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 non-ionizing 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.

Stanford University, Calif.

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[Contribution from the Coates Laboratories of Louisiana State University]

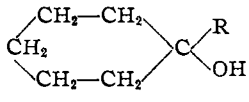
Anomalous Densities of 1-*n*-Alkyl-cyclohexanols

By H. B. Williams[1] and W. R. Edwards, Jr.

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 non-cyclic 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).

TABLE II

PHENYL URETHANS OF 1-*n*-ALKYL-CYCLOHEXANOLS

Alkyl	M. p., °C.[a]	% N[b] Calcd.	% N[b] Found
C_2H_5[c]	82.5	..	..
C_4H_9	110.0	5.09	5.08
C_6H_{13}	84.5	4.62	4.54
C_7H_{15}	75.5	4.42	4.30
C_8H_{17}	76.5	4.23	4.22
$C_{12}H_{25}$	73.5	3.61	3.64

[a] Melting points listed are mean values of melting range of 1° or less. [b] Analyses are averages of duplicate determinations. [c] M. p. 83°, Sabatier and Mailhe (ref. 3).

cyclohexanes,[4] the 1-*n*-alkyl-cyclopentanols[2] and the *n*-alkyl-cyclopentanes[2] are included. Definite breaks at the hexyl occur in the curves derived from the alkyl-cyclohexanols and the alkyl-cyclohexanes. These curves are similar in general form to those derived from the analogous cyclopentyl compounds, but the density curves for the latter break at the heptyl.

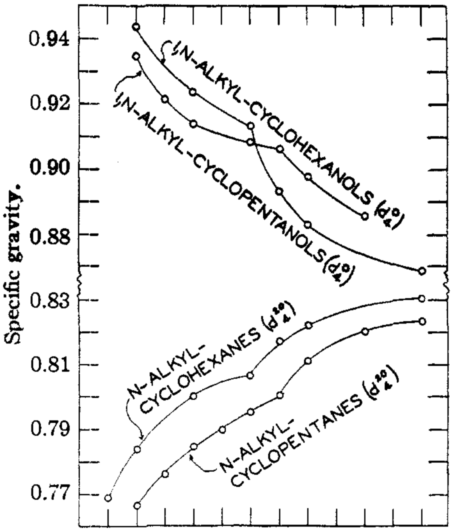

Fig. 1.

These results show that the phenomenon is not the exclusive attribute of five-membered ring systems, or of strained ring systems. McLellan and Edwards' tentative explanation of their observations in the cyclopentyl series assumed a shift in dominance, from ring to alkyl group, at the point at which the break occurs the dominant group being defined as the one which in any way constitutes the major obstacle to closer packing of the molecules. It is now evident that such dominance is not determined solely by the masses of the respective groups; since in that case the break in the cyclopentyl series should have come at the pentyl or the hexyl point, and that in the cyclohexyl series at a later point. More specifically, it appears that the cyclopentyl group possesses greater dominating power than the heavier cyclohexyl one. This might be ascribed to the rigidity of a 5-carbon ring, incapable of much adaptability in packing, as contrasted to the relative elasticity and adaptability of aliphatic 6-carbon rings and normal chains.

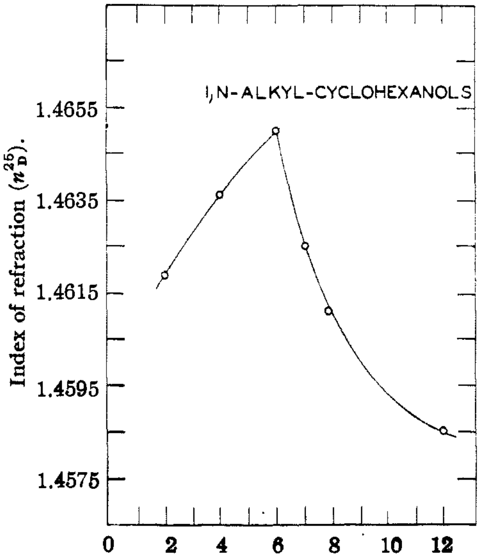

Fig. 2.

An alternative explanation may be suggested, however. The configuration conducive to maximum compactness in the packing of molecules such as are under consideration here appears to be one in which the alkyl chains arrange themselves in slowly-ascending spirals, as nearly parallel as possible to the planes occupied by the cyclopentyl rings, or approximately congruent to larger rings. As long as such an arrangement is possible, the configuration of the entire molecule, and hence its density, should conform to the pattern set by the ring. When the chain attains a length requiring marked divergence from this configuration, a corresponding marked change in density increments should result. In the cyclopentyl series, the first complete circuit of such a hypothetical spiral might be achieved at or near the seventh carbon atom of the chain. At this point, to avoid steric hindrance, it might be necessary for the spiral to rise more steeply, or to give place to some other configuration. In the cyclohexyl series, the three-dimensional character of the ring (particularly in the "boat" form) might cause such hindrance to develop before the spiral had achieved a complete circuit, quite possibly at the sixth carbon atom of the chain.

The data available at this time do not exclude other possible interpretations. Measurements of other properties (such as dipole moments, vis-

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(4) M. P. Doss, "Physical Constants of the Principal Hydrocarbons," Technical and Research Division of The Texas Company, New York, N. Y., 1942.

cosities, thicknesses of unimolecular films and surface pressures) and studies of other series, including appropriate non-cyclic ones, may be of assistance in developing an authentic explanation of the abnormality. Further investigation is contemplated.

In Fig. 2, refractive indices of the 1-*n*-alkylcyclohexanols are plotted against numbers of carbon atoms in the alkyl groups; here, also, there is an abrupt break at the hexyl. Where the densities of the members of an homologous series drop suddenly, other factors remaining constant, the rate of change of index of refraction with respect to increase in the number of carbon atoms should decrease. A curve of this sort, therefore, was to be expected.

Experimental

1-*n*-Alkyl-cyclohexanols.—These compounds were prepared from cyclohexanone and the appropriate alkyl bromides by the method of Zelinski and Gutt.[5] The ethyl, butyl, hexyl and octyl compounds were purified by repeated fractional distillation at pressures ranging from 760 to 0.2 mm.

It was impractical to purify the 1-*n*-heptylcyclohexanol adequately in this manner, because at no pressure at which distillation was possible without marked decomposition was there more than two degrees difference between its boiling point and that of *n*-tetradecane formed in the original synthesis. The crude product was distilled, therefore, and a fraction collected at 116–118° (11 mm.) was dissolved in twice its volume of 95% ethyl alcohol and cooled to −30°. At this temperature white plates of *n*-tetradecane precipitated. The supernatant liquid was removed by suction through a fritted glass crucible. The chilling and separation were repeated five times, until no more solid tetradecane separated. The ethyl alcohol was then distilled off under reduced pressure, and the remaining liquid containing the 1-*n*-heptylcyclohexanol redistilled.

The dodecyl member of the series could not be purified by fractional distillation, because of the ease with which it underwent dehydration when heated. Its ethereal solution was shaken several times with saturated sodium bisulfite solution, and then washed repeatedly with warm water. The ether was removed by evaporation and the crude tertiary alcohol purified by selective solvent action, employing, first, 95% ethyl alcohol at −25°, and, second, an ethyl alcohol–water mixture at room temperature, each step being repeated several times. The ethyl alcohol and water were distilled off under reduced pressure at a temperature of 50°, and the residual 1-*n*-dodecylcyclohexanol was desiccated at 5 mm. for forty-eight hours.

All members of this series were colorless liquids with camphor-like odors. Some, if not all, were supercooled liquids at room temperature. Yields varied from 41 to 72% with the exception of the octyl member, which suffered relatively large loss during purification.

1-*n*-Alkylcyclohexylphenyl Urethans.—Avoidance of elevated temperatures reduced dehydration of these tertiary alcohols sufficiently to permit satisfactory formation of their urethans. In a typical instance, the alcohol (0.01 mole) and phenyl isocyanate (0.02 mole) were placed in a tightly-stoppered 25-ml. flask, kept at room temperature for two days, and then placed in an ice-bath, where, after approximately twenty-four hours, the entire solution solidified, forming a crystalline mass. This was extracted with warm, high-boiling petroleum ether, the extract filtered with suction, and the greater part of the petroleum ether evaporated. The alkyl-cyclohexylphenyl urethan precipitated, forming snowy-white crystals. These were recrystallized from the same solvent, and dried in a vacuum desiccator.

Determination of Boiling Points.—Boiling points were determined by distillation of the purified compounds. Thermal dehydration prevented such determinations over a complete range of pressures with members of the series higher than butyl.

Summary

1. The 1-*n*-alkylcyclohexanols have been characterized as a series through preparation and study of four new members, together with additional characterization of two members previously reported. New phenyl urethans have been prepared from five of these.

2. Densities and refractive indices of these alcohols have been plotted; the former have been compared graphically to densities of other related series; and the peculiar forms of these graphs have been discussed.

BATON ROUGE, LA. RECEIVED JULY 15, 1946

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[5] Zelinski and Gutt, *Ber.*, **34**, 3950–3952 (1901).

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

The Kinetics of the Alkaline Dehydrochlorination of the Benzene Hexachloride Isomers. The Mechanism of Second-Order Elimination Reactions[1,2]

BY STANLEY J. CRISTOL[2a]

The existence of the four known geometric isomers of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) was first demonstrated by the work of van der Linden.[3] The group working in the laboratories of the Imperial Chemical Industries under Slade[4] has recently confirmed the findings of van der Linden and has reported various physical and chemical properties of the several isomers. Interest in the compounds arises from the fact that the *gamma* isomer of benzene hexachloride is a very effective insecticide.[4]

The problem of the structure of the various isomers of benzene hexachloride is similar to that

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[1] The work described in this paper was part of a program conducted under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

[2] This paper was presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 8–12, 1946.

[2a] Present address: Department of Chemistry, University of Colorado.

[3] van der Linden, *Ber.*, **45**, 236 (1912).

[4] Slade, *Chem. Ind.*, 314 (1945).