NRL Report 6579

Effect of the Cation on Solubilization by Oil-Soluble Sulfonates and the Applicability of the Mass Law

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September 5, 1967

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Washington, D.C.

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ABSTRACT

The dinonylnaphthalene sulfonates of cesium, sodium, barium, magnesium, and zinc were studied as solubilizing agents for methanol, normal propylamine, and acetic acid in toluene. By a previously developed gas chromatographic technique, the extent of solubilization of the three species by each of the sulfonates was measured over the range of 0 to approximately 2-wt-% solubilizate. The mass law was shown to be consistent with the experimental observation that the concentration ratio of bound solubilizate to total solubilizer is dependent upon the free solubilizate concentration and independent of the solubilizer concentration. The data and theoretical considerations lead to the additional conclusions that the partition law is not universally applicable to solubilization, and that the size distribution of micelles is fixed by the free solubilizate concentration.

The initial rate of interaction as a function of free solubilizate concentration usually increased with increasing electronegativity of the soap cation. The soaps of zinc and magnesium were exceptions when acetic acid was the solubilizate. This deviation is attributed to the covalent properties of these metals and the bifunctional reactivity of acetic acid.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C02-09
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EFFECT OF THE CATION ON SOLUBILIZATION BY OIL-SOLUBLE SULFONATES AND THE APPLICABILITY OF THIS MASS LAW

INTRODUCTION

Micelle formation and solubilization have been studied extensively in aqueous systems, but much less in nonpolar solvents. Aggregation numbers of the salts (soaps) of dinonylnaphthalene sulfonic acid (HDNNS) in hydrocarbons vary with the cation, although the variation is only about twofold (1-3). In these systems, as the coordinating tendency of the cation increases, the compressive interactions between functional groups distort the sphericity of the micelle and diminish the apparent volume of the dinonylnaphthalene sulfonate anion ($DNNS^-$)(1).

Solubilization of methanol in toluene solutions of sodium and magnesium dinonylnaphthalene sulfonates (NaDNNS and $Mg(DNNS)_2$) reduces micelle size, and at a methanol concentration of 2-wt-% the aggregates contain only one or two sulfonate molecules (4). The interactions holding the soap monomers in micelles are replaced by coordination and hydrogen bonding with methanol molecules, which shield the polar ion pair and render it monomerically soluble. However, solubilization of small polar molecules need not always destroy the integrity of the micelle. Solubilization of water by zinc dinonylnaphthalene sulfonate ($Zn(DNNS)_2$) in benzene increases the aggregation number of the micelle (1). This effect also can be explained by hydrogen bonding of the solubilizate to the soap anion and oxygen bonding to the zinc cation. The water molecules, unlike those of methanol, contain no hydrocarbon group, and do not increase the solubility of the association complexes in benzene, but their bifunctionality allows crosslinking of the hydrated sulfonate molecules to maintain and enlarge the micelle. Measurements of the micelle size of barium dinonylnaphthalene sulfonate ($Ba(DNNS)_2$) by the fluorescence depolarization (5) and ultracentrifugal (6) techniques agree to within less than one monomer per aggregate. Although it might be presumed that the necessary introduction of fluorescent dye for the former technique could disturb the micelle enough to radically alter its size, the striking agreement between the two methods indicates that in this solubilization the dye molecule simply substitutes for a soap monomer in the aggregate.

Concepts of the aqueous micelle have envisioned the integrity of the aggregate as a prerequisite for solubilization, but a broader concept is required for extending the scope to nonaqueous systems. In the most general sense, solubilization is a process occurring in the presence of a solvent, whereby the solubilizing agent diminishes the activity coefficient of the solubilizate, and both species remain soluble thereafter (7). The earlier restricted concept falls within the scope of this definition. The term solubilization is applied here to interactions of substances with the solubilizer irrespective of their solubility in pure solvent, because these interactions depend only in a trivial manner upon the independent solubilities. In early studies of solubilization the typically nonpolar solubilizate was held in the nonpolar interior of the aqueous micelle. There it did not interfere with the aggregation mechanism, which has been described as hydrophobic bonding (8). Nonaqueous micelles, on the other hand, are held together by interactions between the polar ends of monomers in the micelle core, and introduction of small polar molecules can interfere with these interactions.

In the present investigation the dinonylnaphthalene sulfonates of cesium (CsDNNS), sodium, magnesium, barium, and zinc were studied as solubilizers of methanol, acetic acid, and normal propylamine in toluene. Equilibrium vapors over solutions of the solubilizates, with and without soap, were analyzed by a gas chromatographic method

previously described (4,9). The vapor composition, a function of solute activity in the liquid, can be used tc compute concentrations of free and bound (solubilized) solubilizate.

MATERIALS

The HDNNS was a special research grade supplied in moist heptane-methanol solution by King Organic Chemicals, Inc., of Norwalk, Conn. (4,5). Its preparation included a rejection of impurities extracted by a methanol phase (1).

The NaDNNS and CsDNNS were prepared by potentiometric titration of the HDNNS solution with the appropriate aqueous hydroxides after addition of sufficient isopropanol or methanol to prevent phase separation. The water introduced with the hydroxide ensured a satisfactory response of the glass electrode. Each solution was over titrated and carefully back titrated with dilute HDNNS after the exact pH of neutrality had been determined. A small quantity of gelatinous impurity was centrifuged from the nearly neutralized acid solutions (1). After dilution with benzene or hexane the neutralized solution was repeatedly washed with water.

The $Mg(DNNS)_2$, $Ba(DNNS)_2$, and $Zn(DNNS)_2$ were prepared by metathesis from NaDNNS. About 40 g of NaDNNS in 500 cc of aqueous solution containing just enough methanol or isopropanol to prevent turbidity was added dropwise in 3-4 hrs to 2 L of vigorously stirred aqueous solution of twice the requisite weight of chloride or sulfate of the appropriate cation to complete the reaction. Continued agitation agglomerated the curdy soap, and the relatively clear supernatant liquid was discarded. The drained precipitate was taken up in a small volume of methanol or isopropanol, diluted to 500 cc with water and just enough alcohol to clarify the solution, and was reprecipitated as before in 2 L of precipitant of one-fourth the previous concentration. After the supernatant liquid was expressed, the precipitate was washed with a 0.1% aqueous solution of the precipitant, and finally with water which was again expressed. The precipitate was then dissolved in 500 cc of benzene or hexane, and alternately washed with water and centrifuged until the aqueous phase gave no test for the anion of the precipitant.

The ultimate isolation of all the soaps consisted of repeated vacuum evaporations in a rotating evaporator, beginning at ambient temperatures and concluding at 70 to 80°C with additions of dry benzene between evaporations, and then repeated lyophilizations from quickly frozen dry benzene solution to remove the last traces of moisture and solvents. After lyophilization appeared complete, the temperature and pressure were maintained at 80 to 90°C (just below the softening point) and 1μ Hg for at least 1 hr. The isolated soaps were sealed against the atmosphere until used.

The cesium hydroxide used in the preparation of CsDNNS was the purest grade obtainable and was supplied by American Potash and Chemical Co. Their analysis indicated that the metal impurities were rubidium (0.1% as Rb_2O), potassium (0.016% as K_2O), sodium (0.026% as Na_2O), and lithium (0.000% as Li_2O). All other inorganic chemicals used were analyzed ACS reagent grade, selected for the highest purity.

Benzene (Baker's ACS) and toluene (Phillips Petroleum "pure") were percolated through Davison Chemical Co. 950 silica gel to remove polar impurities and water, and were stored over sodium until used. The methanol was a specially selected lot of Baker's ACS grade, containing less than 0.15 mole-% moisture as determined by gas chromatography. The *n*-propylamine was Eastman No. 1216 and was used as received. Its gas chromatogram was free of extraneous peaks except for water, estimated to be present to the extent of 0.1-vol-%. The acetic acid was Baker's ACS reagent grade whose gas chromatogram indicated less than 0.22 mole-% water.

MEASUREMENTS

Equilibrium vapors over the solutions were analyzed by a Perkin-Elmer 154B gas chromatograph. Modifications of the instrument and experimental procedures, except those mentioned here, have been described in earlier publications (4,9). For acetic acid the stainless steel sampling loop of the instrument was replaced with one of glass to avoid unpredictable trapping of the acid vapor. To avoid the excessive retention time of toluene, the column was backflushed as soon as acetic acid peaks were recorded. The chromatographic operating conditions are compiled in Table 1.

Table 1
Chromatographic Operating Conditions

Species Studied	Column Packings*	Operating Temp (°C)	Inlet Pressures (psig)	Carrier-Gas (Helium) Flow Rates (cc/min)
Methanol	Carbowax 400 (polyethylene glycol) 29-wt-% on 60-80-mesh Gas-Chrom P†	80	13	115
n-Propylamine	Armeen SD 16-wt-% on 60-80-mesh Gas-Chrom P†	50	8	145
Acetic acid	Porapak Q‡	116.5	13.5	165

*All columns were 0.64-cm-O.D. stainless steel

†Column length: 1.83 m

‡Column length: 0.25 m

RESULTS AND DISCUSSION

In a previous study (4) solutions of closely equivalent soap concentrations were used to maintain strict comparability among measurements. In the present work the effect of variations in the soap concentration was studied. Methanol was added incrementally to toluene solutions of both NaDNNS and $Ba(DNNS)_2$ containing approximately 2-, 4-, and 6-wt-% soap. Exact concentrations were: for NaDNNS, 1.993%, 2.057%, 3.908%, and 6.046%; for $Ba(DNNS)_2$, 2.021%, 4.080%, and 6.046%. The extent of methanol solubilization as a function of methanol concentration is plotted in Fig. 1. The abscissa is the methanol concentration of a binary toluene-methanol solution whose saturated vapor composition (and methanol activity) equals that of the ternary toluene-soap-methanol solution; it corresponds to the concentration of unsolubilized methanol in the soap solution. The ordinate is the ratio of solubilized methanol to the quantity of soap present. Although three concentrations of each soap are represented, the plots are independent of soap concentration, and the ordinate is clearly a function of the free alcohol concentration. Exact equivalence of soap concentration, therefore, is not a prerequisite to comparability of the data, and dependence upon the free solubilizate concentration implies the applicability of the mass law.

Consider the reaction

$$aM + S_b \rightleftharpoons M_a S_b \ , \tag{1}$$

where M represents a methanol molecule, S represents a soap monomer, b is the aggregation number of the soap micelle, and a is the number of molecules of methanol solubilized by a micelle. According to the mass law

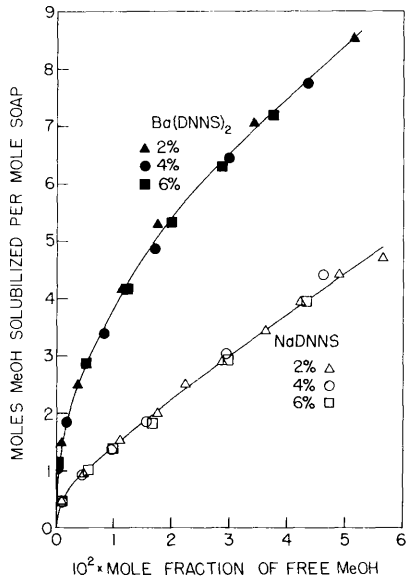


Fig. 1 - Effect of soap concentration; solubilization of methanol by 2, 4, and 6% solutions of sodium and barium dinonylnapthalene sulfonates

$$K = \frac{[M_aS_b]}{[M]^a[S_b]}, \tag{2}$$

where the brackets denote concentration, and K is the equilibrium constant. For any specific value of $[M]$, such as $[M]_1$, the ratio $[M_aS_b]$ to $[S_b]$ must be a constant, irrespective of the total soap concentration, for

$$K[M]^a = \frac{[M_aS_b]}{[S_b]}. \tag{2a}$$

The ordinate in a plot analogous to Fig. 1 can be represented by R, the concentration ratio of solubilized methanol molecules to total soap molecules, where

$$R = \frac{a[M_aS_b]}{b([M_aS_b] + [S_b])}. \tag{3}$$

From Eq. (2) $[M_aS_b] = K[M]^a[S_b]$. By substitution for $[M_aS_b]$ in Eq. (3),

$$R = \frac{a\,K[M]^a[S_b]}{b\,(K[M]^a[S_b] + [S_b])} = \frac{a\,K[M]^a}{b(K[M]^a + 1)}. \tag{4}$$

Equation (4) contains no terms referring to soap concentration, and R is defined by the single variable, $[M]$, and the constants a, b, and K.

Equation (4) is general and does not depend on the nature of the intermediate steps by which M_aS_b is formed from $M + S_b$. It is valid even for interaction of solubilizate with the soap monomer. If the same solution should also contain slightly smaller (or larger) micelles, S_c, an analogous relation would hold, and for this species also, R would be independent of the total soap concentration, although it might have a different magnitude than for S_b micelles. Thus as long as the distribution function for micelle size was independent of soap concentration, the average value of R would be nonvariant with soap concentration. Since R is experimentally independent of soap concentration, it may be concluded that either one micelle size is overwhelmingly predominant in a system of given concentration of unsolubilized alcohol, or that the distribution function

for micelle size at a given free methanol concentration is independent of the total soap concentration. Since, at a given concentration of methanol, [M], the amount of methanol solubilized is directly proportional to the amount of soap present, it might be inferred that there is a valid coefficient for simple partition of solubilizate between the solvent and a soap pseudophase in these systems. An expression based on Eq. (1), and describing the concentration ratio of methanol associated with soap to that independently dissolved in the solvent, is $(a[M_aS_b]/[M_aS_b])/[M]$, or $a/[M]$. Inspection of Fig. 1 shows that the amount of methanol solubilized per mole of soap is not linear with the free methanol concentration, and that $a/[M]$ is not a constant, as it would have to be to satisfy the partition law. Departure from linearity results partly from the approaching saturation of the soap by methanol and partly from changes in the micelle (the pseudophase) induced by solubilization. In view of the foregoing, the formal application of a partition coefficient to solubilization phenomena should be considered only in those systems for which its validity is established.

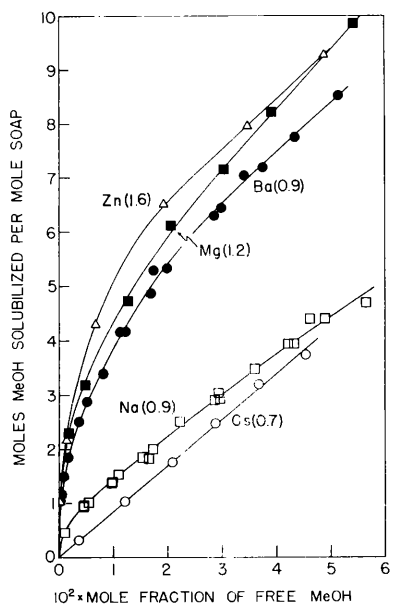


Fig. 2 - Solubilization of methanol by cesium, sodium, barium magnesium, and zinc dinonylnaphthalene sulfonates. (Data for the $Mg(DNNS)_2$ curve are from Ref. 4.)

Figure 2 compares the degrees of solubilization as a function of free methanol concentrations for the five soaps investigated. Weight concentrations of the toluene-soap solutions to which methanol was added were: for CsDNNS, 2.556%; for $Mg(DNNS)_2$, 1.757 to 1.831%; and for $Zn(DNNS)_2$, 2.775%. Concentrations of NaDNNS and $Ba(DNNS)_2$, were reported above. Since it has been demonstrated above that the plot is independent of the stoichiometric soap concentration, all points on the respective curves of Fig. 1 are considered comparable and bear a single symbol in Fig. 2 to simplify notation. The curve for $Mg(DNNS)_2$ is plotted from previously published data (4). In the earlier work an inflection point in the data for NaDNNS was observed and attributed to a stepwise solubilization, but this effect is not confirmed in the present study, which has been more complete. The inflection therefore is believed to have been the result of systematic experimental errors.

The ordinate of these plots can be represented as the extent of solubilization either per mole or per equivalent of soap. Solubilization per mole is used here to highlight the effect of the cation; the alternative plot would emphasize the effect of the anion or approximately the effect per unit weight of soap (9). The influence of varying the cation is most effectively illustrated by the comparative slopes of the curves near the origin (Fig. 2). The intensity of methanol solubilization by soaps of these cations in increasing order is: Cs(0.7), Na(0.9), Ba(0.9), Mg(1.2), and Zn(1.6). (Numbers in parentheses are the respective

electronegativities of these metals.) It is evident then, within this array of data for methanol solubilization, that the intensity of interaction between the cation and methanol correlates well with the electronegatives of the respective elements.

The plot for CsDNNS is linear throughout the experimental range and has the lowest initial slope of the plots in Fig. 2. Cesium has the largest ionic radius and the smallest electronegativity of the cations and therefore should be expected to participate least effectively in coordination interactions. The constant slope indicates that little or no interaction occurs between the cesium and the methanol and that all, or nearly all, of the solubilization occurs at the anion. The linearity in this case satisfies the formal requirement for a partition coefficient in the range studied.

Above a free methanol concentration of about 3×10^{-2} (mole fraction) all the plots are relatively linear, which qualitatively indicates that in this concentration region the effect of the cation is substantially spent; further interaction is essentially a function of the anion which is a large reservoir for solubilization. Extrapolation of the linear region to zero methanol concentration, then, should provide an approximation of the degree to which the cation has associated with the methanol. For sodium the extrapolated value is about one molecule of methanol per cation; for magnesium and barium, about 4; and for zinc, more than 4.5.

Figure 3 compares the solubilization of n-propylamine by the various soaps. Weight concentrations of the soap-toluene solutions to which amine was added were: for CsDNNS, 2.259%; for NaDNNS, 1.839 to 1.889%; for $Mg(DNNS)_2$, 1.822 to 1.911%; for $Ba(DNNS)_2$, 2.000%; and for $Zn(DNNS)_2$, 1.820%. The curves for $Na(DNNS)_2$ and $Mg(DNNS)_2$ are plotted from earlier data (9). The CsDNNS curve reaches a plateau at a small fraction of a molecule of amine solubilized per cation. Neither the cation nor the $DNNS^-$ ion interact appreciably with the amine. The major metallic contaminants found by qualitative spectroanalysis of the CsDNNS were the alkalis; estimates of these by flame photometry were Rb, 0.12%; K, 0.04%; Li, 0.01%; and Na, 0.2%. This estimate is consistent with the presence of one contaminating cation in about 50. It is unlikely that these contaminants account for the solubilization indicated, but at this low level the experimental uncertainties could have resulted in exaggerated estimates of interation.

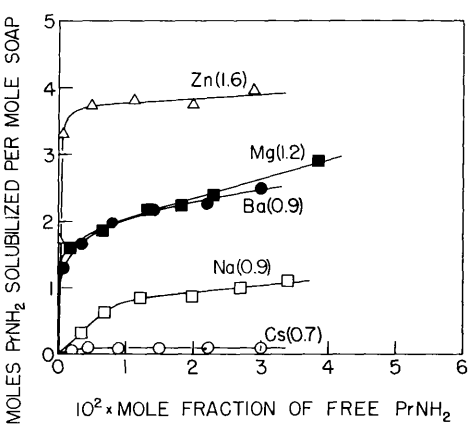


Fig. 3 - Solubilization of n-propylamine by cesium, sodium, barium, magnesium, and zinc dinonylnaphthalene sulfonates. (Data for the $Mg(DNNS)_2$ and $Na(DNNS)_2$ curves are from Ref. 9.) (Numbers in parentheses represent the respective electronegativities.)

Again as in Fig. 2 the initial slopes arrange themselves in order of the electronegativities of the respective cations. All the curves have lesser ultimate slopes than those in Fig. 2. The zinc ion coordinates to its limit with four amine molecules. The ultimate slopes for the sodium, barium, and magnesium soaps suggest that these cations form less stable amine complexes and require higher amine concentrations for saturation.

Figure 4 displays the data for solubilization of acetic acid. Weight concentrations of the soap-toluene solutions to which the acid was added were: for CsDNNS, 2.373%; for NaDNNS, 1.911%; for $Mg(DNNS)_2$, 1.827%; for $Ba(DNNS)_2$, 2.116%, and for $Zn(DNNS)_2$, 1.902%. Although the data resemble results for solubilization of both methanol and n-propylamine, there are substantial dissimilarities. Initial slopes are in the expected order for CsDNNS, NaDNNS, and $Ba(DNNS)_2$, but the relative order for $Mg(DNNS)_2$ and $Zn(DNNS)_2$ is reversed, and the shifted order appears to invalidate conclusions drawn above. The curve

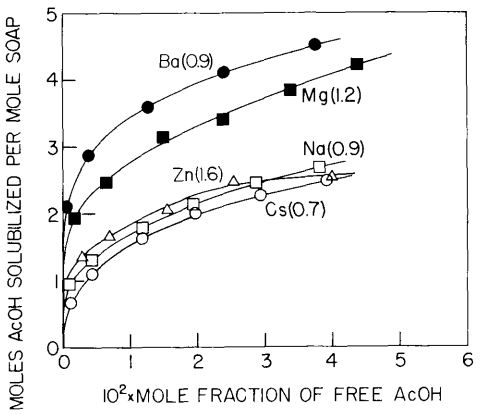
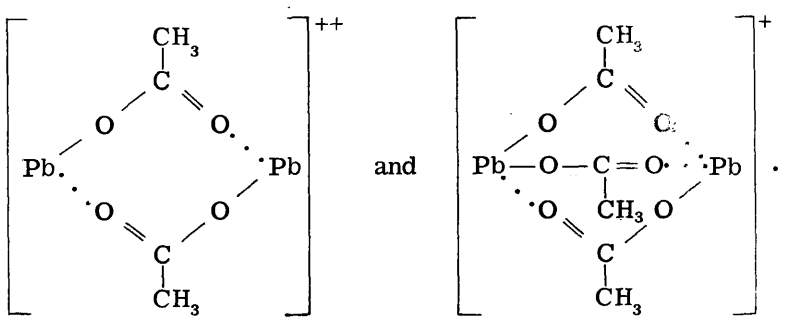


Fig. 4 - Solubilization of acetic acid by cesium, sodium, barium, magnesium, and zinc dinonylnaphthalene sulfonates. (Numbers in parentheses represent the respective electronegativities.)

for $Zn(DNNS)_2$ approaches a plateau within the experimental range, and appears to deny the participation of the $DNNS^-$ ion in these interactions. However, consideration of the specific properties of zinc, magnesium, and acetic acid can reconcile these data with those of Figs. 2 and 3.

Zinc and magnesium both form covalent bonds, as in dialkyls and Grignard reagents, whereas cesium, sodium, and barium are more characteristically electrovalent. Zinc demonstrates its covalent behavior by its amphotericity, but magnesium is less covalent in behavior. The bifunctional properties of acetic acid distinguish it from methanol and *n*-propylamine, and reveal the covalent natures of zinc and magnesium. Stable acetate complexes can result from the binding of two metal atoms, each to one of the carboxylate oxygens (10) such as



Crystals of several metal carboxylates are polynuclear complexes (11-14), and those of zinc acetate dihydrate have been reported to be a chelate rather than a bridged, or polynuclear complex (15), but a variety of copper carboxylates, in the crystalline form and in organic solvents, have been reported to be of bridged structure (16,17).

The $Zn(DNNS)_2$, then, can be visualized as participating in either a bridged or chelate complex, wherein each acetate ion can occupy two sites on a zinc atom or atoms. The proton thus released by acetic acid in a low polarity solvent probably associates itself with a sulfonate anion. Capture of the proton by the $DNNS^-$ ion counteracts reversal of the interaction and maintains electrical neutrality. Because of the marked covalent behavior of the $Zn(DNNS)_2$, two pairs of electrons in the coordination sphere of the zinc atom participate in covalent bonds with the $DNNS^-$ ions and therefore block possible sites for association with acetic acid molecules or acetate ions. This blocking plus the occupation of three active sites by each solubilized molecule of acetic acid limits the availability of the soap for further interaction. The result is that the relative initial slope and ultimate extent of solubilization are less than would be inferred from the behavior shown with methanol and amine.

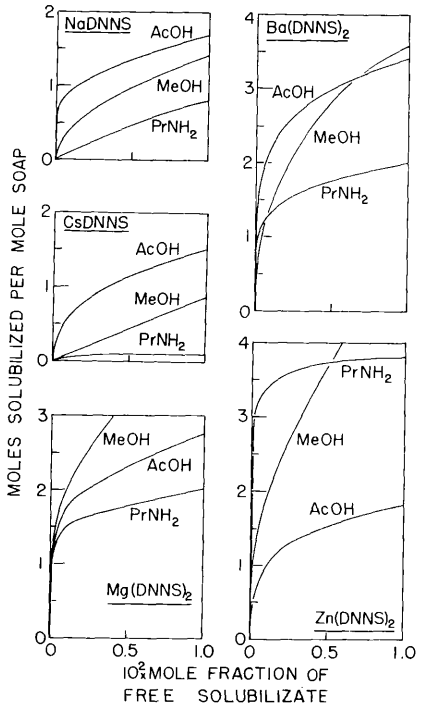


Fig. 5 - Relative affinities of solubilizates (methanol, *n*-propylamine, and acetic acid) for each of five cations (Cs, Na, Ba, Mg, and Zn)

The case for magnesium is much the same as that for zinc, but magnesium is less covalent than zinc. The curve for $Mg(DNNS)_2$, nevertheless, is depressed enough to fall below that for $Ba(DNNS)_2$. The latter soap, by contrast, is distinctly ionic. Thus, its cation and anion can interact independently with acetic acid molecules in the same way that the ions of NaDNNS can, by formation of hydrogen bonds to anion oxygens and by coordination of the cation with the carbonyl oxygen of the acid. The CsDNNS plot for acetic acid is neither linear from the origin as for methanol, nor indicative of negligible interaction as for the amine. Instead, it rises initially and reaches a nearly constant slope. Its shape resembles the methanol plots for the other soaps, suggesting an initial reactivity of the cesium ion which is soon spent, and a continuing interaction of the acid with the anion at higher acid concentrations.

It is revealing to compare interactions of the three solubilizates with a single cation. Figure 5 comprises magnified plots of the data at low solubilizate concentration, where the effect of the cation is most apparent. The slopes show that the intensity of solubilization decreases in the order, acetic acid > methanol > *n*-propylamine, but there are exceptions. There appears to be no question in the case of sodium and cesium, but for barium there may be some question about the validity of the relative slopes for methanol and *n*-propylamine as they are extrapolated to the origin from the data. The combined margins of experimental and extrapolation errors could be responsible for the minimal crossover of the methanol and propylamine curves. There are obvious exceptions, however, for zinc and magnesium. The amine is more firmly bound to the zinc than is methanol, and the low slopes for acetic acid with zinc and magnesium should be interpreted in the light of the preceding discussion of Fig. 4.

Comprehensive rules for predicting solubilization would be premature at this time, although these data can suggest trends. Solubilization can be promoted by specific interactions of the cation and the anion with the solubilizate. The role of the solvent in solubilization has not been studied, but inasmuch as it is a factor in micelle formation (3) it can be expected to affect solubilization.

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13. ABSTRACT

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Micelles						
Nonpolar solvents						
Soaps						

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