[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Cryoscopic Evidence for Micellar Association in Aqueous Solutions of Non-ionic Detergents

BY EMANUEL GONICK[1] AND JAMES W. MCBAIN

A variety of water-soluble soap-like non-electrolytes have become commercially available in the past few years. These compounds are surface active, produce foaming in aqueous solutions, and solubilize otherwise insoluble substances. The present research demonstrates for the first time, by means of cryoscopic evidence, that compounds of this type exhibit colligative properties similar to those of the ionic soaps. The ionic soaps are characterized by a high degree of association into colloidal micelles above a certain concentration, as shown by their abnormally low freezing point depression or vapor pressure lowering, and have been accordingly named "colloidal electrolytes" by J. W. McBain.

Association in solutions of colloidal electrolytes is attributable to the contradictory solubility relations exhibited by the various groups within the molecule. A non-polar hydrocarbon, essentially water insoluble, portion of the molecule is attached to one or more ionic groups whose attraction for the aqueous medium is strong enough to draw the compound into solution but not, except in very dilute solution, sufficient to bring about complete dispersion against the high interfacial tension between hydrocarbon and water.

One would *a priori* expect non-ionic detergents to be similarly constituted in aqueous solution because of their resemblance to typical colloidal electrolytes in their macroscopic properties, on the one hand, and, on the other hand, because of the basic likeness in the molecular constitution of the two classes of compounds.

Of the three compounds investigated here, *viz.*, nonaethylene glycol (mono) laurate, detergent "X," and Triton X-100, the formula of the first only is definitely known. Detergent "X," however, is also known to be a polyethylene oxide with an aromatic hydrocarbon portion attached, and triton X-100 is an alkyl aryl polyethylene oxide. Thus, the condition of polar-nonpolar structure, characteristic of colloidal electrolytes, is fulfilled and micellar association is accordingly to be expected. The average molecular weights were determined by Beckmann freezing points in dry benzene.[2]

Experimental

Materials.—The nonaethylene glycol (mono) laurate was kindly supplied by the Glyco Products Co., and Triton X-100 by Rohm and Haas. The commercial preparations were used after determining, by means of conductivity measurements, that they were free from appreciable amounts of electrolytes. Experiments with colloidal electrolytes have shown that the presence of solubilized water-insoluble impurities (such as would be a possible excess of lauric acid in the nonaethylene glycol laurate) does not affect the colligative properties of detergents.[3,4] Any excess of polyethylene glycol would result in too great a freezing point lowering and would thus tend to mask the evidences of associative tendencies obtained by this method.

Experimental Method.—Freezing point lowerings, except at a few of the higher concentrations, were determined by means of the differential precision method of G. Scatchard,[5] in which the freezing point lowering is measured by means of a multiple junction thermocouple, one leg of which is immersed in a well-stirred mixture of pure ice and conductivity water and the other in a mixture of ice and solution. Measured volumes of solution are withdrawn at suitable intervals and replaced by a like volume of water, thus achieving progressive dilution without the necessity of opening up the apparatus. Concentrations were determined with the Zeiss dipping refractometer in the case of the more concentrated samples and by means of the Zeiss interferometer in the more dilute region. Both instruments were calibrated in advance against solutions of known concentration.

The results are expressed in terms of Bjerrum's osmotic coefficient $g = \theta/1.858 \times m$, *i. e.*, the ratio of the observed to the theoretical freezing point lowering for complete dispersion. Since the depression of the freezing point is determined primarily by the number of solute particles per unit weight of solvent, the osmotic coefficient expresses directly, to a first approximation, the ratio of the true number of solute particles to that obtaining at complete dispersion of the solute and thus gives a measure of the average degree of association into micelles or other aggregates.

X-Ray diffraction photographs were taken by Mr. Sullivan S. Marsden, Jr., and will be described elsewhere.

TABLE I

FREEZING POINT LOWERING, θ, AND OSMOTIC COEFFICIENTS, g, OF AQUEOUS SOLUTIONS OF NONAETHYLENE GLYCOL (MONO) LAURATE

Molal concn.	θ, °C.	g
0.00079	0.00124	0.84
.00132	.00126	.514
.00217	.00168	.417
.00417	.00314	.385
.00930	.00604	.350
.00591	.00397	.362
.00992	.00644	.349
.0159	.0103	.350
.0234	.0151	.347
.0349	.0225	.347
.0525	.0337	.345
.0828	.0530	.342
.1736[a]	.121[a]	.417[a]
.2618[a]	.193[a]	.511[a]
.6572[a]	.688[a]	.563[a]

[a] By Beckmann method; all others by Scatchard method.

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[2] *Cf.* E. Gonick, *J. Colloid Sci.*, **1**, 393 (1946).

(3) J. W. McBain and A. P. Brady, THIS JOURNAL, **65**, 2072 (1943).

(4) S. A. Johnston and J. W. McBain, *Proc. Roy. Soc.* (London), **A181**, 119 (1942).

(5) G. Scatchard, P. T. Jones and S. S. Prentiss, THIS JOURNAL, **54**, 2676 (1932).

TABLE II

FREEZING POINT LOWERING, θ, AND OSMOTIC COEFFICIENTS, *g*, OF AQUEOUS SOLUTIONS OF DETERGENT "X"

Molal concn.	θ, °C.	*g*
0.00126	0.00169	0.722
.00155	.00177	.614
.00245	.00207	.455
.00350	.00256	.394
.00366	.00265	.389
.00510	.00330	.348
.00556	.00339	.328
.00799	.00415	.279
.00855	.00429	.270
.0123	.00613	.268
.0187	.0160	.234
.0270	.0113	.226
.0331	.0134	.218
.0399	.0161	.216
.03858[a]	.043[a]	.261[a]
.1911[a]	.076[a]	.214[a]
.2838[a]	.121[a]	.229[a]
.3767[a]	.196[a]	.280[a]

[a] By Beckmann method; all others by Scatchard method.

TABLE III

FREEZING POINT LOWERING, θ, AND OSMOTIC COEFFICIENTS, *g*, OF AQUEOUS SOLUTIONS OF TRITON X-100

Molal concn.	θ, °C.	*g*
0.000966	0.00174	0.969
.00194	.00196	.544
.00287	.00207	.389
.00410	.00256	.336
.00593	.00295	.268
.00900	.00327	.196
.0274	.00875	.172
.0396	.0117	.159
.0569	.0158	.149
.0979[a]	.032[a]	.176[a]
.261[a]	.091[a]	.188[a]
.371[a]	.128[a]	.186[a]

[a] By Beckmann method; all others by Scatchard method.

Experimental Results and Discussion

The experimental results are summarized in Tables I, II and III and in Fig. 1.

The curves for all three compounds bear a striking similarity to the corresponding ones for colloidal electrolytes.[6] At extremely low concentrations the solute is molecularly dispersed. At a "critical concentration," whose value is approximately 0.00063 *m* for nonaethylene glycol (mono) laurate and 0.0009 *m* for "X" and Triton X-100, a rapid transition to colloidal micelles sets in, as reflected by the abrupt drop in the osmotic coefficient from a value near unity to a fraction of this as the concentration increases. In each case the osmotic coefficient passes through a flat minimum and then rises more or less at higher concentrations, just as is the case with colloidal electrolytes.[4,7]

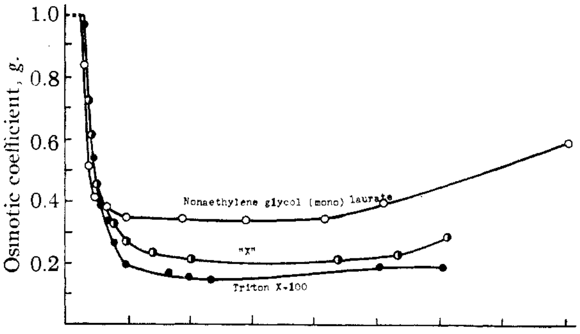

Fig. 1.

Effect of Addition of Salt on Freezing Point Lowering.—The addition of a strong electrolyte is without appreciable effect on the degree of association, as shown by the following data for an experiment in which the freezing points of two solutions, both of which were 0.1798 molal in nonaethylene glycol (mono) laurate, and one of which contained in addition 0.0938 molal potassium chloride, were measured by the Beckmann method:

Theoretical freezing point lowering for 0.0938 *m* potassium chloride	0.324°
Observed lowering for 0.1798 *m* laurate, alone	.135
∴ Expected lowering of laurate plus potassium chloride assuming additivity	.459
Observed lowering for laurate plus potassium chloride	.468
Difference	+ .009

The difference between the expected freezing point lowering for the combined solutes, assuming the separate lowerings to be additive, and the observed value—less than 2%—is without significance since values obtained by the Beckmann method are typically 2–3% high.

X-Ray Diffraction Patterns.—It is not the purpose of this paper to present the results of X-ray diffraction experiments except to state that distinct lines and halos corresponding to first and second order long spacings of the order of 65–75 Å. were obtained at high concentrations, and that the length of these spacings increases with dilution. In the latter respect the micelles behave like those formed in solutions of colloidal electrolytes, and they are probably similar in structure.

Solubilization.—Exploratory experiments made in this Laboratory several years ago[8] and again more recently[9] showed that non-ionic deter-

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(6) J. W. McBain, "Colloidal Electrolytes, Wetting Agents and Detergents," in Vol. 7, "Frontiers in Chemistry; The Organization of Crystals and Micelles of Soap; Solubilization and Detergency." in Vol. 8, "Frontiers in Chemistry," Interscience Publishers Inc., New York, N. Y. (in press).

(7) J. W. McBain and O. E. A. Bolduan, *J. Phys. Chem.*, **47**, 98 (1943).

(8) J. W. McBain, R. C. Merrill, Jr., and J. R. Vinograd, THIS JOURNAL, **63**, 670 (1941).

(9) J. W. McBain and A. A. Green, *J. Phys. Chem.*, communicated.

gents solubilize dyes. The results of these investigations afford additional confirming evidence for the presence of colloidal micelles in aqueous solutions of non-ionic detergents.

Conclusion

The evidence presented here shows that nonionizing detergents, like their electrolytic counterparts, are characterized by micelle formation, a "critical concentration" for the formation of micelles, expansion of the micelle structure with dilution, and a comparable power of solubilization. The phenomena are uncomplicated by ionization effects and are therefore peculiarly well adapted for the study of association in solution. More detailed investigation of this class of compounds may well throw additional light on the problems of colloidal electrolytes.

Summary

1. Measurements of freezing point lowerings of aqueous solutions of three non-ionic detergents of the polyethylene oxide–hydrocarbon type show that these compounds form colloidal micelles similar to those formed by colloidal electrolytes except for the absence of ionization.

2. The addition of potassium chloride to a solution of nonaethylene glycol (mono) laurate caused no significant change in the degree of association of the detergent.

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Anomalous Densities of 1-*n*-Alkyl-cyclohexanols

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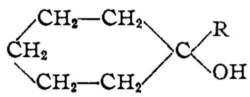
In an earlier paper[2] a remarkable abnormality was shown to exist in the series of 1-*n*-alkyl-cyclopentanols. When the densities of the alcohols were plotted against the numbers of carbon atoms in the normal alkyl groups, a sharp change in the slope of the curve occurred at the seventh carbon atom. The density curve for the *n*-alkyl-cyclopentanes showed a similar abrupt change in slope, but in the opposite direction, at the same point in the series.

The purpose of the present work was to investigate the 1-*n*-alkyl-cyclohexanols in order to determine whether or not an analogous phenomenon occurred in this series, in which an unstrained and less rigid ring was present. One of three possible results was expected: (1) an unbroken density curve, indicating dependence of the phenomenon on a strained ring; (2) a break at the eighth or ninth carbon atom, pointing to the relative masses of the cyclic and noncyclic radicals as the sole or the major factors; or (3) a break at some other point, indicating that the phenomenon is of a general nature, but requiring a less simple explanation than either (1) or (2).

To achieve this end, six compounds of the general type:



were prepared; those in which "R" contained 2, 4, 6, 7, 8 and 12 carbon atoms, respectively. Phenyl urethans were prepared from all six. With the exception of the first two alcohols and the urethan of the first one,[3] these were all new compounds. Tables I and II contain data pertaining to the alcohols, and to their urethans, respectively.

TABLE I

PROPERTIES OF 1-*n*-ALKYL-CYCLOHEXANOLS

Alkyl	B. p., °C., at various *p* in mm. 760	400	100	20	12—1		d^0_4	d^{25}_4	$n^{25}D$	Analyses,[a] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
C_2H_5[b]	166.5	147.0	115.5	77.0	51.2 (5)	60.2 (10)	0.9444	0.9227	1.4621	...	...	...	...
C_4H_9[c]	208.0	186.5[d]	142.0[d]	107.5	89.5 (10)		.9248	.9140	1.4636	76.86	76.76	12.90	12.85
C_6H_{13}	...	218.0[e]	172.4[e]	119.6	107.0 (7)	112.0 (11)	.9152	.8980	1.4650	78.19	78.03	13.13	13.20
C_7H_{15}	...	....	....	131.8	103.5 (1)	117.5 (11)	.8945	.8738	1.4625	78.72	78.72	13.21	13.63
C_8H_{17}	...	....	....	...	109.5 (2)	129.0 (10)	.8848	.8631	1.4611	79.17	79.26	13.29	13.65
$C_{12}H_{25}$	...	....	....	...		[f]	.8691	.8451	1.4585	80.54	80.57	13.52	14.22

[a] Analyses are the averages of duplicate determinations. [b] B. p. 76° (20 mm.), 166° (760 mm.) Sabatier and Mailhe (ref. 3). [c] B. p. 88–91° (7 mm.) Signaigo and Cramer (ref. 3). [d] Interpolated values. [e] With slight decomposition. [f] Pronounced decomposition when distilled at 1 mm.

In Fig. 1, the densities of the 1-*n*-alkyl-cyclo hexanols are plotted against the numbers of carbon atoms in the *n*-alkyl groups. For comparison, the corresponding curves for the *n*-alkyl

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[1] Taken from M. S. Thesis of H. B. Williams, Louisiana State University, May, 1943.

[2] McLellan and Edwards, THIS JOURNAL, **66**, 409 (1944).

[3] P. Sabatier and A. Mahile, *Compt. rend.*, **139**, 343–346 (1904); Signaigo and P. Cramer, THIS JOURNAL, **55**, 3326–3332 (1933).