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Solubility Behavior of Barbituric Acids in Aqueous Solution of Sodium Alkyl Sulfonate as a Function of Concentration and Temperature

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Abstract □ The solubility of 13 barbituric acids was determined in aqueous solutions of sodium alkyl sulfonate. The effects of concentration and temperature were investigated, and the thermodynamic functions of the solubilization process were calculated. An analysis of the location of a solubilized species within a micelle is suggested in terms of the sign and amplitude of the standard entropy of solubilization, which is strongly positive for micelle penetration and negative for adsorption. A solubilization mechanism through adsorption onto the micellar surface is suggested for most of the barbituric acids studied. The enthalpy/entropy compensation phenomenon was identical for barbituric acids in ionic and nonionic (polyoxyethylene lauryl ether) surfactant solutions with a compensation temperature of 270 °K, indicating common behavior of these compounds with respect to micellar solubilization. The concept of molecular surface area was used to correlate the free energy of solubilization of the solutes to their size and structure. A linear relationship was found with an excellent correlation factor for the alkane derivatives of the 5-ethyl-barbituric acids. The specific behavior of some of the barbituric acids investigated is discussed.

Keyphrases □ Solubility—barbituric acids in aqueous sodium alkyl sulfonate, thermodynamics □ Thermodynamics—solubility of barbituric acids in aqueous sodium alkyl sulfonate □ Barbituric acids—solubility in aqueous sodium alkyl sulfonate, thermodynamics

The increase in solubility of poorly soluble preservatives in water by the addition of surfactants has been the subject of a large number of studies (1, 2). This phenomenon is related to the formation of micelles in water, but the availability of the preservative as an active agent is highly dependent on the molecular attachment site, and this subject is still a controversial matter. Opposite views have been proposed for barbituric acids, such as adsorption at the micelle interface (3) or incorporation into the micelle hydrocarbon core (4). However, for simpler molecules like acetone or urea, which may be considered model compounds for barbituric acids, thermodynamic evidence shows that these molecules hardly penetrate the micelle interior, at least at the critical micelle concentration (CMC) and for ionic micelles (5, 6).

BACKGROUND

Studies on the solubilization of barbituric acids have been mostly (7) restricted to the influence of nonionic surfactants (3, 4, 8–10). Few of these studies were concerned with the determination of thermodynamic functions such as free energy, enthalpy, and entropy (3). In fact, few papers have been published on this subject for compounds other than barbituric acids (3, 11, 12).

The present work investigated the solubilization properties of sodium alkyl sulfonate. Its biodegradability and nontoxic properties, even at high surfactant concentration, make it an interesting surfactant in formulation problems (13). The barbituric acids are useful compounds in this respect since the possibility of changing, almost at will, the radicals attached to the malonylurea ring permits the study of the influence of shape and structure on the solubilization process. Thus, previous studies (14) on the molecular surface area concept and the investigation of the effects of temperature on barbituric solutions have indicated the use of the entropy function to deduce the chemical environment of compounds solubilized by micelles.

EXPERIMENTAL

Materials—Sodium alkyl sulfonate[1] was composed of 90.7% (by weight) monosulfonated detergent, 8.8% polysulfonated compound, and 0.5% unsulfonated product. The monosulfonated compound was a mixture of $C_{14}H_{29}SO_3Na$ and $C_{15}H_{31}SO_3Na$, so a molecular weight of 323 was adopted in the concentration calculations. The CMC of the detergent

[1] Produits chimiques de la Montagne Noire, 81100, Castres, France.

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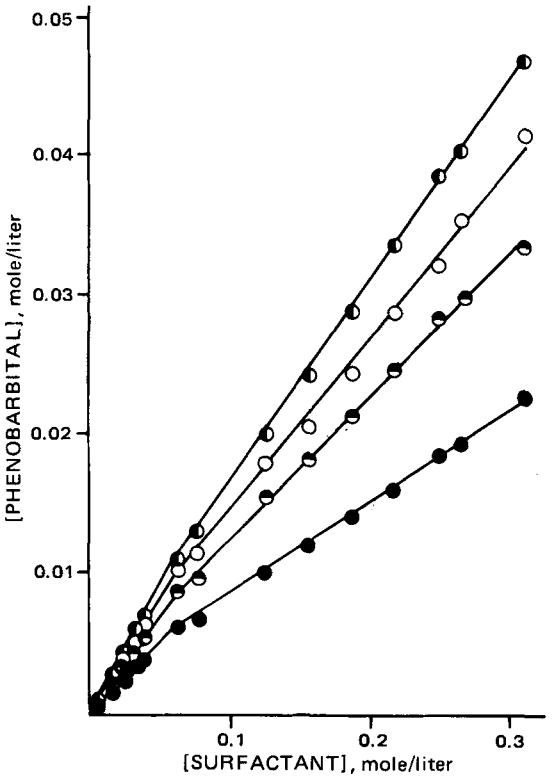

Figure 1—*Variation of the solubility of phenobarbital with sodium alkyl sulfonate concentration at various temperatures. Key:* ◐, *55°;* ○, *45°;* ◓, *35°; and* ●, *25°.*

used was 0.0039 mole/liter, as determined from conductivity measurements at 25°. Highly pure sodium dodecyl sulfate[2] was used without purification. Its CMC at 25° was 0.0081 mole/liter, in excellent agreement with literature values (15).

The barbituric acids were from different sources[3]. Their melting points and solubilities in water at 25° are presented in Table I, although some solubility values in water may be slightly in error due to impurities. However, since the major interest was in partition coefficients, *i.e.*, in ratio of concentrations with and without the added surfactant, the influence of the impurities on the partition coefficient values should be negligible.

Solubility Measurements—The barbiturate solution with the added surfactant was equilibrated for 240 hr (10 days) at a given temperature, and controlled to within ±0.1°. The suspension was filtered and diluted, and the concentration of solubilized solute was determined with a UV spectrophotometer[4].

Solubility Calculations—The pH of the solutions was determined and used with the pKa of each barbituric acid to correct for the variation of solubility due to the pH change of the solution, which occurs with the addition of alkyl sulfonate (16). The classic formula was used:

$$S = S_0 (1 + 10^{pH-pKa}) \qquad \text{(Eq. 1)}$$

where S and S_0 are the total amount of barbituric acid and the intrinsic solubility of the undissociated acid, respectively.

RESULTS AND DISCUSSION

An example of the variation of barbituric acid solubilization with the surfactant concentration is presented at several temperatures in Fig. 1. This behavior was typical of all barbituric acids studied with alkyl sulfonate but had not been observed with nonionic surfactants. It has been interpreted as the result of the presence of mixed micelles of monosulfonated and polysulfonated sodium alkyl sulfonate above the concentration C_2 (17). Below this value, the only micelles present are formed from monosulfonated molecules. The present report concerns only the first part of these curves, *i.e.*, the initial slope above the CMC. In Fig. 1, the maximum concentration of solubilized material is plotted for convenience as a function of the concentration of surfactant used minus the CMC.

In all cases, solubilization increased with increased surfactant concentration in water and with temperature. To quantify, the relative variation of the solubilized solute in water and in the micellar solutions, an apparent distribution coefficient such as:

$$K = \frac{S_m - S_w}{S_w C} \qquad \text{(Eq. 2)}$$

is defined where S_m and S_w are the saturation molarities of solubilized barbituric acid in the micellar solution and in water, respectively, and C is the excess of surfactant above the CMC in moles per liter. The maximum surfactant concentration used in the determination of K was ~0.04 mole/liter (1.3 g/100 ml of solution).

In each case, K was calculated using at least eight experimental points with a least-squares method. As shown in Table II, K decreased as temperature increased, which means that the increase in solubility was faster in water than in the micellar solution. This finding agrees with previous findings (3) for barbituric acids in nonionic polyoxyethylene lauryl ether aqueous solutions but contradicts the results of Ismail *et al.* (10) for the same solutes with the nonionic polyoxyethylene derivative surfactants used (monoalkyl ether, monostearate, and polysorbate).

Thermodynamic Functions and Location of Solubilized Material in Micelles—To discuss the thermodynamic properties of the solutions, the free energy of solubilization may be calculated as:

$$\Delta G_s^\circ = -RT \ln K \qquad \text{(Eq. 3)}$$

where K is an apparent distribution coefficient, uncorrected for volume effects (5).

The standard enthalpy of solubilization is defined by:

$$\partial \frac{\ln K}{\partial T} = \frac{\Delta H_s^\circ}{RT^2} \qquad \text{(Eq. 4)}$$

and:

$$\Delta G_s^\circ = \Delta H_s^\circ - T\Delta S_s^\circ \qquad \text{(Eq. 5)}$$

where ΔS_s° is the standard entropy of solubilization. The results of these calculations are given in Table II. The precision of ΔH_s° is not very good when obtained from indirect determinations (4). Thus, ΔH_s° values should be considered reliable within ±300 cal/mole, while ΔS_s° values are accurate to ±1.0 entropy units.

The same thermodynamic functions are examined in more extreme cases in Table III, using the standard thermodynamic functions of hydrocarbon transfer (18) from water to an aqueous anionic surfactant solution (such as sodium lauryl sulfate of molarity c = 0.06 mole/liter).

Thus:

$$\Delta G_t^\circ = -RT \frac{S}{S^\circ} \qquad \text{(Eq. 6)}$$

As expected, ΔG_t° is more negative the larger the solute molecule since

Table I—Some Physical Properties of Barbituric Acids

Acid	Melting Point	S_w, mole/liter	Molecular Surface Area[d], Å^2
Barbital[b]	186°	0.00401	102.6
Vinbarbital[b]	165°	0.00487	142.0
Butabarbital[b]	168°	0.00407	140.3
Butethal[b]	125°	0.0213	138.8
Pentobarbital[b]	125°	0.00407	158.4
Amobarbital[b]	156–158°	0.00217	160.1
Allobarbital[c]	175°	0.00865	89.2
Aprobarbital[d]	145°	0.0194	117.2
Butalbital[d]	140°	0.00759	135.3
Secobarbital[d]	95°	0.00441	151.7
Phenobarbital[b]	175°	0.00517	152.4
Heptabarbital[b]	175°	0.00100	156.7
Reposal[b]	213°	0.00168	150.0

[a] Molecular surface areas of side chains on the malonylurea ring. [b] A 5-ethylbarbituric acid. [c] A 5-diallylbarbituric acid. [d] A 5-allylbarbituric acid.

[2] Merck "pro analysis."

[3] Barbital, Expandia, Paris; vinbarbital, Schmoller et Bompard, Grasse; butabarbital, Expandia; butobarbital, Rhone Poulenc Chimie, Courbevoie; pentobarbital, Expandia; amobarbital, Expandia; allobarbital, Soprotec, Paris; aprobarbital Expandia; itobarbital, Rhone Poulenc Chimie; secobarbital, Expandia; phenobarbital, Cooperation pharmaceutique française, Paris; heptabarbital, Laboratoire Geigy, Rueil-Malmaison; and reposal, Laboratoire Martinet, Vernouillet, Dreux.

[4] Beckman model 25.

Table II—Partition Coefficients and Thermodynamic Parameters [a] for Barbituric Acids as a Function of Temperature (Molar Scale)

Acid	t	K, moles^{-1}	ΔG_s°, cal/mole	ΔH_s°, cal/mole	ΔS_s°, cal/mole/deg
Barbital	25°	3.8	−790	−2600	−6.0
	35°	3.5	−770		−5.9
	45°	3.2	−720		−5.9
	55°	2.5	−600		−6.0
Vinbarbital	35°	16.0	−1700	−700	+3.2
	45°	16.0	−1750		+3.2
	55°	14.8	−1760		+3.1
Butabarbital	25°	22.4	−1840	−3100	−4.3
	35°	17.8	−1760		−4.4
	45°	15.3	−1720		−4.4
	55°	13.8	−1710		−4.3
Butethal	35°	19.4	−1820	−2100	−0.9
	45°	17.5	−1810		−0.8
	55°	15.7	−1790		−0.6
Pentobarbital	25°	39.3	−2170	−1100	+3.7
	35°	39.4	−2230		+3.5
	55°	33.4	−2290		+3.6
Amobarbital	25°	51.6	−2340	−1700	+2.1
	35°	48.0	−2370		+2.0
	45°	43.0	−2380		+2.0
Allobarbital	25°	9.2	−1310	−2200	−2.9
	35°	8.5	−1310		−2.8
	45°	7.3	−1250		−2.9
	55°	5.9	−1150		−3.1
Aprobarbital	25°	14.4	−1580	−2700	−3.6
	35°	10.1	−1420		−4.0
	45°	9.8	−1440		−3.8
	55°	9.3	−1450		−3.7
Butalbital	25°	21.4	−1810	−2600	−2.6
	35°	19.4	−1820		−2.5
	45°	16.3	−1760		−2.6
	55°	14.6	−1750		−2.5
Secobarbital	25°	80.6	−2600	−4100	−5.9
	35°	60.7	−2510		−6.0
	45°	50.3	−2480		−5.9
	55°	40.6	−2420		−5.9
Phenobarbital	25°	22.7	−1850	−3800	−6.5
	35°	18.6	−1790		−6.5
	45°	12.7	−1660		−6.6
Heptabarbital	25°	33.5	−2080	−2000	+0.3
	35°	27.7	−2030		+0.1
	45°	26.5	−2070		+0.2
	55°	24.2	−2060		+0.3
Reposal	25°	117.6	−2820	−1600	+4.2
	35°	103.9	−2840		+4.2
	45°	97.2	−2890		+4.2
	55°	92.2	−2950		+4.2

[a] Throughout this paper, 1 cal = 4.184 J.

dispersion forces and the hydrophobic effect both increase in magnitude when the surface of contact between the solute and the solvent molecules (here the micelles) increases.

The standard enthalpy of transfer, ΔH_t°, is close to zero and is also size dependent, but the entropy of transfer is strongly positive. Since hydrocarbons dissolve in the micelle interior, the positive entropy change upon solubilization seems a good thermodynamic characteristic of the penetration of a solute from an aqueous to a nonaqueous environment. The cases of ammonium chloride and hydrochloric acid were chosen to illustrate the behavior of a polar or an ionic hydrophilic solute (19). [Methane is presented to illustrate the thermodynamics of transfer of a hydrocarbon from water to an organic component (20). It shows that all thermodynamic functions are of the same order of magnitude whether the transfer is from water to a micellar phase or to an organic solvent in the case of penetration. The same reasoning may be applied to a polar solute.] Table III shows that, for a hydrophilic solute transferred from an aqueous to an organic environment, ΔG_t° is positive and ΔS_t° is negative. Since ammonium chloride or hydrochloric acid prefers water to the organic phase (19), a negative entropy change is associated with nonpenetration of the solute into the organic phase (which can be a micelle). Thus, $\Delta G_s^\circ < 0$ and $\Delta S_s^\circ > 0$ are associated with the penetration into a micelle interior, and $\Delta G_s^\circ > 0$ and $\Delta S_s^\circ < 0$ are associated with an interaction of the solute with the micelle without penetration, *i.e.*, through an adsorption phenomenon.

Table III—Thermodynamic Standard Transfer Functions for Various Solutes from Water to Organic solvents at 25° (Mole Fraction Scale)

Solute	Organic Solvent	ΔG_t°, cal/mole	ΔH_t°, cal/mole	ΔS_t°, cal/mole/deg
Pentane[a]	Micellar solution[b]	−5720	−1100	+15.6
Butane[a]	Micellar solution[b]	−5130	0	+17.2
Propane[a]	Micellar solution[b]	−4230	+1000	+17.5
Ethane[a]	Micellar solution[b]	−3450	+2000	+18.3
Methane[c]	Ethanol	−2650	+1960	+15.4
Methane[c]	Cyclohexane	−2280	+2380	+15.6
Ammonium chloride[d]	Ethanol	+5010	−2830	−26.3
Hydrochloric acid	Ethanol	+4320	−5400	−32.6

[a] Reference 18. [b] Aqueous sodium lauryl sulfate solution; c = 0.06 mole/liter. [c] Reference 20. [d] Reference 19.

Table IV—Partition Coefficients and Thermodynamic Parameters for Butethal in Aqueous Sodium Lauryl Sulfate Solutions (Molar Scale)

t	K, mole^{-1}	ΔG_s°, cal/mole	ΔH_s°, cal/mole	ΔS_s°, cal/mole/deg
25°	29.0	−1990	−3040	−3.5
35°	24.0	−1950		−3.5
45°	21.0	−1930		−3.5
55°	18.0	−1880		−3.5

Examination of the barbituric acids shows that ΔH_s° is negative in all cases and ΔS_s° is negative or zero for nine out of 13 barbiturates. Thus, it may be concluded that solubilization occurs in an environment of mixed water and nonpolar molecules, depending on the particular solute, but with a preference for a predominantly aqueous phase.

To compare solutes dissolved in sodium lauryl sulfate and alkyl sulfonate solutions, the solubilization of butethal was studied at four temperatures in very pure samples of sodium lauryl sulfate. The results were analyzed as for the alkyl sulfonate solutions (Table IV). They are similar in both surfactant solutions. The ΔG_s° values are equal within experimental error, and only the dependence of K with temperature is slightly different with alkyl sulfonate and sodium lauryl sulfate. The ΔH_s° and ΔS_s° values are both somewhat more negative in the alkyl sulfonate solutions, a good example of enthalpy/entropy compensation. In addition, the thermodynamic functions are very much the same in the nonionic polyoxyethylene lauryl ether solutions (deduced from dialysis measurements at several temperatures) and in the anionic alkyl sulfonate solutions. For example, ΔG_s° is systematically more negative by only ~20% in the nonionic solution[5]. This finding should be the result of a number of compensation effects. If, as was previously suggested (3) for polyoxyethylene lauryl ether and as presently proposed for alkyl sulfonate, solubilization occurs through adsorption for barbituric acids in these surfactant solutions, the situations at each micelle surface must be quite different. In particular, the role of the adsorbed sodium counterions in the latter case should be clarified.

Enthalpy/Entropy Compensation Phenomenon—Ionic and nonionic surfactants as solubilizing agents also can be compared by considering the enthalpy/entropy compensation phenomenon. It occurs in most solutions but presents amazing regularities for aqueous solutions. Lumry and Rajendar (21) described the phenomenon by an equation of the type:

$$\Delta H_s^\circ = \alpha + T_c \Delta S_s^\circ \qquad \text{(Eq. 7)}$$

where α and T_c are constants. This equation holds for a given solute in various media or for a series of different solutes in a given medium. The compensation temperature (T_c) is equal to an average value of 285 °K for most aqueous or predominantly aqueous systems, indicating a common mechanism in a given solution process when essentially water molecules are involved. [In organic solvents, Eq. 7 is known as the Barclay–Butler plot (22) with $T_c \approx 910$ °K.]

Figure 2 presents the correlation found for the barbituric acids used in this work and those of Ikeda *et al.* (3) with polyoxyethylene lauryl ether. If the results for barbital and reposal in the ionic solutions and for

[5] The same situation was described with phenobarbital in ionic and nonionic surfactant solutions (7). Unfortunately, the authors did not publish the actual data but only corresponding curves.

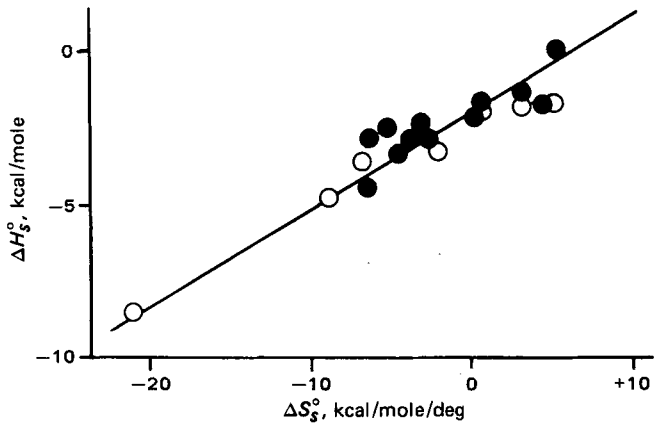

Figure 2—*Enthalpy/entropy compensation plot for barbituric acids in sodium alkyl sulfonate (●), ionic, and polyoxyethylene lauryl ether (○), nonionic, aqueous solutions at 25°.*

secobarbital in the nonionic solutions are discarded, a linear regression on the remaining 18 barbituric acid solutions may be represented at 25° by:

$$\Delta H_s^\circ = -2020 + 269\ \Delta S_s^\circ \qquad \text{(Eq. 8)}$$

with a correlation coefficient of $r^2 = 0.98$. The T_c value of 269 °K is in agreement with the average 285 °K.

The Humphreys and Rhodes distribution coefficients at several temperatures were also analyzed for benzoic acid in aqueous solutions of *n*-alkylpolyoxyethylene surfactants. Benzoic acid is considered as being mostly adsorbed on the micelle surface (23). The derived thermodynamic functions are presented at 25° in Table V. The ΔH_s° and ΔS_s° values are situated on the same line as for the other systems in Fig. 3.

Although speculation on the meaning of the compensation temperature in terms of chemical compensation has been criticized (24), the fact that, for the same chemical process (*i.e.*, solubilization by adsorption onto micellar surfaces), a single line is obtained on a ΔH_s° *versus* ΔS_s° plot should be considered. In the case of benzoic acid, ΔS_s° becomes less negative as the number of oxyethylene group increases, which may be interpreted as an increase in penetration of the benzoic molecule within the micelle mantle. However, ΔS_s° remains negative for the four surfactants, indicating that adsorption still predominates for this system.

Solubilization and Molecular Surface Area Concept—Many approaches have been tested, from the crudest models that correlate distribution coefficients with the number of carbon atoms on the barbituric acid molecule [with corrections for the position of radicals and the malonylurea rings (25)], to the more general approach of Hansch and Anderson (26), who correlated drug activity with the distribution coefficient in octanol–water mixtures, to others who use the regular solution theory to find an index of drug activity (27). An attractive alternative to these approaches may be found in the concept of molecular surface area, as proposed by Herman (14) and extensively used in the case of slightly soluble series of organic compounds in water (28–30). It is based on the idea that, provided no specific interactions take place between solute and solvent molecules and the solute is sufficiently diluted so that solute–solute interactions are negligible, the molecular surface of contact between solute and solvent molecules is proportional to their free energy of interaction. Thus, the logarithm of solubility should be a linear function of the molecular surface area. Implicitly, it is assumed that the same correlation will not be found for any series of compounds. Thus, alkanes, alkynes, or aromatic derivatives may be found on different straight lines.

Table V—Partition Coefficients and Thermodynamic Parameters for Benzoic Acid in Nonionic Surfactant Solutions at 25° (Molar Scale)

Surfactant[a]	*K*, mole	ΔG_s°, cal/mole	ΔH_s°, cal/mole	ΔS_s°, cal/mole/deg
$C_{16}E_{16}$	50.07	−2320	−3700	−4.7
$C_{16}E_{30}$	45.55	−2260	−3100	−2.9
$C_{16}E_{40}$	32.72	−2070	−3100	−3.7
$C_{16}E_{96}$	27.43	−1960	−2300	−1.2

[a] *n*-Alkylpolyethylene C_nE_m, where n = number of carbon atoms and m = number of polyoxyethylene groups.

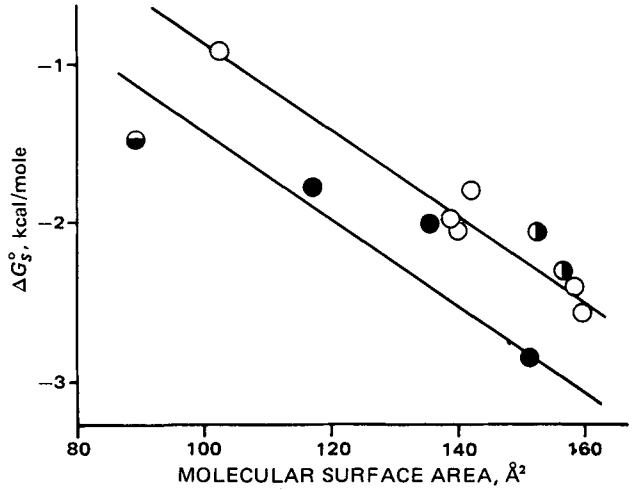

Figure 3—*Variation of the standard free energy of solubilization of barbituric acids with the molecular surface area of their substituted groups at 25°. Key: ○, 5-ethyl (linear); ◑, 5-ethyl (cyclic); ●, 5-allyl; and ◒, 5-diallyl.*

Valvani *et al.* (29) proposed a simplified version of the elaborate method of evaluation of molecular surface area by Herman (14), and the present study used their results whenever possible (28). The heptabarbital ring has been considered as being equivalent to that of cycloheptane (29) minus one methylene group (a quaternary carbon atom has no molecular surface area) and minus the difference between one methylene and one CH group. It was assumed that the molecular surface areas of phenobarbital and cyclobarbital were equivalent to that of a benzene ring minus one methylene group. The molecular surface area of malonylurea was not accounted for since it was assumed to play the same role for each barbituric acid. The results of these calculations are presented in Table I. (Reposal was not calculated because of too many geometrical unknowns. However, a value of ~150 Å² is plausible.)

Figures 3 and 4 correlate ΔG_s° (which is proportional to the logarithm of a ratio of solubilities) and molecular surface area at 25 and 55°. For the eight 5-ethylbarbituric acids, a linear correlation is found at 25° with a standard deviation of $\sigma = 117$ and $r^2 = 0.980$. (If phenobarbital is ignored, $\sigma = 101$ and $r^2 = 0.990$.) At 55°, the correlation is even better if phenobarbital is ignored, with $\sigma = 70$ and $r^2 = 0.995$. This result is as good as the correlation found, for example, between the logarithm of the partition coefficients of alkylbenzenes in octanol–water mixtures and their molecular surface area (28). The standard deviation is of the order of magnitude of the experimental error or better. The three 5-monoallylbarbituric acids stand on a parallel to the preceding line, and the one 5-diallylbarbituric acid is at a still more negative ΔG_s° value. This behavior was observed with other types of correlations, such as those involving the solubility and melting point of a given series of compounds (31).

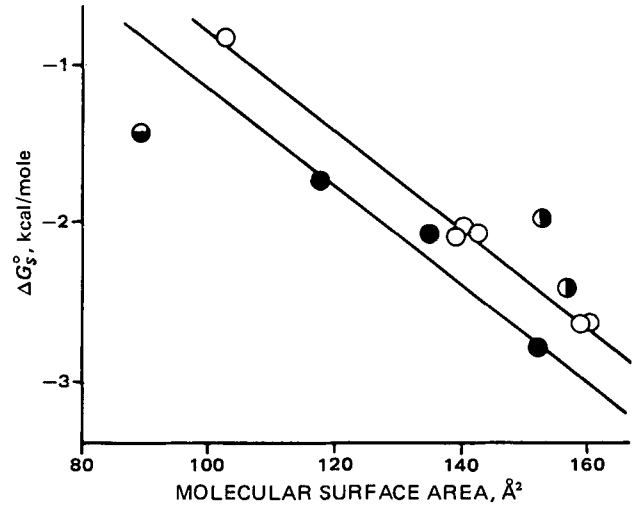

Figure 4—*Variation of the standard free energy of solubilization of barbituric acids with the molecular surface area of their substituted groups at 55°. See Fig. 3 for key.*

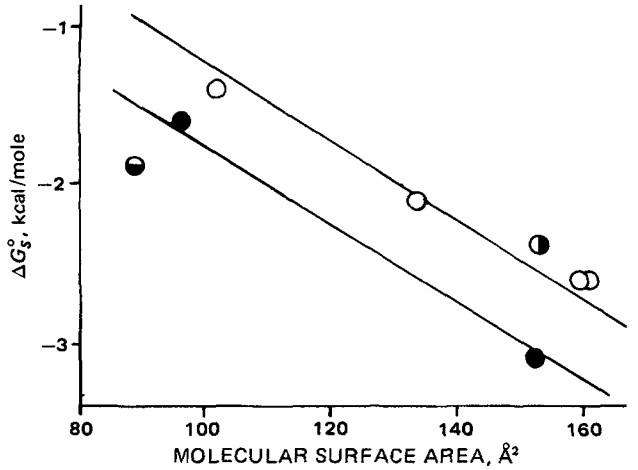

Figure 5—*Variation of the standard free energy of solubilization of barbituric acids with the molecular surface area of their substituted groups at 25°, polyoxyethylene lauryl ether solutions. See Fig. 3 for key.*

Comparison of these results with those of Ikeda *et al.* (3) in polyoxyethylene lauryl ether aqueous solutions (Fig. 5) shows the standard deviation of fit for the five 5-ethyl derivatives is $\sigma = 53$ with $r^2 = 0.996$. It also seems that the two monoallyl and the one diallyl derivatives are in the same position with respect to the 5-ethyl line in polyoxyethylene lauryl ether and alkyl sulfonate solutions.

Since the common behavior of these solutes in nonionic and ionic surfactant solutions has been stressed, some differences should now be pointed out. Some authors noted the specific interaction between phenobarbital and oxyethylene groups at high surfactant concentrations and low temperatures (3, 4), leading to precipitation of this barbituric acid. Such behavior is not found with alkyl sulfonate. However, some specificity is apparent with the observation that, for phenobarbital, ΔG_s° moves off the line corresponding to the 5-ethyl derivatives as the temperature increases. This effect, which is small, is difficult to interpret since specific effects usually decrease as temperature increases. (The correlation between ΔG_s° and molecular surface area is better at 55° than at 25° for the 5-ethylbarbituric acids.) Reposal is more soluble than one might expect from its molecular surface area, although it is the only compound for which precise molecular surface area evaluation could not be made. Finally, a rough correlation may be observed between ΔG_s° and ΔS_s° in a direction indicating that the micellar solubilization is favored by the penetration of the solubilized compounds in the micelle interior. Thus, barbital with the less negative ΔG_s° value and reposal with the most negative ΔG_s° value have the most negative and the most positive ΔS_s° values, respectively. This observation again points out that micellar solubilization is essentially an entropy-related phenomenon.

In conclusion, although this study used an impure surfactant product, the self-consistency of the results, when compared with pure sodium lauryl sulfate solutions or with the nonionic solutions, and the correlations found with the molecular surface area approach justify the general conclusions proposed.

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