

The Solubility of Sodium Soap in Organic Solvents

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J. Chem. Phys. **90**, 6569 (1989); 10.1063/1.456324



between layers in a lamellar micelle, but the change in the intermicellar distance (d_I).

With respect to solubilization, Corrin found that Hartley's spherical model gave much better agreement than this.

The cylindrical model is superior in that its height is measured by the M - or micelle thickness band, and it has a diameter which may be varied and can be calculated approximately at high concentrations from the I -band, or at low concentrations from light scattering (Debye).

In any model the energy relations make it essential to make the interface hydrocarbon chains-water as small as possible, which means that the cylinder may be somewhat distorted at the side to give coverage of the hydrocarbon chains by a few polar-ionic groups of the soap. However, the model is essentially a cylinder with these groups at the ends.

* This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the government's synthetic rubber program.

^{1a} R. W. Mattoon, R. S. Stearns, and W. D. Harkins, submitted for publication (September, 1947); ^b *ibid.* J. Chem. Phys. 15, 209 (1947); ^c W. D. Harkins, R. W. Mattoon, and R. Mittelman, *ibid.* 15, 763 (1947).

² A. E. Alexander, *Colloid Science, A Symposium* (Chemical Publishing Company, Inc., Brooklyn, 1947), p. 43. McBain now considers the "neutral" micelle to be the somewhat ionized "large lamellar micelle."

^{3a} J. W. McBain, *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1942), edited by E. O. Kraemer, p. 124, for extensive references to work on the "large lamellar micelle" see; ^b W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Am. Chem. Soc. 68, 220 (1946), and ^c J. Colloid Sci. 1, 105 (1946).

⁴ M. L. Corrin and W. D. Harkins, J. Am. Chem. Soc. 68, 679, 683 (1947).

⁵ G. S. Hartley and D. M. Runnicles, Proc. Roy. Soc. A168, 420 (1938).

The Solubility of Sodium Soap in Organic Solvents

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November 18, 1947

THE solubility of sodium palmitate and sodium stearate in organic solvents has been determined by several members of the Stanford Group.¹⁻³ These data seem rather difficult to correlate with each other or with other solubility data. The latter is usually most fruitful if the comparison is made on the basis of Hildebrand's relation:

$$\ln a_2 = -\frac{\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right),$$

where ΔH_f the heat of fusion (or transition) and T_f the melting (or transition) temperature.^{4,5}

In view of the fact that the sodium soaps exhibit not only a melting point but a series of transition points in the solid state, the ideal solubility curve changes its slope at as many points. The transition points and the transition heats have been determined by Vold.⁶ It is therefore possible to construct the ideal solubility curve of these soaps. Such a curve for sodium palmitate is shown—marked "ideal"—on Fig. 1. The other curves on the same figure are the so-called T_i curves,⁷ giving the temperature at which the isotropic melt changes into an anisotropic liquid crystal. The proximity of several curves to the Raoult's law curve is rather surprising, since one usually associates "ideality" with simpler physical behavior. It

should be noted that the slope of all solutions in hydroxylic compounds deviates in the low temperature (<180°C) region but little from the slope of the ideal curve, while the slope of the other solutions, particularly in hydrocarbons, is very much steeper. This suggests that the excess free energy of mixing with the alcohols consists of a negligible heat of mixing and a strongly negative entropy of mixing. The solution of soap in hydrocarbons requires on the other hand both rather large (negative) enthalpy and entropy changes. One would hardly have expected that the solubility of stearic acid in similar solvents deviates more from ideality than that of soap, as is evident from the data on Fig. 2. This applies particularly to alcoholic solutions.

In the high temperature region all solutions behave quite similarly in exhibiting solid solution phenomena, as is also apparent in visual observation of these systems. The effect of chemical structure of the solvent on the shape of the solubility curve is sometimes quite marked, as e.g., in the case of the cresols. The position of *p*-cresol solutions is given on the graph. The solubility curve of soap in *o*-cresol, on the other hand, is practically identical with that of cetyl alcohol and has, therefore, not been drawn in. In other cases there is little specificity as is exemplified by the solubility in cyclohexane and in low mole weight aromatic hydrocarbons, or cetane and white medicinal oil.

The humps in the solubility curves which are observed in soap solutions in cyclic (low molecular weight) hydrocarbons, in water, and in glycerol are somewhat reminiscent of the shape of solubility curves of systems forming two immiscible liquid phases in a certain temperature range. While presentation of the soap solubility data in the

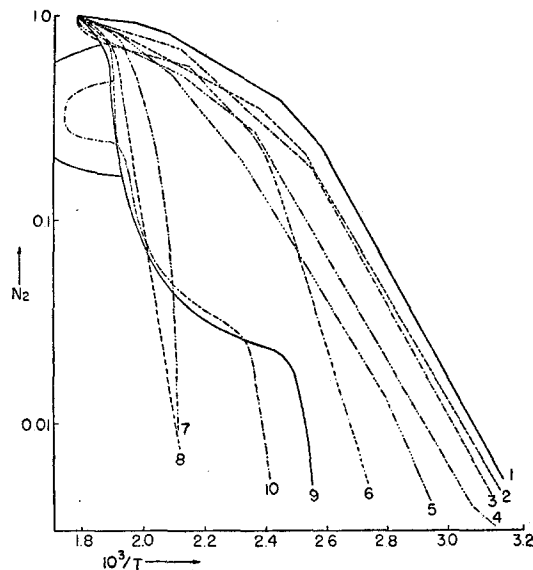


FIG. 1. Solubility of sodium palmitate in various organic solvents (from data of references 1, 2, 3) compared with ideal solubility curve (1).

- | | |
|-----------------------|---------------------------------------|
| (1) Ideal solubility | (6) <i>n</i> -butylamine |
| (2) <i>p</i> -cresol | (7) <i>n</i> -cetane |
| (3) Diethylene glycol | (8) Nujol |
| (4) Ethyl alcohol | (9) Cyclohexane, sodium stearate in |
| (5) Cetyl alcohol | (10) Ethylbenzene, sodium stearate in |

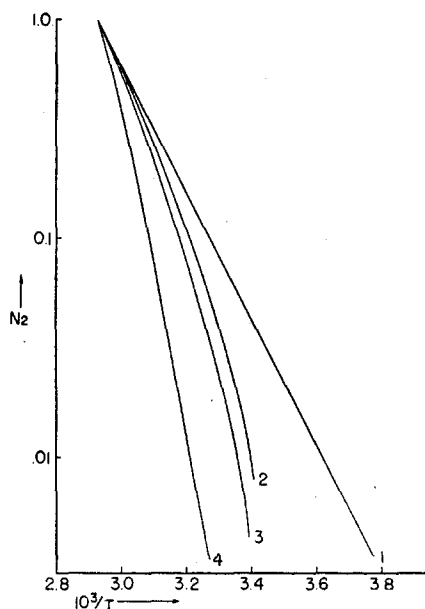


Fig. 2. Solubility of stearic acid in various organic solvents (from data of reference 8) compared with ideal solubility, curve (1).

- (1) Ideal solubility
- (2) Cyclohexane
- (3) *n*-butyl alcohol
- (4) Methyl alcohol

manner shown in Fig. 1 simplifies the discussion of these complicated systems, it leaves many phenomena still unexplained.

The writer was unable to find any solubility data of simpler compounds undergoing phase transition in the solid state, such as camphor, C_2Cl_6 , and the like, to compare with the apparently more thoroughly studied soap systems.

The writer wishes to acknowledge discussions with Professor J. W. McBain and Dr. O. Redlich, which led to this work.

¹ R. D. Vold, C. W. Leggett, Jr., and J. W. McBain, *J. Phys. Chem.* **44**, 1058 (1940).

² C. W. Leggett, Jr., R. D. Vold, and J. W. McBain, *J. Phys. Chem.* **46**, 429 (1942).

³ G. H. Smith, Ph.D. Thesis, Stanford, 1946.

⁴ J. H. Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York, 1936).

⁵ A. Bondi, *J. Phys. Chem.* **51**, 891 (1947).

⁶ R. D. Vold, *J. Am. Chem. Soc.* **63**, 2915 (1941).

⁷ J. W. McBain, L. H. Lazarus, and A. V. Pittner, *Zeits. physik. Chemie* **A147**, 87 (1930).

⁸ C. W. Hoerr and A. W. Ralston, *J. Org. Chem.* **9**, 329 (1944).

The Triplet State of Ethylene

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December 9, 1947

IN dealing with the separation between the ground and triplet states of ethylene, Laidler¹ has drawn attention to the remarkable agreement existing between the experimental value of 74 kcal. obtained by Lewis and Kasha,² and the calculated value of 72 kcal. found by Hartmann³ by the method of antisymmetrical molecular orbitals.

It is not, however, indicated in Hartmann's paper what

values were used for the various integrals that occur, and in treating the same problem by the same approximation during the course of other work, the writer has obtained a considerably greater value for the singlet-triplet separation. Using values for the integrals obtained by interpolation between the values given by Sklar and Lyddane,⁴ the singlet-triplet separation comes out to be 95 kcal. or greater, the exact value depending on the assumptions made about the configuration of the triplet state. Therefore, there is probably not the good agreement between calculated and experimental values that Hartmann's value suggests. Hartmann's value for the excited singlet state, given in the same paper, appears to be in error due to the use of a wrong wave function, and the corrected value again proves to be considerably greater than the experimental.

The values for the integrals used in these calculations are so closely in agreement with those given recently by Griffing⁵ that there is no need to quote them here.

¹ K. J. Laidler, *J. Chem. Phys.* **15**, 712 (1947).

² G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944). These authors commented that Hartmann's value was improbably low.

³ H. Hartmann, *Zeits. physik. Chemie* **B53**, 96 (1943).

⁴ A. L. Sklar and R. H. Lyddane, *J. Chem. Phys.* **7**, 374 (1939).

⁵ V. Griffing, *J. Chem. Phys.* **15**, 421 (1947).

Erratum: Infra-Red Spectrum and Depolarization Factors of the Raman Lines of Spiropentane and the Raman and Infra-Red Spectra of 1,1-Dimethylcyclopropane, 1-Methylcyclobutene, and Methylene cyclobutane

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[*J. Chem. Phys.* **15**, 742 (1947)]

DUE to a faulty distillation and an oversight, the infrared spectrum of methylenecyclobutane reported in Table IV of the above paper contains spurious bands at 782, 990, 1051, and 1155 cm^{-1} , which correspond to the prominent bands of spiropentane. If these are deleted, the remaining bands are those of methylenecyclobutane. (It should also be noted that the strongest band of spiropentane is nearly coincident with the 877- cm^{-1} band of methylenecyclobutane.) The Raman data, however, were obtained with another sample which was pure enough not to show the strongest line of the spiropentane.

This correction of the experimental data necessitates the following changes in the assignments for eight of the weak bands: the combination or overtone frequencies whose values are given in the last column of Table IV as 801, 1509 or 1510, 1883, 2013, 2061 or 2063, 2118 or 2109, 2177 or 2188, 2310, and 2416 should be deleted; they may be replaced by the combination frequencies 1167-373=794, 354+1167=1521, 728+1167=1895, 954+1070=2024, 895+1167=2062, 954+1167=2121, 1029+1167=2196, and 1029+1395=2424. Thus eight of the nine carbon skeleton frequencies and eighteen of the twenty-four C-H frequencies are now tentatively assigned.