

Unusual Solubilization Behavior of a Maleic Acid–Hexyl Vinyl Ether Copolymer

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An intriguing previous observation concerning some unusual solubilization effects in a polysoap system was explored further. The polysoap system consisted of a maleic acid–hexyl vinyl ether copolymer in an aqueous LiCl solution. The extent of micellization of the polysoap is known to decrease with increasing pH due to repulsion between ionized acidic groups on the polymer backbone. Accordingly, the solubilization of pyrene and several other water-insoluble organic compounds diminished with rising pH; moreover, the pH dependence of the solubilization was essentially identical for these compounds. However, surprisingly, the solubilization of benzophenone remained constant with changing pH. For the present investigation, we employed additional solubilizates, expanded the pH range, and added a tetramethylammonium chloride supporting electrolyte system. Nevertheless, only the same two types of behavior were observed in the LiCl system. One group of solubilizates comprised eight compounds, all of which behaved like pyrene in that their solubilization changed with pH in an essentially identical manner, thereby furnishing a novel method for estimating the extent of micellization of the polysoap. The other group, containing benzophenone and three other solubilizates, exhibited constant solubilization with changing pH, indicating that, for this group, a mechanism besides the micellar one must contribute to the solubilization. In the tetramethylammonium chloride system, however, results were quite different. The “pyrene group” compounds no longer shared a common pH dependence, while the “benzophenone group” compounds still exhibited a common behavior, but showed a maximum with increasing pH. This newly observed behavior is ascribed to the possible cosolubilization of the tetramethylammonium ion in the interior of the polysoap molecules.

Introduction

Polysoaps constitute a particular class of polyelectrolytes possessing hydrophobic side chains that can form intramolecular micelles in aqueous solution.¹ Like micelles formed from monomeric surfactants, polysoap micelles have the ability to enhance the water solubility of normally sparingly soluble organic compounds. In earlier work, we determined the size of the micelles suspended from hexyl polysoap molecules by fluorescence quenching.² Use of this technique necessitated that we determine the solubilities of selected organic compounds in polymer solutions under a variety of conditions. In so doing, we observed some unexpected solubilization behavior.

The polysoap was an alternating copolymer of maleic acid and hexyl vinyl ether dissolved in an aqueous 0.1 M LiCl solution. By a number of experimental methods, including viscosimetry,³ potentiometry,³ calorimetry,⁴ solubilization⁵ and fluorescence probing,^{6,7} it had previously been established that Θ_m , the fraction of polysoap in micellized form, is pH-sensitive; it is greatest at low pH and decreases with increasing pH as a result of macromolecular expansion caused by the repulsion between ionized carboxylate groups. Consistent with this behavior, the solubilization limits of pyrene and several other water-insoluble organic compounds were all found to decrease uniformly by a factor close to 0.6 as the pH was raised from 4.5 to 5.7. This factor was taken to be a measure of the relative

degrees of micellization of the polysoap. Surprisingly, however, the solubilization limits of benzophenone and some closely related compounds remained constant with this change in pH.²

To explore this unexpected behavior further, we have expanded the pH range in the LiCl solvent, added a significant number of new solubilizates, and extended the type of supporting electrolyte system by including experiments in a 0.1 M tetramethylammonium chloride (TMACl) solvent at various pH values. The latter electrolyte system was chosen because the lithium ion has been shown to be site-bound to the completely deprotonated dicarboxylate ion,⁷ which limits the expansion of the macroion beyond half-neutralization,^{7,8} whereas the tetramethylammonium ion is not site-bound and therefore does not impose such a limit on the macromolecular expansion.^{7,8} We have also expanded the number of solubilizates in order to obtain further information about the effects of chemical structure on solubilization behavior. The results of this investigation are presented here.

Experimental Section

Two samples of maleic anhydride–hexyl vinyl ether copolymer (hexyl copolymer, Figure 1) were used. One was our sample BRB#2, described previously.² The other was our sample PN#1, synthesized in this laboratory by P. Nguyen. The degree of polymerization (DP) of BRB#2 was 1100, and, by means of a comparison of viscosities in tetrahydrofuran, that of PN#1 was estimated to be close to 1000. Trial solubilization runs with several organic compounds indicated that both copolymer samples behaved alike under identical conditions. Polymer solutions were prepared as described previously.² The

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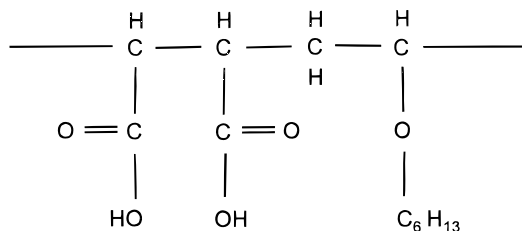
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TABLE 1: Solubilization in Hexyl Copolymer Solutions Containing 0.1 M LiCl

| solubilizate | $S_{4.5} \times 10^3$ ^a | $S_{5.7} \times 10^3$ ^a | $S_{6.8} \times 10^3$ ^a | $R_{5.7}$ ^b | $R_{6.8}$ ^b |
|--------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------|------------------------|
| pyrene | 4.13 | 2.55 | 2.18 | 0.62 | 0.53 |
| 9-methylanthracene | 9.12 | 5.63 | | 0.62 | |
| biphenyl | 12.8 | 8.01 | 6.46 | 0.63 | 0.50 |
| fluorene | 5.90 | 3.54 | 3.01 | 0.60 | 0.51 |
| cyclohexyl phenyl ketone | 8.54 | 5.34 | | 0.63 | |
| naphthyl phenyl ketone | 22.4 | 13.7 | | 0.61 | |
| nonyl phenyl ketone | 48.8 | 32.5 | | 0.67 | |
| 2-bromonaphthalene | 70.6 | 44.1 | | 0.62 | |
| benzophenone | 19.6 | 19.7 | 19.8 | 1.01 | 1.01 |
| 4-bromobenzophenone | 8.81 | 8.56 | 8.68 | 0.97 | 0.99 |
| fluorenone | 12.3 | 12.8 | 12.2 | 1.04 | 0.99 |
| 1,1-diphenylethanol | 35.3 | 36.3 | | 1.03 | |

^a S_{pH} = moles solubilizate per mole polyacid repeat unit at saturation at indicated pH. ^b $R_{pH} = S_{pH}/S_{4.5}$.

**Figure 1.** Structure of the repeat unit of the hydrolyzed copolymer of maleic anhydride and hexyl vinyl ether.

concentration of the copolymer throughout this paper is denoted by C_p and expressed in moles of repeat units per liter of solution. For solubilization experiments, saturated solutions of the solubilizates were prepared by adding excess amounts of large crystals to known volumes of hexyl copolymer solutions previously adjusted to the desired pH and electrolyte concentration. The mixtures were allowed to equilibrate for 20 days at 23 ± 1 °C by slow inversion on a rotary mixer, protected from light. After filtration followed by centrifugation, the concentrations of the solubilizates were determined by absorption spectrometry, diluting with ethanol where necessary. Solubilities in the supporting electrolyte solvents were determined similarly. Titrations were performed at 23 ± 1 °C using a Radiometer Model PHM64 Research pH meter equipped with a Ross combination electrode. A two-point calibration was performed against standard pH 4 and pH 10 buffer solutions. Aqueous solutions of LiOH in 0.1 M LiCl and TMAOH in 0.1 M TMACI were standardized against ultrapure potassium acid phthalate by titration to a phenolphthalein endpoint. Dilute HCl (0.2 N) was then standardized against the LiOH solution by titration to a phenolphthalein endpoint. A Gilmont microburet calibrated in 0.1 μ L increments was used to deliver the titrant. Sample solutions and blanks were covered with water-saturated N_2 which had been scrubbed free of CO_2 and O_2 . Blanks were identical to samples in composition, except they contained no copolymer. Sample solutions and blanks were first acidified to pH 2.8 using a measured volume of dilute HCl, and then titrated to pH 11.2 with base.

Results and Discussion

The solubilization results obtained in 0.1 M LiCl solution are summarized in Table 1. The quantity S_{pH} represents the number of moles of compound solubilized per mole of polyacid repeat unit at saturation at the indicated pH.^{2,9} For convenience, the structures of the solubilizates are given in Figure 2. The results in Table 1 show that the solubilizates fell into two distinct groups, with the compounds in each group exhibiting nearly identical values of R_{pH} , the ratio of S_{pH} to $S_{4.5}$, at any given pH but differing in how R_{pH} depends on changes in pH. For group

TABLE 2: Extent of Micellization in 0.1 M LiCl

| pH | α | Θ_{ms} ^a | Θ_{mt} |
|-----|----------|----------------------------|---------------|
| 4.5 | 0.43 | 0.97 | 0.99 |
| 5.7 | 0.87 | 0.60 | 0.60 |
| 6.8 | 1.20 | 0.51 | |

^a Using pyrene data.

I (eight compounds in the upper part of the table), the values of R_{pH} decrease with increasing pH, while for group II (four compounds at the bottom of the table), the values of R_{pH} remain essentially constant with changing pH. For all compounds, solubilization behavior was independent of C_p , which ranged from roughly 0.01 to 0.05 M. These findings confirm and extend our previously reported results, which had been obtained with a smaller number of solubilizates and over a more limited pH range.²

We interpret these results to indicate that the R_{pH} values of group I are a relative measure of Θ_{ms} , the extent of micellization of the polysoap.¹⁰ Thus, Θ_{ms} is given by the relation

$$\Theta_{ms,pH} = R_{pH} \Theta_{ms,pH4.5} \quad (1)$$

Our previous work showed that maximum solubilization in LiCl is attained when $pH \leq 4.2$ and that at pH 4.5 the solubilization is about 97% of its maximum. The values of Θ_{ms} for pyrene are given in Table 2 as a function of pH and α , the degree of deprotonation obtained by potentiometric titration and defined to be unity at half-neutralization. They agree closely with values of Θ_{mt} ,¹⁰ an independent estimate of the extent of micellization, obtained as described previously³ using the relation

$$\Theta_{mt} = (\alpha_r - \alpha)/(\alpha_r - \alpha_c) \quad (2)$$

where α_c and α_r are the values of the hypothetical compact and random coil states at each pH corresponding to the experimental values of α . The α_c values are obtained by extrapolation of a modified form of the titration curve of the polyacid from its compact form into its transition region; the α_r values are obtained from the experimental titration curve of the maleic acid–ethyl vinyl ether copolymer.³ For the polyacids used here, this procedure works well up to half-neutralization but, because of complications due to specific effects of alkyl group size on the interactions involving deprotonated dicarboxylate groups,¹¹ it is unsatisfactory beyond that point. Consequently, no values of Θ_{mt} are given for $\alpha > 1$.

We have no satisfactory explanation for the strange behavior of the four compounds in group II. The striking invariance of the solubilization to changes in pH could indicate that the decrease in micellization is compensated for by the attendant increase in ionization, which may play a role in attracting these

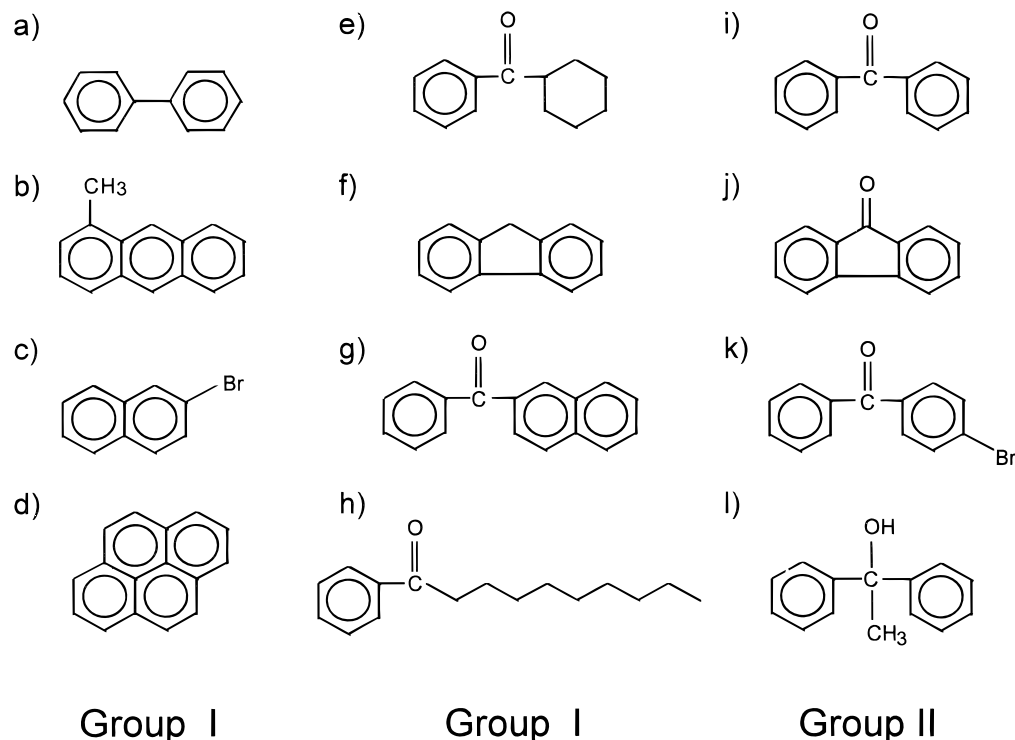


Figure 2. Compounds used in solubilization experiments in hexyl copolymer solutions: (a) biphenyl; (b) 9-methylantracene; (c) 2-bromonaphthalene; (d) pyrene; (e) cyclohexyl phenyl ketone; (f) fluorene; (g) naphthyl phenyl ketone; (h) nonyl phenyl ketone; (i) benzophenone; (j) fluorenone; (k) 4-bromobenzophenone; (l) 1,1-diphenylethanol.

dipole-containing molecules. An examination of the structures portrayed in Figure 2 illustrates that relatively small changes in chemical structure can bring about the profound differences in solubilization behavior shown by compounds in groups I and II. For instance, changing a methylene group to a carbonyl group converts fluorene, which shows group I behavior, to fluorenone, a ketone which shows group II behavior. However, ketones can also show group I behavior. Thus, while benzophenone belongs in group II, substitution of one of its phenyl groups by the bulkier naphthyl group or by the aliphatic cyclohexyl or nonyl group, produces structures found in group I.

A clue to understanding the Group II behavior may be that each of the foregoing chemical transformations results in enhanced water solubility for the compound in group II relative to that in group I.¹² Since there is some evidence that in micelles polar compounds, such as are found in group II, have their locus of solubilization at the water–micelle interface,¹³ it is possible that somehow these interface regions are preserved, even as the micelles disappear with increasing ionization of the polyacid.

It should be noted that the maleic acid–butyl vinyl ether copolymer did not produce the unusual solubilization effect for benzophenone.⁹ That is, at pH 4, where this polyacid is known to be almost completely micellized,^{7,11} it solubilized benzophenone as expected, but at pH 7, where this polyacid is in a nonmicellized random coil state, it did not.

The solubilization results obtained in 0.1 M TMACl are shown in Table 3. The pH values were chosen to produce values of α close to those in the LiCl system. The four compounds at the top, selected from the LiCl group I, show solubilization behavior similar to their behavior in LiCl only in that their R_{pH} values decrease with increasing ionization. However, quantitatively, none of the trends are alike.

In contrast, the R_{pH} values of the three compounds at the bottom of the table, selected from the LiCl group II, follow a

TABLE 3: Solubilization in Hexyl Copolymer Solutions Containing 0.1 M TMACl

| solubilize | $S_{4.5} \times 10^3$ ^a | $S_{6.1} \times 10^3$ ^a | $S_{8.0} \times 10^3$ ^a | $R_{6.1}$ ^b | $R_{8.0}$ ^b |
|---------------------|------------------------------------|------------------------------------|------------------------------------|------------------------|------------------------|
| pyrene | 4.60 | 4.55 | 1.79 | 0.99 | 0.39 |
| 9-methylantracene | 7.68 | 6.27 | 2.20 | 0.82 | 0.29 |
| biphenyl | 17.5 | 13.7 | 6.93 | 0.78 | 0.40 |
| fluorene | 8.09 | 7.85 | 4.48 | 0.97 | 0.55 |
| benzophenone | 44.2 | 53.1 | 33.8 | 1.20 | 0.76 |
| 4-bromobenzophenone | 8.37 | 10.3 | 6.50 | 1.23 | 0.78 |
| fluorenone | 17.4 | 21.5 | 13.9 | 1.24 | 0.80 |

^a S_{pH} = moles solubilize per mole polyacid repeat unit at saturation at indicated pH. ^b $R_{\text{pH}} = S_{\text{pH}}/S_{4.5}$.

TABLE 4: Extent of Micellization in 0.1 M TMACl

| pH | α | Θ_{mt} |
|-----|----------|----------------------|
| 4.5 | 0.46 | 0.99 |
| 6.1 | 0.90 | 0.57 |
| 8.0 | 1.23 | |

common trend in passing through a maximum with increasing pH, although this, too, differs from their behavior in the LiCl system. Neither does this maximum follow the trend in Θ_{mt} , the extent of micellization determined by the titration method, which decreases from 0.99 at pH 4.5 to 0.57 at pH 6.1, as shown in Table 4.

A comparison of the solubilization behavior of the two groups of compounds in polysoap samples in LiCl and TMACl electrolyte solutions is shown in Table 5. Clearly the counterions exert specific effects not only on the ionization of the polysoap, as indicated by the difference in pH required to reach comparable values of α and Θ_{mt} , but also on the relative solubilities of each compound, as well as on the responses of these solubilities to changing conditions of α and Θ_{mt} . From a quantitative point of view it is worth noting that all values in the middle column are larger than unity and larger than the corresponding values in the outside columns, indicating that any

TABLE 5: Comparison of Solubilization in TMAcI and LiCl

| solubilizate | $S_{4.5,\text{TMA}}/S_{4.5,\text{Li}}$ | $S_{6.1,\text{TMA}}/S_{5.7,\text{Li}}$ | $S_{8.0,\text{TMA}}/S_{6.8,\text{Li}}$ |
|---------------------|--|--|--|
| pyrene | 1.13 | 1.78 | 0.82 |
| 9-methylanthracene | 0.84 | 1.11 | |
| biphenyl | 1.36 | 1.72 | 1.07 |
| fluorene | 1.37 | 2.22 | 1.31 |
| benzophenone | 2.20 | 2.70 | 1.71 |
| 4-bromobenzophenone | 0.97 | 1.20 | 0.80 |
| fluorenone | 1.42 | 1.68 | 1.17 |
| α (average) | 0.45 | 0.89 | 1.22 |

TABLE 6: Partition Coefficients at pH 4.5

| solubilizate | Q_{aq}^a | LiCl | | TMAcI | |
|--------------------------|-----------------------|-----------------------|-------------|-----------------------|-------------|
| | | $S_{4.5} \times 10^3$ | $K_{4.5}^b$ | $S_{4.5} \times 10^3$ | $K_{4.5}^b$ |
| pyrene | 7.65×10^{-7} | 4.13 | 5400 | 4.66 | 6090 |
| 9-methylanthracene | 3.38×10^{-6} | 9.12 | 2700 | 7.68 | 2270 |
| biphenyl | 3.22×10^{-5} | 12.8 | 398 | 17.5 | 543 |
| fluorene | 9.00×10^{-6} | 5.90 | 656 | 8.09 | 900 |
| cyclohexyl phenyl ketone | 6.18×10^{-5} | 8.54 | 138 | | |
| naphthyl phenyl ketone | 1.52×10^{-4} | 22.4 | 148 | | |
| nonyl phenyl ketone | 7.15×10^{-6} | 48.8 | 6830 | | |
| 2-bromonaphthalene | 5.18×10^{-5} | 70.6 | 1360 | | |
| benzophenone | 3.65×10^{-4} | 20.1 | 55.1 | 44.2 | 121 |
| 4-bromobenzophenone | 2.99×10^{-5} | 8.81 | 295 | 8.37 | 285 |
| fluorenone | 8.02×10^{-5} | 12.3 | 153 | 17.4 | 217 |
| 1,1-diphenylethanol | 1.08×10^{-3} | 35.3 | 32.7 | | |

^a Q_{aq} = solubility limit (mol/L) in aqueous 0.1 M LiCl. ^b $K_{4.5} = S_{4.5}/Q_{\text{aq}}$.

solubilization enhancement by TMA⁺ relative to Li⁺ passes through a maximum with decreasing extent of micellization. Furthermore, from the evidence available so far, it appears intriguing that 9-methylanthracene and 4-bromobenzophenone, the two solubilizates with the significantly smaller ratios, both have symmetry-destroying side groups.

Since solubilization involves an equilibrium between two liquid states, namely the polysoap molecules and the aqueous medium, the partition coefficient between these states indicates

the intrinsic affinity between the polysoap and the solubilizate. These partition coefficients, denoted by K_{pH} and defined as the ratio of S_{pH} to Q_{aq} , the solubility limit in the aqueous phase, are given for pH 4.5 in Table 6. There is no obvious correlation between the K_{pH} values and the relative effects of TMA⁺ and Li⁺ on the solubilization behavior.

Conclusions

The findings presented here demonstrate some significant variety in polysoap behavior. With LiCl as the supporting electrolyte, the solubilizates can be classified into just two groups, one being quantitatively sensitive, the other apparently completely insensitive to intramolecular micelle formation. In contrast, the tetramethylammonium ion elicits a remarkable diversity of individual responses by the solubilizates in their affinity for the polysoap, somewhat reminiscent of the specificities exhibited in macromolecular biological processes. This may be the result of a combination of hydrophobic character and positive electric charge that causes the tetramethylammonium ion itself to be solubilized in the hydrophobic regions of the polysoap anion. The resulting large fluctuating dipoles would then lead to the observed specificities.

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