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The Solubility of Oil-Soluble Dyes in Aqueous Solutions of Stable Protecting Colloids as Examples of True Reversible Equilibrium

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Not only are many important colloids truly stable in that they form spontaneously and enter into reversible equilibrium with crystalloidal constituents and crystals, but colloids which are usually unstable may also exhibit similar properties characteristic of true stability when sufficient stable protective colloid is present.[1]

In the present experiments, 40 g. of water and 2 cc. of toluene are placed in a thermostat at 25° upon a pivoted table whose normal very slowly describes a small cone, thus imparting to the system an extremely slow swirling motion that avoids all emulsification or breaking of the surface. The water contains a given amount of soap or other detergent or colloid. Systems of identical total composition were always studied together in quadruplicate. In one pair the dye was first dissolved in the toluene, and in the other pair it was first dissolved in the aqueous detergent. At least forty-eight hours is required for both pairs to arrive at the same equilibrium, from opposite sides. Analysis of the toluene layer was made by evaporating to dryness and weighing; that of the aqueous layer colorimetrically, often against a standard dichromate solution. Whenever the aqueous layer of soap was turbid through hydrolysis, this was first clarified by addition of a small amount of solid potassium hydroxide.

The ultramicroscope shows the dye to be plentifully present in the aqueous layer in the form of colloidal particles which are invisible in the microscope. A toluene solution of dye is clear in the ultramicroscope.

It is found that within the experimental error, all the data with soap or detergents up to 5 or 10% may be approximately represented by the equation

$$D_{\text{aq.}} = KD^{2/3}_{\text{tol.}}S^{2/3}_{\text{aq.}}$$

where D is the concentration of dye in the aqueous and toluene layers, respectively, and S is the concentration of the soap or other protective colloid referred to the water present. The values of K depend upon the nature of the colloid and of the dye. Most of the experiments have been carried out with Yellow AB (benzene-azo-β-naphthylamine) or Scarlet X 9995 (benzene-azo-β-naphthol), both kindly supplied by the Calco Chemical Company. All concentrations are expressed in g./100 g. of solvent, whether water or toluene, except that for Yellow AB $D_{\text{tol.}}$ is expressed in g./100 cc. of toluene.

Further proof that true reversible equilibrium is reached independent of previous history is given by experiments in which the oleate radical, as oleic acid, was placed in the toluene leaving the potassium hydroxide in the water. At the end of forty-eight hours, the distribution of dye

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[1] McBain and Laing McBain, THIS JOURNAL, **58**, 2610 (1936), of which the present paper is a continuation. Subsequent work is reported by Hartley in the Leather Trades' Chemists' Symposium on "Wetting and Detergents," 1937 (in press), and by Lawrence, *Trans. Faraday Soc.*, **33**, 325 and 815 (1937). Details of the work of Miss Parsons and Hartley on azobenzene and its crystalline derivatives in solutions of paraffin chain salts are not yet published.

was the same as in the usual experiments with the potassium oleate originally all in the water. Likewise when all the potassium oleate was placed with the dye in the toluene, although during the first few minutes twice the equilibrium concentration of dye went into the water, this went back to the usual equilibrium within the next few days. Twenty-four hours is always insufficient to attain equilibrium from both sides, but it is nearly reached in forty-eight hours.

Experimental Results

The systems with potassium oleate were examined in greater detail. A large number of commercially available and other detergents and colloids were then examined in 1 and 5% concentration with two amounts of Yellow AB. Scarlet X was used in early experiments, but it bleaches distinctly on long exposure to light in soap solution, whereas Yellow AB does not.

In most of the experiments on soaps of the alkali metals, the aqueous layer contained also 0.0407 *N* hydroxide. The solubility of the dyes is negligible in water, or in aqueous alkali, or in solutions of trisodium phosphate or in aqueous sodium silicate. Solutions of potassium oleate were studied in 0.1, 0.5, 1, 5, and 10% concentration, each with 100, 40, and 10 mg. of Scarlet X. One typical result with 5% and 100 mg. was 0.0294, 0.0292, 0.0251, and 0.0253 g., respectively, found in the toluene layer after forty-eight hours, with 0.0613, 0.0613, 0.0674, and 0.0674 g. in the aqueous soap layer. A mean of each quadruplicate result was taken and the fifteen resulting simultaneous equations were solved; first for the exponent of $D_{\text{tol.}}$, maximum 0.74, minimum 0.54, mean 0.67; and then in pairs for K and the exponent of S_{aq}. Hence the exponent of $S_{\text{aq.}}$ is maximum 0.89, minimum 0.53, mean 0.67; and $100\,K$ is maximum 5.70, minimum 3.68, mean 4.73.

Since the solubility of Scarlet X is 15.0 g. in 100 g. of toluene, substitution in the equation shows that 100 g. of 5% potassium oleate solution at 25° if saturated with dye would carry 0.843 g. of Scarlet X. This is 1 g. of dye to 6 g. of soap, or one molecule of dye to 4.6 of soap. A 1% solution would dissolve 0.288 g. and a 0.1% solution 0.062 g. Similarly since the solubility of Yellow AB is 13.54 g. in 100 cc. of toluene, the solubility of Yellow AB in a 1% potassium oleate solution is 0.330 g. per 100 g. Potassium oleate has a distinctly higher protective and solvent action than potassium laurate, as shown by the fact that $100\,K$ for Scarlet X is 4.73 for potassium oleate, whereas for potassium laurate it is 3.56.

We long ago showed that a slight excess of alkali or fatty acid improves the detergent power of a soap as measured by the carbon black method. The value of $100\,K$ for Yellow AB and 1% or 0.033 *N* sodium oleate is 5.34. When 0.01 *N* sodium hydroxide is also present, this becomes 5.48, and with 0.05 *N* sodium hydroxide it is 5.81. With 0.01 *N* oleic acid it is 5.19, and with 0.05 *N* oleic acid it is 5.04. There is thus only a steady increase in $100\,K$ as the solution passes from acid soap to strongly alkaline soap, with no suggestion of a maximum or minimum.

The values of $100\,K$ for a large number of commercially available or technical detergents and emulsifiers are given in Table I. Our thanks are due to the firms, including E. I. du Pont de

Table I

Values of $100\,K$, Showing the Protective or Solvent Action of Various Materials Added to Water in Dissolving the Water-Insoluble Dye, Yellow AB

Detergent	$100\,K$ from 1%	$100\,K$ from 5%	$100\,K$
Potassium oleate, Kahlbaum[a]	5.80	..	5.80
Sodium oleate, Kahlbaum[a]	5.69	5.65	5.67
"75% Turkey red oil"	6.22	5.96	6.09
Sodium sulforicinoleate	4.12	4.11	4.12
Highly sulfonated olive oil	6.18	6.24	6.21
Tech. sodium stenyl sulfate	9.74	9.81	9.78
Tech. sodium octyl sulfate[a]	2.96	2.94	2.95
Tech. sodium lauryl sulfate	3.94	3.90	3.92
Tech. sodium oleyl sulfate[a]	4.16	4.14	4.15
Ammonium lauryl sulfate	5.93	6.04	5.99
Sodium lauryl sulfate	5.06	5.18	5.12
Sodium sulfonate of Igepon type	6.15	6.22	6.18
Trimethyldodecylammonium bromide	6.74	6.72	6.73
By-product of India coir fiber	0.15	0.14	0.14
An Igepon product	6.85	6.92	6.89
A sodium alkyl sulfate	5.75	5.75	5.75
Aliphatic ester sulfate	8.86	8.60	8.73
Another commercial synthetic salt	5.83	5.76	5.80
Oleo glyceryl sulfate	8.45	8.26	8.36
Diglycol laurate	5.63	5.63	5.63
Synthetic non-electrolytic polymer	6.60	6.58	6.59
Polyglycerol ester	..	4.15	4.15
Polyhydroxyether, technical	..	3.62	3.62
Trisodium phosphate	0	0	0
Sodium silicate ($SiO_2/Na_2O = 3.2$)	0	0	0
Sodium hexametaphosphate (Calgon)	0	0	0
Triethanolamine	0	0	0
Ethyl alcohol	0	0	0
Sodium alginate	0	0	0

[a] In presence of 0.0407 *N* alkali.

Nemours and Company, Lever Brothers Company, Shell Development Company, and others, who supplied these materials or through whom they were obtained. The names given are those of the main constituent when stated and supplied by the maker, but where the samples were procured indirectly only an indication of the type of synthetic commercial product is given. The proportion of active material in all the technical preparations varies greatly and in many cases is unknown to us. The potassium and sodium oleates were special preparations by Kahlbaum. In each case measurements were made at forty-eight hours in quadruplicate approaching the equilibrium from both sides with solutions containing 1 and 5 g. of detergent per 100 g. of water. The agreement between results for these 1 and 5% solutions shows that the formula given is of general applicability.

TABLE II

THE TRUE SOLUBILITY OF YELLOW AB IN 1 AND 5% AQUEOUS SOLUTION OF PROTECTIVE COLLOIDS, MAINLY AS PROTECTED COLLOIDAL SOLUTION OF DYE

	G. of dye in 100 g. of aqueous solution of detergent	
Detergent	1% soln.	5% soln.
Potassium oleate, Kahlbaum[a]	0.3300	...
Sodium oleate, Kahlbaum[a]	.3154	0.9432
"75% Turkey red oil"[b]	.3463	1.0130
Sodium sulforicinoleate	.2342	0.6846
Highly sulfonated olive oil	.3531	.8201
Tech. sodium stenyl sulfate	.5554	1.6240
Tech. sodium octyl sulfate[a]	.1680	0.4913
Tech. sodium lauryl sulfate	.2224	.6505
Tech. sodium oleyl sulfate[a]	.2362	.6908
Ammonium lauryl sulfate	.3402	.9947
Sodium lauryl sulfate	.2914	.8521
Sodium sulfonate of Igepon type	.3516	1.0280
Trimethyldodecylammonium bromide	.3824	1.1185
By-product of India coir fiber	.0831	0.2429
An Igepon product	.3914	1.1445
A sodium alkyl sulfate	.3361	0.9535
Aliphatic ester sulfate	.4961	1.4510
Another commercial synthetic salt	.3296	0.9638
Oleo glyceryl sulfate	.4751	1.3890
Diglycol laurate	.3203	0.9362
Synthetic non-electrolytic polymer	.3742	1.0940
Trisodium phosphate	0	0
Sodium silicate (SiO_2/Na_2O = 3.2)	0	0
Sodium hexametaphosphate (Calgon)	0	0
Triethanolamine[c]	0	.005
Ethyl alcohol	0	0

[a] In presence of 0.0406 N alkali. [b] Solubility of Yellow AB directly determined in Turkey red oil 7.32 g.; in 5% 0.9880 g.; in 1% 0.291 g. [c] Solubility of Yellow AB in the triethanolamine alone is 4.86 g.; in 5% aqueous solution 0.005 g.

Five per cent. aqueous solution of alcohol or of triethanolamine remains practically colorless when placed in contact either with solid dye or with a solution of dye in toluene. Thus the dye does not form a colloidal solution in water containing small percentages of these non-colloidal liquids.

However, the dye is freely soluble in alcohol or triethanolamine alone and if these dye solutions are suddenly diluted with water they form the familiar von Weimarn type of unstable colloidal solution. It is of great importance to note that if these unstable colloidal sols are exposed to a toluene layer in the usual manner, all of the dye enters the toluene and leaves the water colorless, definitely proving their lack of stability.

In Table II is given the total amount of dye which 1 and 5% aqueous solutions will dissolve reversibly; that is, the true saturation value which may be obtained by contact with excess of dye or by releasing supersaturation by deposition of dye or by contact with a saturated solution in another solvent.

When Nujol (medicinal paraffin) is shaken with solutions of trisodium phosphate or of sodium silicate, some emulsification appears to occur in both phases. There is no spontaneous emulsification without shaking. Phenol, containing 5% lauric acid and 95% phenol, is only partially miscible with aqueous 0.02 N sodium hydroxide, but is miscible with 0.1 N potassium hydroxide.

Discussion

Most of these detergents carry into aqueous solution an appreciable fraction of their own weight of dye, the proportion increasing with dilution of detergent. Elsewhere[2] we have shown that lauric acid dissolved in Nujol temporarily carries into aqueous alkali 1.9 parts by weight of Nujol, but that much of this Nujol finally collected as emulsified droplets, in contrast to the present measurements which deal strictly with true reversible permanent equilibrium. It is interesting that Gurwitsch found that aqueous solutions of the pure naphthenates which favor aqueous soap type emulsions break water-in-oil emulsions of natural petroleum, but that the aqueous naphthenate is without effect if it has already dissolved mineral oil.[3]

From the general regularity of the results, particularly with regard to concentration for all the detergents studied, it is evident that we have

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[2] McBain, *Proc. Roy. Soc.* (London), **A163**, 182 (1937).

[3] L. Gurwitsch, *Kolloid-Z.*, Ergänzungsband **36**, 197 (1925).

here isolated one, but only one, of the many factors entering into detergent action. There is, for example, here no optimum concentration of detergent, or maxima and minima, such as have been observed with the carbon black method or in the work of Donnan and Potts on emulsification.[4]

What has been measured here is the protective action of the detergent on matter originally presented to it in molecular form. It is concurrently organized into stable colloidal particles. This must be closely related to, but is distinctly different from, the stabilization or formation of a protective coating upon preëxisting particles or pieces of dirt. In the latter case, the size and disposition of the particles is largely determined by fortuitious previous history, whereas here the result is wholly independent thereof. This therefore forms a true measure of the intrinsic protective effect of the stable colloid.

It is instructive to compare and contrast, as in Table III, the dye numbers for the usual unstable unprotected colloidal sol, made by throwing a solution of dye in alcohol into water; the dye number after this has been subsequently stabilized with Turkey red oil, which immediately clarifies the turbid sol; that when the turkey red oil is present from the beginning; and finally that with Turkey red oil alone. In the first three cases ethyl alcohol was used in the proportion of 5 cc. to 95 cc. of water.

TABLE III

STABILITY OF UNSTABLE AND STABILIZED SOLS OF YELLOW AB MEASURED BY DYE NUMBER (100 K)

Usual unprotected hydrosol, 5% alcohol	0
Subsequently stabilized by Turkey red oil	1.46
Stabilizer present throughout	1.44
Stabilizer present, without alcohol	6.09

It is noteworthy from Table III that the presence of the 5% of true solvent, alcohol, militates against the protective action of the Turkey red oil. This is not due to alcohol dissolving in the toluene, since from Goldsmith's[5] measurement of distribution between water and benzene, the alcohol remains almost wholly in the aqueous layer. Nor is it probable that the constitution of the aqueous solution of Turkey red oil can be much altered by this small amount of alcohol, which likewise is too dilute to dissolve an appreciable amount of dye. Rather, the effect must be due to a partial displacement of protective colloid from the particles of dye in a manner somewhat analogous to the interference of similar liquids with the free foaming of soap solutions.

When 5% ethyl ether is used instead of ethyl alcohol, in the presence of the 5% Turkey red oil, the value of 100 K is appreciably less, namely, 0.92, probably on account of the relative insolubility of ether in water. When care is taken to avoid evaporation, the ethereal solution of dye spontaneously emulsifies in the aqueous solution, sending down long myelin streamers in the complete absence of stirring.

The solubility curve of the dye for a detergent solution containing a constant amount of water is proportional to the two-thirds power of the concentration of the detergent between 1 and 5% for all the cases studied. This has the form of a sorption isotherm, but with exponent independent of the nature of the detergent. Undoubtedly, when the concentration of detergent is very great or approaches 100% a much higher proportion of solubility may in some cases be expected, for there the detergent is itself acting as a solvent. However, this is definitely not true of Turkey red oil.

Triethanolamine and Turkey red oil are both good solvents for dye. Nevertheless, on dilution with water, triethanolamine deposits almost all of its dye, whereas the Turkey red oil on similar dilution dissolves much more of the water-insoluble dye. The very striking difference is due to the triethanolamine not being colloidal, but only an ordinary solvent; whereas Turkey red oil in water is an excellent protective colloid. When the true solution of dye in triethanolamine is diluted, the dye is almost quantitatively converted to colloid suspension of the von Weimarn, or unstable, type, which ultimately is converted to a crystalline sediment.

The solubility of dye in Turkey red oil, as shown in Table II, is 1 part of dye to 14 parts of oil; but when diluted to 5% oil and 95% water it dissolves 1 part of dye to 5 parts of oil, and in 1% solution this rises to 1 part of dye to 3 parts of oil; and this ratio rises still farther, according to the formula given, with further dilution.

A third type of solvent might be found intermediate between the triethanolamine type and the excellent protective Turkey red oil type, where an intermediate dilution with water would reduce the solvent power more than the protective power could compensate so that a part of the dye would be fully protected and stabilized and the excess

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[4] Donnan and Potts, *Kolloid-Z.*, **7**, 208–214 (1910).

[5] Goldsmith, *Z. physik. Chem.*, **31**, 242 (1899).

released as unstable suspension. In all cases where the formula given applies, the protective solvent power of a given weight of colloid increases steadily with dilution, as far as this has been followed.

Lawrence has recently published[1] a study of the effect of water soluble substances such as alcohols in wholly or partially preventing the curding of soap solutions. He considers that some complex formation occurs between alcohol and soap, the amount being relatively greatest for anhydrous soap. On account of the very different method of approach and very different solubility relations it is difficult to determine the exact relation between those results and the phenomena here described.

Hartley's extensive discussion[1] in the Symposium touches upon a large number of factors which have to be considered. Like Lawrence, he has omitted reference to the previous publication of McBain and McBain, and his conclusions rest too much upon one particular case and are of doubtful applicability to all the substances which we have here shown to exhibit parallel behavior. It is also difficult to ascribe any definite meaning to the suggestion that the dye forms a liquid solution in the micelle, especially in view of its appearance in the ultramicroscope. There is little, or no, evidence that colloid particles of soap are liquids. We are fully in agreement that the phenomena are not similar to that of an organic liquid miscible with water. For example, Mrs. McBain in measuring the solubility of Yellow AB in mixtures of water and ethyl alcohol in all proportions found results which are very similar to those here described for triethanolamine. That is, the solubility is almost negligible at first up to 30% alcohol where it is still only 0.01%. Only above 50% alcohol does the solubility rise rapidly to substantial amounts to become 2.4% in pure alcohol.

The pioneer work of Pickering and Lester Smith does not serve as a good basis for quantitative interpretation because the experiments do not refer to proved reversible equilibrium, but from the nature of the procedure must in many cases depart very widely therefrom. Lawrence[1] has also commented on Pickering's results and has repeated and extended his observations. For all the materials to which the formula here given applies, the behavior departs markedly from that of Hartley's particular case where the amount of azobenzene per molecule of hexadecane was constant over a wide range of concentration, instead of being proportional to the two-thirds power and therefore much larger than that for the pure solvent. Miss Parsons found, indeed, that *p*-dimethylaminoazobenzene was proportionately five times more soluble than in pure hexadecane.

Opportunity may here be taken in connection with Powney's communication in the Symposium[1] on the penetration of fabrics by detergent solutions to point out that many years ago we observed with a very tightly packed Hele-Shaw streamlined filter that soap solutions passed freely through when the packing was impervious to water under compression. Likewise Meltzer recently has observed in this Laboratory that the rate of ultrafiltration of a long chain sulfonic acid, even where much of the latter is being held back, may be much greater than that of pure water.

Finally, it is evident from Tables I and II that good detergent properties have no necessary connection with electrolytic dissociation or ionization, even the surface tension curves being very similar when suitable non-electrolytes and colloidal electrolytes are compared. Equal protective action likewise may be conferred through cationic or anionic constituents of colloidal electrolytes, or by non-electrolytes.

Summary

Extensive measurements show that water-insoluble dyes dissolve in aqueous detergents in proportion to the two-thirds power of the concentration of the detergent, and in proportion to the two-thirds power of the concentration of dye in a toluene layer in equilibrium with them. This proportionality factor or "dye number" may be regarded as a measure of the true intrinsic protective power of the stable colloid. These true reversible equilibria are wholly independent of previous history, and depend solely upon the total composition of the system.

Unprotected colloidal solutions of the von Weimarn type show their instability by losing the dye to a toluene layer. In the presence of a small percentage of a true solvent, the dye number, and stability, is the same irrespective of whether the original suspension is subsequently stabilized by addition of a protective colloid or whether the protective colloid was present from the first; however, the dye number is noticeably less than when the protective colloid alone is present.

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