

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.

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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 toluenes² and the infrared spectra.⁶

TABLE I

OBSERVED RAMAN SHIFTS AND INTENSITIES			
Toluene- α - <i>d</i>	Toluene-2- <i>d</i>	Toluene-3- <i>d</i>	Toluene-4- <i>d</i>
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) 867(1)	764(3) 878(2)	784(5)
1003(10)	988(10)	1005(10)	987(10)
1026(3)	1031(1) 1044(2)	1049(2)	1028(1)
1200(1)	1205(2) 1379(1)	1209(3) 1377(1)	1178(1) 1209(2) 1379(1) 1470(1/2)
1605(1) ^a	1600(3) 2261(2)	1606(3) 2271(2)	1601(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

(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.

(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).

ring deuterated toluenes in the 2260 to 2288 cm^{-1} region. There should be only one fundamental frequency in this region, but two lines are observed in toluene-4-*d*. It is postulated that this doubling is due to Fermi resonance of the deuterium valence-stretching vibration with the combination $1493 + 784 = 2277 \text{ cm}^{-1}$. Since the 2266 cm^{-1} line appears with greater intensity than the 2288 cm^{-1} line, the 2266 cm^{-1} line must retain a greater resemblance to the deuterium valence-stretching frequency. The deuterium frequency must be Class A_1 ; thus, the 1493 cm^{-1} line must belong to Class A_1 also, if this postulate is correct. Presumably, resonance would not take place in the case of toluene-2-*d* or that of toluene-3-*d* since the deuterium vibration would belong to a symmetry class different from that of the combination. The 1493 cm^{-1} line and corresponding lines in the other deuterated toluenes have been observed by Nance⁶ in the infrared.

The measured frequencies show that the deuterium atom is held more tightly in the meta

position than it is in the ortho position; the possibility of Fermi resonance leaves the condition of the para position in doubt.

A Raman spectrograph is currently under construction for use in the extension of this investigation to benzyl chloride, benzal chloride and benzotrichloride. The infrared spectra of these compounds are being measured.

Summary

The Raman spectra of the deuterated toluenes have been measured and compared with the infrared spectra. Examination of the frequencies in the region of the C-D stretching frequencies indicates that doubling in the spectrum of toluene-4-*d* is due to Fermi resonance with the combination $1493 + 784$. This implies that the 1493 cm^{-1} band belongs to symmetry class A_1 .

The C-D stretching frequencies also indicate that the C-H force constant in the meta position is larger than the corresponding constant for the ortho position.

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Diffusion of Sucrose in Supersaturated Solutions

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Introduction

As far as we are aware there have never been any successful measurements of diffusion coefficients in supersaturated solutions although Van Hook and Russell,² realizing the importance of diffusion data in the supersaturated range for the interpretation of the kinetics of crystallization, attempted to measure diffusion coefficients of sucrose in supersaturated solutions using the Northrop³-McBain⁴ porous disk technique, but "only irregular and unreliable results were realized"—probably due to crystallization induced by sharp edges or irregularities in the porous disk. It occurred to us that the Foucault-Toepler schlieren⁵ method of observing refractive index and hence concentration gradients could be profitably applied to diffusion measurements in the supersaturated region just as it had been in the region of dilute solutions by a number of investigators.⁶

During the preliminary stages of the investiga-

tion⁷ a new optical method for the determination of diffusion coefficients was developed in this country by Longworth,⁸ and Kegeles and Gosting⁹ and in Great Britain by Coulson, Cox, Ogston and Philpot.¹⁰ In the present research we have tried both methods as described below. We have also developed a diffusion cell particularly suitable for the highly viscous solutions with which we have had to deal.

Experimental

Part A: The Schlieren Method.—The optical components of the Longworth-Tiselius electrophoresis apparatus were purchased from the Klett Manufacturing Company and were used as received after installation of a lens of the correct focal length in the camera.

Our first diffusion cell was a modified Neurath⁸ type, but one with which we experienced the following difficulties: leakage troubles, due to areas of short distance between the diffusion channel and the water-bath, crystallization difficulties arising from impurities, grease, etc., which squeezed out the glass-metal contact zone into the diffusion channel, and the production of swirls and eddies in

(1) Department of Chemistry, University of Kentucky, Lexington, Kentucky.

(2) A. Van Hook and H. D. Russell, *THIS JOURNAL*, **67**, 370 (1945).

(3) J. H. Northrop and M. L. J. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(4) J. W. McBain and T. H. Liu, *THIS JOURNAL*, **53**, 59 (1931).

(5) The technique of this method is extensively discussed by L. G. Longworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

(6) See the review by H. Neurath, *Chem. Rev.*, **30**, 357 (1942).

(7) This research was started by J. J. Josephs during the academic year 1945-1946, but for reasons beyond our control, it was not resumed until the fall of 1947 by A. C. English. We wish to acknowledge the aid of Dr. Josephs in the early stage of development.

(8) L. G. Longworth, *THIS JOURNAL*, **69**, 2510 (1947).

(9) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947); L. J. Gosting, E. M. Hanson, G. Kegeles and Margaret S. Morris, *Rev. Sci. Instrument*, **20**, 209 (1949); L. J. Gosting and M. S. Morris, *THIS JOURNAL*, **71**, 1998 (1949).

(10) C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc.*, **A192**, 382 (1948).