Refractive Indices of Soaps and Detergents

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An example of the practical application of the method for rapid particle size determinations is given in Table I which contains data on the variation of the particle diameter of polymer with percent conversion of monomer to polymer in agitated styrene-isoprene reaction mixtures which were kept in bombtubes at 50°C, in presence of 0.2 percent of potassium caprylate as emulsifier. The calibration curve differs here from that in Fig. 1 (in <1.23).

* The work reported in this abstract was done at the University of Chicago in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation. Details of the method and results are given in the restricted reports Comptes rendus 87, 124, 237 (1943); 470 (1944); 845, 846, 858, 888 (1945).
† Present address: Firestone Tire and Rubber Company, Akron, Ohio.
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Spectrophotometric Studies on Solubilization of Hydrocarbons*

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A STRONGLY light scattering emulsion is formed on exceeding the limiting concentration of hydrocarbon, c_1, which defines its solubility in a soap solution. A quantitative spectrophotometric method for studies on solubilization was based on this known fact. c_1 is characterized by a minimum in light scattering which facilitates the measurements. Special joint studies with H. Oppenheimer showed that the minimum is caused by a decrease in size of molecular aggregates of soap, with increasing oil concentration, at concentrations $<c_1$. Solubilization studies on ethylbenzene gave the following results valid at 20°–25°C.

(1) c_1 increases with time, particularly in concentrated solutions where a practically final value is reached only after 60 hours.

(2) The number of moles of ethylbenzene, dissolved per mole of soap, R_m, increases for a given soap concentration, with increasing chain length of the soap molecules. R_m, implicitly, increases with a decrease in the "critical soap concentration," c_{cr}, above which micelles are formed. Considering 15 percent soap solutions, the following R_m (c_{cr}) values were found: KC$_6$: 0.0031 (1.62); KC$_8$: 0.080 (0.395); KC$_{10}$: 0.207 (0.100); KC$_{12}$: 0.433 (0.023); KC$_{14}$: 0.870 (0.007). The c_{cr} values, in moles of soap per liter were determined in supplemental experiments by other methods.

(3) With an increase in concentration of a given soap, R_m first decreases, reaches a minimum, and then increases nearly linearly without definite indication of approaching saturation at a 15 percent concentration. The minimum value of R_m, is reached at c_{cr}, providing thereby a new method for determining c_{cr} from solubilization measurements. c_{cr} thus found for KC$_{12}$ is 0.025 mole per liter.

(4) Adopting the concept of the lamellar micelle structure,[1a,1b] using cross-sectional areas of soap molecules as obtained from x-ray measurements and assuming that the density of ethylbenzene absorbed in the micelles is, in the first approximation, identical with that of liquid ethyl-

benzene, one can calculate from R_m—corrected for oil dissolved by micelles only—the thickness (spacing) of the individual intermicellar ethylbenzene layers. For KC$_{12}$, one thus finds, by interpolation, that the oil layer is equivalent to a completed monomolecular layer and a bimolecular layer at a soap concentration of 0.09 and 0.50 mole per liter, respectively. According to extrapolation, a trimolecular layer would be completed at a concentration of 1.08 moles per liter. The corresponding spacings are $2.7+2\epsilon$, $5.4+2\epsilon$, and $8.1+2\epsilon$A, respectively, where ϵ, a fraction of one A, represents the unknown distance, at a minimum of potential energy between the hydrophobic ends of the oriented soap molecules and the neighboring ethylbenzene molecules.

* The work reported in this abstract was done at the University of Chicago in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation. The methods used were developed early in 1943.
† Present address: Firestone Tire and Rubber Company, Akron, Ohio.
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Refractive Indices of Soaps and Detergents*

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A CCORDING to Hess, Philippoff, and Kiessig,[1] the variation in the refractive indices with the concentration for various soaps is characterized by an intersection of two linear functions. The authors believe that this intersection represents the critical micelle concentration above which micelles are formed. These experiments were repeated and expanded using a Haber-Loewe type of interferometer (layer thickness, 160.290 mm, $T=23.5°C$) using both cationic and anionic soaps or detergents; a few preliminary data are given below.

The results reported here are those obtained with lauryl amine hydrochloride (LA-HCl) and with potassium laurate (KC$_{12}$). The former was kindly supplied by the Research Laboratories of Armour and Company and was subsequently recrystallized five times; the latter was prepared by multiple fractionation of the methyl ester of lauric acid, followed by saponification and repeated recrystallizations.

The refractive indices change in the case of LA-HCl between 1.332849 and 1.336065 and for KC$_{12}$ between 1.332828 and 1.335640 over a concentration range from 0.10 percent to 2.00 percent. Plotting of this data gives two straight lines for each series which intersect at 0.29–0.30 percent for the LA-HCl and at 0.61–0.62 percent for the KC$_{12}$ solutions. The refractive increment, $(n_t-n_m)/c$, where n_t is the refractive index of the solution, n_m the refractive index of the medium, and c the concentration in grams per hundred grams solution, reaches a maximum value at 0.29–0.30 percent and at 0.61–0.62 percent for LA-HCl and KC$_{12}$, respectively.

More significant is the change with concentration in the refractive index of the solute itself (n_s). These values were obtained by use of the new mixture rule reported recently by Heller.[2] These results are plotted in Fig. 1. In both cases,
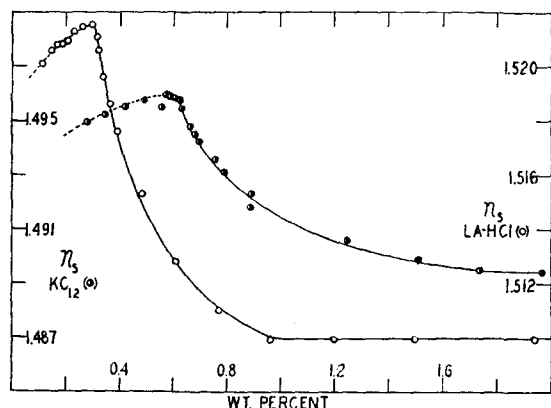
FIG. 1. The change in the refractive indices of lauryl amine hydrochloride (LA–HCl) and potassium laurate (KC₁₂) with concentration. The dotted portion of the curve is the region in which there is as yet no certainty that the equation used here is valid.

n_s increases slightly and then decreases suddenly, apparently then approaching a constant value at concentrations above 1.2–1.3 percent. Ralston and Hoerr[3] reported a discontinuity in the equivalent conductivity curve at a concentration of 0.29 percent for the LA-HCl. This agreement between the two methods regarding the concentration at which a discontinuous change in the properties of soap and detergent solutions occurs, is significant. In the case of KC₁₂, the values obtained by Bury and Parry[4] from density measurements indicate that this discontinuity occurs at about 0.9 percent at 25°C. Recently, from measurements of the spectral shifts of cyanine dyes, a value of 0.54–0.57 percent has been reported as the critical micelle concentration for KC₁₂.[5]

If one were to consider these and other similar discontinuities as indicative of a formation of a new phase in soap solutions, then the value of n_s at concentrations below the break point would represent the refractive indices of molecularly dispersed soaps or detergents or of a simple micelle, and the asymptotic values of n_s at concentrations above the maximum, the refractive indices of micellar soap or of aggregates of micelles. The values between these two regions may be caused by mixtures of these various forms, or by a gradual change in form or aggregation. Further, it may prove possible, if the first hypothesis is correct, to determine the relative amounts of molecular and micellar soap present in this intermediate region when more data are available.

Comparison of the discontinuities observed for various properties of soap solutions shows that the discontinuity observed in n_s is particularly interesting because it is characterized by a considerable change in the slope, whereas in most other experimental results there is only a small change in slope.

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On the Dissociation Energies of CO, N₂, NO, and CN

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GAYDON and Penney tried to obtain dissociation schemes with respect to CO, N₂, NO, CN by a systematic application of the non-crossing rule of the energy eigenvalue curves of the two-center problem to the potential curves of the molecule.[1] Their paper shows that even their correlation leads to contradictions with such a non-crossing rule for the excited states since they consider the correlation of the molecular ground state to the atomic ground states as a necessary consequence of this rule. For instance in Herzberg's CO dissociation scheme there are also crossings of the same species with respect to the potential curves of the states $a'\,^3\Sigma^+$ and $A\,^1\Pi$ with the corresponding repulsive curves. Moreover, the dissociation schemes given by Gaydon and Penney do not seem to be reconcilable with other spectroscopic arguments.

Schmid and Gerö have pointed out several times that the non-crossing rule cannot be applied to the correlation of molecular terms to the atomic term combinations, strong spectroscopic arguments being adducible both in the use of the molecules mentioned and in the case of diatomic hydride and deuteride molecules.[2] In addition, theoretical considerations show,[3] that from the non-crossing of the energy eigenvalue curves of the two-center problem one cannot deduce the sequence of the discrete energy levels of the molecule, and the possibility of the violation of a non-crossing rule does not have to be specially postulated. The potential curves of unperturbed electronic states, resulting by an averaging of the interactions with respect to the electronic motions which can also be influenced by the nuclear motion, cannot, in general, be identified with the energy eigenvalue curves of the two-center problem.

Table I shows the dissociation energies and dissociation products of CO, N₂, NO, CN as given by Schmid and Gerö. The corresponding dissociation schemes can be regarded as taking into consideration all the spectroscopic data. The bond energies are to be counted from the atomic term

TABLE I.

Molecular ground state	Dissociation products	Bond energy cm⁻¹	Lowest atomic term combination	Dissociation energy cm⁻¹
CO $X^1\Sigma^+$	C(^{1}D)+O(^{1}D)	81,660	C(^{3}P)+O(^{3}P)	55,600[a–c]
N₂ $X^1\Sigma_g^+$	N(^{2}D)+N(^{2}D)	78,750	N(^{4}S)+N(^{4}S)	40,350[d,e]
NO $X^2\Pi$	N(^{2}D)+O(^{3}P)	53,800	N(^{4}S)+O(^{3}P)	34,600[d–f]
CN $X^2\Sigma$	C(^{1}D)+N(^{2}D)	61,100	C(^{3}P)+N(^{4}S)	31,700[g]

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