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THE SOLUBILITY OF ALKALI-METAL DINONYLNAPHTHALENE SULFONATES IN VARIOUS TYPES OF SOLVENT, AND A THEORY FOR THE SOLUBILITY OF OIL-SOLUBLE SOAPS

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ABSTRACT

The solubility of the alkali-metal (group I) dinonylnaphthalene sulfonates in low-polarity solvents is roughly parallel to that of dinonylnaphthalene in the same solvents. This indicates that, to a first approximation, the outer hydrocarbon sheath of the micelle determines compatibility with a solvent. The solubility behavior in nonpolar solvents is most readily correlated by comparison of the Hildebrand solubility parameter of the solvent with that estimated for the hydrocarbon exterior of the micelle. In systems showing limited solubility the data indicate that (a) the condensed soap phase behaves as an extremely viscous liquid and (b) the equilibrium is characteristic of a liquid/liquid system in which the limited solubility of the two components in each other increases with rising temperature to a critical solution temperature; above this temperature the soap and solvent are miscible in all proportions. For ordinary oil-soluble soaps in common hydrocarbons, the critical solution temperature lies well below room temperature. Micelle size in low-polarity solvents decreases as the solubility parameter increases, probably because such a variation improves the match in solubility parameter between micelle and solvent by exposing more of the polar core.

In solvents having Hildebrand parameters above 10, the solvent, with a few exceptions, appears to associate with the monomer (or dimer) solute molecule to modify the latter's solubility parameter and to maintain high solubility of the sulfonate as an equilibrium mixture of monomer, dimer, and possibly higher units. In hydrogen bonding solvents of high dielectric constant, the association of the solvent with both ions leads to dissociation of ion pairs and high electrolytic conductivity.

Pure crystalline alkali-metal carboxylates do not show high solubility in hydrocarbons unless they are heated to a temperature at which they pass over to a liquid-like phase; noncrystalline carboxylates, or mixed crystals of many different branched chain carboxylate species, have high or unlimited solubilities and appear to behave as liquid/liquid systems in much the same way as the alkali sulfonates.

PROBLEM STATUS

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

AUTHORIZATION

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THE SOLUBILITY OF ALKALI-METAL DINONYLNAPHTHALENE SULFONATES IN VARIOUS TYPES OF SOLVENT, AND A THEORY FOR THE SOLUBILITY OF OIL-SOLUBLE SOAPS

INTRODUCTION

The military and commercial importance of oil-soluble soaps as special-purpose additives in various oil systems is well established. For example, such compounds have found wide application as detergents in oils, as gelling agents for fuels in incendiaries, in rust inhibition, and as bodying agents in paints. This Laboratory has been engaged for some time in a research program aimed toward the production, purification, and study of high molecular weight organic salts in important oil systems with a view toward elucidating their specific function in these systems.

Previous reports (1,2) have laid the foundation for the basic understanding of an important family of such salts, the dinonylnaphthalene sulfonates, in a particular model solvent, benzene. This report is concerned with sulfonate behavior in a variety of solvent types. A systematic investigation has been made of the influence of (a) cation, (b) water, and (c) solvent type upon the apparent solubility (defined as the combined solubility of associated and nonassociated sulfonate-derived species which are in thermodynamic equilibrium) of these sulfonates. The model sulfonates selected for the investigation were the dinonylnaphthalene sulfonates of representative group I cations, in particular, lithium, sodium, and cesium.

The published data on the solubility of soaps in various solvent environments is often difficult to interpret, each soap-solvent system appearing to have its own individual character (3-10). Winsor (11) has attempted to clarify and classify some of this work. His theory, however, refers primarily to solutions containing water as an important component, and it is most readily exemplified in systems of high soap content.

The need for a more comprehensive theory of soap behavior in nonaqueous systems continues to exist, and it is toward this objective that this work is directed.

EXPERIMENTAL

Preparation of Materials

The lithium, sodium, and cesium salts of a special grade of dinonylnaphthalene sulfonic acid (HDNNS), abbreviated LiDNNS, NaDNNS, and CsDNNS, respectively, were prepared by neutralization of an aqueous alcoholic solution of the acid by the appropriate base. The soaps were then lyophilized and stored in a desiccator over P_2O_5 until use. This acid and its salts have been described previously (1). The dinonylnaphthalene (DNN) was molecularly distilled from a commercial sample of dinonylnaphthalene obtained from King Chemical Co.

All of the solvents used were ACS grade or better, except for the 0.65-, 1-, 2-, and 10-centistoke silicones which were commercial samples. All solvents were passed through Linde molecular sieve materials and Florisil in order to remove water and polar contaminants. A check on the efficiency of the percolations was made in the case of dioxane

by means of a Karl Fischer titration. No water could be detected within the precision of the method. The cyclohexane used was of very high purity (99.92 mole percent) and was obtained by fractional crystallization. The dimethyl siloxanes were specially prepared monodisperse species available from the Dow-Corning Corporation. The nitroparaffins were fractionally distilled from the best available grade of Eastman Kodak solvents; their boiling points and refractive indices corresponded closely to the literature values. The preparation and purification of the fluorocompounds have been described (12). All solvents were stored over molecular sieve pellets in glass-stoppered bottles and were used as soon as possible after percolation.

Measurement Techniques

Figure 1 illustrates the apparatus used for the determination of the apparent soap solubility in the various solvents. It consists of a stationary NBS-certified tenth-degree thermometer upon which is mounted a baffle to promote agitation. The rotator turns the solution cell within an air space surrounded by a bath of controlled temperature. A magnetic stirrer provides agitation of the bath, while a copper heat-exchange coil permits easy change of temperature conditions by means of the thermostated reservoir. A solubility determination was made as follows. A sulfonate solution of known molality was made up at a higher temperature and allowed to cool at a rate of 0.1°C per minute in the vicinity of the temperature at which precipitation would occur. The rate of cooling was controlled by means of the bath temperature setting. Rates of cooling from 0.05°C to 0.2°C per minute gave the same results within the experimental error of ±0.2°C. The point at which precipitation occurred was determined by visual observation of the turbidity in a concentrated light beam directed at a right angle to the observer.

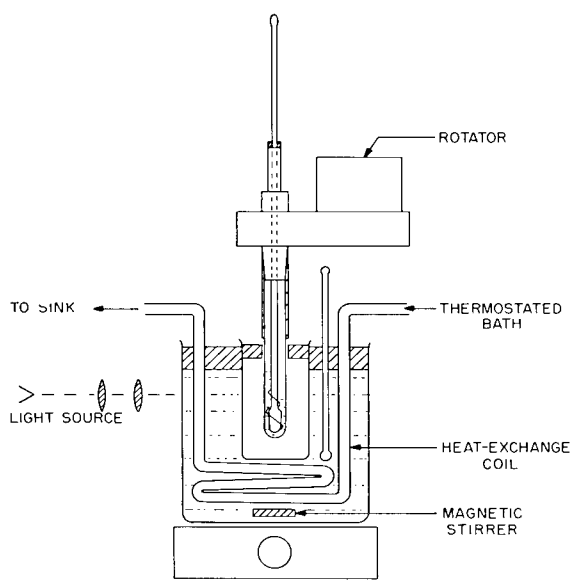

Fig. 1 - Schematic of apparatus used for solubility determinations

Vapor pressure lowering data were obtained by means of a commercial thermoelectric device, the Mechrolab Model 301A Osmometer. In all cases a drying agent, Linde molecular

sieves, was added to the solvent cup in order to maintain a water-free solvent atmosphere in the measuring chamber. Some difficulty was experienced with the osmometer in measuring solutions containing significant concentrations of ions. This was due to the fact that since the thermistor leads of the nonaqueous-type-probe support are not insulated, there is apparently ionic conductance taking place between the leads. Substitution of a matched pair of glass-probe-type thermistors for the glass-bead type, furnished with the commercial unit, eliminated this difficulty.

Figure 2 is a diagrammatic representation of the experimental arrangement used for the liquid crystal determinations and is self-explanatory.

Conductivity measurements were made with a portable conductivity bridge, Industrial Instruments, Inc., type RC16B1. Measurements were made at 35.02±0.02°C in a cell protected from atmospheric humidity by means of molecular sieve materials. The cell was surrounded by an oil bath.

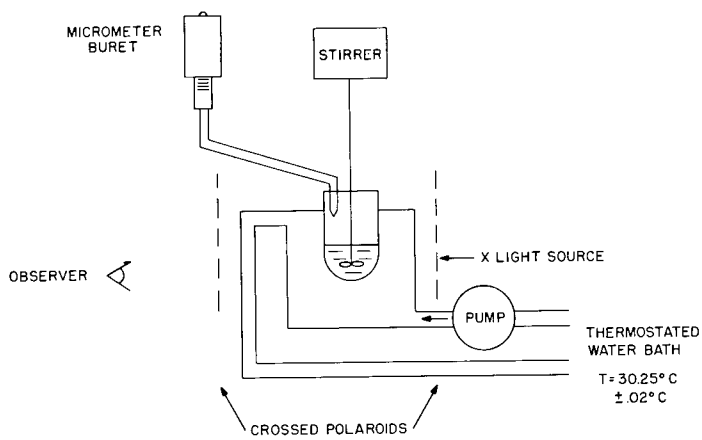

Fig. 2 - Schematic of essential apparatus for liquid crystal studies

RESULTS

In order to facilitate discussion of the experimental results, the sulfonate solvent systems have been divided into four rather arbitrary classes based upon their experimental behavior.

Type 1: Sulfonate is Miscible with the Solvent in all Proportions; Aggregation Number is Constant in a Given Solvent

Table 1 shows the degree of sulfonate solubility in type-1 solvents, and Fig. 3 presents the data obtained from vapor pressure lowering measurments in terms of osmotic coefficient versus concentration. Two generalizations may be made, and they are consistent with results previously obtained by Kaufman and Singleterry (2) on benzene solutions of lithium and sodium dinonylnaphthalene sulfonates. First, the aggregation number is independent of the concentration, and second, the aggregation numbers of the lithium and sodium salts are identical within the precision of the method. It should be stated here that aggregation numbers in benzene at 35°C were lower ($n = 7$) than those obtained from fluorescence

Table 1
Solubility of Sodium Dinonylnaphthalene Sulfonate (NaDNNS)
at Two Temperatures in Type-1 Solvents

Solvent	Dielectric Constant ϵ*	Solubility of Indicated (Molal) Solution			
		NaDNNS (25°C)	NaDNNS (-78°C)	DNN (25°C)	DNN (-78°C)
N-Heptane	1.924	∞†	∞	∞	∞
Cyclohexane	2.01	∞	f‡	∞	f
Siloxane Dimer	2.2	∞	∞	∞	∞
Dioxane	2.21	∞	f	∞	f
Carbon Tetrachloride	2.24	∞	f	∞	f
Benzene	2.27	∞	f	∞	f
Chloroform	4.81	∞	f	∞	f

*At 25°C.
†∞ = miscible in all proportions.
‡f = solvent freezes at -78°C or higher.

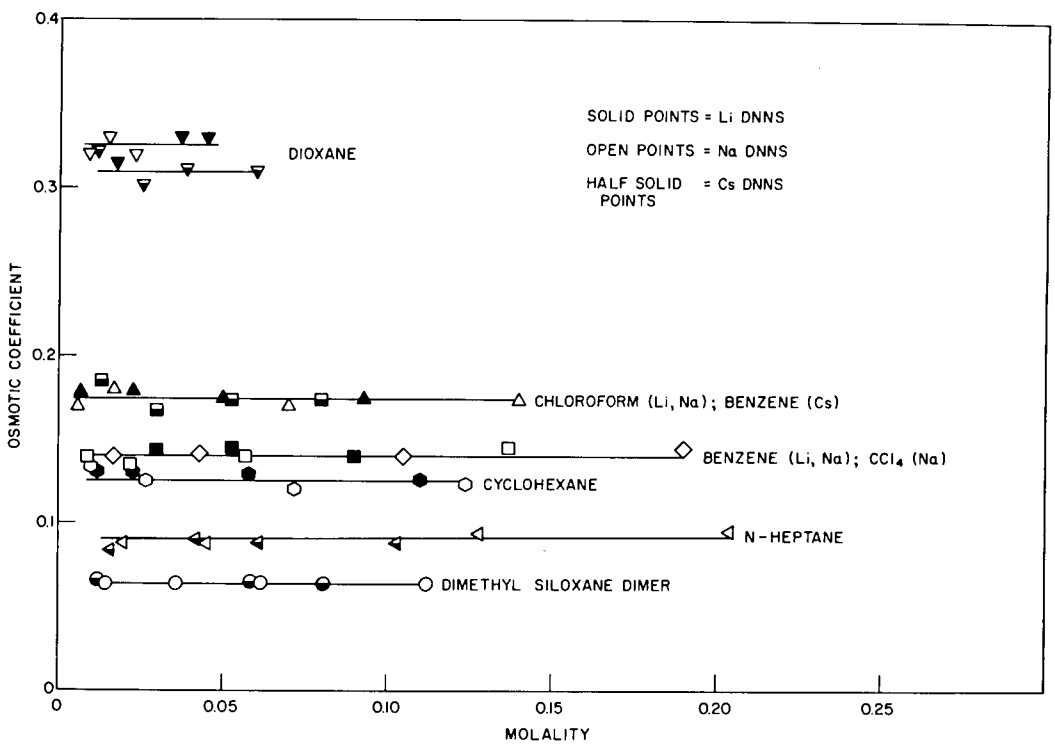

Fig. 3 - Osmotic coefficient vs concentration for sulfonates in low-polarity type-1 solvents at 35°C

depolarization studies ($n = 10$) at 25°C (2). The discrepancy is slightly greater than the absolute uncertainty estimated by Singleterry and Weinberger for the fluorescence depolarization method (13). The consistency of results obtained by either method alone is much better, so the relative aggregation numbers reported by the osmometer method are believed reliable to ± 1 or better. The difference in aggregation number obtained by the two methods, however, merits further study.

Precise conductivity measurements on sulfonate solutions in solvents of this type were not possible with the simple conductivity bridge used in this work. It is sufficient for purposes of this study to state that the specific conductivity of the solutions was less than 8×10^{-8} mhos/cm, indicating that ionic concentrations of any soap species in solvents of this type must be extremely low. Table 5 shows conductance results obtained for four of the type-1 solvents.

Type 2: Sulfonate is Miscible with the Solvent in all Proportions, but the Extent of Association and/or Dissociation is Concentration Dependent

Table 2 shows the degree of sulfonate solubility in type-2 solvents, and Fig. 4 illustrates the osmotic behavior which is characteristic of this solvent group. The sulfonates form conducting solutions in these solvents, as is shown by the data of Table 5 and in Fig. 5. Solutions in ethanol showed the highest conductance, whereas solutions in ethyl acetate showed the lowest. The decrease in the ability of the solvent to dissociate ion pairs reflects the decrease of dielectric constant. Two distinct processes appear to control osmotic behavior of sulfonate solutions from this solvent class, namely, ionic dissociation and molecular association. Low sulfonate concentrations and high dielectric constants promote the first process, moderate to high concentrations and low dielectric constants favor the second. The equilibria which apply in solvents of this type probably involve simple ions, ion pairs, triple ions, associated ion pairs, and larger clusters which are perhaps both charged and neutral.

In ethanol, an analysis of the data indicates that the equilibrium involves predominately simple ions and ion pairs. An apparent equilibrium constant of $7.0 - 7.6 \times 10^{-3}$ was found to fit the osmotic data for NaDNNS solutions over the experimental range of 0.002 to 0.04 molal, assuming the ion ion-pair model. Because the ethanol used contained some foreign ions which could not be removed by percolation, no serious attempt was made to determine the thermodynamic equilibrium constant, which would require measurements in solutions so dilute as to permit serious interference by the foreign ions.

In acetone, methyl isobutyl ketone, and ethyl acetate, association products larger than simple ion pairs appear to be formed. In acetone solutions the osmotic coefficient data indicate the formation of association products equivalent to sulfonate dimer and trimer (not necessarily neutral in charge); in ethyl acetate solutions, association products corresponding to clusters containing the equivalent of three and four sulfonate molecules (again not necessarily neutral in charge) appear to exist. Solvents of this type may or may not differentiate between the osmotic behavior of lithium and sodium soaps (see Fig. 4).

In water, the equilibrium appears to involve ions and much larger aggregates-probably aqueous micelles. This conclusion is supported by the following evidence: (a) high conductance at low soap concentrations (see Table 5), (b) high light scattering power of the dispersions, (c) ability to solubilize an oil-soluble dye (Sunbeam Yellow), and (d) easy passage of the dispersions through a 100-mμ Millipore filter.

Table 2
Solubility of NaDNNS at Two Temperatures
in Type-2 Solvents

Solvent	Dielectric Constant ϵ*	Solubility of Indicated (Molal) Solution			
		NaDNNS (25°C)	NaDNNS (-78°C)	DNN (25°C)	DNN (-78°C)
Ethyl acetate	6.02	∞†	∞	∞	∞
Methyl isobutyl ketone	13.11(20°)	∞	∞	∞	∞
Acetone	20.7	∞	0.12	∞	0.03
Ethanol	24.3	∞	∞	0.09	i‡

*At 25°C, unless otherwise indicated.
†∞ = misicible in all proportions.
‡i = insoluble.

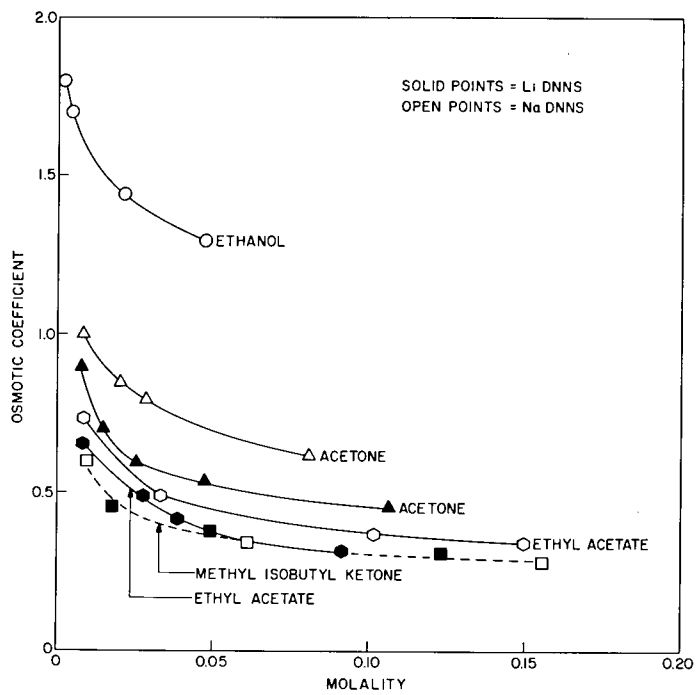

Fig. 4 - Concentration dependence of sulfonate osmotic coefficients in polar type-2 solvents at 35°C

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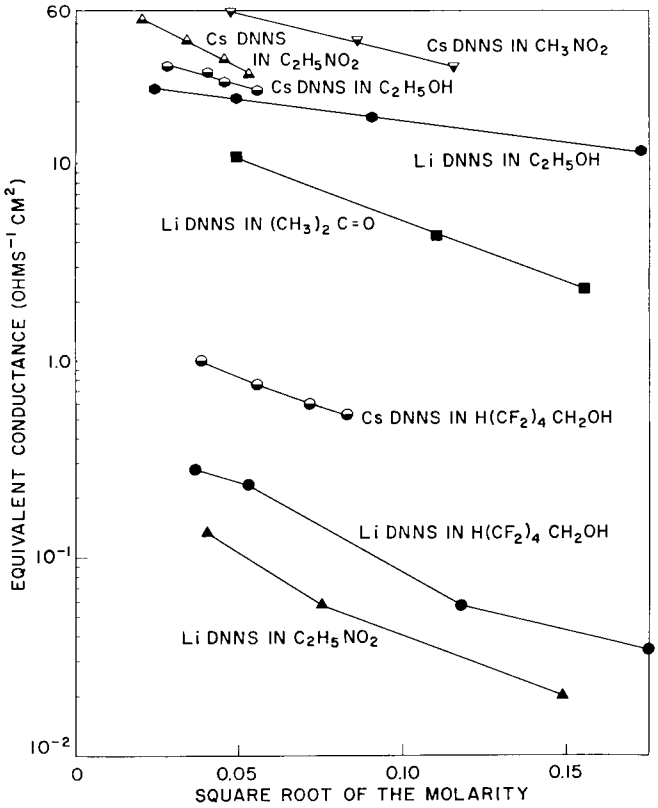

Fig. 5 - Equivalent conductance of sulfonates in high-polarity solvents at 35°C

Type 3: Solubility is Limited, and the Solubility Limit Varies with Temperature

Table 3 shows the degree of solubility in type-3 solvents. The dinonylnaphthalene sulfonates exhibit a positive temperature coefficient for the solubility limit in solvents of type 3. That is, the systems absorb heat when the sulfonates undergo solution in these solvents, and solubility increases with temperature. Figure 6 exemplifies, in a very general way, the type of behavior shown by the soaps in solvents of this type. Four solvent families belong to this group: (a) the higher members of the polymethyl siloxanes, (b) fluorinated esters, (c) nitroparaffins, and (d) alkyl cyanides. It will be convenient to consider these families separately.

Polymethylsiloxanes — The dinonylnaphthalene sulfonates are dissolved by the lower homologues of the polydimethyl siloxanes in all proportions; this solubility extends up to the hexamer siloxane in the case of the lithium and sodium salts, and to the trimer in the case of the cesium salt. The sulfonates exhibit limited solubility in the higher polysiloxane homologues (Fig. 6), and Fig. 7 illustrates the effect of solvent homology upon the dinonylnaphthalene sulfonates. The most complete data are shown for the cesium salt. The plot of $\log_{10}$ of the saturating molality vs N, the number of siloxane units in the polymer chain, led to the following descriptive equation for data taken at 45°C:

$$\log_{10} m = -0.289\ N + 0.225.$$

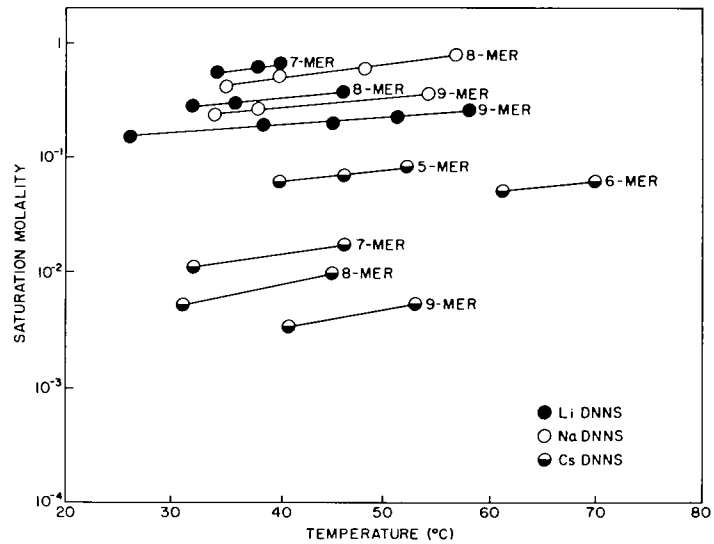

Fig. 6 - Solubility of the sulfonates in low molecular weight dimethyl siloxane polymers as a function of temperature

Initial slopes for the NaDNNS and LiDNNS lines were found to be -0.247. The data for the cesium sulfonate over the experimental range 30° to 65°C may be summarized to within 8 percent of the experimental data by the empirical relation

$$\log_{10} m = A/T + BN + C,$$

where A = -1304, B = -0.289, and C = 4.33. Differential heats of solution were not calculated from the solubility data because the activity of the sulfonates was not known.

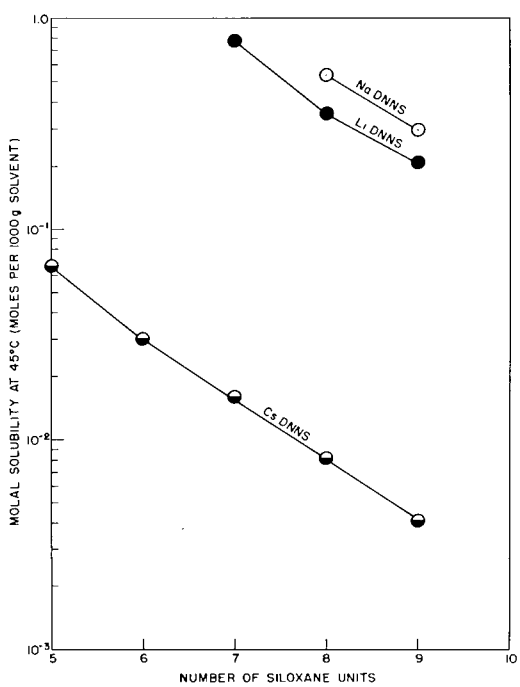

Fig. 7 - Solubility of the sulfonates in siloxane polymers at 45°C as a function of polymer size

Nitroparaffins and Alkyl Cyanides – The solubility behavior of the sodium sulfonate in the first three nitroparaffins is shown in Table 3. Solubility increases as the proportion of hydrocarbon in the solvent molecule is increased, going from barely detectable solubility in nitromethane to miscibility in all proportions with 1-nitropropane (not shown).

The cesium sulfonate (not shown in the table) is much more soluble in nitroethane than either the lithium or sodium sulfonates. The cesium salt, moreover, has a moderate, though limited, solubility in nitromethane.

The conductance behavior of cesium sulfonate solutions as compared with lithium sulfonate solutions is of interest (Table 5). In the solvent series ethanol, nitroethane, and nitromethane, the limiting conductance of the cesium

salt increased along with the increase in dielectric constant in accordance with the Nernst-Thompson rule. On the other hand, the conductance of the lithium salt is two orders of magnitude less in nitroethane than in ethanol. While the cesium salt readily dissociates in nitroethane, the lithium salt does not. Osmotic measurements, moreover, indicate that the lithium salt may be associated in the nitroethane. The difference in conductance reflects the difference in cation radii; the small radius of the lithium ion favors coordination bonding to the sulfonate oxygen, which opposes ion dissociation. As would be expected, the solubility of the sulfonates in the nitroparaffin family increases very rapidly as the hydrocarbon radical is increased in size, paralleling the increased solubility of the parent hydrocarbon molecule DNN. (Dinonylnaphthalene is completely miscible with nitroethane at 25°C; the sulfonates were also found to be completely miscible with 1-nitropropane at 25°C.)

The experimental results obtained with the nitroparaffins suggested still another solvent family of similar electrical and physical properties – the alkyl cyanides. Although data are incomplete at the time of this writing, preliminary experiments indicate that both the sulfonates and dinonylnaphthalene have a limited solubility in the first member (acetonitrile) of this family.

Fluorocompounds – Table 3 lists the solubility characteristics of NaDNNS and of DNN in a fluoroalcohol and in several fluoroesters. Again, the low solubility of the dinonylnaphthalene parallels that of the sulfonates. Although the cesium and lithium salts formed conducting solutions in the ψ' amyl alcohol, the limiting conductance was low as a result of the lower dielectric constant (16.93) and high viscosity of the alcohol.

Type-4: Soap May Show No Detectable Solubility Effect

Solvents in this class (Table 4) include fluorocarbons and higher molecular weight silicones. The insolubility of the sulfonate again approximately parallels the immiscibility of the dinonylnaphthalene.

Table 3
Solubility of NaDNNS at Two Temperatures in Type-3 Solvents

Solvent	Dielectric Constant ϵ*	Solubility of Indicated (Molal) Solution			
		NaDNNS (25°C)	NaDNNS (-78°C)	DNN (25°C)	DNN (-78°C)
Siloxane Nonamer	2.5-2.6	0.20	i†	∞‡	s§
Siloxane Octamer	2.5-2.6	0.30	i	∞	s
Siloxane Heptamer	2.5-2.6	s	i	∞	∞
Bis(ψ'-Heptyl)β-Methyl Glutarate	6.1(20°)	0.0001	f¶	s.s.**	f
Ethyl Perfluorobutyrate	——	0.0001	i	s.s.	i
Bis(ψ'-Amyl)Diphenate	8.0(20°)	0.001	f	s.s.	f
Bis(ψ'-Propyl)Diphenate	9.70(20°)	0.01	f	s.s.	f
ψ'-Amyl Alcohol	16.93(20°)	0.04		i	
Nitroethane	28.6	>1	i	∞	0.006
Nitromethane	36.6	<0.001	f	s.s.	f
Acetonitrile	36.7	<0.001	f	s	f
Water	78.54	d††	f	i	f

*At 25°C, unless otherwise indicated.
†i = insoluble.
‡∞ = miscible in all proportions.
§s = soluble.
¶f = solvent freezes.
**s.s. = slightly soluble.
††d = disperses.

Table 4
Solubility of NaDNNS at Two Temperatures
in Type-4 Solvents

Solvent	Solubility of Indicated (Molal) Solution			
	NaDNNS (25°C)	NaDNNS (-78°C)	DNN (25°C)	DNN (-78°C)
Silicones {10 cs and higher}	{i* i}	{i i}	{∞† solubility	S‡ decreases}
Monochloropentadecafluorodimethylcyclohexane	i	i	i	i

*i = insoluble.
†∞ = miscible in all proportions.
‡S = soluble.

Table 5
Equivalent Conductance of Dinonylnaphthalene
Sulfonate Soaps at 35°C

Solvent	Solvent Type	Dielectric Constant ϵ*	Soap	Soap Concentration (Molar)	Equivalent Conductance (cm^2/ohm)
Cyclohexane	1	2.01	LiDNNS	0.01	< 0.005
Dioxane	1	2.21	LiDNNS	0.01	< 0.005
Carbon tetrachloride	1	2.24	LiDNNS	0.01	< 0.005
Benzene	1	2.27	LiDNNS	0.01	< 0.005
Ethyl acetate	2	6.02	NaDNNS	0.018	0.036
1,1,5 Trihydroperfluoroamyl alcohol	3	16.93(20°)	LiDNNS	0.002	0.18
1,1,5 Trihydroperfluoroamyl alcohol	3	16.93(20°)	CsDNNS	0.002	0.97
Acetone	2	20.7	LiDNNS	0.002	12.2
Ethanol	2	24.3	LiDNNS	0.002	23.5
Ethanol	2	24.3	CsDNNS	0.002	27.7
Nitroethane	3	28.6	LiDNNS	0.002	0.13
Nitroethane	3	28.6	CsDNNS	0.002	36.4
Nitromethane	3	36.6	CsDNNS	0.002	63.2
Water	3	78.54	LiDNNS	0.002	72.2

*At 25°C, unless otherwise indicated.

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Effect of Water on Solutions of the Dinonylnaphthalene Sulfonates

The effect of water on solutions of dinonylnaphthalene sulfonates depends upon whether the solvent mixes with water freely and upon whether the salt shows limited or unlimited solubility in the solvent. It is convenient to discuss the effects of water-immiscible and water-miscible solvents separately.

Water-Immiscible Solvents — Simple water titrations indicate that water is solubilized in solutions of the dinonylnaphthalene sulfonates in excess of the amount soluble in the pure solvent. Solubilization of water by sulfonates in hydrocarbon solvents has been reported previously by Mathews and Hirschhorn (14) and by Kaufman and Singleterry (2). Continued addition of water leads to a stable water-in-oil emulsion, and finally, upon addition of a large excess of water, oil-in-water emulsions result which are partly stabilized by films of precipitated soap. When a small amount of water was added to sodium sulfonate swollen with about 5 percent of benzene, the viscous mixture became flow birefringent. The further addition of a small amount of benzene destroyed the birefringence.

Water-Miscible Solvents — Water added to a concentrated solution of the DNNS soap in a solvent which was completely miscible with water led to the precipitation of liquid crystals. Six different solvents were found which gave this effect: ethanol, dioxane, acetone, glycerol, n-butylamine, and pyridine. Only two conditions seem necessary in order to produce the effect in the case of the dinonylnaphthalene sulfonates: (a) high solubility of the sulfonate in the solvent and (b) miscibility of the solvent and water in all proportions. Additional experiments with the DNNS salts and water alone indicate that even the water-miscible solvent itself is not needed to secure the effect since it was found that a thick paste of the sulfonate mixed with water in a mortar and pestle was birefringent. This liquid crystal, however, is not necessarily equivalent to the liquid crystal which precipitates from the solvent upon addition of water. Aqueous solutions of the dispersed sulfonates are easily precipitated by the addition of a chloride solution of the corresponding cation. Although the coagulum was not initially birefringent, it could be made so by smearing it on a glass slide. These generalizations pertain only to the dinonylnaphthalene sulfonates; the arylstearates form liquid crystals under quite different conditions (15).

A region where liquid crystal formation is observed for the NaDNNS-ethanol-water system near the water vertex of its Gibbs triangle is shown in Fig. 8; a birefringent gel region of undetermined boundaries is indicated by a single experimental point. Rheopectic properties were shown by the NaDNNS-dioxane-water system at mole percentages of 0.1, 1.0, and 98.9. The birefringent gel slowly transformed over a 24 hour period into an isotropic liquid (which showed flow birefringence). Gentle agitation of the liquid immediately regenerated the gel, which again slowly reverted to the isotropic liquid.

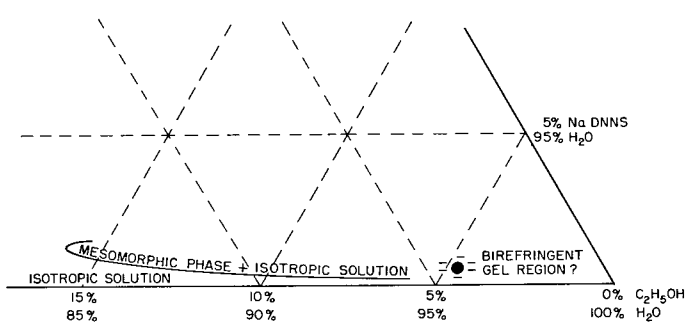

Fig. 8 - Partial phase diagram of the NaDNNS-C_2H_5OH-H_2O system

DISCUSSION

A Theory of Micellar Solubility in Nonaqueous Solvents

The solubility phenomena exhibited by oil-soluble soaps are too complex and depend upon too many factors to justify any hope of systematizing all the data by means of one simple theory. Nevertheless, the data available as a result of this and previous studies encourages an attempt to develop a theory applicable at least to the oil-soluble DNNS salts of the alkali cations. The attempt is especially promising for those solvents in which the sulfonate can be shown to exist in solution preponderantly as micelles whose size is independent of solute concentration. The solvents meeting this qualification include all of those listed as Type 1 solvents and those solvents of Type 3 having dielectric constants below 10 (siloxanes and fluoroesters).

The data of this report suggest the following hypotheses about the solubility of the alkali-metal sulfonates and their properties in micellar solutions in low-polarity solvents:

1. The equilibrium between solution and "solid" is effectively an equilibrium between sulfonate micelles of a characteristic size and a solvent-swollen sulfonate phase which is essentially a highly viscous liquid rather than a crystalline phase. The solubility phenomena observed are those characteristic of binary liquid systems.

2. The solubility characteristics of the sulfonate are determined by the composition and properties of that exterior part of the micelle which is located so that it can interact with the molecules of the solvent. To a very rough first approximation this portion of the micelle consists of the DNNS radical; the cation and the charged sulfonate portion of the anion are considered to be located in the central region of the micelle. As a result of this structure, the solubility in the specified systems parallels that of the hydrocarbon dinonylnaphthalene, again to a rough first approximation (see Fig. 9).

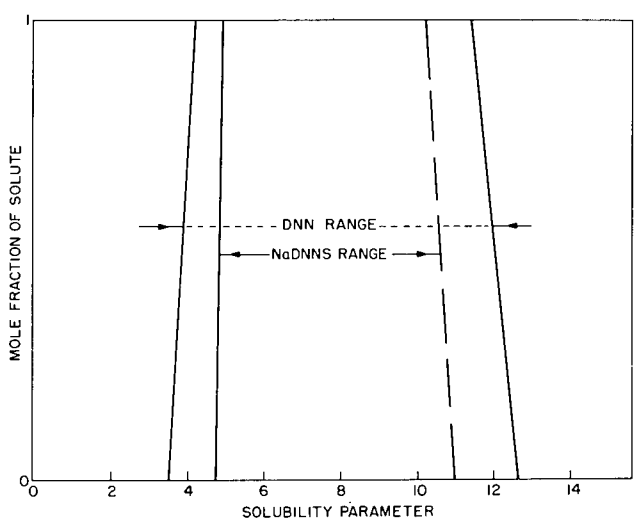

Fig. 9 - The range of complete miscibility for dinonylnaphthalene (DNN) and NaDNNS. (Polar solvents of a high solubility parameter which solvate the ion pair do not conform to this diagram.)

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3. The solubility parameter of Hildebrand and coworkers (16), rather than the dielectric constant or the dipole moment, is the property of a solvent which most accurately forecasts the micellar solubility of the alkali sulfonates in that solvent. As the solubility parameter of the solvent is increased, the micelles tend to assume a smaller size. This size reduction gives a looser packing of the DNNS tails and, thus, exposes the more interactive aromatic and polar parts in such a way as to reduce the difference between the solubility parameter of the solvent and the effective solubility parameter of the solvent-accessible portions of the micelle.

4. As the solubility parameter of the solvent increases, this tendency to match solubility parameters leads to the breakdown of the micellar regime and produces systems which are most readily treated as concentration-dependent equilibrium mixtures of the monomer, dimer, trimer, and possible tetramer. In solvents of high dielectric constant there may also be substantial dissociation into ions of various compositions. The interaction of the polar heads with the polar solvent molecules may also lead to solvation, which modifies the effective solubility parameter of the solute.

The available data are generally consistent with these hypotheses (see Table 6). With all solvents having solubility parameters between 5 and 10, the alkali-metal dinonylnaphthalene sulfonates are miscible in all proportions. Dinonylnaphthalene, with a solubility of 7.5, is similarly miscible with these same solvents although, as a result of the lower molecular volume, miscibility in the case of dinonylnaphthalene extends to slightly lower and higher values of the solubility parameter. Miscibility in all proportions is characteristic of liquid pairs whose solubility parameters do not differ by more than approximately 3.5 units (16). The degree of mismatch tolerated is less if the effective molecular volumes differ by an order of magnitude, as in the case of the sulfonate micelles in a volatile solvent. Unlimited miscibility is not often encountered for pairs consisting of a crystalline solid and a liquid. The belief that the alkali-metal sulfonates behave essentially as liquids in the presence of organic solvents is supported by the nature of the temperature composition diagram observed for one case of limited sulfonate solubility, as shown in Fig. 10. Here the compositions of the two equilibrium phases are plotted as a function of the temperature for the case of LiDNNS in the dimethyl siloxane heptamer. The curve is typical of a pair of liquids having a critical solution temperature (consolute temperature), above which they are miscible in all proportions. The sulfonate-rich equilibrium fractions at temperatures below the consolute point are seen to contain substantial amounts of silicone, although their viscosities are so high that casual inspection might have classified them as soft solids. In the other cases of limited solubility examined, complete data were collected only for the composition of the solvent-rich phase, but these data are consistent with the picture developed for the LiDNNS in siloxane heptamer. In several cases the critical solution temperature has been established.

The fact that practical oil-soluble soaps are usually either miscible with a solvent in all proportions or essentially insoluble is another observation which accords with the hypothesis that the oil-soluble soaps have the solubility characteristics of liquids. The range of solubility parameter mismatch permitting appreciable, but limited, miscibility is narrow. It corresponds to those pairs having critical solution temperatures only moderately higher than ambient. When the mismatch of parameters is greater, the consolute temperature is high and the mutual solubilities of solvent and soap become negligible. (The case of crystalline soaps is special and requires separate consideration.)

The Relation of Solubility Parameter to Micelle Size

Figure 11 shows that the micelle size of sodium dinonylnaphthalene sulfonate decreases approximately linearly with increasing solubility parameter δ of the solvent in the range of

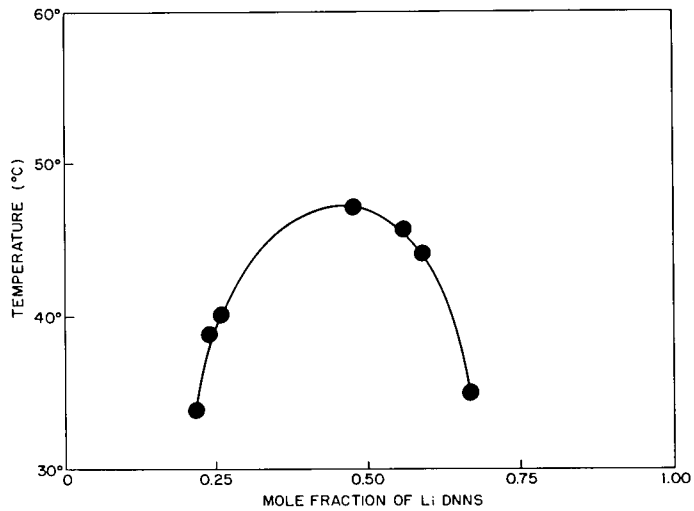

Fig. 10 - Mutual solubility of LiDNNS and dimethyl siloxane heptamer

solvent solubility parameters between 6.5 and 10. A similar solvent effect has been noted by other workers (17-20), although over a much shorter range of solubility parameter, for solutions of Aerosol OT, nonaethylene glycol laurate, monocaprin, and calcium dinonylnaphthalene sulfonate (see Table 7).

In solvents with solubility parameters lower than 6.5, the sulfonates exhibit limited solubility of the liquid/liquid type. Examination of molecular models suggests that an aggregate containing 15 to 20 DNNS units is as large as can be formed without radical deformation of the micelle towards a prolate or oblate spheroid of high eccentricity. This limit exists because the polar head of the sulfonate molecules has a smaller cross section than the branched hydrocarbon tail. If such a size limit is operative, the limited or negligible solubility in solvents of lower solubility parameter reflects the inability of the micelle to go further in adjusting its external shell to match the properties of the solvent. It may be expected that the micelle size of sulfonates showing limited solubility in solvents of lower solubility parameter will all lie near the limiting value noted above.

In an attempt to explain the observed relation of aggregation number n to solubility parameter δ on a semiquantitative physical basis, a conceptual model was devised on the basis of five specific assumptions. These assumptions include those already made in the foregoing qualitative theory of soap solubility (monodisperse micelles, having a central polar core, and a liquid-like structure for the condensed sulfonate phase), plus the following two additional assumptions:

1. When the sulfonate molecules associate to form aggregates or micelles, their polar heads are shielded so that the solubility parameter of the aggregate tends to approach the solubility parameter of the solvent.

2. When a sulfonate molecule is added to an aggregate, the degree of shielding is increased so that the solubility parameter of the aggregate is reduced by the amount K. The change in solubility parameter $\Delta\delta_2$, for n molecules forming an aggregate would be $(n-1)K$. It is recognized that this assumption may be an oversimplification, although it corresponds to the general trend of the shielding effect.

Table 6
Physical Properties of Selected Solvents

Solvent	Solubility Parameter δ*	Dielectric Constant ε*	Dipole Moment	DNN Solubility §	Molar Volume	Surface Tension*
DC 200, 10-cs Silicone		~ 2.6	0‡	m.a.p.		
Siloxane Octamer	4.72 v†	2.5	0	m.a.p.	668.4	18.03
Siloxane Hexamer	5.0 v	2.5	0	m.a.p.	516.8	17.42
Siloxane Pentamer	5.2 v	2.5	0	m.a.p.	441.4	17.08
Monochloropentadecafluorodimethyl-cyclohexane	6.1 h	Low	0	i	~215	-
Siloxane Dimer	6.5 v	2.2	0	m.a.p.	213.0	14.82
Ethyl Perfluorobutyrate	6.8 n	-	-	s.s.	173.7	19-20?
Bis(ψ'Heptyl)β-Methyl Glutarate	6.8 s	6.1(20)	3.83	s.s.	469.7	25.6(20)
Squalane	7.1 s	Low	0	m.a.p.	517.4	28.6
Bis(ψ' Amyl) Diphenate	7.2 s	8.0(20)	4.06	s.s.	429.1	28.4(20)
Diethyl Ether	7.4 h	4.34(20)	1.1	m.a.p.	104.7	17.0(20)
N-Heptane	7.45 h	1.924	0	m.a.p.	146.5	19.27(30)
Dinonylnaphthalene	7.5 s	Low	0	m.a.p.		31.2(20)
Bis(ψ'Propyl) Diphenate	7.8 s	9.7(20)	3.84	s.s.	327.9	31.1(20)
Hexadecane	8.0 h	Low	0	m.a.p.	292.7	27.4(20)
Cyclohexane	8.2 h	2.01	0	m.a.p.	108.03	25.3(20)
ψ' Amyl Alcohol	8.3 n	16.93(20)	2.88	i	139.4	25?
N-Butyl Amine	8.5 n	5.3	1.40	m.a.p.	98.97	19.7(41)
Carbon Tetrachloride	8.6 h	2.24	0	m.a.p.	96.51	27.0(20)
Isopropyl Biphenyl	8.9 s	Low	0	m.a.p.	200.5	34.8
Benzene	9.15 h	2.27	0	m.a.p.	88.86	29.02(20)
Chloroform	9.3 h	4.81	1.2	m.a.p.	80.18	27.1(20)
Methyl Isobutyl Ketone	9.5 n	13.11(20)	-	m.a.p.	125.04	23.64(20)
Acetone	9.9 h	20.7	2.7	m.a.p.	73.42	23.7(20)
Ethyl Acetate	9.9 n	6.02	1.7	m.a.p.	97.78	24.3(20)
Dioxane	10.0 h	2.21	0.45	m.a.p.	85.20	32.20(30)
Pyridine	10.7 h	12.3	2.2	m.a.p.	80.46	38.0(20)
1-Nitropropane	10.2 n	23.2(30)	3.6(vapor)	m.a.p.	88.82	29.28
Nitroethane	11.1 h	28.6	3.3	m.a.p.	71.35	32.3(20)
Acetonitrile	11.9 h	36.7	3.5	s	52.43	29.3(20)
Nitromethane	12.6 h	36.6	3.19	s.s.	53.96	36.8(20)
Ethanol	12.9 v	24.3	1.7	0.09	58.39	22.75(20)
Glycerol	13.2 s	42.5	2.56	i	73.02	63(20)
Methanol	14.4 h	32.63	1.66	i	40.45	22.6(20)
Water	23.8 h	78.54	1.84	i	18.0	72.75(20)

*At 25°C, unless otherwise indicated.
†Calculation of δ values

h - Hildebrand and Scott
v - Heat of vaporization data
n - Hildebrand rule
s - surface tension data.

‡Calculation of the dipole moment of the silicones from their dielectric constants by the Onsager equation (J. B. Romans and C. R. Singleterry, J. Chem. and Eng. Data 6:56 (1961)) gave values of 0.0±0.01.
§Solubility notations

m.a.p. = miscible in all proportions
i = insoluble
s = soluble
s.s. = slightly soluble.

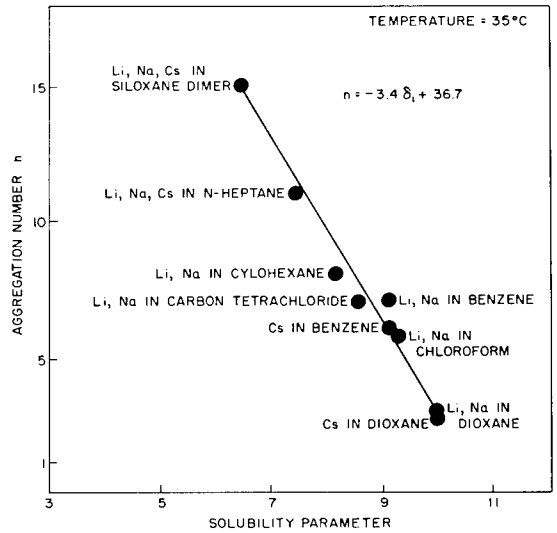

Fig. 11 - The dependence of the aggregation number of sulfonate micelles upon the solubility parameter of the solvent

Table 7
Effects of Solvent Solubility Parameter δ
on Degree of Association

Compound	Solvent	Aggregation Number n	Technique	Reference
Aerosol OT	benzene (δ = 9.15)	24	light scattering	A. Kitahara et al., J. Phys. Chem. 66:363 (1962)
	cyclohexane (δ = 8.2)	56	light scattering	A. Kitahara et al., J. Phys. Chem. 66:363 (1962)
$Ca(DNNS)_2$	benzene (δ = 9.15)	5	fluorescence depolarization	S. Kaufman and C. R. Singleterry, J. Colloid Sci. 12:465 (1957)
	dodecane (δ = 7.8)	12	ultracentrifuge	F. M. Fowkes, J. Phys. Chem. 66:1843 (1962)
nonaethylene-glycol laurate	benzene (δ = 9.15)	1	freezing point depress.	E. Gonick, J. Colloid Sci. 1:393 (1946)
	cyclohexane (δ = 8.2)	4	freezing point depress.	E. Gonick, J. Colloid Sci. 1:393 (1946)

Debye and Coll [J. Colloid Sci. 17:220 (1962)] observed that the order of association of monocaprin in various solvents is in the order $C_6H_{12} > CCl_4 > C_6H_6 > CHCl_3$, which would be in accordance with the vapor pressure lowering results for the DNNS soaps.

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The basic equation to be operated upon is Hildebrand's expression for the free energy of mixing of two liquids (16):

$$\Delta F^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + V_m(\delta_1 - \delta_2)^2 \phi_1 \phi_2, \tag{1}$$

where ΔF^M = free energy of mixing
R = gas constant
T = absolute temperature
X_i = mole fraction
V_m = volume of mixing
δ_i = solubility parameter
ϕ_i = volume fraction.

If the solute molecules are predominantly in the associated state as monodisperse micelles, the mole fraction of micelles having an aggregation number n will be $X_2' \cong X_2/n$. The free energy of mixing of sulfonate micelles and solvent then becomes

$$\Delta F^M = RT\left[\left(1 - \frac{X_2}{n}\right)\ln\left(1 - \frac{X_2}{n}\right) + \frac{X_2}{n}\ln\frac{X_2}{n}\right] + V_m[\delta_1 - \bar{\delta}_2 + (n-1)K]^2 \phi_1 \phi_2, \tag{2}$$

where $\bar{\delta}_2$ refers to the solubility parameter of the nonassociated soap molecule. The free energy of mixing is then minimized with respect to the aggregation number, holding temperature, solvent mole fraction and solvent solubility parameter essentially constant:

$$\left(\frac{\partial(\Delta F^M)}{\partial n}\right)_{X_1 T \delta_1} = -\frac{X_2 RT}{n^2}\ln\left(\frac{X_2}{n - X_2}\right) + 2V_m K \phi_1 \phi_2 [\delta_1 - \bar{\delta}_2 + (n-1)K] = 0. \tag{3}$$

Rearrangement yields

$$n = \frac{-\delta_1}{K} + \frac{1}{K}\left\{\bar{\delta}_2 + \left(\frac{RTX_2}{2\phi_1\phi_2 V_m K n^2}\right)\left[\ln\left(\frac{X_2}{n - X_2}\right)\right]\right\} + 1. \tag{4}$$

This compares with the experimentally observed relation

$$n = -3.4\delta_1 + 36.7 \tag{5}$$

for sulfonates of the periodic group I cations.

Comparison of Eq. (4) and (5) leads to values of $K = 0.295$ and $\bar{\delta}_2 = 10.5$ for aggregation numbers of 5 or greater. Evaluation of the complex term in Eq. (4) showed that it amounted to three percent of the $\bar{\delta}_2$ value, or less, for aggregation numbers of 5 or greater. A simplified working form of Eq. (4) for aggregates of 5 or more monomers would then be

$$n = \frac{-\delta_1}{K} + \frac{\bar{\delta}_2}{K} + 1. \tag{6}$$

Equation (4) is not applicable at high dilutions of solute, i.e., in the region of the critical micelle concentration, since the assumption can no longer be made that $X_2' \cong X_2/n$. The extrapolation of the linear relation shown in Eq. (6) to $n < 3$ is not strictly justifiable because the degree of hydrocarbon shielding is decreased by a much larger fraction in passing from $n = 3$ to $n = 2$ than in any step between adjacent higher values of n. The effect is even more pronounced if we pass to $n = 1$, and in addition, the isolation of the ion pair dipole from other dipoles with which it would interact will further increase the relative polarity of the monomer. It must therefore be expected that δ for the unsolvated monomer will be substantially greater than the 10.5 indicated by the extrapolation.

In order to determine whether a $\bar{\delta}_2$ value of 10.5 or somewhat greater was a reasonable value, a crude calculation was devised in which the heats of vaporization at 298°K of typical group I ionic compounds were estimated from their boiling points using the Hildebrand Rule. A solubility parameter of 36 was estimated for the ionic head, and the volume-fraction combination of this value with the value of 7.5, determined for dinonylnaphthalene from surface tension measurements, leads to an estimated value of 12.0 for the average solubility parameter of the soap molecule. Although the Hildebrand Rule was not intended for estimating parameters of ionic compounds, yet the estimated parameter is in good agreement with the one derived from the semi-theoretical treatment of the data and tends to validate the association model.

Nonmicellar Solubility of Dinonlynaphthalene Sulfonates in Polar Solvents

When the solubility parameter of the solvent exceeds 10, it would be expected from the analogy with the solubility of dinonylnaphthalene hydrocarbon that sulfonate solubility would become limited. A few cases were in fact found in which the sulfonate solubility paralleled the decreasing solubility of the dinonylnaphthalene. Two of these solvents were nitromethane (δ = 12.6) and nitroethane (δ = 11.1). Acetone (δ = 9.9) permits mixing in all proportions at room temperature, but allows only limited solubility at -78°C. In most solvents of high solubility parameter, however, the dinonylnaphthalene sulfonates were soluble in all proportions.

The solubility of the dinonylnaphthalene sulfonates in polar solvents having solubility parameters substantially higher than that estimated for the sulfonate monomer results from at least two causes. One is that the ionic end of the sulfonate molecule is solvated by coordination and/or hydrogen bonding with functional groups of the solvent in such a way as to improve the solubility parameter match between solvent and the solute units. The other cause is believed to be tail-to-tail association, which increases the relative contribution of the polar heads to solute-solvent interaction in the more polar liquids. In the extreme case of water this association leads to the formation of large aqueous micelles in which the polar heads lie on the exterior of the micelle. The behavior in polar solvents may thus be understood as extending the association mechanism for matching the solubility parameter of the solute unit to that of the solvent, but as modified by concurrent association of the solute molecule's polar head with solvent molecules.

It is recognized that the application of the solubility parameter concept to polar compounds goes beyond the original definition of δ in terms of London forces alone, but such as extension, which takes account of dipole forces as well as dispersion forces, has been made by Hildebrand and Scott (16). Estimates of δ by the Hildebrand Rule for polar molecules automatically include the electrostatic effects.

Solvents capable of coordination or hydrogen bonding include acetone, methyl isobutyl ketone, ethyl acetate, ethanol, and methanol. The work of Kaufman (21) has shown that alcohols are strongly solubilized from toluene solutions by sodium sulfonate and that hydrogen bonding of the solubilized alcohol can be detected by infrared examination. He found evidence of solubilization for acetone also (22), but the effect was weaker. When the ketone is present in overwhelming proportions as the solvent species, even a modest tendency of the ketonic oxygen to coordinate with the cation will lead to substantial solvation. The osmotic coefficients of Fig. 4 suggest that the solvated dimer and, to a lesser extent, the trimer are the predominant solute species, but that at low sulfonate concentrations appreciable proportions of the solvated monomer may exist. These conclusions apply particularly to solutions in methyl isobutyl ketone and ethyl acetate, whose dielectric constants are below 14. Acetone (ϵ = 20.7) forms strongly conducting solutions for both LiDNNS and NaDNNS, the effect being greater for the sodium salt. Thus an ionic dissociation is imposed on the monomer-dimer-trimer equilibrium of the low-conductance

systems. The dissociation is much stronger for the cesium soap than for the lithium soap, as could be expected from the relative diameters of the unhydrated cations. With ethanol the ability of the solvent molecules to solvate both anion and cation by hydrogen bonding and oxygen coordination, respectively, coupled with the dielectric constant of 24.3, leads to extensive ionic dissociation. Thus the number of osmotically active solute particles exceeds the total number of sulfonate molecules present, even though the monomer-dimer association may still be operative.

It is of interest to examine the solubility and micellar phenomena observed for the group I dinonylnaphthalene sulfonates in relation to the general theory of micelle formation advanced by Winsor (11). Winsor considers systems containing an amphipathic compound in the presence of varying proportions of water and a hydrocarbon and postulates an equilibrium of the form

$$\begin{bmatrix} \text{Aqueous} \\ S_1 \text{ Micelles} \end{bmatrix} \begin{matrix} \rightarrow \\ \leftarrow \end{matrix} \begin{bmatrix} \text{Lamellar Large (or liquid crystals)} \\ \text{G Micelles} \end{bmatrix} \begin{matrix} \rightarrow \\ \leftarrow \end{matrix} \begin{bmatrix} \text{Nonaqueous} \\ S_2 \text{ Micelles} \end{bmatrix}.$$

Such an equilibrium is most readily demonstrated in concentrated solutions in which the amphipath has a suitable balance of lipophilic and hydrophilic components.

In the sulfonate systems of the present study, the transition from hydrocarbon to water environment was obtained by choosing a series of pure solvents of increasing polarity rather than by varying the proportions of water and hydrocarbon present. Under these conditions the S_2 micelle decreases in size as the polarity of the liquid is increased, approaching monomeric dispersion in the lower alcohols, and forms typical S_1 micelles only in water. Progressive additions of water to dilute hydrocarbon solutions of the sulfonate does not lead to the separation of a liquid crystalline phase but, after a substantial solubilization of water, to the formation of water-in-oil or oil-in-water emulsions stabilized by precipitated sulfonate. However, the addition of a small and critical amount of water to the solvent-free sulfonate, or to a sulfonate containing less than 10 percent of benzene, does produce a birefringent phase. Birefringence appears to depend upon some specific action of water; it was encountered in no system from which water was absent. The S_1 and S_2 micelles and the G liquid crystals of Winsor's model thus can be demonstrated in suitably chosen hydrocarbon/water/sulfonate systems, but the intermediate liquid crystalline phase can exist only in the presence of an overwhelming preponderance of the sulfonate. No indication of an intermediate G structure involving aggregates larger than the S-type micelles was found in any water-free solvent of intermediate polarity.

Solubility Behavior of Crystalline Soaps

The relation of soap crystallinity to soap solubility has been discussed briefly by Kaufman and Singleterry (23). They noted that the solubility of crystalline sodium 2-ethylhexyl sebacate in benzene was undetectably small at room temperature, but that it increased sharply in the neighborhood of 47°C to give miscibility of soap and solvent in all proportions. This behavior recalls that of aqueous soap systems at the Krafft point. Similar sharp transitions in solubility have been reported for zinc laurate and stearate in various solvents (24). Murray and Hartley (25) have explained the Krafft point in aqueous soap solutions as the temperature at which the solubility of the crystalline soap reaches the CMC for micelle formation. Therefore, at temperatures higher than the Krafft point the crystalline phase cannot exist in equilibrium with micelles. The same explanation is applicable, in principle, to the sudden increases in solubility noted for amphipathic salts in low-polarity solvents. However, as Winsor (11) has pointed out, the critical increase in solubility may sometimes occur as a sudden large increment accompanying a change of state from solid to liquid crystalline or liquid phases, either of which is likely to have a solubility greater than the CMC for the micellar form. It should be noted that the temperature of a phase change (such as melting or the formation of liquid crystals) is lowered by the presence of a solvent which

can swell or dissolve in one or both of the phases involved in the transition. This shift in the temperature of a phase transition is illustrated by the behavior of lithium stearate in the formation of greases from lubricating oils by the hot-kettle process. In this process a homogeneous solution of the soap in hot oil is chilled to produce the characteristic grease structure of precipitated soap crystals. It is noted that the temperature required for isotropic solution of the soap is lower as the solubility parameter of the oil rises. In the case of a slightly phenylated siloxane, the solution temperature is as high as the melting point of the dry soap (205°C), but as bis(2-ethylhexyl) sebacate is added to the siloxane the solution temperature falls; in the presence of the diester alone it may be only 180°C.

Kissa (26-28) has reported extensive data on the solubility of crystalline lithium salts of aliphatic and alicyclic acids at 27.0°C, a temperature much below that usually required for the transition to high solubility in organic solvents. He reports also some solubilities for salts of other alkali cations. Briefly, he found that: (a) all pure crystalline salts of either branched or straight chain acids had solubilities below 10^{-4} moles/liter in n-heptane, isooctane, or benzene with the straight chain acids showing the lowest solubilities; (b) salts of branched chain or alicyclic acids could be solubilized by the addition of the corresponding acids, with the amount solubilized being nearly proportional to the amounts of acid added; salts of straight chain acids were not solubilized by the presence of either the corresponding acid or of branched chain acids effective in solubilizing branched or alicyclic salts; and (c) mixtures of branched chain salts had solubilities greater than the sum of their separate solubilities; the excess solubility increased as the number of component salts was increased (the most complex mixtures examined formed gels in concentrated solutions); salts of mixed isomeric branched acids derived from commercial intermediates showed moderate to high, or unlimited, solubility.

Although Kissa's data are for carboxylates, which do not always form the small isometric micelles characteristic of the sulfonates (15,29,30), the theory proposed for the sulfonates appears capable of extension to the carboxylates. It may be noted that when Kissa mixed lithium salts of nine pure branched chain acids, the solubility was increased 400 fold over the sum of their separate solubilities. The major change in the thermodynamic situation when the pure salts are mixed is that the condensed salt phase becomes a solid solution of geometrically unlike molecules and approaches the character of the viscous liquid phase just postulated for the sulfonates. The solubility then becomes that appropriate to a liquid/liquid mixture. Kissa reported difficulty in reaching equilibrium solubilities with some mixtures. It is thus not clear whether these mixed salt systems were above or below their critical solution temperatures. In the case of the nine-salt mixture the fact that the solution passed to a gel as the concentration was increased suggests that this system was above the critical temperature and so was miscible in all proportions. The salts of isomeric mixed acids obtained from commercial sources had solubilities as much as 1000 times that of some of the pure single salts of which they were composed. They appear to have been miscible with isooctane in all proportions but to have had limited liquid/liquid solubility in benzene, except for the lithium tridecanoate mixture which formed gels in concentrated solutions.

The differences in solubility behavior of the pure crystalline salts and of mixtures of the same pure salts are most readily understood if we focus attention on the different free energies of the solid phases involved rather than on changes in micelle stability or structure as a result of mixing species. Straight chain aliphatic acids can pack closely in the crystal, allowing strong dispersion-force interactions between the methylene groups of the chain (31). The standard free energy decrease for a molecule passing from hydrocarbon solution into the crystal is relatively large and the solubility is accordingly small. Mixing straight chain acids causes only a minor decrease in the amount of interaction between chains, so mixtures of straight chain acids show no enhanced solubility. In the small nonaqueous micelle the hydrocarbon chain must be in rather intimate contact with the disordered solvent molecules, rather than adlineated to each other as in the crystal, so the standard free energy change for micelle formation is less than that for crystal formation.

Consequently, the micellar phase is unstable with respect to the crystal until the temperature of the system approaches the melting point of the soap, at which point there is usually a sharp transition to unlimited solubility.

When the carboxylate molecules are branched the molecules cannot pack so closely in the crystal, and there is less dispersion-force interaction between chains. In addition, the branched chains contain additional methyl groups, which interact less strongly than methylene groups. Thus branched chain crystals are formed from the hydrocarbon solution with a smaller decrease in free energy than are straight chain crystals, so a higher proportion of soap molecules remains in solution at equilibrium. Mixing branched chain species results in a further decrease in geometrical economy of packing and in an increase in entropy, which still further minimizes the free energy of solid formation and increases the equilibrium solubility. As the complexity and heterogeneity of the molecules in the solid carboxylate phase are increased, a point is reached at which the mixture is in equilibrium with a higher concentration of dissolved species than is required for the formation of micelles. The solid phase then passes over completely to the micellar state unless the system is below the critical solution temperature, in which case a solvent-swollen "solid" phase equilibrates with the micellar solution, i.e., there is limited micellar solubility.

The solubilization of pure branched or alkyl alicyclic salts by the addition of the corresponding acid, as reported by Kissa, is also understandable in the light of the general theory proposed here. The presence of acid in the equilibrium solid phase results in the dilution of the ion pair interactions in the crystal, and so reduces the free energy difference between molecules in the crystal and molecules in solution. Kissa found that the branched chain carboxylate acid mixtures formed micelles in the hydrocarbon phase. The presence of the acid in the micelles dilutes the polarity of the micelle core and improves core shielding, which improves the solubility parameter match of the micelle with hydrocarbon solvents. This again contributes to increased solution of the carboxylates in the presence of the corresponding acids.

SUMMARY

A study of the solubility of alkali dinonylnaphthalene sulfonates in a wide variety of organic solvents has led to the following generalizations about their solubility relations. These generalizations are considered to be applicable to many other oil-soluble organic salts.

1. The alkali dinonylnaphthalene sulfonates are micelle forming in all low-polarity solvents in which they are soluble.

2. The solubility or compatibility of the sulfonate with a solvent depends upon the closeness of match of the Hildebrand solubility parameter of the solvent with that of the hydrocarbon exterior of the nonaqueous micelle. DNNS solubility roughly parallels that of the parent hydrocarbon, dinonylnaphthalene, in the same low-polarity solvents.

3. Micelle size is nearly independent of the alkali cation present but is strongly dependent upon the solubility parameter of the solvent. The micelle size decreases as the solubility parameter increases. Decreasing size increases the exposure of the polar micelle core to the solvent and, so, improves the parameter match between solvent and solute.

4. The condensed phase of the alkali dinonylnaphthalene sulfonates behaves as a viscous liquid rather than a crystalline solid in solubility equilibria, e.g., in cases of limited sulfonate solubility in silicones or fluoroesters. With good solvents the sulfonates are miscible in all proportions, as would be expected for a pair of liquids having comparable solubility parameters.

5. Crystalline organic salts are sparingly soluble in low-polarity solvents if they consist of a single molecular species even though the molecular weight may be large. The low solubility results because the molecular interactions in the crystal give a lower free energy state than is found in the liquid-like micelle. Chain branching and mixing of branched molecular species degrade the crystal structure toward the liquid state and cause increased solubility, or even miscibility of soap and solvent in all proportions.

6. In most polar solvents the alkali dinonylnaphthalene sulfonates are soluble in all proportions. Compatibility of solute and solvent appears to be achieved by sulfonate association to dimer or trimer and by solvation through coordination or hydrogen bonds.

7. In solutions having strong solvating action and dielectric constants above 15, the dinonylsulfonates show substantial ionic dissociation and electrical conductance, the effects varying in magnitude with the particular cation present. The hydrogen bonding solvents methanol and ethanol give the most strongly conducting solutions. In water the sulfonates give rise to aqueous-type micelles.

8. Alkali sulfonates in water-miscible solvents separate readily upon the addition of suitable amounts of water to form three-component liquid crystalline phases. At extremely high sulfonate concentrations a liquid crystalline benzene/water/sulfonate system has been obtained which completes the formal analogy between these systems and Winsor's model of an equilibrium:

$$\left[\begin{array}{c}\text{Nonaqueous}\\ \text{Micelles}\\ \text{in}\\ \text{hydrocarbon}\end{array}\right] \begin{array}{c}\rightarrow\\ \leftarrow\end{array} \left[\begin{array}{c}\text{Lamellar}\\ \text{Liquid}\\ \text{Crystal}\end{array}\right] \begin{array}{c}\rightarrow\\ \leftarrow\end{array} \left[\begin{array}{c}\text{Aqueous}\\ \text{Micelles}\\ \text{in}\\ \text{water}\end{array}\right]$$

The investigation of the solubility of oil-soluble emphipaths is being extended to include other cation types and to study in more detail ion dissociation in nonaqueous polar solvents.

UNCLASSIFIED

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