chromium nitrate (10⁻² M) in 1:1 mixtures of alcohol and organic solvents (except for pyridine alcohol mixture in which chromium nitrate did not dissolve). In all these solvents violet-coloured solutions were obtained which turned into light green on keeping for 2–3 hr. The absorption studies of each solution were made after the development of stable green colour. In these solutions two maxima at 430 and 580 m$\mu$

TABLE V

| Solvent | Soap | Reqd. g | Chemical analysis | | Spectrophoto-metric method | |
|---|---|---|---|---|---|---|
| | | | Found g | % Error | Found g | % Error |
| Benzene | Cr(iii)-stearate | 0.093 | 0.083 | 10.7 | 0.094 | 1.05 |
| | | 0.0294 | 0.0194 | 34.0 | 0.029 | 0.0 |
| | Cr(iii)-palmitate | 0.0779 | 0.0680 | 12.7 | 0.0772 | 0.89 |
| | | 0.0246 | 0.0205 | 16.7 | 0.02466 | 0.0 |
| Toluene | Cr(iii)-stearate | 0.093 | 0.086 | 7.0 | 0.092 | 1.0 |
| | | 0.0294 | 0.21 | 28.9 | 0.0294 | 0.0 |
| | Cr(iii)-palmitate | 0.0779 | 0.0727 | 6.6 | 0.0789 | 1.2 |
| | | 0.0246 | 0.0194 | 21.2 | 0.0246 | 0.0 |
| Xylene | Cr(iii)-stearate | 0.093 | 0.0856 | 7.0 | 0.092 | 1.0 |
| | | 0.0294 | 0.0220 | 28.5 | 0.0294 | 0.0 |
| | Cr(iii)-palmitate | 0.0779 | 0.0745 | 4.3 | 0.0772 | 0.89 |
| | | 0.0246 | 0.0213 | 13.0 | 0.0246 | 0.0 |
| Carbon tetra-chloride | Cr(iii)-stearate | 0.0930 | 0.0825 | 10.7 | 0.0920 | 1.0 |
| | | 0.0294 | 0.0220 | 25.9 | 0.0294 | 0.0 |
| | Cr(iii)-palmitate | 0.0779 | 0.0731 | 6.1 | 0.0760 | 1.2 |
| | | 0.0246 | 0.0205 | 16.7 | 0.0246 | 0.0 |
| Pyridine | Cr(iii)-stearate | 0.1258 | 0.1156 | 8.0 | 0.1256 | 0.1 |
| | | 0.0325 | 0.0395 | 17.9 | 0.0325 | 0.0 |
| | Cr(iii)-palmitate | 0.0973 | 0.0956 | 1.7 | 0.0973 | 0.0 |
| | | 0.0307 | 0.0285 | 7.2 | 0.0307 | 0.0 |

were obtained. Although these maxima existed at the same wavelengths as those for the chromic soaps, there was a large difference in the O.D. values, so much so that the order of absorption was almost reversed. Here the O.D. were larger at the lower wavelength than at the higher wavelength. Hence it was concluded that the behaviour of chromic soaps in these solvents is quite different from that of the corresponding salts. For pyridine as the solvent chromic chloride instead of chromic nitrate was used. Here the maxima were realised at 460 m$\mu$ and 630 m$\mu$, respectively, instead of 425 and 580 m$\mu$.

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# Studies on the Behaviour of Chromium (iii) Soaps. II. Solubility and Viscometric Studies with Chromium Stearate and Palmitate in Nonaqueous Solutions

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## Abstract

The colloid chemical behaviour of the chromium stearate and palmitate in nonaqueous solutions have been investigated by solubility and viscometric methods. Chromium stearate and palmitate form no micellar aggregate in pyrindine but aggregate into micelles in benzene, toluene, xylene and carbon tetrachloride in the concn range of ca. 0.7–1.5 × 10⁻² mole/liter. Viscometric studies can be utilized in estimating the concn of the metal soaps in fairly concd solution: 0.822–27.431 g/liter.

CHROMIUM SOAPS have found use in industry (1) and technology, especially in the preparation of paints and varnishes (2) and dewaxing agents (3). Their use in lubricating oils has also been reported. It is, however, surprising that fundamental research on these soaps have not been undertaken until now. Recently we took up systematic investigations in this direction, dealing with the physicochemical behaviour of these soaps in different organic media. Encouraging results were obtained on the basis of polarographic

(4,5) and spectrophotometric (6,7) studies with pyridine and o- and m-toluidines as organic solvents. There it was found that both the polarographic and spectrophotometric methods can be usefully employed for the estimation of metal content in soaps when highly dilute solutions are meant for analysis.

Next we attempted a more critical study of the properties of chromium stearate and palmitate. In the first instance we attempted to determine the critical micelle concentration (CMC) values of these soaps in a number of organic solvents. In this communication the results obtained from the solubility and viscometric data are described. Further work dealing with the composition of the metal soaps is in progress and would form the basis of a future communication.

## Experimental

Palmitic and stearic acids were reagent grade British Drug House (BDH) products purified by repeated crystallization. A.R. samples were chrome alum, chromium nitrate, chromium chloride and sodium hydroxide benzene, toluene, xylene, carbontetrachloride

TABLE I

Amount of Chromium Stearate and Chromium Palmitate in Benzene at Different Temps.

| Temp (°C) | Amount of soap in g/100 g solvent | |
|---|---|---|
| | Chromium stearate | Chromium palmitate |
| 15 | 1.949 | 2.754 |
| 20 | 1.995 | 3.311 |
| 25 | 1.995 | 3.981 |
| 30 | 2.089 | 4.897 |
| 35 | 3.548 | 6.165 |
| 40 | 6.025 | 10.000 |
| 45 | 10.000 | 15.849 |

and pyridine (BDH) were doubly distilled. Sodium stearate and sodium palmitate were obtained by refluxing stearic acid, palmitic acid and sodium hydroxide in alcohol for 10 to 12 hr on a water bath. They were further purified by alcoholic crystallization.

The metal soaps were prepared by the precipitation method (8). Small portions of warm solutions of sodium stearate and sodium palmitate (1000 ml, 1.5%) in water were added to chrome alum solution (500 ml, 1.0%) with constant stirring at 50 to 60C. The light grey precipitate thus obtained was filtered and was successively washed with hot water and alcohol. The metal content of the soap, to test its purity, was determined iodometrically by converting it into sodium dichromate after fusion with sodium peroxide. On analysis metal content in Cr (iii) stearate and Cr (iii) palmitate was found 5.23%, 6.32%, respectively (theoretical 5.7% and 6.45%).

Solutions (2 × $10^{-2}$ M) of Cr(iii) palmitate and Cr (iii) stearate were prepared by dissolving 16.4586 g/litre and 20.00 g/litre of respective soaps in benzene, toluene, xylene, carbon tetrachloride and pyridine.

Viscosities of nonaqueous solutions of chromium soaps were determined by Scarpa's method (9) modified by Farrow (10) and improved by Prasad, Mehta and Desai (11). The formulae used takes into account time $t_1$ and $t_2$ required for filling and emptying the bulb of the Ostwald's type viscometer under a definite pressure P, with V as the vol of the bulb, R the radius of the capillary and L its length.

$$\eta = \frac{PR^4}{8LV} \times \frac{t_1 t_2}{t_1 tt_2} = K \frac{t_1 t_2}{t_1 tt_2}$$

If the same temp and pressure were employed, the value of the constant K for a particular viscometer could be determined by measuring $t_1$ and $t_2$ for a liquid of known viscosity. The measurements were performed several times and the average values were adopted. Temp was maintained with ±0.05C in a thermostatic water bath.

The solubility of Cr(iii) stearate and palmitate were determined by the usual method of preparing a saturated solution of the two soaps in benzene at different temps and analysing the supernatant liquid by weighing. The solutions attained equilibrium after a long time. Clear supernatant liquid was obtained only after keeping the chromium palmitate for 2 hr and chromium stearate for 5 hr.

## Results and Discussion

It is well known that there is an abrupt change at a definite temp in the slope of the solubility temp curve of micelle-forming substances. The temp at which this abrupt change occurs is known as Krafft point and the concn at the Krafft point is taken as the CMC of the given substance. The solubility method, there-
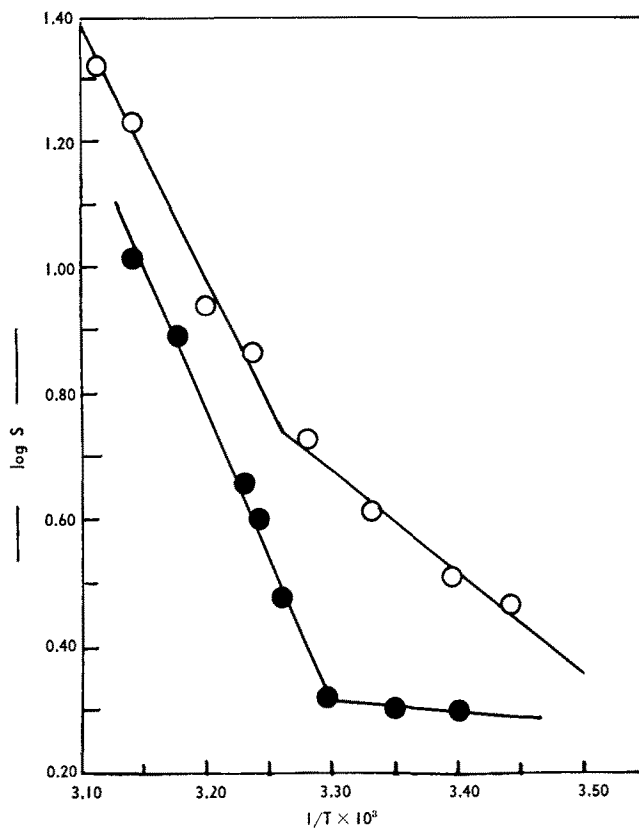


FIG. 1. Log S ~ 1/T curves for chromium stearate (●) and chromium palmitate (○) in benzene.

fore, gives one of the direct measure of micelle formation. The solubility data of chromium stearate and chromium palmitate in benzene at different temps are given in Table I.

The solubility curves of chromium stearate and chromium palmitate are not exponential in nature but show an abrupt change (marked increase in solubility) at 33 and 31C, respectively. On plotting log S against
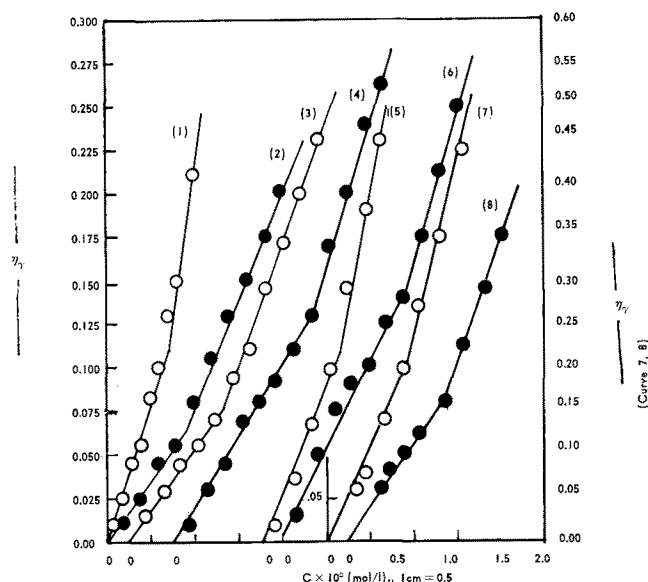


FIG. 2. The variation of relative viscosity with the concn of benzene (1,2), toluene (3,4), carbon tetrachloride (5,6), and xylene (7,8) solutions of chromium stearate (●) and chromium palmitate (○) at 30C.
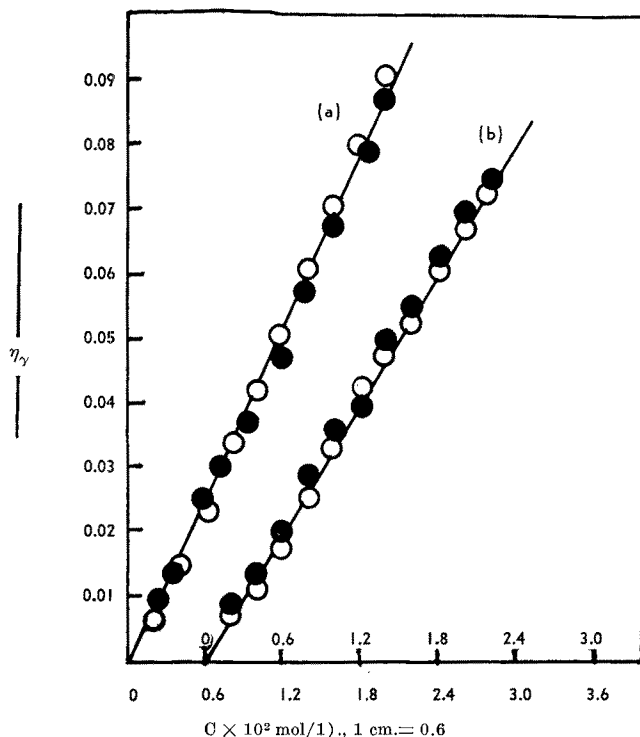
FIG. 3. The variation of relative viscosity with concn of the pyridine solution of (a) chromium stearate at 30C (○) and 35C (●), (b) chromium palmitate at 30C (●) and 35C (○).

the reciprocal of the absolute temp T, a change in slope takes place at 33 and 30C (Fig. 1), pointing towards the existence of micellar aggregates above these temps for chromium palmitrate and chromium stearate, respectively. The apparent heat of solutions can be calculated from Van't Hoof reaction isochore expression $\dfrac{d \log_e S}{dT} = \dfrac{Q}{RT^2}$ where S is the solubility in moles per liter and Q is the heat of solution. Assuming that Q is independent of temp this expression yields, on integration, $\log_{10}S_2 - \log_{10}S_1 = \dfrac{Q(T_2 - T_1)}{2.303 \times 1.99 \times T_2 T_1}$

The average values of apparent heat of solution were obtained in chromium palmitate and chromium stearate (11.429, 31.79 Kcal/mol; 9.977, 1.035 Kcal/mol), respectively, above and below Krafft point.

The variations in viscosity with concns are almost similar with benzene, toluene, xylene and carbon tetrachloride as the solvent (typical curves shown in Fig. 2) but in the case of pyridine as the solvent a

TABLE II

Critical Micelle Concn of Chromium Stearate and Chromium Palmitate at Different Temp in Different Organic Solvents

| Solvent | Temp °C | CMC values of | |
|---|---|---|---|
| | | Cr(iii) stearate | Cr(iii) palmitate |
| | | $10^{-2}$ M/liter | $10^{-2}$ M/liter |
| Benzene | 30 | 0.90 | 0.70 |
| | 34 | 1.00 | 0.80 |
| Toluene | 30 | 1.60 | 1.10 |
| | 35 | 1.80 | 1.40 |
| Xylene | 30 | 1.08 | 0.865 |
| | 35 | 1.35 | 1.08 |
| Carbon tetra- | | | |
| chloride | 30 | 1.45 | 0.90 |
| | 35 | 1.50 | 1.00 |
| Pyridine | 30 | | |
| | 35 | | |

TABLE III

Concn Range Studied of Chromium Stearate and Chromium Palmitate in Different Organic Solvents

| Solvent | Concn of soap in g/liter | |
|---|---|---|
| | Chromium stearate | Chromium palmitate |
| Benzene | 1.0–20.0 | 0.8225–16.45 |
| Toluene | 2.0–20.0 | 1.6450–16.45 |
| Xylene | 3.3–33.3 | 2.700–27.431 |
| Carbon tetra- | | |
| chloride | 2.0–20.0 | 1.6450–16.45 |
| Pyridine | 4.0–40.0 | 3.2900–32.90 |

linear relationship is observed (Fig. 3a and 3b). Unlike the other solvent the influence of temp on the viscosity values is not marked in the case of chromium soaps and pyridine mixtures. From these results it may be concluded that CMC values can be determined from a variety of hydrocarbons but not with organic bases. The CMC values so determined are listed in Table 2.

With regard to the behaviour of chromium stearate and chromium palmitate in pyridine, it appears that colloid chemical factors do not seem to be operative here. On the other hand, complex formation between the two take place and it is due to this fact that an abrupt change corresponding to micelle formation is not observed. The lower viscosity values also lend support to this viewpoint.

In order to ensure that the viscosity variations are solely due to soap solutions and not simply to the presence of metallic content, viscosity experiments with chromium chloride and chromic nitrate solution were done under strictly identical conditions, employing 50% alcoholic solutions for different solvents (metal salts as such are insoluble in pure solvents). The nature of the curves in this case is quite different from those obtained from the soap solutions. This again confirms the colloid chemical behaviour of chromium soaps in organic media.

Another interesting fact emerges from the viscometric studies, viz., the possibility of the estimation of the metal soap by the viscometric method. The use of this method appears to have a distinct advantage over the polarographic and spectrophotometric methods reported earlier (4–7) insofar as estimations can be made both with highly dilute and concd solutions. In our previous methods we could only go to lower concn limit. The analytical data are summarized in Table III.

From the Table III it is evident that in pyridine and xylene the solubility of chromium soap is higher than in other solvents. These solvents should therefore, be more suitable for carrying out estimations in fairly concd solutions.

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