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Some Physical Properties of Soap/Solvent Systems and Their Relation to the Solubility Parameter of the Solvent

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ABSTRACT

Certain solubility-linked physical properties of soap/solvent systems have been shown to be functions of the solubility parameter of the solvent. The lowest critical solution temperatures for zinc and lead stearates occur in solvents having a solubility parameter of 8.9. Maximum swelling of lithium and sodium stearate/solvent systems occurs at a solvent solubility parameter of 9.3. In addition, the gel/jelly-or-sol transition temperatures for aluminum dilaurate/solvent systems have been shown to be an approximately linear function of solvent solubility parameter. A qualitative explanation for the observed results is based upon an analogy to high polymer/solvent systems.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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INTRODUCTION

The successful application of the solubility parameter concept (1) to the solubility of oil-soluble sulfonates (2) suggests that other modes of soap/solvent interaction should be examined in terms of this concept. Relevant physical properties to be studied might include such solubility-linked phenomena as critical solution temperatures of soap/solvent systems, solvent-induced swelling of soaps, or other phase equilibria of soap/solvent systems.

Although the literature data on soap/solvent systems is considerable, much of the work done has been in mineral oils of different and sometimes ill-defined types and in soap/solvent systems of unknown water content. Nonetheless, selected results (3-6) have shown systematic trends when examined in terms of the solubility parameter concept with these results amplified where necessary with additional experimental data. The analogy between soap solubility and the solubility of high polymers suggested in an earlier paper (2) is used to explain some of the experimental results.

EXPERIMENTAL MATERIALS AND METHOD

Zinc and lead stearates were dried under vacuo. Their respective melting points were 124° and 107°C. All solvents were percolated over Linde molecular sieve materials to remove water.

Critical solution temperatures (C. S. T.) were determined according to the arbitrary technique of Tughan and Pink (7). The critical solution temperatures were reproducible to within one degree.

SOLVENTS EXCLUDED FROM CONSIDERATION

Lower molecular weight alcohols have been excluded from the set of solvents considered since they have been shown to have an extraordinary dissociating effect on the sulfonate soaps (8). Hydrogen bonding of the alcohol to the soap anion and extensive dissociation of a soap into its constituent ions prevents meaningful application of the solubility parameter concept to soap/lower alcohol systems. Mineral oils have also been excluded because of possible variation in their composition and the difficulty of assigning a solubility parameter for a given grade of mineral oil.

CRITICAL SOLUTION TEMPERATURES: ZINC AND LEAD STEARATES

Lawrence (9) has investigated solutions of a wide variety of metal soaps in Nujol. He found that the soaps dissolved at sufficiently high temperatures to form clear solutions. In most cases, solutions of the alkali metal, alkaline earth metal, and heavy metal soaps set to gels upon cooling. A smaller group of soaps which included zinc and lead soaps did not form gels. Moreover, the solubility of the zinc soaps has been determined in several

solvents and their critical solution temperatures tabulated (3). The absence of gel formation suggested a simple system which might show significant trends upon application of the solubility parameter concept to the data.

Figure 1 shows a plot of the critical solution temperature of the soap/solvent system versus the solubility parameter of the solvent for both zinc and lead stearates. In each case the maximum lowering of the critical solution temperature corresponds to a δ (solubility parameter) of 8.9. This minimum lies 29 degrees below the melting point for the zinc soap and 34 degrees below the melting point for the lead soap. The existence of a minimum and the general shape of the curve can be qualitatively inferred from thermodynamic considerations. Two processes contribute to the breakdown of the soap lattice: (a) swelling caused by solvent penetration with resultant weakening of the lattice structure and (b) additional weakening of the lattice resulting from increased thermal agitation as the temperature is increased, ultimately terminating in dissolution of the lattice as the critical solution temperature is reached. The free energy of swelling is expressed or defined by the well-known relation:

$$\Delta F = \Delta H - T\Delta S.$$

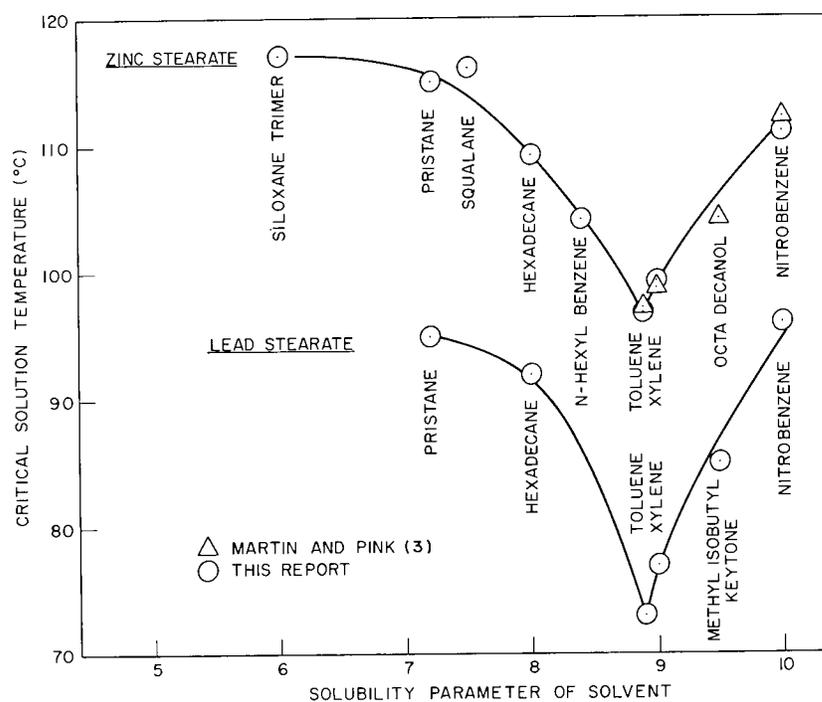


Fig. 1 - Critical solution temperatures of zinc and lead stearates vs solubility parameter

Spontaneous swelling requires that the free energy change be negative: the more negative the free energy term the greater the degree of swelling. In nonpolar systems the driving force for swelling arises from the $-T\Delta S$ term. A maximum free energy change will be found for those systems having a minimum enthalpy term. The enthalpy of swelling becomes increasingly positive as the solubility parameter difference between solute and solvent increases and thus the free energy of swelling progressively decreases in magnitude. In order to increase the degree of swelling, it is necessary to progressively increase

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the $-\Delta S$ term by increasing T . Although these considerations appear to predict the general trend of the $C. S. T./\delta$ relation, it should be recognized that actual dissolution of the swollen soap lattice must, in addition, depend upon the state of the soap in solution and the free energy change produced by micelle formation in the solvents considered.

SWELLING PHENOMENA

Swelling and Sedimentation Volumes of Lithium and Sodium Stearates

The sensitivity of many metal stearates in Nujol to traces of water in the system has been demonstrated by Lawrence (9). He showed that gelation is closely linked to the water content of the soap/solvent systems and that truly anhydrous sodium stearate/Nujol systems do not gel. Because of this possible complication in the literature data, only swelling data have been considered in the case of the alkali metal stearates. Figure 2 shows a plot of sedimentation volume (5) versus the solvent solubility parameter. Figure 3 shows a plot of swelling volume (4) versus solubility parameter. Maxima for the sodium stearate data occur at $\delta = 9.3$ and 9.2 for sedimentation volume and swelling data, respectively. Sedimentation volume data for lithium stearate are less complete but nevertheless a maximum near $\delta = 9:2$ appears to be indicated.

It should be noted that the swelling and sedimentation data were measured at $130^\circ C$ (relative to $20^\circ C$) and $20^\circ C$, respectively. Although several factors affect the sedimentation volume, it is of interest to note the excellent correlation between the swelling data and the sedimentation data as regards the appearance of the maximum at $\delta = 9.2$ to 9.3 , indicating

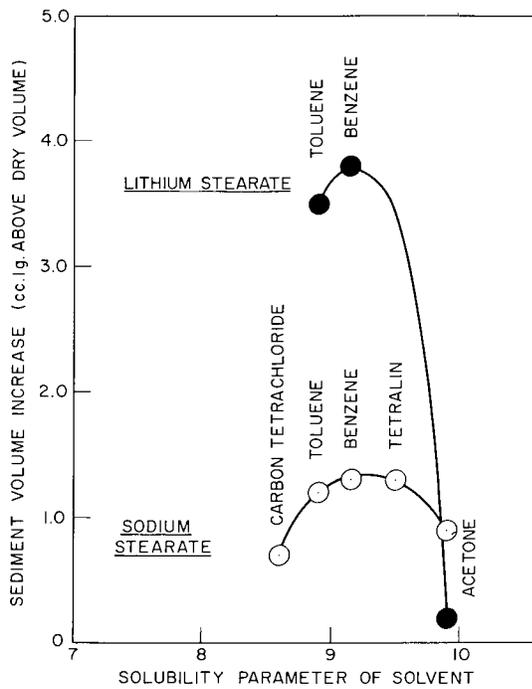


Fig. 2 - Sediment volumes of lithium and sodium stearates vs solubility parameter

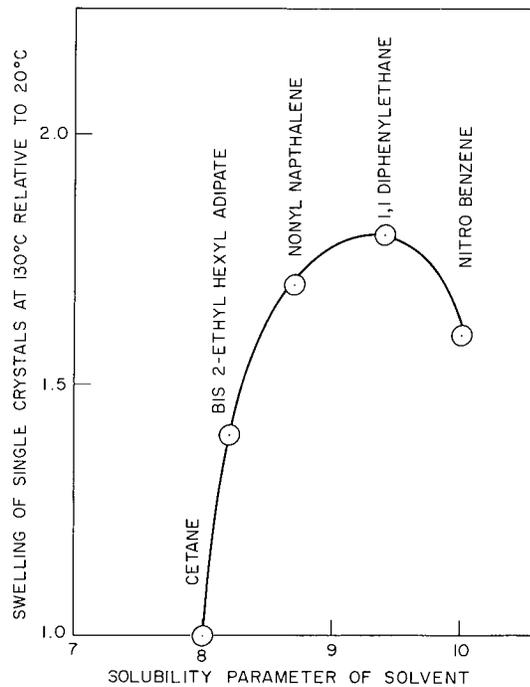


Fig. 3 - Swelling volume of sodium stearate vs solubility parameter

that, at least to a first approximation, volume change of the sedimented particles themselves is a major factor. It was suggested in the section on critical solution temperatures that swelling would be a maximum when the δ 's of solvent and solute were closely matched in analogy to the interpretation of swelling for certain solvent/high polymer systems (1). The maximum solvent effect for zinc and lead stearates occurs at $\delta = 8.9$, while for lithium and sodium stearates it occurs at $\delta = 9.2$ to 9.3 . These apparent solubility parameters for the soap molecules indicate that the polar part of the soap molecule plays a significant role in determining the optimum solvent solubility parameter for maximum swelling since the δ value for the stearate hydrocarbon tails alone is only 8.0 . The difference in apparent δ 's for the heavy metal soaps vs the alkali metal soaps may reflect the decreased polarity of the partially covalent linkage of the former (3) as against the ionic linkage of the alkali metal soaps. In addition, the decreased volume of the polar group in the former case results in a smaller contribution to the overall solubility parameter of the soap molecule. It is interesting to compare the apparent δ values obtained for the carboxylates with the value of 10.5 obtained from the extrapolation of sulfonate data (2). The larger δ value for the alkali metal dinonylnaphthalene sulfonates is consistent with the larger volume fraction contribution of the polar group to the soap molecule and the aromatic contribution to the hydrocarbon tail. It is recognized that the interpretations of carboxylate soap/solvent behavior presented here are formulated by analogy to high polymer/solvent behavior and may need to be modified as the body of data on soaps increases and theory improves.

Gel/Jelly-or-Sol Transitions of Anhydrous Aluminum Dilaurate. in Hydrocarbons

The data of McBain, Mysels, and Smith (6) on aluminum soaps in pure hydrocarbons and their gel/jelly-or-sol transformations are particularly useful since special care was taken to maintain the dryness of the soap/solvent systems. McBain defines the gel, jelly, and sol states as follows (10): Gels are systems of two or more components involving a crystalline phase of swollen soap intermeshing regions of a second phase which may be liquid crystalline, a jelly, or a sol. Jellies and sols are single phase isotropic transparent colloidal systems. Most soap greases are gels in which only a trace of soap is dissolved, the rest remaining as insoluble fibers whose degree of dispersion and of independence determines whether the grease is buttery or firm. The transition of the desired gel at a particular temperature or temperature interval into a sol or jelly of unfavorable rheological properties is of fundamental importance in lubrication technology.

Systems containing 2.5% of crystalline aluminum dilaurate were studied in various hydrocarbons and the swelling volumes and gel/jelly-or-sol transition temperatures recorded. The swelling volume was four times the dry soap volume in isooctane ($\delta = 6.8$), six times in n-heptane ($\delta = 7.4$), and fifty times in cyclohexane ($\delta = 8.2$) following the trend shown by the alkali metal stearates. McBain and his coworkers found that a smooth curve was obtained when the swelling volumes were plotted against the gel/jelly-or-sol transition temperatures thus emphasizing the correlation between swelling data and gel stability.

Figure 4 shows the relation between the transition temperature and the solvent solubility parameter for aluminum soap/solvent systems. It can be seen from the graph that a variation in solubility parameter of 0.5 unit changes the transition temperature by eight degrees. Other soap/solvent systems might be expected to show similar variations. It appears, therefore, that knowledge of the solubility parameter of an oil used to make up a grease formulation is of some importance in determining the temperature range of the grease.

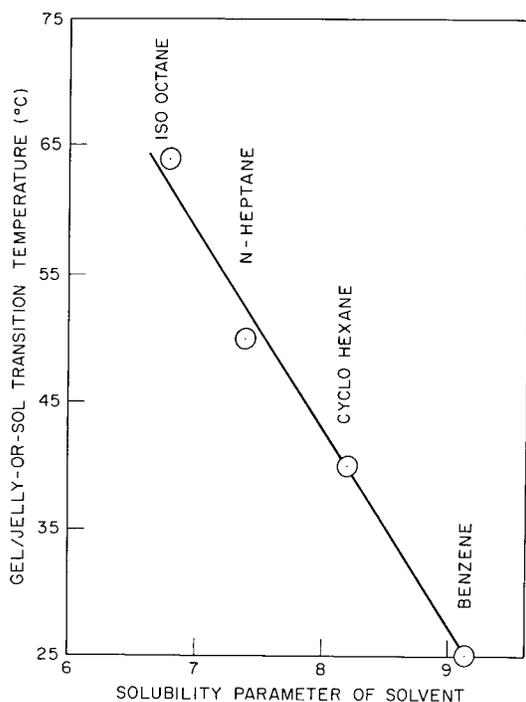


Fig. 4 - Gel/jelly-or-sol transition temperatures of aluminum dilaurate/hydrocarbon systems vs solubility parameter

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