The Solubility of Heavy Metal Soaps In Co-Solvent Mixtures of Chloroform and Propylene Glycol

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VERY meager data exist for the solubility of metallic soaps (1,2,3). The problem is to dissolve a soap consisting of a polar end and a hydrocarbon body. This can be done by using a solvent which dissolves one part of the molecule so strongly that the rest follows, as in an aqueous solution of sodium soap. Another method is to use a solvent whose groups include one capable of dissolving one part of the molecule and another capable of dissolving the other. A third method is that of co-solvency (4). Two co-solvents are chosen such that the first can dissolve one part of the molecule and the second the other part. The solvents capable of dissolving the polar end are typified by the glycols, and the body of the soap then requires a solvent for hydrocarbons. These two co-solvents are referred to as G and H, respectively. In the present study the G-H co-solvent mixture used is propylene glycol (G) and chloroform (H). It is found (5) that not only do such G-H mixtures dissolve soaps freely even when the soaps are practically insoluble in either co-solvent alone, but that the co-solvents themselves are frequently made miscible in all proportions if sufficient soap is present. Ethylene glycol and chloroform are made miscible in all proportions by sodium soaps but the blending power of the metallic soaps is generally insufficient to make them completely miscible.

The purpose of the present paper is to study such co-solvency with metallic soaps of magnesium, calcium, barium, zinc, and lead and to compare their behavior with sodium soaps. All these are of importance in such industries as the manufacture of lacquers and of lubricating greases.

Experimental

Eastman Kodak Company propylene glycol was fractionated and the portion boiling between 186.5 and 187.0° C. was used. Chloroform, U. S. P., was washed six times with water to remove alcohol and acid, dried with Drierite ($CaSO_4$), and fractionated through a 1-foot Vigreux column.

The metallic soaps were prepared by double decomposition between sodium or potassium soaps and an excess of the pure chloride of the metal (acetate in the case of lead) near 40° C. in a high-speed mixer. The precipitated soap, about 25 gms. in each run, was washed with warm water until completely free from chloride (ten washings each with 2 to 2.5 liters of water). The soap was then dried overnight at 75° C. to get rid of practically all of the water, powdered, and then dried at 105° C. for 3 hours. A snow-white product in a very fluffy and finely divided state was obtained by this procedure in all cases except with lead laurate and myristate, which melted somewhat in the final treatment.

These soaps were not absolutely pure but showed on analysis a metal content usually to within 1-3% of the theoretical value. Some typical values are: calcium laurate: calcium 9.04% (theory, 9.09); calcium myristate: calcium 7.97% (theory, 8.07); barium laurate and myristate: barium 25.2% and 22.9%, respectively (theory, 25.6 and 23.2); magnesium laurate, myristate, and palmitate: magnesium 5.57%, 4.97%, and 4.42%, respectively (theory, 5.72, 5.05, and 4.53); zinc laurate: zinc 13.94% (theory 14.03); lead laurate and lead myristate: lead 35.08 and 31.83%, respectively (theory, 34.09 and 31.20). The free fatty acid content was analyzed for a few soaps by acetone extraction and the values were about 0.2% by weight.

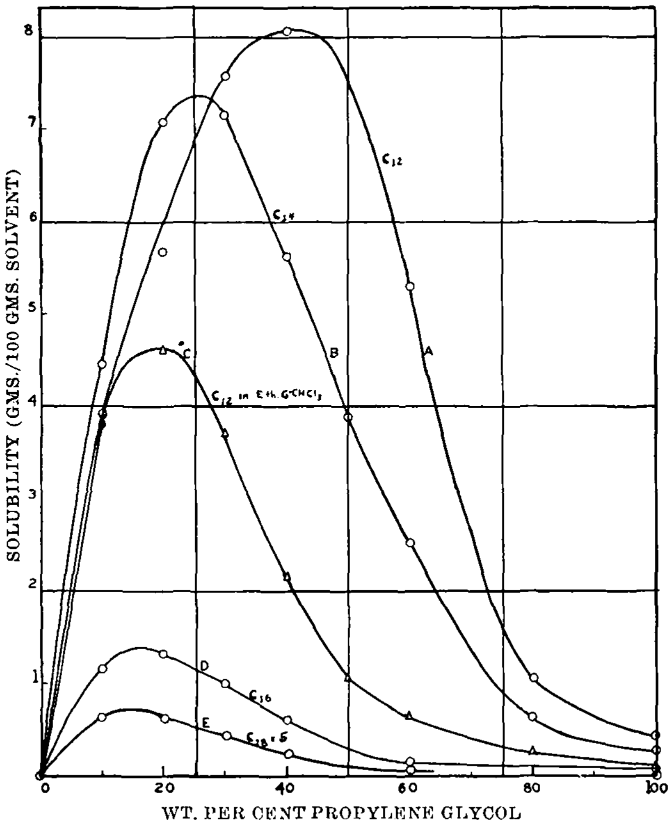

FIG. 1. Co-solvency curves for calcium soaps in propylene glycol-chloroform mixture, 25°C.; A, calcium laurate; B, calcium myristate; D, calcium palmitate; E, calcium stearate (ordinates five-fold magnified); C, calcium laurate in diethylene glycol-chloroform mixture.

The procedure for solubility determination was as follows: Twenty grams of the solvent mixture (10 gms. if the solubility exceeded 15%) and a slight excess of soap were delivered from a 10 cc. buret, calibrated against the weight of the solvent delivered, into 1-oz. Bakelite-top, screw-cap bottles. The bottles were shaken vigorously for 8 hours in a mechanical shaker in an air thermostat maintained between 27 and 28° C. The solutions after thermostating at 25° C. ± 0.05, for a minimum of 12 hours were filtered through coarse filters in an air thermostat at 25 to 25.5° C., taking care to reduce any loss of solvent by evaporation to a minimum. Solutions which were

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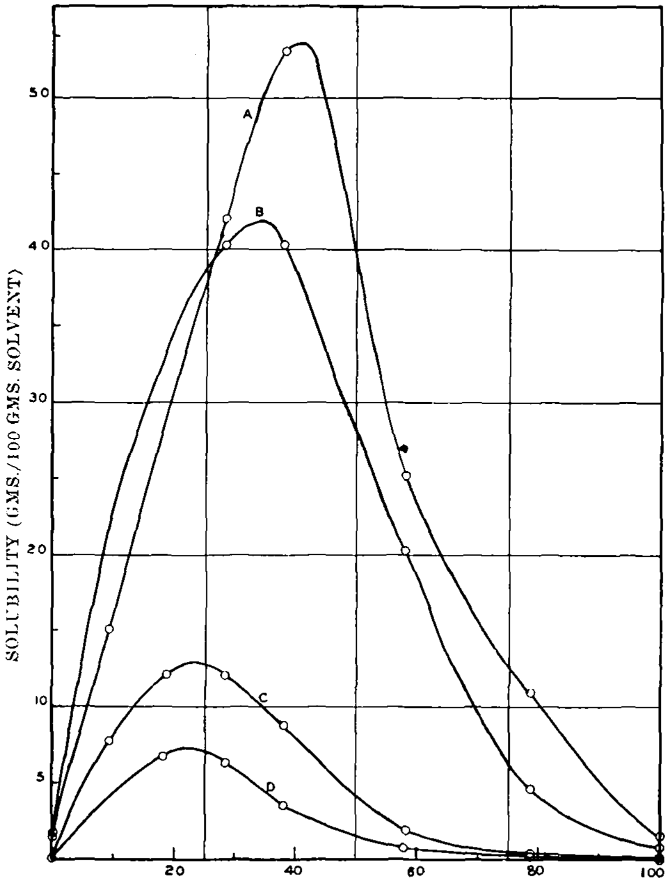

FIG. 2. Co-solvency curves for magnesium soaps in propylene glycol-chloroform mixture, 25°C.; A, laurate; B, myristate; C, palmitate; D, stearate.

very viscous, e.g., magnesium soaps and some calcium soaps, were filtered in small fritted glass Buchner filters under air pressure of 25 pounds. The filtrates, after diluting with propylene glycol-chloroform mixture in case the solution was too concentrated, were analyzed.

The analysis was done by direct titration with standard perchloric acid (0.2 N) in propylene glycol-isopropyl alcohol mixture. The suitability of this method for titrating sodium soaps has already been established (6). The indicator used in the direct titration method was thymol blue instead of the usual methyl red, which was found to show a very sharp color change from yellow to red at the endpoint. Its use was checked by a few potentiometric titrations in G-H solvents by the procedure described elsewhere (7) and it was found to correspond to the true endpoint. As a further check two barium soaps were analyzed by this direct titration method and by the gravimetric method, and the results agreed very well. The values obtained for a sample of barium laurate are 22.89 and 22.96% barium, and for a sample of barium myristate, 25.20 and 25.33% barium, respectively, by the two methods.

Results and Discussion

Table I presents the data for the solubility of saturated soaps of calcium, magnesium, barium, zinc, lead, and sodium in mixtures of propylene glycol and chloroform at 25° C., and it also includes the data for calcium laurate in mixtures of diethylene glycol and chloroform. These data are plotted in Figures 1-5.

In all cases the soaps are dissolved by the mixture even when they are insoluble, or nearly so, in the chloroform and glycol separately. For example, calcium laurate is insoluble in chloroform and only 0.4% soluble in glycol, but its solubility reaches 8% in the mixture. Magnesium laurate is soluble to only 1½% in the separate solvents but in the mixture

TABLE I.

Solubility of Soaps of Calcium, Magnesium, Barium, Zinc, Lead, and Sodium in Propylene Glycol-Chloroform, at 25°C.

	Solubility = gms. soap/100 gms. solvent							
	Per cent glycol in the solvent mixture							
	0	*10*	*20*	*30*	*40*	*60*	*80*	*100*
Calcium laurate	0.00	3.92	5.67	7.58	8.07	4.96	1.06	0.43
Calcium myristate	0.00	4.46	7.08	7.16	5.63	2.52	0.63	0.27
					3.88**			
Calcium palmitate	0.00	1.16	1.31	1.00	0.60	0.15	......	0.07
		1.33*						
Calcium stearate	0.00	0.126	0.124	0.088	0.050	0.015	......	0.00
Calcium laurate (in diethylene glycol-chloroform)	0.00	3.82	4.60	3.70	2.14	0.64	0.25	0.12
					1.06**			
	Per cent glycol in the solvent mixture							
	0	9.3	18.8	28.4	38.1	58.1	78.7	100
Magnesium laurate	1.43	15.05	......	42.04	53.47	25.19	10.97	1.5
Magnesium myristate	1.73	......	......	40.31	40.69	20.64	4.58	0.59
Magnesium palmitate	0.00	7.75	12.04	12.07	8.80	1.89	0.36	0.09
Magnesium stearate	0.00	6.02	6.65	6.31	3.52	0.69	0.12	0.03
Barium laurate	0.00	3.47	5.42	6.60	6.28	2.75	1.20	0.47
Barium myristate	0.00	1.63	2.13	2.06	1.81	0.81	0.35	0.21
Zinc laurate	0.06	0.729	0.721	0.568	0.395	0.149	0.043	0.02
Zinc stearate	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Lead laurate	1.23	7.40	9.24	8.75	5.57	1.79	0.61	0.32
Lead myristate	0.26	1.86	2.17	1.90	1.00	0.32	0.11	0.07
Lead stearate	0.08	0.20	0.12	0.11	0.07	0.04	0.02	0.01
Sodium laurate	0.00	......	7.15	......	12.21	14.34	13.21	12.19
Sodium myristate	0.00	......	5.18	......	8.21	8.44	6.41	4.94
Sodium palmitate	0.00	......	3.95	......	5.61	4.77	2.90	1.89
Sodium stearate	0.00	......	2.65	......	3.52	2.50	1.30	0.92

* 15% propylene glycol.
** 45% propylene glycol.

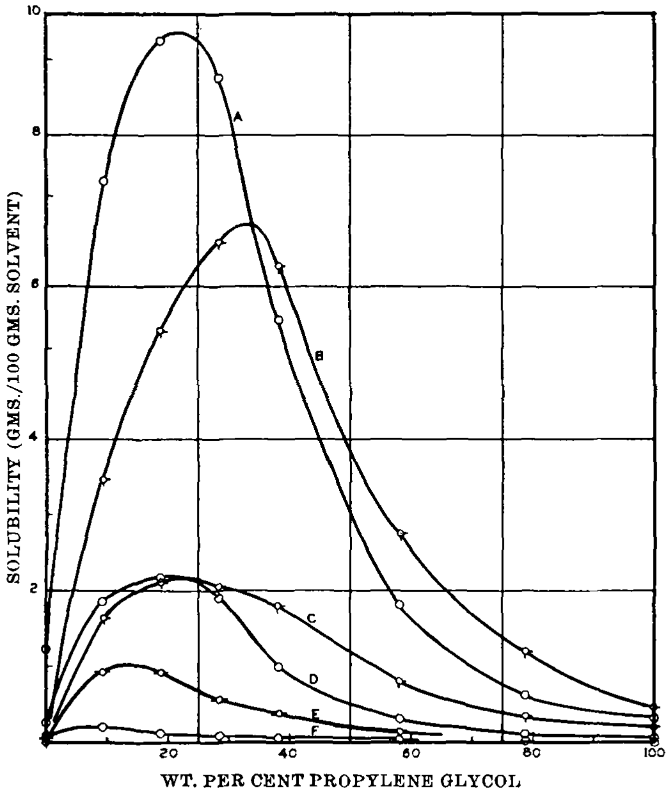

FIG. 3. Co-solvency curves for metallic soaps of lead, barium and zinc in propylene glycol-chloroform mixture, 25°C.; A, lead laurate; B, barium laurate; C, barium myristate; D, lead myristate; E, zinc laurate; F, lead stearate.

attains a solubility of 54%. The magnesium soaps are the most soluble, followed at much lower values by the sodium, lead, calcium, barium, and zinc soaps.

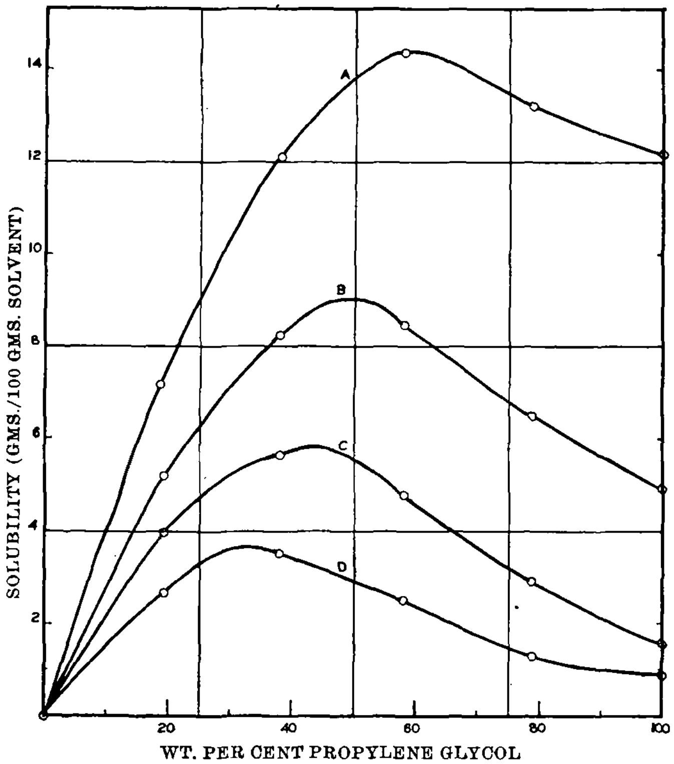

FIG. 4. Co-solvency curves for sodium soaps in propylene glycol-chloroform mixture, 25°C.; A, laurate; B, myristate; C, palmitate; D, stearate.

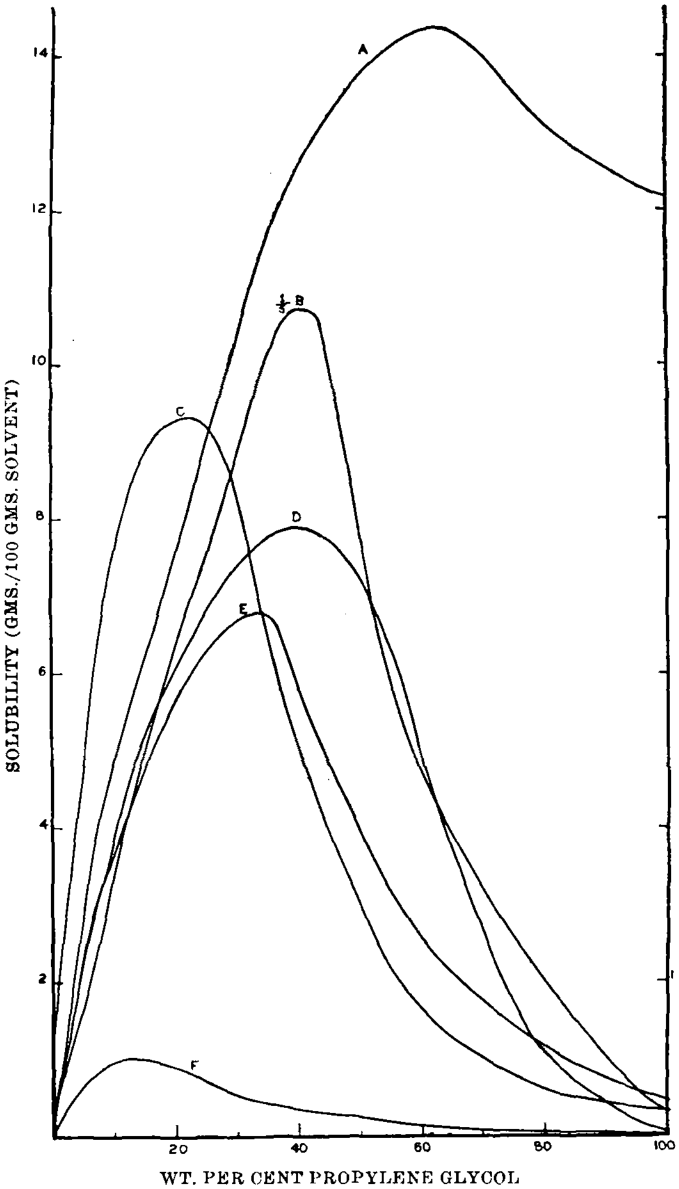

FIG. 5. Co-solvency curves for laurates of different metals in propylene glycol-chloroform mixture, 25°C.; A, sodium; B, magnesium (the solubility values have been divided by five to accommodate the curve within the scale of the figure); C, lead; D, calcium; E, barium; F, zinc.

In all cases the laurate is the most soluble and the stearate least. Indeed zinc stearate is practically insoluble throughout.

The H of the G-H mixture is the hydrocarbon solvent. The higher the molecular weight of the soap itself, the greater the proportion of hydrocarbon therein and the more it needs H co-solvent. In accordance with this the optimum proportion of G-H mixture for stearate contains more chloroform than the optimum for laurate, with the intermediate homologs in between.

Probably for a similar reason the myristate is more soluble than laurate in the chloroform-rich mixtures.

Diethylene glycol is not as good a co-solvent as propylene glycol, as is shown by the solubility of calcium laurate being much less and the optimum lying much further toward the chloroform side.

Heavy metal soaps tend to dissolve in many organic solvents, whereas sodium soaps are soluble in water (at sufficiently high temperatures). The sodium soaps are much more soluble in the glycol than the corresponding metal soaps. In the co-solvent mixtures, the optimum for the sodium soaps is towards the middle of the diagram, whereas for all the heavy metal soaps it lies well towards the chloroform side. The position of the optimum composition of co-solvent mixtures lies increasingly towards the side of chloroform as one passes from sodium to magnesium, calcium, barium, and lead, which is in accordance with increasing atomic weight. However, for zinc, with far lower atomic weight than the latter two, the optimum is still further towards chloroform. As far as actual solubility is concerned this decreases with increasing atomic weight, if the high solubility for lead and the extremely low solubility for zinc soaps are taken as exceptions. However, the solubility of lead laurate is less than that of all the other soaps except zinc if the glycol present exceeds 35%. The authors consider that such behavior can throw light upon the nature of the polarity of the valency bonds and the molecular structure of the soaps.

The heavy metal soaps show co-solvency in mixtures of benzene and alcohol, especially at higher temperatures, and more particularly magnesium and aluminum soaps. A stiff non-flowing gel or jelly of aluminum soaps in hydrocarbons may be converted into a thin clear fluid by addition of less than 1% of methyl alcohol.

Summary

The solubilities of the myristates, laurates, palmitates, and stearates of magnesium, lead, calcium, barium, and zinc have been measured at 25° C. in chloroform and in propylene glycol and in their mixtures. Even where they are sparingly soluble in the solvents separately, they dissolve freely in mixtures of the two.

For each metal the solubility is greatest for laurate and least for stearate and it is very low for zinc soaps, particularly zinc stearate.

Heavy metal soaps may be directly titrated with acid in mixtures of propylene glycol and chloroform using thymol blue as indicator (yellow to pink).

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An Investigation of the Crystalline Phases in the System: Sodium Myristate-Water*

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Introduction

ONLY recently has there been recognition of the fact that solid soaps are aggregates of crystalline phases and that the collection of phases in the aggregate differs with differing treatment. While the science of soap phases is in its infancy, it is now evident that soaps of different properties can be prepared from one and the same soap stock by varying their preparation.

In an earlier contribution (1) we have outlined the general occurrence of crystalline soap phases in simple soap-water systems. In this paper we discuss the conversion of one soap phase to another in such systems and give experimental results obtained in the system sodium myristate-water.

Soap phases are difficult to identify because they show more resemblances than differences. Their optical properties are nearly identical insofar as these have been investigated (2) and this is a consequence of the generally similar manner in which the molecules are packed in the structures of the soap crystals. It is only in detail that the packing schemes of the structures differ. One of the best ways of investigating differences in structure is by X-ray diffraction. "Powder" photographs of soap phases provide a means of "fingerprinting" them and thus of distinguishing between them as they occur in soaps.

Phase Transformations in Soap Systems

McBain has shown that simple soap-water systems conform with the phase rule insofar as the non-solid phase fields are concerned and has investigated the nature and distribution of the phase fields for a number of such systems (3). Our own investigations have been concerned chiefly with the regions of the phase diagrams in which solid phases predominate. These regions have not been discussed in detail by McBain. We now realize, in retrospect, that such regions cannot be investigated by the classical static methods for reasons which will appear very shortly.

To anticipate our general results somewhat, in order to make them the basis of discussion, we find that the predominantly solid regions of soap-water systems are partitioned into fields (1). In the cases of systems of pure soaps with water such fields are limited by phase rule considerations to solid solution fields and two-phase fields. In more complex soap-water systems additional phases may appear within a single field.

We have ascertained that it is not generally possible to shift the state of the system in these regions by merely changing its coordinates only, i.e., by merely adding or removing water or by changing its temperature (except as noted below). Indeed, *equilibrium can be attained, in general, following a change of coordinates, only when the change is accompanied by violent working.* (An exception to this is that equilib-

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