repressed. A more detailed discussion of the chemical equilibria involved in these complex solutions will be given elsewhere (*5*).

Literature Cited

(1) R. C. Carlston, M. M. Schieber, and W. F. Schnepple, *Mater. Res. Bull.*, **11**, 959 (1976).
(2) J. P. Joly and I. F. Nicolau, *Spectrochim. Acta, Part A*, **35**, 281 (1979).
(3) J. J. Lindberg and J. Kenttamma, *Suom. Kemistil. B*, **33** 104 (1960).
(4) J. J. Lindberg and I. Pietila, *Suom. Kemistil. B*, **35** 30 (1962).
(5) I. F. Nicolau and J. P. Joly, *J. Cryst. Growth*, in press.

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A Correlation between the Solubility of Aromatic Hydrocarbons in Water and Micellar Solutions, with Their Normal Boiling Points

Mats Almgren, Franz Grieser, James R. Powell, and J. Kerry Thomas*

Chemistry Department, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

A linear correlation between the logarithm of the solubility in water of aromatic hydrocarbons and their normal boiling points is shown. Similarly, the logarithm of the distribution ratio of aromatic hydrocarbons in aqueous micellar solution is shown to be linearly related to the boiling points of the hydrocarbons.

Introduction

In previous studies on the water solubility of various groups of sparingly soluble hydrocarbons, e.g., alkanes or aromatics, attempts have been made to correlate the solubility with some property of the hydrocarbons. Possibly the most successful has been the linear correlation between either the partial molar volume[1] or the cavity surface area of the hydrocarbons[2,3] and the logarithm of their solubility in water.

A useful aspect of such correlations is that they provide a means of estimating the solubility of other hydrocarbons with sufficient accuracy for a number of purposes, e.g., solubility values in environmental studies.

We show in this note that there is a linear correlation between the logarithm of the water solubility of aromatic hydrocarbons and their boiling point. A similar correlation is also found for the solubilization of aromatic hydrocarbons in several micellar systems.

Experimental Section

There is a large amount of reliable data available in the literature[4-9] on the solubility of various hydrocarbons in water. We have used these data to obtain the plot shown in Figure 1.

The solubility of the aromatic hydrocarbons in micellar solutions was measured by using the technique described in detail elsewhere.[10] Briefly, it involves the saturation of a micelle solution with the hydrocarbon, usually equilibrated for several days, and measurement of the total concentration in the solution by absorption spectrometry.

The data for the solubilization of aromatic hydrocarbons in cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (NaLS) solutions are taken from ref 10. These data are compared with solubilization in the bile surfactants sodium tauro cholate (Calbiochem, >96% (TLC)) and sodium cholate (Calbiochem, >97% (TLC)). With the latter two surfactants some solubilization measurements were made with concentrations below the critical micelle concentration[11] (cmc). Below the cmc the additive was found to be only slightly more soluble than in pure water. However, above the cmc, the solubilization increased linearly with an increase in the micelle concentration. This indicates that there is no specific binding of the arene with a monomer unit but that a micelle environment is required for solubilization.

The solubilization of naphthalene in Brij-35 (polyoxyethylene lauryl ether, Pierce Chemical Co. (specially purified)), and in a vesicle solution of didodecylammonium bromide (DDAB, Eastman Chemical) was also measured to compare with the other surfactant systems.

The source and quality of all chemicals used that have not been listed here are given in ref 10.

Discussion

In Figure 1, the logarithm of the water solubility of a variety of aromatic hydrocarbons has been plotted as a function of their normal boiling points.[12] Where there is a large discrepancy in the values reported in the literature, both values are shown, otherwise a single value is plotted, generally from the most recent measurement. The references cited in the previous section give a list of all the original data. A linear least-squares analysis of the plot gives

$$\log S = 0.0138 T_b + 0.76 \qquad (1)$$

with a correlation coefficient of 0.97.

S is the solubility in water in mol dm^{-3} and T_b the normal boiling point of the arene in °C. Similar relationships also exist for most of the alkanes, alkenes, alkynes, and cyclic hydrocarbons; all these groups have similar slopes but different constant values. The relationship in these cases is only useful in extrapolating to longer chain lengths, since at small carbon numbers and on addition of various substituent groups to the basic hydrocarbon unit a marked deviation from the linear trend is observed.

With the aromatic hydrocarbons, addition of a substituent such as a halogen or small alkyl groups to the basic ring structure does not appear to cause a large deviation from the general trend. A marked exception to this is anthracene, chrysene, and the butylbenzenes. These compounds were not included in the least-squares plot. For most other aromatics eq 1 is a reasonable description of the water solubility of the hydrocarbons. It allows one to estimate how the solubility of an aromatic will change with either the addition of a functional group to the basic ring or an alteration in the position of a side group.

The reason for the empirical relationship of the water solubilities with the boiling point of the aromatic hydrocarbons can be understood, qualitatively, from the discussions by Hermann,[2] Harris et al.,[3] and Tanford et al.[13] of the correlations between

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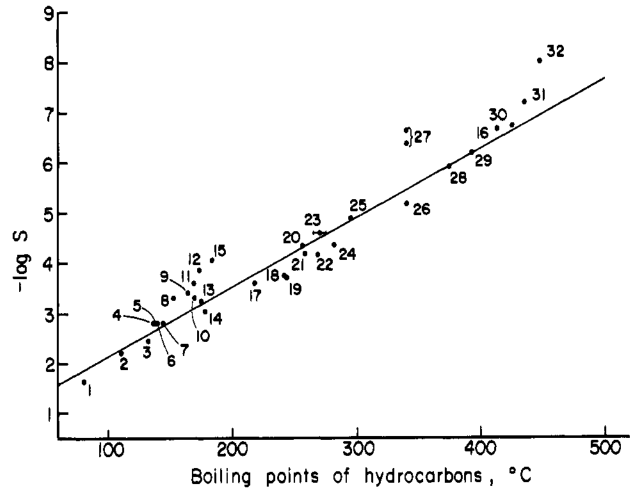

Figure 1. The logarithm of the solubility in water of aromatic hydrocarbons at 25 °C, as a function of their normal boiling points: (1) benzene, (2) toluene, (3) chlorobenzene, (4) ethylbenzene, (5) *p*-xylene, (6) *m*-xylene, (7) *o*-xylene, (8) isopropylbenzene, (9) 1,3,5-trimethylbenzene, (10) 1,2,4-trimethylbenzene, (11) *tert*-butylbenzene, (12) *sec*-butylbenzene, (13) 1,4-dichlorobenzene, (14) indan, (15) *n*-butylbenzene, (16) 1,2-benzofluorene, (17) naphthalene, (18) 2-methylnaphthalene, (19) 1-methylnaphthalene, (20) biphenyl, (21) 1-ethylnaphthalene, (22) 1,4-dimethylnaphthalene, (23) acenaphthalene, (24) 1-bromonaphthalene (at 21 °C), (25) fluorene, (26) phenanthrene, (27) anthracene, (28) fluoranthrene, (29) pyrene, (30) triphenylene, (31) 1,2-benzanthracene, (32) chrysene.

solubilities and surface area of the compounds and some additional arguments.

Hermann,[2] Harris et al.,[3] and Tanford et al.[13] have shown that the logarithm of the water solubilities, as well as some other solubility parameters, of hydrocarbons are linearly related to the surface areas of the solutes (the correlation lines are different for aromatic and aliphatic hydrocarbons). As discussed by Hermann,[2] the free energy of transfer of a solute molecule from the pure liquid to water is related to the surface areas of two cavities, one in the pure liquid phase from which the solute molecule is taken and one in the water. Hermann shows that the effective surface areas of these two cavities are linearly related.

Let us now consider the vapor pressure over the pure liquid phase at a temperature T. The logarithm of this pressure is a measure of the free-energy change going from the gas phase to the liquid.

$$RT \ln (P/P_0) = \mu_l{}^\circ(T) - \mu_g{}^\circ(T)$$

P_0 is the reference standard state of 1 atm. This free-energy change would be expected to be a linear function of the molecular surface area, about as well as the free-energy change in the transfer from liquid to water (since most of the compounds listed in Figure 1 are solid at 25 °C, this vapor pressure of the liquid is not easily accessible). The vapor pressure at T and the boiling point T_b are interrelated by the expression

$$RT \ln (P/P_0) = -\int_T^{T_b} \Delta\bar{S}^\circ{}_{\mathrm{vap}}\, \mathrm{d}T$$

If we, approximately, assume (1) $\Delta\bar{S}^\circ{}_{\mathrm{vap}}$, the entropy of vaporization, to be independent of temperature and (2) Trouton's rule is valid ($\Delta\bar{S}^\circ{}_b = 21.2$ cal deg^{-1} mol^{-1}), then we have

$$RT \ln (P/P_0) = -\Delta\bar{S}^\circ{}_b(T_b - T)$$

Thus, at a given temperature T, both the logarithm of the solubility in water, S, and the logarithm of the vapor pressure over the pure liquid, P, are linearly correlated to the molecular surface area. Since ln P is linearly related to the boiling point T_b, it follows that this should apply to ln S as well.

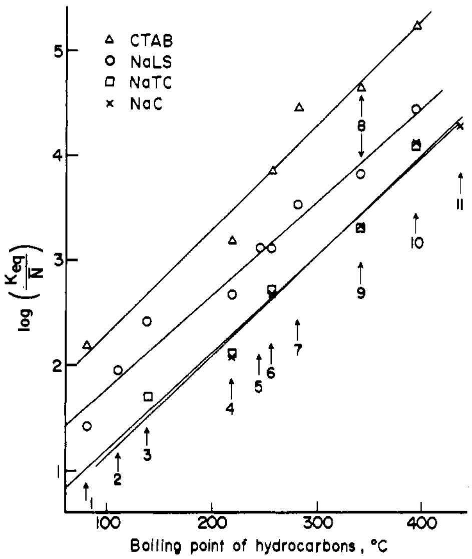

Figure 2. The logarithm of the distribution ratio of aromatic hydrocarbons in micellar solutions as a function of their normal boiling points: (1) benzene, (2) toluene, (3) *p*-xylene, (4) naphthalene, (5) 1-methylnaphthalene, (6) biphenyl, (7) 1-bromonaphthalene, (8) anthracene, (9) phenanthrene, (10) pyrene, (11) 1,2-benzanthracene.

Table I. Least-Squares Parameters for the Solubilization of Aromatic Hydrocarbons in Aqueous Solution Systems at 21 ± 1 °C

surfactant	$10^2 A$, °C^{-1}	C	r^2 [a]
CTAB	1.0	1.32	0.96
NaLS	0.89	0.89	0.97
NaTC	0.93	0.27	0.97
NaC	0.96	0.16	0.95

[a] r^2 is the correlation coefficient.

Further use of the empirical relationship can be gained if coupled with data from micelle solubilized aromatics.

The solubility in a micelle system can be described as an equilibrium between the bulk water and the micelles, i.e.

$$A + M \rightleftharpoons MA$$

$$K_{eq} = [MA]/([A][M])$$

where $[M] = ([\text{surfactant}] - \text{cmc})/\bar{N}$ and [MA] is the concentration of the micelle solubilized aromatic A. For the saturation measurements the concentration of A is taken as the solubility in pure water. The aggregation number $\bar{N}$ is the average number of surfactant molecules forming a micelle. Since the aggregation number of a particular surfactant may change with the amount of hydrocarbon that is solubilized, the distribution constant is best expressed as $K_{eq}/\bar{N}$, and this value is used as a comparison among the aromatics. It should be noted that the cmc may also be altered with a large amount of solubilized hydrocarbon. The effect can be gauged by using different surfactant concentrations or completely negated by making [surfactant] >> cmc. One of these procedures has been followed in the case of the more soluble aromatics, e.g., benzene or toluene. The realibility of the $K_{eq}/\bar{N}$ values is estimated to be about 15%.

In Figure 2 plots of log ($K_{eq}/\bar{N}$) as a function of the boiling points of the hydrocarbons in several micellar systems are shown. In the systems of NaTC and NaC with the more soluble aromatics, benzene, toluene, and *p*-xylene, opaque solutions were formed, indicating the formation of an immiscible new phase. Distribution ratios, therefore, could not be determined by the saturation method.

In all systems the distribution constant can be calculated from the empirical expression

$$\log (K_{eq}/N) = AT_b + C \qquad (2)$$

Table II. Solubility of Naphthalene in Several Surfactant Systems at 21 ± 1 °C[a]

surfactant	solubility[b] in the micelle pseudophase, mol dm^{-3}	molar vol,[c] dm^3 mol^{-1}
CTAB	1.1	0.292
NaLS	0.38	0.227
Brij-35	0.43	0.277[d]
DDAB	0.90	0.454
NaTC	[0.054]	[0.515][e]
NaC	[0.063]	[0.41][e]

[a] Solubility in water is 2.2×10^{-4} M (*9*) and in hexane 0.91 M (*15*). [b] The micelle solubility is calculated from $[[P]_{total} - [P]_{aq}]/([surfactant] - cmc)V$. V is the molar volume of the surfactant. $[P]_{total}$ is the concentration of naphthalene at a particular surfactant concentration above the cmc and $[P]_{aq}$ the concentration of naphthalene in pure water. This equation applies to any micelle solubilized molecule; see ref 10. [c] Molar volumes calculated from hydrocarbon densities are given in ref 12. [d] Molar volume of this polyethylene oxide micelle core is from the data given in ref 14. [e] No literature value for the density of these compounds could be found, so a density of 1 has been used in the calculation.

where A and C from a linear least-squares analysis take the values given in Table I.

The data given in Figure 2 clearly show that CTAB is by far the best surfactant in solubilizing aromatic compounds. This is further seen in Table II where the solubility of naphthalene in various surfactant micelles is shown.

In the comparison of the solubility of naphthalene in the micelle pseudophase, the volume of which is estimated as the volume of the hydrocarbon tails of the surfactant monomers to that in a hydrocarbon solvent, hexane, it appears that in both CTAB micelles and DDAB vesicles the solubility is the same within the experimental uncertainty, whereas in the other surfactants the solubility is considerably lower. For the solubility to be as high as in a hydrocarbon phase is surprising since, the Laplacian pressure in a micelle core (estimated to be several hundred atmospheres[16]) and the lower microviscosity would both tend to reduce the solubility relative to a bulk hydrocarbon solvent. This relatively high solubility in CTAB and DDAB can be explained if one assumes that there is some specific binding of naphthalene with the quaternary ammonium head group. Such an interaction seems to be the case with pyrene.[10] The bile acid salts form aggregates of about 4 units, which have a microviscosity (measured with 2-methylanthracene as probe)[17] of 675 cP. This can be compared with other micelles: 30 cP for CTAB[18] and DDAB[19] and 15 cP for NaLS.[20] Thus the very much lower solubility in NaC and NaTC micelles is probably due to the comparatively low fluidity in these aggregates.

The data from the solubility in water of these aromatic hydrocarbons coupled with their solubilization in micellar systems can be used to calculate, at least approximately, the maximum amount of compound that will be solubilized by a given amount of surfactant. Some inaccuracy is introduced into the calculation because of the temperature difference of the water solubilities (25 °C) and micelle solubility (21 °C) data. This is, however, only minor, since the solubility in water will only change slightly in the temperature range cited.

For the less solubilized aromatics the aggregation number should not be greatly altered compared to the pure surfactant solution, as has been shown for some compounds, nor will the distribution ratio.[10,19] Consequently the distribution ratio can be used as a guide in nonsaturated solutions to determine the ratio of the concentration of compound solubilized to that in the aqueous phase. This case is particularly useful in interpreting results from photochemical and reaction rate studies of solubilized compounds in micellar systems.

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Literature Cited

(1) C. McAuliffe, *J. Phys. Chem.*, **70**, 1267 (1966).
(2) R. B. Hermann, *J. Phys. Chem.*, **76**, 2754 (1972).
(3) M. J. Harris, T. Higuchi, and J. H. Rytting, *J. Phys. Chem.*, **77**, 2694 (1973).
(4) C. Sutton and J. A. Calder, *J. Chem. Eng. Data*, **20**, 320 (1975).
(5) R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951).
(6) D. Mackay and W. Y. Shiu, *J. Chem. Eng. Data*, **22**, 399 (1977).
(7) R. D. Wauchope and F. W. Getzen, *J. Chem. Eng. Data*, **17**, 38 (1972).
(8) H. Stephen and T. Stephen, Eds., "Solubilities of Inorganic and Organic Compounds", Vol. 1, Part 1, Pergamon Press, New York, 1963, p 55–79.
(9) F. P. Schwarz, *J. Chem. Eng. Data*, **22**, 273 (1977).
(10) M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **101**, 279 (1979).
(11) P. Mukerjee and K. J. Mysels, "Critical Micelle Concentrations of Aqueous Surfactant Systems", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No 36** (1971).
(12) "Handbook of Chemistry and Physics", 56th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1971–1972.
(13) J. A. Reynolds, D. B. Gilbert, and C. Tanford, *Proc. Natl. Acad. Sci. USA*, **71**, 2925 (1974).
(14) K. Shinoda, T. Nakagowa, B-I Tamamushi, and T. Isemura, "Colloidal Surfactants", Academic Press, New York, 1963, p 136.
(15) A. Seidell "Solubilities of Organic Compounds", 3rd ed., D. Van Nostrand, New York, 1942.
(16) P. Mukerjee, *Ber. Bunsenges. Phys. Chem.*, **82**, 931 (1978).
(17) M. Chen, M. Grätzel, and J. K. Thomas, *J. Am. Chem. Soc.*, **97**, 2052 (1975).
(18) M. Shinitzky, A.-C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, **10**, 2106 (1971).
(19) R. McNeil and J. K. Thomas, unpublished data.
(20) M. Grätzel and J. K. Thomas, *J. Am. Chem. Soc.*, **95**, 6885 (1973).
(21) S. J. Dougherty and J. C. Berg, *J. Colloid. Interface Sci.*, **48**, 110 (1974).

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Liquid–Liquid Equilibrium for the Ternary System $NaOH–H_2O–t\text{-}BuOH$

J. L. Zepeda,* F. Lozano, and F. J. Garfias

Facultad de Química, Universidad Nacional Autônoma de Mêxico, Mêxico D. F., Mêxico

The ternary diagram for the system $NaOH–H_2O–t\text{-}BuOH$ was determined by a combination of NMR and potentiometric titration. NaOH is extracted only slightly by *tert*-butyl alcohol from aqueous solution.

Introduction

tert-Butyl alcohol has some unique properties which are of interest in the study of phase equilibrium (*1*). *tert*-Butyl alcohol is the highest molecular weight of the saturated monohydroxy

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