

form. The figure near each point on the graph indicates the percentage conversion. The plots are linear only up to about 50% conversion and beyond that stage the shape of the curves indicates that the values of k_3 decrease with time and that the reaction is inhibited by hydrogen bromide, as suggested by Robertson *et al.*¹

Figure 2† shows plots for pseudo-second order kinetics, using equation (5) in the appropriate form. The plots are linear even up to about 80% conversion and therefore, no inhibition by HBr is indicated.

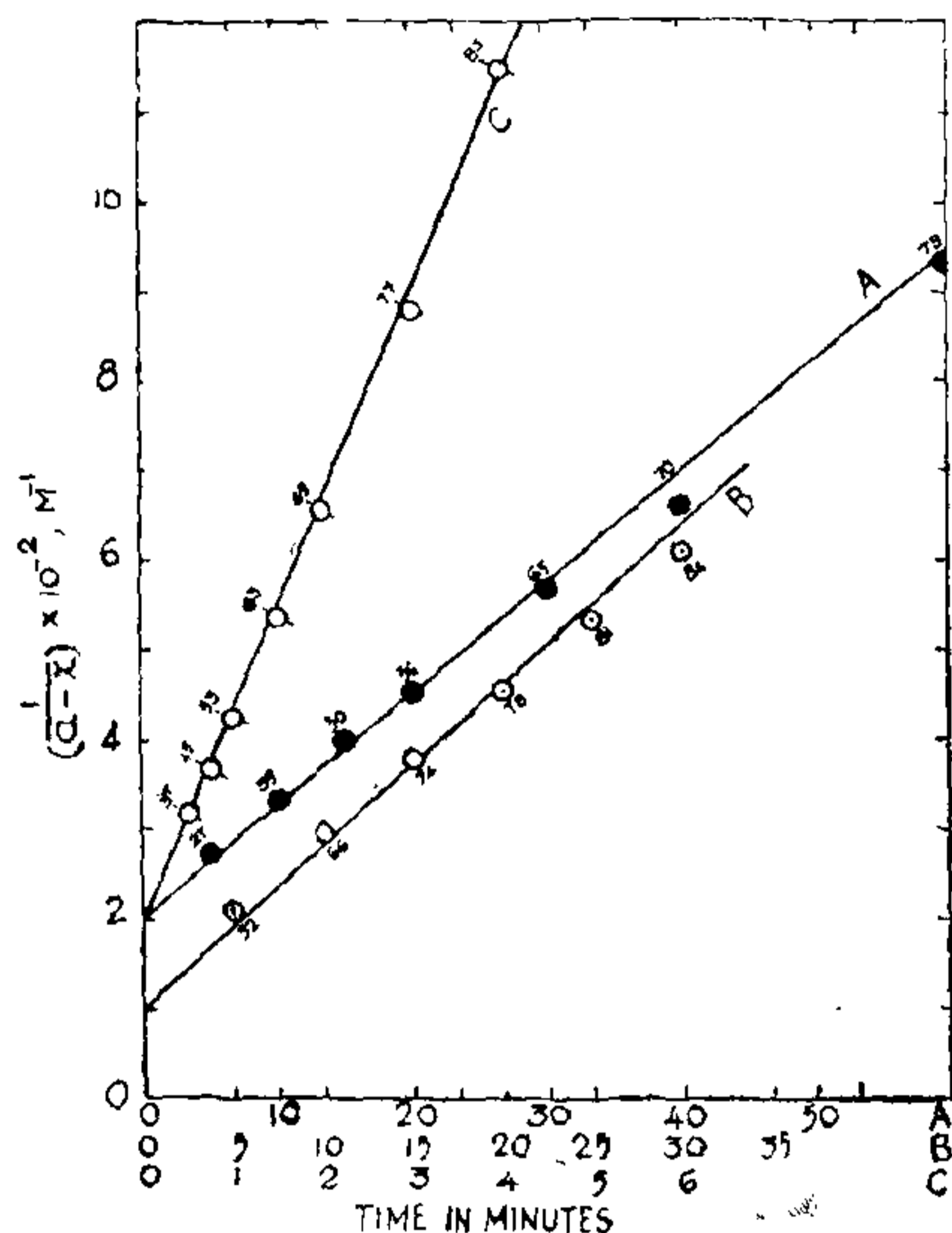


FIG. 2. Plots showing pseudo-second order kinetics with respect to bromine in acetic acid at 30°C.; A, paradimethoxybenzene-bromine reaction, $[\text{ArH}]_0 = 0.1 \text{ M}$, $[\text{Br}_2]_0 = 0.005 \text{ M}$; B, paradimethoxybenzene bromine reaction, $[\text{ArH}]_0 = 0.2 \text{ M}$, $[\text{Br}_2]_0 = 0.01 \text{ M}$; C, anisole-bromine reaction, $[\text{ArH}]_0 = 0.1 \text{ M}$, $[\text{Br}_2]_0 = 0.005 \text{ M}$.

If the reaction is retarded by the formation of HBr_3 , then the shape of the lines in Fig. 2 should be similar to that in Fig. 1. Since our experimental finding is different, we have to conclude that the reaction is inhibited not by the formation of HBr_3 but due to some other reason. We propose the following explanation. The aromatic compound and hydrogen bromide form a π -complex which has the probable composition $\text{ArH}\cdot\text{HBr}$. When the concentrations of the reactants are equal (Fig. 1), a substantial amount of the aromatic compound is converted

into $\text{ArH}\cdot\text{HBr}$ (especially after about 50% conversion) and $[\text{ArH}]$, available for the reaction, decreases. Hence, the rate constant also decreases with time. When the aromatic substrate is present in a large amount (Fig. 2), the formation of $\text{ArH}\cdot\text{HBr}$ does not affect $[\text{ArH}]$ in the reaction system, even when there is cent per cent. conversion. No inhibition is, therefore, observed.

Both hydrogen bromide and bromine form π -complexes with aromatic molecules.⁴ Since HBr is more polar than Br_2 , the complex $\text{ArH}\cdot\text{HBr}$ will be more easily formed than $\text{ArH}\cdot\text{Br}_2$. Hydrogen bromide is dissociated to a small extent in acetic acid⁵; $\text{HBr} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOH}_2^+ + \text{Br}^-$. π -Complexes such as $\text{ArH}\cdot\text{CH}_3\text{COOH}_2^+$ and $\text{ArH}\cdot\text{H}^+$ may also be formed. They will affect the overall kinetics in the same manner as $\text{ArH}\cdot\text{HBr}$.

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* $k_2' = k_2 [\text{ArH}]$.

† $[\text{ArH}]_0$ and $[\text{Br}_2]_0$ denote initial concentrations.

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COMPOSITION AND STABILITY OF NICKEL-DIETHYLDITHIOCARBAMATE

Job's method¹ of continuous variation, the mole ratio method of Yoe and Jones³ and the slope ratio method of Harvey and Manning² can be applied to determine the formula of the complex and its stability constant. In the present work, attempt has been made to determine the formula of the complex formed by nickel ions with sodium diethyldithiocarbamate (NaDDC). The effect of pH on the stability of the complex is also studied.

EXPERIMENTAL

The wavelength of maximum absorbance was determined by studying the absorbance of a mixture of cation and the chelating agent (in excess). It was 385 m μ .

For Job's method, different ml. of NiCl_2 0.002 M was taken and to it varying amounts of 0.002 M NaDDC were added so as to have

the total mixture 2.5 ml. The complex being insoluble in water, 7.5 ml. ethyl alcohol was added to make it soluble and the alcohol content to be 75%. Exact half the concentrations were also employed.

For the slope ratio method, 0.002 M NiCl₂ and 0.02 M NaDDC and 0.02 M NiCl₂ and 0.002 M NaDDC were prepared. In one set, excess of NaDDC was taken and in the other, excess of NiCl₂. The alcohol percentage was 75.

For the mole-ratio method, 0.002 M NiCl₂ and 0.002 M NaDDC were prepared. To a fixed amount of NiCl₂, different amounts of NaDDC were added. Ethyl alcohol content was 75%. Experiments were repeated with exactly half the concentrations.

The data with all the three methods are not given for the sake of brevity.

For the study of stability of the complex at various pH, the absorbance of the mixtures with different buffers was measured at zero and twenty-four hours.

The results are shown graphically (Fig. 1).

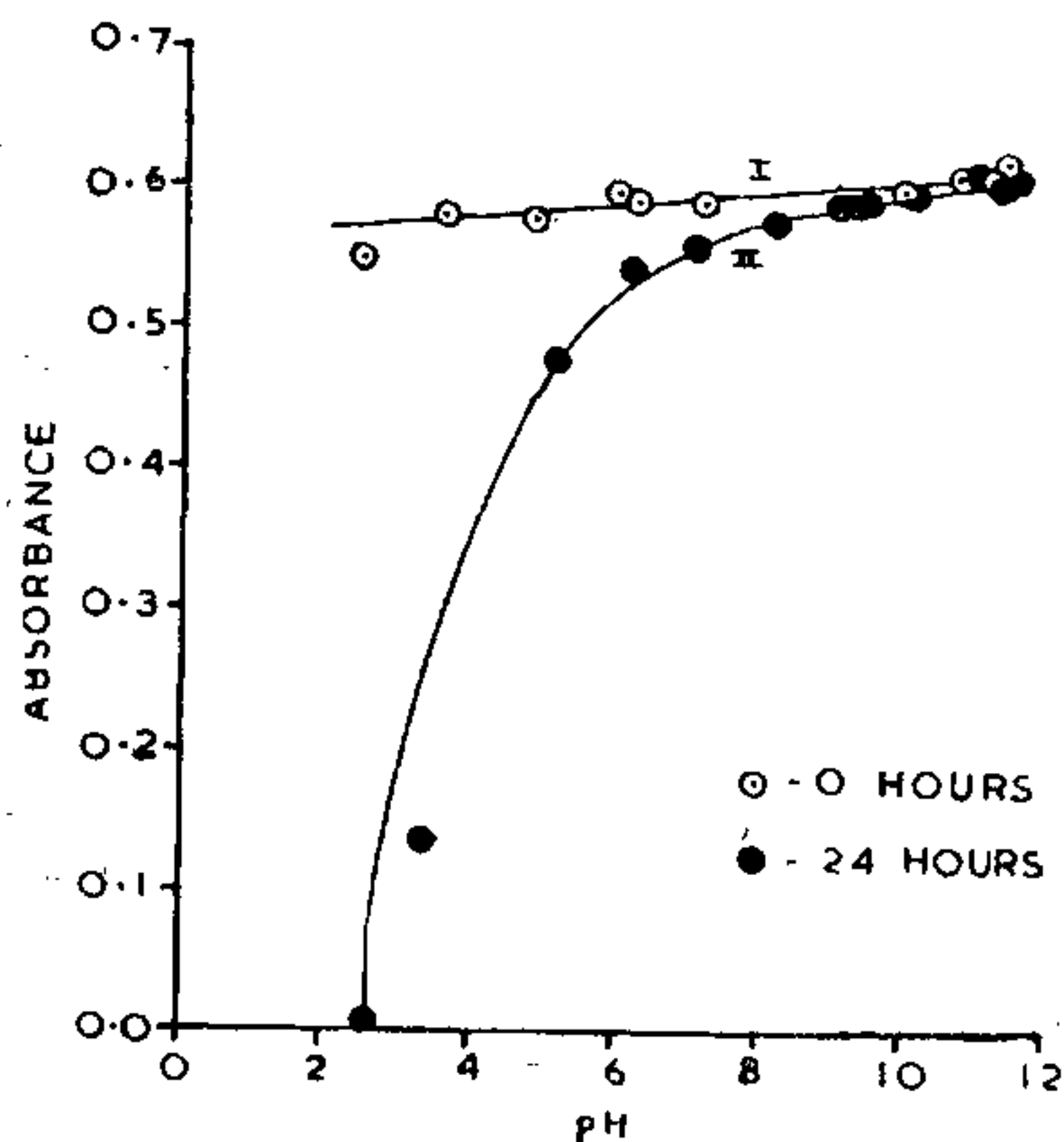


FIG. 1. Effect of pH on stability of Ni(OOC)₂.

DISCUSSION

It was observed that the optical density was maximum for the mixture having the cation and NaDDC in the ratio 1 : 2. Thus, Job's method gave the formula Ni(DDC)₂.

The slopes of the graphs were 0.448/0.4 and 0.220/0.4. According to the method of slope ratio, the ratio of two slopes was nearly equal to 1 : 2. Thus this method also gave the formula of the complex as Ni(DDC)₂.

Mole ratio method showed a good break when the concentration ratio of the metal ion to NaDDC was 1 : 2. Hence, this method also gives the formula as Ni(DDC)₂.

As regards the effect of pH on stability, it is found that the complex is stable down to pH 6, below which it is unstable (Fig. 1).

None of the methods was successful for the calculation of stability constants. This may be due to (i) very low solubility of the complex even in 75% ethyl alcohol, (ii) very high stability of the complex and (iii) decomposition of the complex at lower pH.

Thanks are due to Dr. A. M. Trivedi for interest in the work and to Dr. R. D. Desai for the laboratory facilities.

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COMPOSITION AND STABILITY OF METAL-1-(O-ARSONOPHENYLAZO)-2-NAPHTHOL-3:6-DISULPHONIC ACID CHELATES OF TRIVALENT ALUMINIUM, GALLIUM AND INDIUM IN AQUEOUS SOLUTION

1-(O-ARSONOPHENYLAZO)-2-naphthol-3 : 6-disulphonic acid (APANS) has been extensively used as a chelating agent in the determination of thorium¹ and of many other metals.² In spite of the large amount of work done on the chromogenic properties of the reagent, the composition and stability of metal chelates involving APANS, have not received sufficient attention. In the present communication the composition and stability of the trivalent aluminium, gallium and indium have been described. The compositions were determined and were found to be 1 : 2 (metal : ligand) in each case, by employing the method of continuous variations, the mole ratio and the slope ratio methods. The Al-APANS was studied at 530 m μ (pH 4.0), Ga-APANS at 520 m μ (pH 3.35) and In-APANS at 520 m μ (pH 3.5). By Vosburgh and Copper's method,³ λ_{max} of the complexes were found to be 490 m μ for all the three