Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. VII. Effects of Solvents on Cobalt Soaps. Solubilities and Color Changes of Cobalt Soaps in Solvents, and Adsorption of Water Vapor on Cobalt Soaps

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(Received March 29, 1961)

Cobalt stearates with red and blue colors have been prepared and investigated in the previous papers[1]. Cobalt soaps do not readily dissolve in common solvents when cold, as has been stated in Part V. Boner[2] dissolved cobalt stearate in hot paraffinic oils and observed gelatinization after cooling. He described how cobalt stearate, dissolved in pyridine, made a red complex with the pyridine which decomposed in air on being heated. Lawrence[3] used this complex as a means of the purification of cobalt soaps. Koenig[4] described how cobalt stearate showed solubilities over 1% in chloroform, carbon tetrachloride, liquid paraffin, *n*-heptane, benzene, toluene, amyl alcohol and pyridine, and of about 0.01% in ethyl ether and carbon disulfide. It was stated to be insoluble in methanol, acetone and ethyl acetate.

In preliminary observation, some typical solubility characteristics were observed. Cobalt soaps did not dissolve in water. Because water did not wet them, they floated on its surface. Ethanol did wet them, but they did not show any solubility in it, even if it was hot. If cobalt soaps were immersed in cold ethanol for a long time, they changed purple, as stated in Part III. In benzene, cobalt soaps did not dissolve at room temperatures, but in hot benzene, a blue solution was obtained which appeared silky when it was stirred. A purple jelly was obtained after cooling. In hot toluene, cobalt soaps dissolved considerably, but the colors of the solutions changed to a dirty yellow.

In the present paper, the solubility characteristics and color changes of cobalt soaps in various solvents will be observed. Additionally, the adsorption of water vapor on cobalt soaps will be measured.

Experimental

Materials.—The same cobalt stearates were used as in previous papers[1]. Solvents (cf. Table I) were chemically pure reagents. They were used without special purifications.

Observations on Solubilities and Color Changes.—An amount (usually 10 mg.) of cobalt soap was sealed and shaken with various solvents (usually 5 ml.) in glass tubes. The changes in appearance and color were observed at cold temperatures. Then the solutions were heated in an air bath at 90~100°C for 3~4 hr. and cooled again. They were observed occasionally during these processes.

Adsorption of Water Vapor.—The same quartz spring balance was used as in determining the amount of hydrate water in Part II. The relative humidity (RH) in the atmosphere of the sample was controlled by aqueous solutions of sulfuric acid. Measurements of the amount of adsorbed water, x(g.), were carried out at room temperatures at about 25 and 30°C. The saturated vapor pressure, p_s, was obtained from International Critical Tables. The weight of the sample, m(g.), was 40~100 mg. Specific adsorption, x/m, was calculated and plotted against relative humidity to get an adsorption isotherm.

Results and Discussion

Solubilities.—The solubility characteristics of red dihydrate and blue anhydrate of cobalt stearate were almost identical. Although, in a cold solution, the red soap swelled and suspended more easily in many solvents than blue soap, at higher temperatures the difference of color did not significantly affect the appearance of the soaps. The results of observations on the changes in appearance of red cobalt soaps were tabulated in Table I. Much the same data were obtained for blue soap. The differences in characteristics between these tables were so minor that the latter table was eliminated.

There were several solvents in which cobalt soaps showed considerable solubilities. Among the solvents investigated, pyridine and bromoform were the most effective solvents for cobalt soaps, followed by benzyl alcohol, nitrobenzene, chlorobenzene and aniline.

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1) H. Kambe, This Bulletin, **34**, 1786, 1790, 1794 (1961); **35**, 78 (1962); H. Kambe and I. Mita, ibid., **34**, 1797 (1961); H. Kambe, T. Ozawa, M. Onoue and S. Igarashi, ibid., **35**, 81 (1962).

2) C. J. Boner, *Ind. End. Chem.*, **29**, 56 (1937).

3) A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 669 (1938).

4) A. E. Koenig, *J. Am. Chem. Soc.*, **36**, 951 (1914).

TABLE I. SOLUBILITY CHARACTERISTICS OF RED COBALT STEARATE DIHYDRATE IN VARIOUS SOLVENTS*
(10 mg. soap/5 ml. solvent)

Solvent	At room temp.	At 90°C	After cooling
Water	insol. float.	insol. melting	insol. float.
Methanol	insol. cloudy dispers. pink ppt.	sol. yellow soln.	colorless soln. pale pink ppt.
Ethanol	alm. insol. cloudy dispers. purple ppt.	sl. insol. gray susp.	colorless soln. violet ppt.
Butanol	insol. cloudy dispers. purple ppt.	sol. yellow soln.	
Benzyl alcohol	insol. brown ppt.	sol. pink soln.	brown soln. violet ppt.
Phenol	insol. float. dispers.	sol. brown soln.	
Ethylene glycol	alm. insol. float. indispers.	alm. insol. pink soln. ppt.	cloudy dispers.
Diethylene glycol	alm. insol. float. indispers.	insol. pink soln. ppt.	cloudy dispers.
Dioxane	alm. insol. cloudy dispers. red ppt.	sol. yellow soln.	brown soln. black ppt.
Methyl Cellosolve	alm. insol. dispers.	sol. yellow soln.	brown ppt.
Chloroform	insol. float. dispers.	sol. light blue soln.	pink susp.
Bromoform	alm. sol. brown soln.	sol. green soln.	yellow soln.
Carbon tetrachloride	insol. float. dispers.	sol. colorless soln.	colorless jelly
1, 2-Dichloro-ethane	alm. insol. dispers. brown ppt.	alm. sol. brown soln.	brown soln.
Trichloroethylene	alm. insol.	alm. sol.	pink jelly
Acetone	alm. insol. dispers. purple ppt.	insol. white susp.	colorless soln. pink ppt.
Ethyl methyl ketone	insol.	sol. brown soln	yellow soln. ppt.
Isoamyl acetate	alm. insol.	sl. insol. cloudy pink ppt.	red ppt.
n-Butyl acetate	insol.	sol. pink soln.	brown susp.
Ethyl ether	insol.		colorless soln. dark red ppt.
Benzene	insol. dispers. purple ppt.	sol. purple soln.	pink jelly
Toluene	insol. dispers. purple ppt.	sol. dark blue soln.	
p-Xylene	sl. insol. cloudy red ppt.		green soln. black ppt.
Chlorobenzene	sl. insol. dispers.	sol. blue soln.	
Nitrobenzene	sl. insol. dispers.	sl. insol. dark red soln.	
Aniline	sl. insol. float.	sol. yellow susp.	dark red ppt.
Pyridine	alm. sol. pink soln.	sol. violet soln.	yellow soln.
Cyclohexane	insol. purple ppt.		red jelly cloudy
n-Heptane	insol. cloudy purple ppt.		brown jelly cloudy

* sol.: soluble; insol.: insoluble; alm.: almost; sl.: slightly; ppt.: precipitate; soln.: solution; susp.: suspension; dispers.: dispersible; indispers.: indispersible; float.: floating.

Water showed absolutely no influences on cobalt soaps. Acetone was also a relatively indifferent solvent to them. In a hot state, halogen compounds and aromatic hydrocarbons were fairly good solvents for cobalt soaps. Glycols were poor.

When hot solutions in some comparatively good solvents were cooled, jellies were obtained. These solvents were carbon tetrachloride, trichloroethylene, benzene, toluene and chlorobenzene. Sometimes solutions became a dirty yellow or brown in which dark precipitates appeared.

As cobalt soaps did not readily dissolve in common solvents, it was difficult to get a single crystal from these solvents, as has been stated in Part V.

Color Change.—Several types of color change were observed. (i) No change of color was observed in water or in acetone. (ii) The color of red soap turned blue or gained a tinge of blue in ethanol, and violet in benzene. The color of blue soap in these solvents approaches to the color of changed red soap. (iii) The color of blue soap turned pale pink in methanol, and red in pyridine. Red soap also approached these colors in them. (iv) The color changed to a dirty yellow, brown, or green in *n*-butanol, toluene, *p*-xylene, *n*-heptane, dioxane (at first, red), cyclohexane (at first, blue), and in ethyl ether. The absorption spectra of solutions of cobalt stearates in dioxane and in xylene are shown in Fig. 1. Absorption maxima appeared

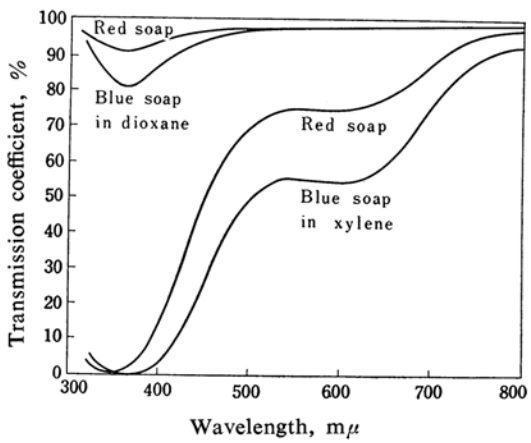

Fig. 1. Absorption spectra of cobalt stearate solutions in xylene and in dioxane.

at 360 mμ. In these systems, the addition of water did not recover soaps of the original color. It is suggested that some change in the electronic configuration of cobalt ion occurred in these solutions. (v) The solution gelatinized after cooling. Purple jelly was obtained in benzene, but dirty yellow or brown jellies grew in toluene, *n*-hexane, *p*-xylene and cyclohexane. These jellies were thixotropic and syneretic and gradually recovered their fluidities for a long time. (vi) In hot pyridine, cobalt stearates dissolved easily, but they soon turned red. Red crystals precipitated on cooling. These were complexes of cobalt soaps with pyridine[2].

In aqueous ethanol the color of blue cobalt soap gradually turned red. The effects of the addition of electrolytes to these systems were examined. Suspensions of red and blue cobalt stearate in mixtures of ethanol with water in 80, 50 and 40 wt.%, with the addition of potassium chloride, potassium nitrate, cobalt chloride and cobalt nitrate, were shaken with a machine at room temperatures. Cobalt stearates in all systems turned completely red after two or three days. Some bluish tint remained in red soaps in systems to which potassium salts had been added without regard to concentrations of ethanol. In other systems red soap did not change its color. In absolute ethanol, red and blue soaps became pale purple in systems with potassium salts, but with cobalt salts the color turned violet.

In benzene, hot solutions of cobalt soaps gelatinized after cooling. Red or blue cobalt soap was sealed in glass tubes with benzene, at various concentrations of 0.05～5.00 wt.%. When they were heated at 100°C for one hour, pale blue solutions were obtained in which some gelatinized mass floated. After subsequent cooling, they gelatinized soon. These processes were repeated three or four times. The appearances of jellies were observed. Below concentration of 0.12 wt.%, the jelly showed a considerable fluidity at 20°C, but above this concentration the system solidified as purple jelly. Red soap in benzene systems with concentrations above 0.28% were heterogeneous and turbid. Blue soap systems were clear and transparent.

When ethanol was added to benzene, the gelatinization was much suppressed. When various amounts of ethanol above 2 vol.% were added, solutions of cobalt stearates in benzene, with a concentration of 0.3%, did not solidify. Purple flocculates grew within the solution. Long after, the color of soap remained a reddish violet in pure benzene, but in other systems soap turned blue completely.

In pyridine red and blue soap dissolved above 10% and reddish violet solutions were obtained. Red crystals of complex precipitated from the solution.

Adsorption of Water Vapor.—The amounts of water adsorbed on red and blue cobalt stearates are shown in Table II and in Fig. 2. Red soap adsorbed much more water than blue soap, but the difference of temperature at

TABLE II. ADSORPTION OF WATER VAPOR ON COBALT STEARATES

Red soap, at 30°C
m=42.3 mg. p_s=31.8 mmHg

RH p/p_s %	Adsorbed amount x mg.	Specific adsorption x/m %
86	1.1	2.6
74	0.5	1.2
63	1.1	2.6
49	0.8	1.9
40	0.5	1.2
29	0.5	1.2
14	0.3	0.7
8	0.1	0.2

Blue soap, at 25°C
m=94.7 mg. p_s=23.8 mmHg

RH p/p_s %	Adsorbed amount x mg.	Specific adsorption x/m %
91	0.9	0.95
77	—	—
59.5	0.4	0.42
37.5	0.1	0.1
16.5	0.1	0.1
2.5	—	—

measurement must also be considered. The forms of the adsorption isotherm are apparently different from each other. The mechanisms of adsorption seem also to be different. Since the accuracy of measurement is insufficient, however, particularly in blue soap, the significance of these results must be minimized.

Summary

The effects of various solvents on cobalt soaps were investigated. The solubility of cobalt soap was low in general. In pyridine and bromoform, it showed a considerable value. In a hot state, several solvents dissolved cobalt soaps fairly well. In some solvents, jellies were obtained on cooling. In other solvents, the color changed to a dirty yellow. Absorption spectra showed that the absorption maxima in these solutions were displaced for a shorter wavelength. This means that a change of the electronic configuration occurred.

Adsorption of water vapor on cobalt soaps was measured. Red dihydrate seemed to adsorb much more water vapor than blue anhydrate.

The author expresses his gratitude to Professor Bunnosuke Yamaguchi for his advice throughout this work, and to Mr. Itaru Mita for his help in the measurement of solubility.

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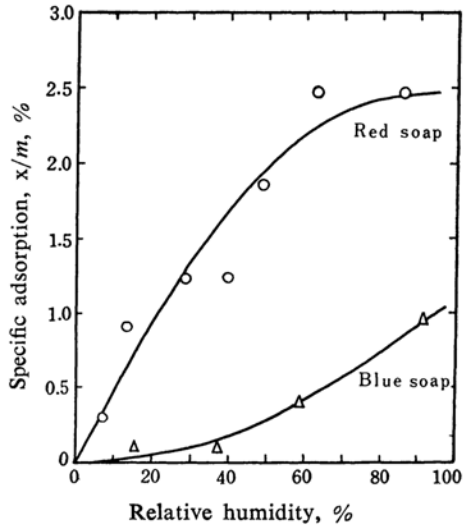

Fig. 2. Adsorption isotherms of water on cobalt stearates.