fat are symmetrical. Polymorphic data for the one synthetic and two natural oleyldipalmitins here reported are extremely similar except for rate of transformation of beta prime-2 to beta-3 as illustrated in Table V.

Table V

Formation of Beta-3 in POP

Treatment	Synthetic POP	Stillingia tallow POP	Piquia fat POP
Melt, chill, 2–3 weeks 32°	β-3	β'-2	β'-2 and β-3
Melt, chill, 1 day each 27, 32, 35°	β-3	β'-2	Mainly β-3
Solvent crystallized from acetone	β-3	β-3	β-3

This suggests that the POP from piquia fat was more nearly pure than that from stillingia tallow. In this connection, it might be added that beta prime-2, as in the case of other glyceride forms, has been observed to increase in m. p. on storage. This was particularly evident for the form from stillingia tallow which remained beta prime on 32° storage although its m. p. rose above 35°.

Since the only identified oleyldistearins of nature are symmetrical, as are the present oleyldipalmitins, it would be of considerable interest to establish how general is the occurrence of symmetrical disaturated glycerides in nature.

Summary

The polymorphism of synthetic 2-oleyldipalmitin (POP) has been studied by X-ray and thermal means and compared with that of oleyldipalmitin from two natural sources, namely, stillingia tallow and piquia fat. Results confirmed the conclusions of previous workers, based on thermal examination, that these two natural oleyldipalmitins are symmetrical.

The following forms were obtained for POP: alpha-2 (m. p. 18.1°), sub beta prime-2 (26.5°), beta prime-2 (33.5°), and beta-3 (38.3°). These results differ in important details from both thermal and X-ray evidence of others. Much of the difficulty involves the question of the existence of so-called vitreous forms of fats, unconfirmed in this Laboratory for POP or any other glyceride.

In contrast to the implications of earlier workers, POP was found to show a number of characteristic differences from 2-oleyldistearin which has shown, on crystallization from the melt, alpha-3, sub beta-3 (formerly called X-3) and beta-3 forms.

Cincinnati 17, Ohio Received September 29, 1949

[Contribution from the Research Laboratory of Armour and Company]

The Solubilities of Dodecylammonium Chloride and its N-Methyl Derivatives in *n*-Hexane, Benzene and 95.0% Ethanol[1]

By F. K. Broome and H. J. Harwood

A recent paper[2] has reported the conductivities of aqueous solutions of dodecylammonium chloride and its N-methyl derivatives. The present paper extends the study of this group of salts to their solubilities in one polar and two non-polar organic solvents. Earlier studies from this Laboratory[3,4] have considered the solubilities of the primary salt in two of these solvents, but the present work has extended the range of concentrations somewhat, and has uncovered new information on the polymorphic behavior of this salt.

Experimental

Preparation of Materials.—The preparations of the dodecylammonium chloride[5] and the methyl and dimethyl derivatives[2] used herein have been described. Trimethyldodecylammonium chloride, prepared as previously described,[6] was further dried over phosphorus pentoxide *in vacuo*. Because of its hygroscopicity, this compound was handled in a desiccated box equipped with a window and sealed-in rubber gloves.

The *n*-hexane used was Phillips Technical *n*-hexane purified by treatment with sulfuric acid, fractionation in a Stedman-packed column, and drying with sodium wire. Thiophene-free benzene was dried over sodium. Commercial absolute ethanol was diluted to 95.0% by weight with conductivity water. Its content of ethanol was checked with a pycnometer.

Procedures.—The procedures are essentially those described elsewhere.[3,7,8] Weighed portions of salt and solvent were sealed in small glass tubes, dissolved by heating, thoroughly mixed, and then cooled below the crystallization point. Solution temperatures were observed during slow heating of these samples, rotated in a regulated water- or oil-bath. Temperatures up to 100° were estimated to 0.01° on a thermometer checked against a similar thermometer calibrated by the National Bureau of Standards, and were reproducible within a few hundredths of a degree. Temperatures above 100° were measured to 0.1° with an iron–constantan differential thermocouple calibrated against a certified platinum resistance thermometer, and were reproducible within less than 0.1°.

Where polymorphic forms were detected, the lower liquidus was obtained by cooling a homogeneous sample below the higher liquidus, chilling the tip of the tube with Dry Ice to induce crystallization, and immediately plunging the tube back into the regulated bath. Repeated trials at slightly varying temperatures sufficed to establish

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[2] Ralston, Broome and Harwood, This Journal, **71**, 671 (1949).

[3] Hoerr and Ralston, *ibid.*, **64**, 2824 (1942).

[4] Sedgwick, Hoerr and Ralston, *J. Org. Chem.*, **10**, 498 (1945).

[5] Ralston and Eggenberger, This Journal, **70**, 436 (1948).

[6] Reck, Harwood and Ralston, *J. Org. Chem.*, **12**, 517 (1947).

[7] Ralston, Hoffman, Hoerr and Selby, This Journal, **63**, 1598 (1941).

[8] Harwood, Ralston and Selby, *ibid.*, **63**, 1916 (1941).

the solution temperatures of the unstable forms, defined as the temperatures at which the Dry Ice-seeded crystals just returned to solution. In most cases, the unstable form converted rapidly to the stable form at any temperature below the lower liquidus. However, in the dodecylammonium chloride systems a progressive increase in the stability of the lower form with increasing concentration rendered the obtainment of the higher form difficult. This was particularly true in benzene. To effect the transition, it was necessary in some cases to hold partially solid samples for three days at a temperature about one degree below the lower liquidus. In samples 2% or less below the enantiotropic transition point, crystals of both forms will exist side by side in benzene for considerable periods of time. Upon heating, the more-soluble, amorphous-appearing material dissolves at its liquidus, leaving less-soluble, shiny crystals of the other form, which then dissolve along the higher liquidus. Since the solid salt before mixing with solvent was in the stable crystalline form, some attempts were made to use the temperature of solution during the initial mixing operation as the higher liquidus. However, despite slow heating such temperatures were always slightly high.

Results and Discussion

***n*-Hexane.**—Solubilities in this solvent were not accurately determined, but the following limits may be indicated. Dodecylammonium chloride is soluble at 95° to <0.35%, and dimethyldodecylammonium chloride at the same temperature to <0.07%. It has been reported[6] that trimethyldodecylammonium chloride is soluble to <0.2% at 95°.

Benzene and 95.0% Ethanol.—The solubilities of the four salts in benzene and 95.0% ethanol are presented in Tables I–VII and Figs. 1 and 2. (The single value obtained for trimethyldodecylammonium chloride in benzene is shown in Fig. 1 at 84.05° and 0.06%.) The various breaks in the curves for the several systems are summarized in Table VIII.

TABLE I

SOLUBILITY OF DODECYLAMMONIUM CHLORIDE IN BENZENE

Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable	Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable
0.25	38.45	45.53	17.53	55.63	56.67
.57	41.59	48.08	18.02	55.98	56.79
.93	43.23	49.19	18.67	56.41	57.04
4.93	48.66	52.98	18.83	56.56	57.23
9.91	51.81	54.89	19.51	57.02	...
10.33	52.12	55.05	20.03	57.40	57.41
12.18	53.12	55.31	22.11		59.09
14.92	54.42	56.00	24.97		61.33
15.11	54.44	56.13	29.86		65.16
15.94	54.77	56.26	35.01		69.71
17.05	55.27	56.55	39.93		74.28

TABLE II

SOLUBILITY OF METHYLDODECYLAMMONIUM CHLORIDE IN BENZENE

Wt. % salt	Solution temp., °C.	Wt. % salt	Solution temp., °C.	Wt. % salt	Solution temp., °C.
0.06	20.93	4.65	49.39	12.57	59.50
.10	24.60	6.09	51.09	14.94	62.59
.16	28.37	7.03	52.05	17.43	65.54
.49	35.36	7.55	52.49	20.20	68.60
1.05	39.94	8.03	52.93	25.16	73.80
1.42	41.99	9.02	54.01	29.92	78.33
3.06	46.71	10.06	55.79		

TABLE III

SOLUBILITY OF DIMETHYLDODECYLAMMONIUM CHLORIDE IN BENZENE

Wt. % salt	Solution temp., °C.	Wt. % salt	Solution temp., °C.	Wt. % salt	Solution temp., °C.
0.15	15.05	1.73	57.21	6.20	75.24
0.30	26.97	2.51	62.56	7.61	78.38
0.70	41.84	3.43	66.73	8.69	80.01
1.13	49.40	4.93	71.99		

TABLE IV

SOLUBILITY OF DODECYLAMMONIUM CHLORIDE IN 95.0% ETHANOL

Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable	Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable
7.19	3.73	13.14	63.65	...	59.19
19.84	22.45	30.79	65.77	...	61.94
20.05	22.68	30.81	67.06	...	63.53
30.60	31.29	39.32	69.23	...	66.97
45.70	43.03	48.67	70.83	...	69.43
56.04	51.56	...	72.63	...	73.40
59.35	54.71	56.14	74.46	...	77.79
61.71	57.20	57.46			

TABLE V

SOLUBILITY OF METHYLDODECYLAMMONIUM CHLORIDE IN 95.0% ETHANOL

Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable	Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable
10.13	11.68	11.95	60.71	55.05	55.09
20.05	23.18	23.45	65.10		59.01
30.08	31.75	31.81	68.03		64.53
40.33	39.20	39.50	71.11		72.77
50.54	...	46.78	75.09		84.75

TABLE VI

SOLUBILITY OF DIMETHYLDODECYLAMMONIUM CHLORIDE IN 95.0% ETHANOL

Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable	Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable
30.24	4.72	6.96	62.38	33.32	34.46
34.78	9.17	10.47	66.94	37.54	39.21
39.94	13.51	14.83	71.79		47.44
47.74	19.63	21.04	72.25		48.66
52.28	23.84	24.94	74.88		60.29
53.81	25.38	26.55	75.44		62.77

TABLE VII

SOLUBILITY OF TRIMETHYLDODECYLAMMONIUM CHLORIDE IN 95.0% ETHANOL

Wt. % salt	Solution temp., °C. Unstable	Solution temp., °C. Stable	Wt. % salt	Solution temp., °C. Stable
44.91	6.43	7.00	76.15	59.59
51.90	16.81	17.29	77.34	74.77
60.95	31.47	32.25	78.70	91.34
65.41	39.82	40.13	79.99	107.5
72.42		53.26		

It is of interest to note the pairing of the curves, particularly within the ethanol series. In the conductivity study[2] it was shown that the

TABLE VIII

BREAK POINTS IN THE SOLUBILITY CURVES

Alkylammonium chloride	Benzene		95.0% ethanol	
	Wt. % salt	Temp., °C.	Wt. % salt	Temp., °C.
Dodecyl-	16.4 20.1	54.8 57.4[a]	61.9 70.4	57.5[a] 68.2
Methyldodecyl-	8.7	53.4	66.4	60.2
Dimethyldodecyl-			71.0	44.3
Trimethyldodecyl-			76.2	59.6

[a] Enantiotropic transition point.

greatest difference between successive members of this series occurs between the tertiary and quaternary salts. From this evidence and a consideration of the structural formulas of the four salts, a similar separation of properties might have been expected here. Quaternary ammonium salts are usually considered quite different from other substituted ammonium salts. It appears, however, that the lone hydrogen has less influence than the three alkyl groups on the solubility characteristics of the tertiary salt.

Dodecylammonium chloride exists in two enantiotropic forms whose transition temperature, as given by the intersection of their solubility curves in both figures, is 57.5°. Crystals of this salt were obtained at room temperature from both benzene and 95.0% ethanol. Microscopic observation of these crystals between crossed Nicols during slow heating (*ca.* 0.4°/min.) confirms this transition point. The initial brilliant interference colors begin to change at about 56.5°, and the loss of color is complete by 57.5–58°. Above this point the originally transparent crystals are opaque to unpolarized light and show a black and white pattern between crossed Nicols. No further change occurs up to 101°. Similar observation of the other salts disclosed no changes of form over the temperature ranges of this study. However, the secondary, tertiary and quaternary ammonium chlorides all have two monotropic solubilities in aqueous ethanol over the low portions of the diagram. The two curves for methyldodecylammonium chloride are not separated in Fig. 2, since the one curve drawn is broad enough to cover both sets of points (*cf.* Table V). Perhaps the difficulty in inducing the transition from the unstable form in the primary salt as compared to the other three salts is related to the fact that the former is enantiotropic and the last three are monotropic.

With the exception of the intersection of the curves of dodecylammonium chloride at its transition point, all the breaks shown in both series are consequences of solvent–solute interaction. Crystals of methyldodecylammonium chloride obtained from sample tubes represented by points on the lower portions of the solubility curves in both benzene and ethanol showed no change when heated to 105°. Breaks in the solubility curves therefore cannot be attributed to the existence of solvates. Further study will be required to elucidate the meaning of these breaks or even to decide whether the reason for them is the same in all systems. Attention should be called to the difference in the behavior of dodecylammonium chloride in benzene and aqueous ethanol. In both systems a break occurs only in the curve for the polymorphic form stable above 57.5°. However, in the benzene system this break appears in the unstable region, whereas in the ethanol system it appears in the stable region.

The difficulty in inducing the metastable form of dodecylammonium chloride in benzene to transform to the stable form has been emphasized in a practical way. This salt is customarily purified by crystallization from benzene to which has been added a small amount of ethanol or methanol, since experience has shown that well-defined crystals are not obtained from benzene alone. The presence of a little alcohol induces a

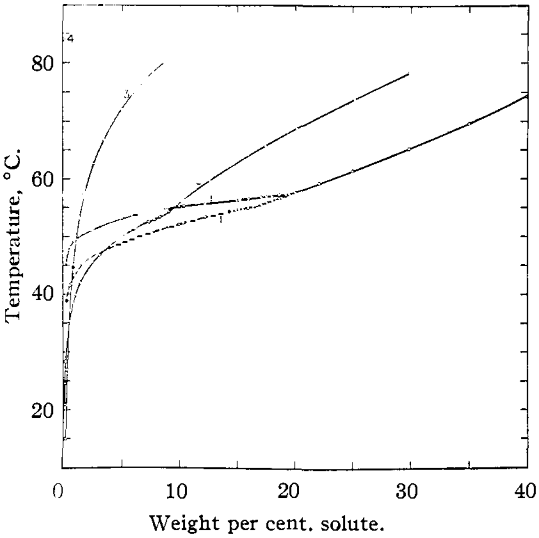

Fig. 1.—Solubilities in benzene: 1, dodecyl-; 2, methyldodecyl-; 3, dimethyldodecyl-; 4, trimethyldodecylammonium chlorides.

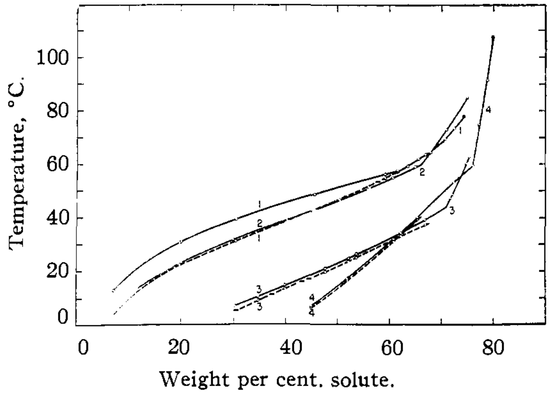

Fig. 2.—Solubilities in 95.0% ethanol: 1, dodecyl-; 2, methyldodecyl-; 3, dimethyldodecyl-; 4, trimethyldodecylammonium chlorides.

rapid transition to the stable form, and the crystals obtained are large and easily filtered.

Summary

1. The solubilities have been determined for dodecyl-, N-methyldodecyl-, N,N-dimethyldodecyl- and N,N,N-trimethyldodecylammonium chlorides in *n*-hexane, benzene and 95.0% ethanol.
2. Dodecylammonium chloride exists in two enantiotropic forms with a transition temperature of 57.5°.
3. The secondary, tertiary and quaternary salts exhibit monotropism in 95.0% ethanol.
4. Breaks due to solvent–solute interaction occur in all solubility curves in 95.0% ethanol and in two of those in benzene. This interaction is not solvation.

CHICAGO 9, ILL. RECEIVED SEPTEMBER 29, 1949

CONTRIBUTION FROM THE COATES LABORATORIES, LOUISIANA STATE UNIVERSITY, AND FROM THE CHEMICAL LABORATORIES OF LOUISIANA POLYTECHNIC INSTITUTE]

The Raman Spectra of the Monodeuterated Toluenes.

BY C. H. SMITH,[1] A. R. CHOPPIN AND O. A. NANCE

This study of the Raman spectra of some deuterated toluenes is a part of the general attack on the spectra and structure of polyatomic molecules. It offered particular interest since the valence-stretching vibration of the deuterium atom in a deuterated toluene should be uncoupled from other fundamental vibrations, because of large frequency differences. Any frequency variations among the deuterium valence-stretching vibrations of the different compounds should be due to variations among the C–D force constants. The force constant was expected to be smaller in toluene-*α*-*d* than in the parent compound and the force constants in the ortho, meta and para positions because of the postulated existence of "formal" charges on the carbon atoms. These formal charges supposedly direct an entering group to the ortho or para positions in toluene. Thus, the spectra of the deuterated toluenes are expected to provide a test of the theory of orientation during substitution in the benzene ring.

Experimental

Preparation of Compounds.—The method used was that previously described by Choppin and Smith.[2] No ordinary toluene could be detected in the ultraviolet absorption spectrum of the vapor of toluene-3-*d*. The toluene-2-*d* and toluene-4-*d* showed about 4–5% ordinary toluene. None of the Raman lines of ordinary toluene were detected in the Raman spectra of the deuterated toluenes.

Spectroscopic Procedure.—The Raman spectra of the liquids were determined using a Bausch and Lomb Large Littrow Spectrograph, a ring of six General Electric Type H-11 mercury vapor lamps, and Eastman Type I-B Spectrographic Plates. The spectrograph was equipped with a glass prism which gave a dispersion of 34.5 cm.$^{-1}$ per millimeter in the center of the region studied. Exposure times of two days to one week were necessary because of the relatively small aperture of the instrument. The spectrograph was placed in an air-conditioned room held at constant temperature. Wave numbers were determined by interpolation between the wave numbers of the lines of the iron arc. Intensities were determined by means of a Leeds and Northrup Recording Photoelectric Microphotometer. The intensities are given an arbitrary scale for each compound with the strongest Raman line assigned a relative intensity of 10. They represent relative transmittance, not integrated intensities. Nearly all of the lines were measured as shifts from both the 4047 and the 4358 Å. mercury lines. The experimental arrangement did not yield sufficiently dense spectra to allow the measurement of position of lines having an intensity less than 0.5 or permit polarization measurements to be made.

Experimental Results.—The observed Raman shifts and their intensities are given in Table I. They should be compared with the Raman spectrum of toluene,[3,4,5] the ultraviolet spectra of the deuterated toluenes[2] and the infrared spectra.[6]

TABLE I

OBSERVED RAMAN SHIFTS AND INTENSITIES

Toluene-*α*-*d*	Toluene-2-*d*	Toluene-3-*d*	Toluene-4-*d*
211(2)[a]	211(2)	211(2)	208(1)
			338($^1/_2$)
			453($^1/_2$)
513(2)	515(2)	520(3)	517(3)
623(1)	619(2)	618(2)	616(2)
774(4)	785(6)	764(3)	784(5)
	867(1)	878(2)	
1003(10)	988(10)	1005(10)	987(10)
1026(3)	1031(1)		1028(1)
	1044(2)	1049(2)	
			1178(1)
1200(1)	1205(2)	1209(3)	1209(2)
	1379(1)	1377(1)	1379(1)
			1470($^1/_2$)
1605(1)[a]	1600(3)	1606(3)	1601(2)
	2261(2)	2271(2)	2266(1)
			2288($^1/_2$)
2925(3)	2918(3)	2922(4)	2922(2)
3052(6)	3051(6)	3056(5)	3054(6)

[a] Frequencies somewhat in doubt because of diffuse or weak images.

Discussion of Results.—The deuterium valence-stretching frequencies were observed in the

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[1] American Chemical Society Post-doctoral Research Fellow at Louisiana State University during most of this work.

[2] Choppin and Smith, THIS JOURNAL, **70**, 577 (1948).

[3] Howlett, *Can. J. Research*, **5**, 572 (1931).

[4] Kohlrausch and Wittek, *Monatsh.*, **74**, 1 (1941).

[5] Cleveland, *J. Chem. Phys.*, **13**, 101 (1945).

[6] The infrared spectra of the deuterated toluenes have been determined by Nance. The results have not yet been published.