Studies on the Behaviour of Chromium (iii) Soaps. I. Spectrophotometry of Chromium Stearate and Palmitate in Nonaqueous Solutions

W. U. MALIK and S. I. AHMAD, Chemical Laboratories, University of Roorkee, Roorkee, India

Abstract

Studies on the spectrophotometry of chromium stearate and chromium palmitate in benzene, toluene, xylene, carbon tetrachloride and pyridine solvents provide evidence for the existence of complex ion formation. It has been found that this property can be applied successfully for the estimation of chromium in the concn range 1 to 11 mM/liter at 425 and 580 mμ. The method can be employed for the higher concn ($>$ 11 m M/liter) range also but the Beer-Lambert's law is applicable only at 425 mμ.

In our earlier communications we have demonstrated the utility of the polarographic (1–4) and spectrophotometric (5) methods in estimating the metal content of heavy metal soaps (6). Among the different metal soaps so studied, little attention was paid to the study of chromium soaps (6). Preliminary work on these soaps was recently taken up in this laboratory using o- and m-toluidine as solvents (7) where it was found that the behaviour of these soaps is markedly different from other metal soaps with regard to their solubility in organic solvents. They not only go readily into solution in pyridine but show marked solubility in different hydrocarbons. The present communication deals with our results on the spectrophotometry of *chromium* stearate and palmitate in benzene, toluene, xylene, carbon tetrachloride and pyridine.

Experimental

A. Material

Sodium Stearate and Palmitate. Stearic acid and palmitic acid (British Drug House) were recrystallized by alcohol and distilled at 226–228C/10 mm Hg and 182–186C/10 mm Hg, respectively. Stearic acid (142.23 g/liter) and palmitic acid (128.2 g/liter) were dissolved in alcohol with sodium hydroxide (20 g/liter). Refluxing on a water bath for 10–12 hr, sodium stearate and sodium palmitate were obtained. These soaps were further recrystallized with alcohol. Sodium stearate: mp 139C; sodium palmitate: mp 190C.

Chromium Stearate. This was prepared by direct metathesis at 50–55C from the corresponding sodium soap (1.5% 500 ml) and chrome alum (1.0% 500 ml) A.R. The soap precipitated was washed with distilled water and then with ethanol to remove free precipitant and acid respectively. This soap was dried in vacuum. Soap obtained was of grey colour with mp 165C. The chromium content in the soap was found by chemical analysis converting chromium into the dichromate and titrating it iodometrically. The result of elementary analysis was as follows:

TABLE I[a]

Solvent	Chromium stearate	Chromium palmitate	Colour
Benzene			
Cold	S	S	Violet
Hot	H.S.	H.S.	Violet
Toluene			
Cold	s	S	Violet
Hot	S	H.S.	Violet
n-Hexane			
Cold	s	S	Violet
Hot	S	H.S.	Violet
Petroleum ether			
Cold	s	s	Violet
Hot	S	H.S.	Violet
Paraffin (liquid)			
Cold	I	I	
Hot	s	S	Violet
Carbontetrachloride			
Cold	s	S	Violet
Hot	S	H.S.	Violet
Chloroform			
Cold	S	S	Violet
Hot	H.S.	H.S.	Violet
Carbon disulfide			
Cold	S	S	Violet
Hot	H.S.	H.S.	Violet
Methyl alcohol			
Cold	I	I	
Hot	I	s	Violet
Isopropyl alcohol			
Cold	I	I	
Hot	s	s	Violet
Iso-butyl-alcohol			
Cold	s	S	Violet
Hot	S	H.S.	Violet
n-Amyl alcohol			
Cold	s	s	Violet
Hot	S	S	Violet
Ether			
Cold	I	s	Violet
Hot	s	S	Violet
Ethyl methyl ketone			
Cold	I	I	
Hot	s	s	Violet
Ethyl acetoacetate			
Cold	I	I	
Hot	I	I	
Turpentine oil			
Cold	s	S	Violet
Hot	S	H.S.	Violet
O-, m-toluidine			
Cold	I	I	
Hot	S	S	Red with violet tinge
Pyridine			
Cold	S	S	Violet
Hot	H.S.	H.S.	Violet
Piperidine			
Cold	s	s	Violet
Hot	S	S	Violet

[a] s=Slightly soluble.
H.S.=Highly soluble.
S=Soluble.
I=Insoluble.

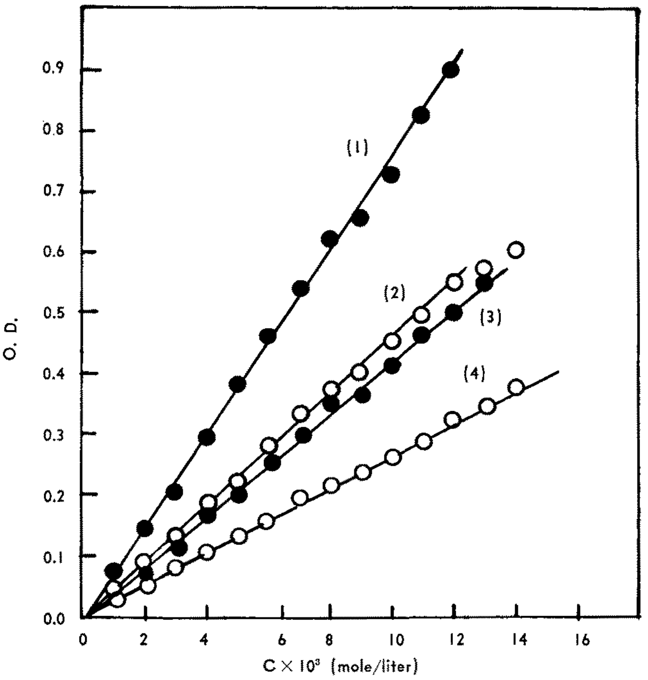

FIG. 1. The variation of O.D. with concn of the benzene solution of chromium stearate (○) and chromium palmitate (●) at 425 mμ (3,4) and 580 mμ (1,2), respectively.

Calculated as $Cr(C_{17}H_{35}COO)_3$ Cr, 5.76%. Found: Cr, 5.23%.

Chromium Palmitate. This could be prepared by metathesis at 45–46C from corresponding sodium soap (1.5% 500 ml) and chrome alum (1.0% 500 ml). The soap precipitated was washed with water and alcohol to remove precipitant and acid, respectively. The soap obtained was of grey colour with mp 120C. The metal content was found iodometrically. The result of elementary analysis was as follows:

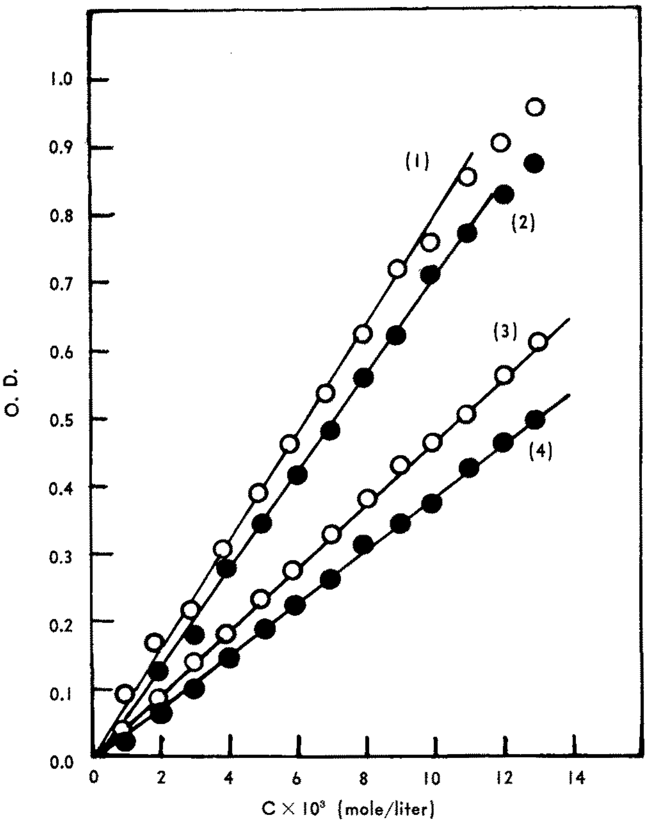

FIG. 2. The variation of O.D. with concn of toluene solution of chromium stearate (○) and chromium palmitate (●) at 425 mμ (3,4) and 580 mμ (1,2), respectively.

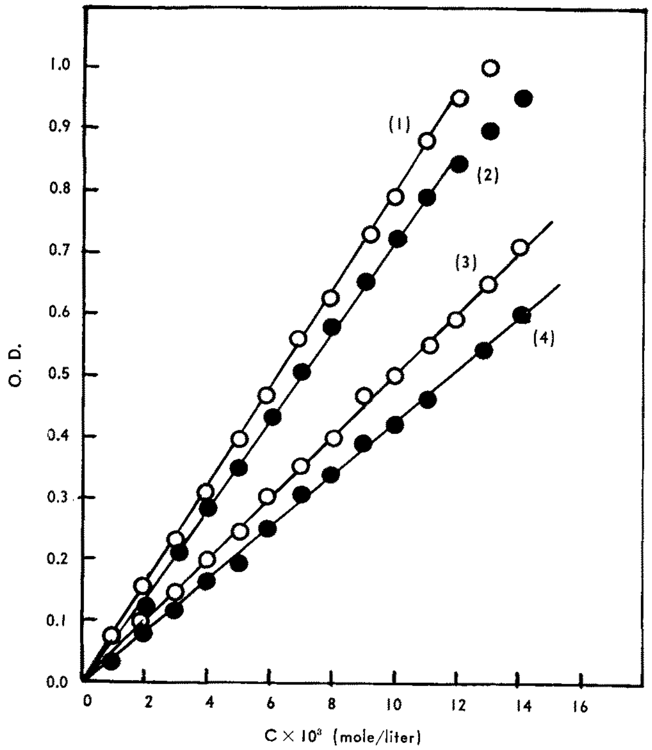

FIG. 3. The variation of O. D. with concn of xylene solution of chromium stearate (○) and chromium palmitate (●) at 425 mμ (3,4) and 580 mμ (1,2), respectively.

Calculated as $Cr(C_{15}H_{31}COO)_3$ Cr, 6.35%. Found: Cr, 6.32%.

Solubility. The solubility of the chromium soaps in different solvents was seen after shaking small portions of the finely powdered salt with a few milliliters of the solvent. After standing for several hours, a portion of the liquid was evaporated on a watch glass. The solubility in hot solvent was seen by warming the mixture on a water bath for about an hour. The results are given in Table I.

B. Apparatus

A Bausch & Lomb "Spectronic 20" was employed for absorption measurements. A red filter was used for carrying out experiments in the longer wavelength regions (650–975 mμ).

TABLE II
Absorption Maxima of Chromium Stearate and Palmitate in Organic Solvents

Medium	Max. with Cr.(iii)-stearate	Remark	Max. with Cr.(iii)-palmitate	Remark
Benzene	425 & 580mμ	Well-defined max	425 & 580 mμ	Well-defined max
Toluene	425 & 580mμ	Well-defined max	425 & 580 mμ	Well-defined max
Xylene	425 & 580mμ	Well-defined max	425 & 580 mμ	Well-defined max
Carbon tetrachloride	425 & 580mμ	Well-defined max	425 & 580 mμ	Well-defined max
Pyridine	425 & 580mμ	Well-defined max	425 & 580 mμ	Well-defined max

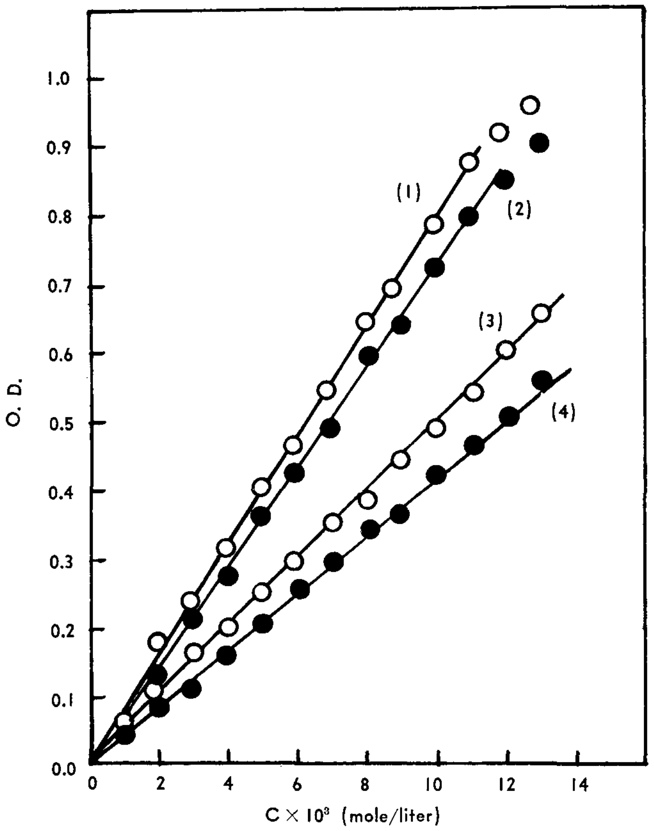

Fig. 4. The variation of O.D. with concn of carbon tetrachloride solution of chromium stearate (○) and chromium palmitate (●) at 425 mμ (3,4) and 580 mμ (1,2), respectively.

Results and Discussion

Koening (8) has shown that chromium stearate and palmitate are insoluble in cold benzene, toluene, xylene, carbon tetrachloride, chloroform and ether. From Table I it is evident that chromium stearate and palmitate are soluble in most of the solvents provided they are warmed for some time. Under this condition solutions of concn up to 2% are readily obtained. The hot solutions of stearate and palmitate of chromium after cooling or on evaporation separate out as a sticky amorphous masses which change to glossy solids after some time.

The results of absorption max for chromium stearate and chromium palmitate in different organic solvents are given in Table II.

On plotting a graph between O.D. (where max occurs) and molar concns of metal soaps at the two wavelengths, a linear relationship was found to exist proving the validity of Beer-Lambert's law over a wide concn range (Fig. 1–5; typical results for xylene are found in Table III). From Table III and also from Figures (1–5), it is evident that the estimation can be carried out at both wavelengths, 425 mμ and 580 mμ, in the low concn range (1–11 mM/liter) but the law is not strickly followed in the higher concn (> 11 mM/liter) at 580 mμ. However, this is possible at the other wavelength, viz., 425 mμ. In Table IV the concn ranges suitable for estimations in different solvents are summarized.

TABLE III

Absorption Values of Chromium Stearate and Palmitate in Xylene at 425 mμ and 580 mμ

Concn (C x m M/liter)	425 mμ		580 mμ	
	Cr(iii)-stearate	Cr(iii)-palmitate	Cr(iii)-stearate	Cr(iii)-palmitate
1	0.05	0.03	0.13	0.06
2	0.09	0.08	0.15	0.12
3	0.13	0.11	0.22	0.20
4	0.19	0.16	0.30	0.28
5	0.24	0.19	0.39	0.35
6	0.30	0.24	0.46	0.43
7	0.35	0.30	0.55	0.50
8	0.39	0.33	0.61	0.58
9	0.47	0.39	0.72	0.65
10	0.50	0.42	0.79	0.72
11	0.55	0.46	0.88	0.79
12	0.58	0.50	0.97	0.85
13	0.65	0.53	1.04	0.95
14	0.71	0.60	1.10	1.07

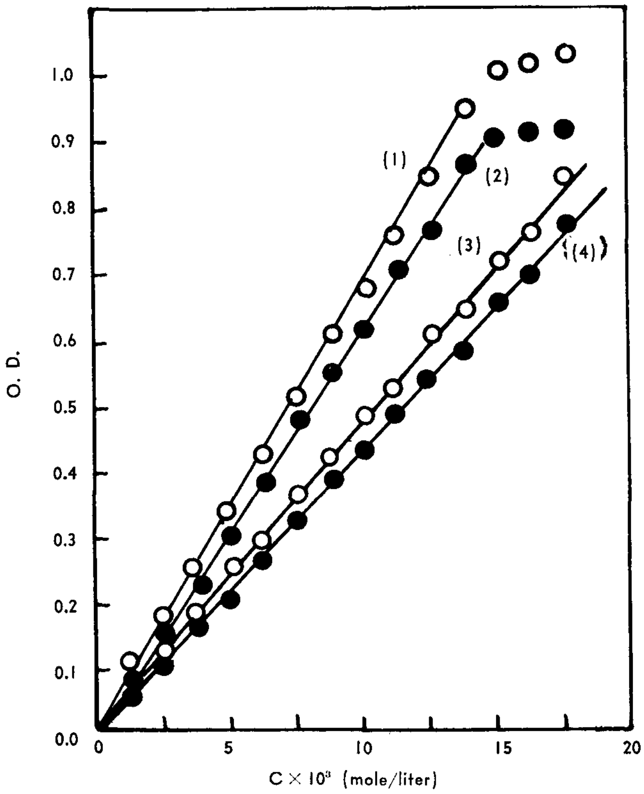

Fig. 5. The variation of O.D. with concn of pyridine solution of chromium stearate (○) and chromium palmitate (●) at 425 mμ (3,4) and 580 mμ (1,2), respectively.

The method of chemical analysis (9–11) in the case of chromium soaps fails to give good and reliable results with respect to spectrophotometric method when content in the soaps is sufficiently low. It is only in the concd solution that some concordance in data of chemical analysis and spectrophotometric is realised.

In order to ensure that the maxima existed due to chromium soap complex with different organic solvents and not because of the formation of metal-solvent complex, absorption studies were made with

TABLE IV

Concn Range for Chromium Content in Cr(iii)Stearate and Palmitate

Solvent	Concn range of the metal ion g/liter
Benzene	0.0717 — 0.7170[a] 0.0725 — 0.7250[b]
Toluene	0.0465 — 0.4650[a] 0.0674 — 0.6740[b]
Xylene	0.0717 — 0.7170[a] 0.0725 — 0.7250[b]
Carbon tetrachloride	0.0465 — 0.4650[a] 0.0674 — 0.6740[b]
Pyridine	0.0818 — 0.8180[a] 0.0906 — 0.9060[b]

[a] Chromium stearate. [b] Chromium palmitate.

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 mμ 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 mμ and 630 mμ, respectively, instead of 425 and 580 mμ.

TABLE V

Solvent	Soap	Reqd. g	Chemical analysis		Spectrophotometric 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 tetrachloride	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

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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

W. U. MALIK and S. I. AHMAD, Chemical Laboratories, University of Roorkee, Roorkee, India

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