

do not agree with the experimental values. Even RKR Franck-Condon factors of the Werner bands (Spindler¹¹⁻¹³) are not in complete agreement with experimentally determined relative band strengths. Hence we conclude that in spite of the improved molecular parameters available for H₂ and D₂, the inconsistency in the theoretical and experimental results of radiative lifetimes is due to the fact that the Werner band system is completely perturbed and the new equation cannot be fully applied.

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Department of Physics,
T.N.B. College,
Bhagalpur 812 007 (India),
and

Department of Physics,
Bhagalpur University,
Bhagalpur 812 007 (India),
September 15, 1978.

B. K. SINHA.

A. N. PATHAK.

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EXTRACTION PHOTOMETRIC DETERMINATION OF IRON(III) WITH SALICYLALDOXIME

EXTRACTION of iron(III) as salicylaldoximate complex into *n*-butanol was studied at pH 7. The red-orange iron(III) complex is measured at 410 nm. The colour of the organic phase is stable

for several weeks. The system obeyed Beer's law in the range 0–10 μgms/ml, with a standard deviation of 0.005. The molar absorptivity, Sandell sensitivity, the composition and stability constant of the extracted species are 3.3×10^3 moles⁻¹ cm⁻¹ litre, 0.017 μg cm⁻², 1:1 and 7.4×10^4 respectively. Mn(II), Zn(II), U(VI), Mo(VI) and Cu(II) do not interfere.

The colour reaction between the ferric iron and salicylaldoxime was reported by Ephraim¹ in as early as 1930. Howe and Mellon² employed the colour reaction for the direct photometric determination of iron. However uranium(VI), molybdenum(VI) and copper(II) interfere seriously in the determination³. A survey of literature revealed that no work except the casual mention by Gorbach and Pohl⁴ was reported on the extraction photometry of ferric iron with the oxime. The results of the photometric determination of iron with the oxime, in *n*-butanol are reported in this communication.

The extraction studies carried out in the pH range 1.0 to 9.0 showed that there was no extraction below pH 3 and quantitative extraction occurred in the pH range 6 to 8. pH 7 was selected for the determination of the metal since it is observed that at this pH, the absorbance of the organic phase showed the highest value at 410 nm. The absorbance is constant for several weeks. It is observed that the oxime is to be present in at least 20 fold excess.

Recommended Procedure

5 ml of 5% ammonium acetate (pH adjusted to 7) 1 ml of sodium perchlorate (1 M), 1 ml of oxime solution (10⁻¹M) and different aliquots of the iron(III) solution (10⁻³M) are taken in a 25 ml separatory funnel. The above sequence of addition is essential for high colour intensity and reproducible results. The volume of the aqueous phase is maintained at 10 ml by adding distilled water. Ten ml of *n*-butanol is then added to the contents of the funnel and shaken well for five minutes. After equilibration, the organic layer is separated, dried over anhydrous sodium sulphate and the absorbance measured against solvent blank. The organic phase obtained in the extraction with the aqueous solution devoid of the metal ion was used as the solvent blank.

The linear plot obtained between the amount of the metal ion and the absorbance showed that iron can be determined by the present method accurately in the range 0–10 μgms/ml. The molar absorptivity (ϵ) and the Sandell sensitivity (S) at 410 nm are 3.3×10^3 mole⁻¹ cm⁻¹ litre and 0.017 μg cm⁻² respectively. The standard deviation is 0.005. Manganese(II) (300 fold), zinc(II) (100 fold), uranium(VI) (30 fold), molybdenum(VI) (10 fold)

and copper(II) (2 fold) did not interfere in the determination. Higher amounts of copper could be tolerated if toluene is added to butanol. Nickel(II), vanadium(V) and tungsten(VI) interfere if their concentration exceeds twice that of iron.

The Coleman⁵ graphical analysis of the organic layer showed that only a single species of the complex is extracted. The results obtained in Job's method applicable to two phase system, indicated that the metal to ligand ratio is 1:1. This is further confirmed by log-log plot. The stability constant of the complex calculated from the data obtained in the Job's method is 7.4×10^4 .

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Department of Chemistry, P. B. SANKARA REDDY.

Autonomous Post-Graduate S. BRAHMAJI RAO.

Centre,

Anantapur 515 003 A.P.,

May 10, 1978:

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GENERAL SPRAY REAGENTS FOR NATURALLY OCCURRING HIGHER FATTY ACIDS AND THEIR METHYL AND ETHYL ESTERS

MANY spray reagents have been in use for detecting the presence of fatty acids and their methyl and ethyl esters¹⁻³. Since these reagents very often do not produce pronounced colour, it was considered necessary to search for the sensitive spray reagents suitable for detecting the presence of fatty acids and their methyl and ethyl esters. This was achieved by paper chromatographic procedures involving the use of Whatman No. 1 filter-paper, impregnated with 2% solution of olive oil in benzene⁴, and 90% ethanol as the developing solvent. The developed chromatograms were dipped in 1% solution of curcumin, whereupon the chromatograms became yellow. The yellow chromatograms were then dipped in (1) 10% aqueous caustic soda solution or (2) 10% aqueous sodium arsenite solution or (3) 10% aqueous potassium ferrocyanide solution or (4) benedict's solution (BDH) or

(5) saturated solution of borax whereupon the colour of the chromatograms changed to reddish brown but the colour of the spots of fatty acids and their esters remained yellow, probably due to adsorption of curcumin. The colour of the spots became more pronounced after the chromatograms were dried in air. The R_f values are: oleic acid 0.04, stearic acid 0.16, palmitic acid 0.21, myristic acid 0.52, ethyl oleate 0.28, ethyl-stearate 0.87, methyl palmitate 0.85 and ethyl myristate 0.32.

The above paper chromatographic procedure has successfully been extended to the quantitative estimation of the fatty acids and their esters in a klett-summerson photoelectric colorimeter using blue filter (420 nm) with the help of standard curves of authentic acids and their esters. Two sets of standard solutions of mixture of (1) oleic acid, stearic acid, myristic acid, ethyl myristate and methyl palmitate (20 mg each in the same 100 ml ethanol) and (2) palmitic acid, ethyl oleate, ethyl stearate (20 mg each in the same 100 ml ethanol) were prepared and 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml and 1.0 ml of each set containing 40, 80, 120, 160, 200 μ g of each compound present in the above two sets of mixtures were chromatographed and the colour was developed by making use of the above spray reagents. The coloured spots were cut out and eluted by immersing in methanol (5 ml each) and the colour intensity of each eluate measured. The concentration of oleic acid, stearic acid, myristic acid, ethyl myristate, methyl palmitate, palmitic acid, ethyl oleate and ethyl stearate were found to be 86%, 82%, 85%, 84%, 86%, 82%, 83% and 85% respectively of the theoretical value from the standard curves.

Department of Chemistry,

M. MASOOD.

University of Allahabad,

R. N. CHOUDHARY.

Allahabad, India,

K. P. TIWARI.

June 13, 1978.

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TERPENIC KETONES AS CHELATING LIGANDS: SPECTROPHOTOMETRIC INVESTIGATION ON VANADIUM (IV) COMPLEX WITH α -CYCLOCITRYLIDINE ACETONE

THE metal complexes of terpenic ketones have not been investigated so far. A review of literature shows that metal complexes of α -cyclocitrylidine