R. J. P., *J. Chem. Soc.*, 1953, p. 3192.
4. Murakami, Y., Nakamura, K. and Tokunaga, M., *Bull. Chem. Soc. Japan*, 1963, 36, 669.
5. Johnston, W. D. and Frieser, H., *Analytica Chim. Acta*, 1954, 11, 302.

DETERMINATION OF MICRO AMOUNTS OF BROMATE COLORIMETRICALLY USING RESACETOPHENONE OXIME—AN INDIRECT METHOD

It is reported that ferric iron reacts quantitatively with resacetophenone oxime in slightly acidic solutions giving a purple colored soluble complex of considerable stability¹⁻³. The reactivity between ferrous iron and potassium bromate coupled with the fact mentioned above is employed to develop a colorimetric procedure for the determination of micro-amounts of bromate. The results obtained are presented in this communication. Since thiocyanate reacts with ferric iron giving deep red colour, the studies are also repeated with thiocyanate for the purpose of comparison. The results obtained with the oxime as well as thiocyanate are presented in Fig. 1.

The standard deviation, molar absorptivity and Sandell sensitivity⁴ are 9.3×10^{-3} , 9.5×10^{12} lit. mole⁻¹ cm⁻¹, 5.9×10^{-2} μ gm/cm²; 5.1×10^{-3} , 2.1×10^{13} lit. mole⁻¹ cm⁻¹, 2.6×10^{-2} μ gm/cm² respectively for the oximate and thiocyanate complexes. Even though satisfactory results are obtained with thiocyanate, the method employing the resacetophenone oxime is preferred in view of the fact that iron(III) forms complexes of different composition depending upon thiocyanate concentration⁵.

Reagents

Resacetophenone oxime is prepared by the standard procedure^{6,7}. All other chemicals used are of A.R. Grade.

Recommended Procedure

2.5 ml of iron(II) solution (0.1 M) in sulphuric acid (0.03 M) is pipetted out into each of 25 ml volumetric flasks containing different aliquots of bromate solution (0.05 mg/ml). About 20 to 30 minutes are allowed to make sure that the oxidation of iron(II) is complete. Then 2.5 ml of the oxime solution (0.1 M) is added to each of the flasks and the contents are made up to the mark. Absorbances of the solutions are measured at 500 nm using water as blank.

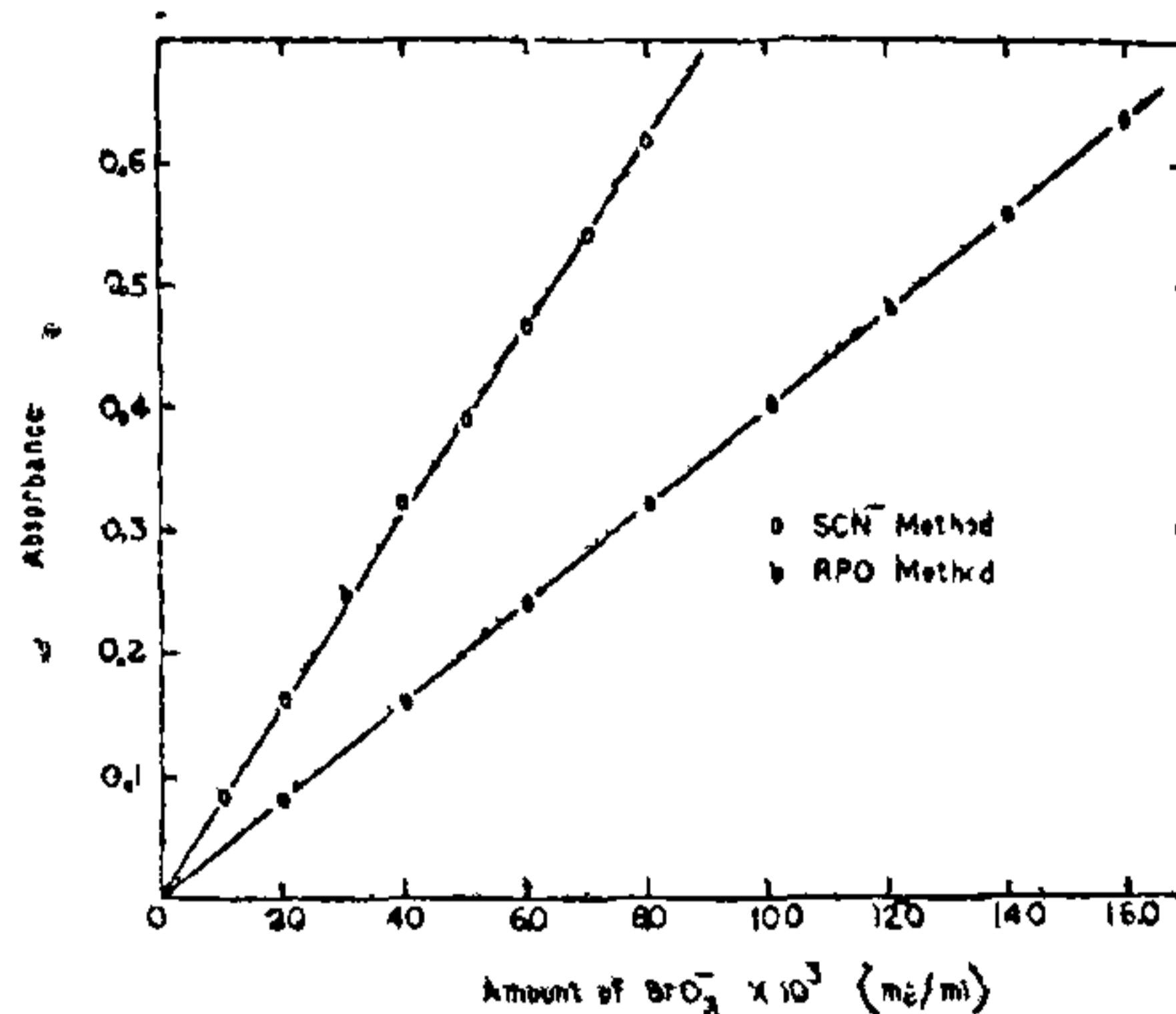


FIG. 1

Similar procedure is adopted for ferric thiocyanate method. The acid concentration is maintained at 0.08 M. Absorbance measurements are however carried out at 450 nm.

Effect of Acidity

In the oximate method, the color intensity decreases with the increase of acid concentration. Lower acid concentrations though improved the color intensity, are undesirable since minimum acidity is required to suppress hydrolysis and to facilitate the oxidation of iron(II). Hence the optimum overall concentration is to be maintained at 0.003 M.

Interferences

Ca²⁺, Mg²⁺, Na⁺, K⁺ nitrate, chloride, bromide did not interfere even when present in large excess.

The method is simple and rapid compared to the colorimetric methods reported in literature⁸ for the determination of bromate employing organic reagents, such as methyl orange, phenol red, fluorescein, etc. Reagents like methyl orange, methyl red suffer from the drawback that they are acid-base sensitive. The other reagents are either less sensitive or suffer from other defects (*loc. cit.*).

Moreover, the present method is very sensitive since the redox reaction involved between iron(II) and bromate is a multi-electron process.

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1. Neelakantam, K. and Sitaraman, M. V., *Curr. Sci.*, 1945, 14, 320.
2. Bhatki, K. S. and Khabadi, M. V., *Proc. Ind. Acad. Sci.*, 1963, 58A, 197.
3. Raja Reddy, G., Kadarmandalgi, S. G. and Murthy, A. S. R., *Ibid.*, 1964, 59A, 159.
4. Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience, New York, 1959.
5. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, Longman Group Ltd., London, 1975, p. 785.
6. Dey, B. B. and Sitaraman, M. V., *Laboratory Manual of Organic Chemistry*, 1952, p. 264.
7. Vogel, A. I., *A Text Book of Practical Organic Chemistry*, 1948, p. 341.
8. Boltz, D. F., *Colorimetric Determination of Non-metals*, Interscience, New York, 1958, p. 185

MECHANISM OF THE SYNERGISTIC EFFECT IN THE ANION EXCHANGE UPTAKE OF Co(II) IN MIXED SOLVENT MEDIA

THE anion exchange adsorption of cobalt(II) chlorocomplex in mixed solvent media is compared with the solubility data and spectral data of quaternary ammonium chlorocomplex of cobalt (II) and the similarity is pointed out.

The anion exchange adsorption of cobalt(II) at a lower hydrochloric acid concentration in mixed solvent media has been reported by the authors¹. The present studies have been carried out to understand the mechanism of the synergistic effect.

Ryan² in his studies of the species involved in the anion exchange adsorption of quadrivalent nitrates $\text{Pu}(\text{NO}_3)_6^{4-}$ and $\text{U}(\text{NO}_3)_6^{4-}$ compared their anion exchange adsorption of these complexes with the solubility data. He found that a marked similarity exists between the anion exchange of these metal complexes and the solubility of the quaternary ammonium salts of these complexes.

Kraus and Michelson³ determined the solubility of tetramethyl ammonium and benzyl trimethyl ammonium chloroaurate in hydrochloric acid and lithium chloride and found that the solubilities of these are reminiscent of anion exchange behaviour of gold in these media.

In the light of above observations, it is considered worthwhile to examine the anion exchange uptake of cobalt from acetone-alcohol mixtures of different compositions in terms of solubility and spectral data.

Experimental

Preparation and Analysis of the complex:

Phenyl trimethyl ammonium chloride and anhydrous cobalt(II) chloride dissolved in alcohol are mixed in the ratio of 2:1 and HCl vapours are passed through this mixture while the solution is cooled. A blue crystalline precipitate separated on further cooling which is finally recrystallised from the ethanol, dried under vacuum and analysed (mp 208°C).

	C	H	CO ₃ O ₄
Found	45.59	6.18	0.53
Required for (C ₆ H ₅ (CH ₃) ₃ N) ₂ CoCl ₄	45.68	5.90	0.55

The cobalt and the chloride ratios are determined by the volumetric method using EDTA and by Volhard's method respectively. The Cl/Co ratio is found to be 4.

Solubility determination :

About 1 g of (phenyl trimethyl ammonium)₂ CoCl₄ complex is shaken with 10 ml portion of the 85% mixture of acetone and ethyl alcohol containing 1.5 M hydrochloric acid in a stoppered flask for one hour. After allowing the solid to settle down an aliquot of the clear supernatant liquid is taken out and the cobalt content is estimated colorimetrically with Nitroso-R-Salt on a Hilger Spekker Absorptiometer using 520 nm colour filter. The solubility determinations in different acetone-ethanol mixtures are repeated until reproducible values are obtained.

Ion exchange distribution coefficients (K_d) were determined as already published¹.

Spectral data:

Spectra of the complex in mixed solvent media are taken on a Unicam SP 600 spectrophotometer.

Results and Discussion

The plot of the solubility of the cobalt complex in solvents of different compositions vs. mole fraction of acetone is given in Fig. 1. In the same figure the $1/K_d$ values of cobalt on the anion exchange resin as a function of solvent composition are also plotted. It can be seen that the curves show a trend similar to that observed by Ryan² in the case of actinide nitratocomplexes in aqueous media.

The spectra of the complex in solvents of different compositions (Fig. 2) indicate that the ϵ values are