



Water solubilities of tetradecanol and hexadecanol by gas-liquid chromatography
by Clark Samuel Hoffman

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

The water solubilities of 1-tetradecanol and 1-hexadecanol were measured by gas-liquid chromatography at several temperatures in the 4 to 61°C. range. The magnitudes involved are illustrated by the 61°C. values: 44.9×10^{-6} and 4.06×10^{-6} gram per 100 ml. for 1-tetradecanol and 1-hexadecanol, respectively. The experimentally determined solubilities at 25°C. were found to be appreciably smaller than the values obtained by extrapolating data for the lower homologs. Estimates of heats of solution above and below the melting point were made for each alcohol. They indicate that the amount of water in an alcohol rich phase at equilibrium with a water rich phase is not negligible.

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BY GAS-LIQUID CHROMATOGRAPHY

by

CLARK SAMUEL HOFFMAN, JR.

A thesis submitted to the Graduate Faculty in partial
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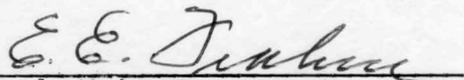
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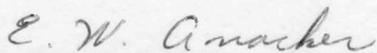
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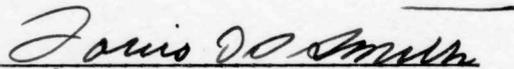
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ABSTRACT

The water solubilities of 1-tetradecanol and 1-hexadecanol were measured by gas-liquid chromatography at several temperatures in the 4 to 61°C. range. The magnitudes involved are illustrated by the 61°C. values: 44.9×10^{-6} and 4.06×10^{-6} gram per 100 ml. for 1-tetradecanol and 1-hexadecanol, respectively. The experimentally determined solubilities at 25°C. were found to be appreciably smaller than the values obtained by extrapolating data for the lower homologs. Estimates of heats of solution above and below the melting point were made for each alcohol. They indicate that the amount of water in an alcohol rich phase at equilibrium with a water rich phase is not negligible.

INTRODUCTION

One-sixth of the available water supply in the Great and Colorado River Basins is lost annually through evaporation (1). The water stored in a large reservoir is especially susceptible to this fate. The loss can be minimized by locating the reservoir at as high an elevation as is feasible, shaping it so as to make the surface area to storage volume ratio as small as is practicable, covering the surface with an impervious barrier, and shielding it with windbreaks (2). Because considerations of cost, convenience, and the need for recreational area often rule out these measures, we are forced to search for practical alternatives. One possibility involves the spreading of a chemical film on the water surface (3). At present monomolecular layers of the long-chain primary alcohols tetradecanol through eicosanol are being intensively investigated for this purpose (4,5).

Before any chemical can be seriously considered for use as an evaporation retardant in a public water supply, it must be shown to have little or no deleterious biological effects. The United States Public Health Service has checked the human health aspects and has approved the use of hexadecanol and octadecanol monolayers for evaporation control (6). The results of several studies (7,8,9) indicate that long-chain alcohols do not pose serious problems for plankton, most insects, aquatic plants, game fish, or waterfowl.

In addition to satisfying minimum health standards, a suitable evaporation retardant must also meet certain economic criteria. One of these is

a reasonable period of service in the monolayer. Long monolayer life depends on the minimization of alcohol attrition. Alcohol may leave through evaporation (10), bacterial action (6,8,9), oxidation induced by the sun's radiation (11,12), and through solubilization in the water (5,10). It is with this last avenue of escape that the present work is chiefly concerned.

In order to make reliable estimates of alcohol loss from solubilization, one needs fairly accurate solubility values as a function of both temperature and chain length. The rate at which alcohol is consumed by bacteria could be more important than the solubility in determining the quantity of alcohol required to keep a reservoir covered with a monolayer. The development of effective and inexpensive bactericides, however, would make bacterial action irrelevant. Some work has already been done in this area (6). If alcohol solubilization were an extremely slow process, solubility data would have only minor significance in loss calculations. The results of this study indicate that the movement of alcohol from the surface to the interior of the water phase is not an extremely slow process and that saturation can occur in a relatively short time.

Solubilities of long-chain primary alcohols have been estimated from logarithm of solubility vs. carbon number plots of C_4 to C_{10} homologs (13,14,15). Such plots are linear and may easily be extrapolated to give the solubilities of the higher molecular weight homologs. According to Kinoshita, Ishikawa, and Shinoda (15),

$$\ln C = -1.39 n + 5.53$$

where C is the solubility in moles/liter at 25°C. of a primary alcohol containing n carbon atoms. The water solubilities of tetradecanol, hexadecanol,

octadecanol, and eicosanol as calculated from this equation are given in Table I.

Table I
Extrapolated Solubilities

<u>Alcohol</u>	<u>Solubility--(moles/liter):10⁹</u>
1-tetradecanol	890
1-hexadecanol	55
1-octadecanol	3.4
1-eicosanol	0.21

Extrapolated values, while providing estimates of the solubilities of long-chain alcohols, can be misleading. At 25°C. the alcohols of Table I are solids, whereas the equation of Kinoshita et al summarizes solubility experiments for alcohols which are liquids at this temperature. Since the temperature dependence of a compound's solubility below the melting point can differ appreciably from the temperature dependence above the melting point, reliable solubility values require direct determination. Two approaches were initially considered by the author, a carbon-14 tracer technique and a gas chromatographic technique. The carbon-14 work has been summarized elsewhere (16). Difficulties in obtaining alcohol solutions free of labeled impurities and colloidal alcohol particles prevented the determination of accurate solubility values. The carbon-14 experiments were terminated when Krause and Lange reported successful determinations of dodecanol, hexadecanol, and octadecanol solubilities by a radiotracer

procedure (17). Research efforts were then concentrated on the gas chromatographic technique. All research described hereinafter concerns the solubility of tetradecanol or hexadecanol in a 50 parts per billion (ppb.) aqueous silver nitrate solution. The silver nitrate solution was used in lieu of water to prevent certain common bacteria, e.g., pseudomonas, from ingesting the alcohols (6,18). For reasons which will be discussed later, no attempts were made to measure the solubilities of octadecanol and eicosanol.

EXPERIMENTAL

Instrumentation

The instruments used in this work included an analytical gas chromatograph, a preparative gas chromatograph, and a 90° light scattering photometer. The analytical gas chromatograph, an F & M Biomedical Model #400, was employed to check alcohol purity and to determine quantitatively injected alcohol weights. Experimental details are given in Table II and on page 15. The preparative gas chromatograph, a Wilkins Aerograph Autoprep #A-700, was used solely for purifying tetradecanol. The purification details are given in Table III. The light scattering photometer has been described by Anacker and Ghose (19).

Materials

Hexadecanol purity was checked by thin layer and gas-liquid chromatography. The checks verified a purity of 99.8+% which was claimed by the distributor, Applied Science Laboratory. The tetradecanol used was purchased from Matheson, Coleman & Bell, and was purified by preparative gas chromatography. The chromatographed alcohol purity was determined to be 99.5+%.

The water used in all experiments was doubly distilled, the second distillation being carried out over alkaline potassium permanganate. Baker and Adamson reagent grade silver nitrate, without further purification, was used to prepare all silver nitrate solutions. Eighty-five mole percent minimum hexane, purchased from the Phillips Petroleum Company, was

Table II

Operating Conditions---F & M Biomedical #400

Detector	Flame ionization
Column:	122 cm. x 6 mm. glass 1% SE-30 on 80/100 Chromosorb W
Column Temperature:	a.) tetradecanol, 120°C. b.) hexadecanol, 140°C.
Flow Rate:	a.) helium, 75 ml./min. b.) hydrogen, 35 ml./min. c.) air, 475 ml./min.
Chart Speed:	$\frac{1}{2}$ inch/min.

Table III

Operating Conditions---Wilkins Aerograph Autoprep #A-700

Detector:	Thermal Conductivity
Column:	10' x 3/8" stainless steel 20% Carbowax 20-M on 60/80 KOH washed Chromosorb W
Column Temperature:	250°C.
Flow Rate:	helium, 200 ml./min.
Filament Current:	150 milliamperes
Chart Speed:	$\frac{1}{2}$ inch/min.

redistilled before use. The hydrogen, helium, nitrogen, and compressed air used in the course of this work were all of a standard grade supplied by National Cylinder and Gas.

Auxiliary Equipment

Various microliter syringes from the Hamilton Syringe Co., Inc. were employed. Models 705-N and 710-N were used in the dilution steps described on pages 18 and 27. A 10 μ l. 701-N was used to inject 1 μ l. samples into the F & M gas chromatograph for analysis. The technique employed is worth describing. First, approximately 1 μ l. of hexane was drawn into the syringe. Then, approximately 2 μ l. of air were drawn in. Finally, 1 μ l. of the alcohol sample, solvent hexane, was drawn into the syringe, the two menisci of the sample coinciding with two syringe graduations 1 μ l. apart (Figure 1). This technique, while difficult to master, gave better reproducibility in this work than one employing a 10 μ l. Hamilton Syringe equipped with a Chaney Adapter, Model 701-NCH.

A 30 cc. hypodermic syringe equipped with a Luer-Lok tip was used in conjunction with the Swinny Hypodermic Adapter to filter the alcohol-water mixtures employed in the initial solubility experiments. The Swinny adapter was first loaded with a 13 mm., white, type HA, 0.45 μ . pore diameter, Millipore Filter and then attached to the syringe tip. Approximately 20 ml. of alcohol solution were poured into the syringe, the plunger was set in place, and the solution was filtered by depression of the plunger. In addition to the initial solubility work, this procedure was followed in the light scattering experiment, page 23.

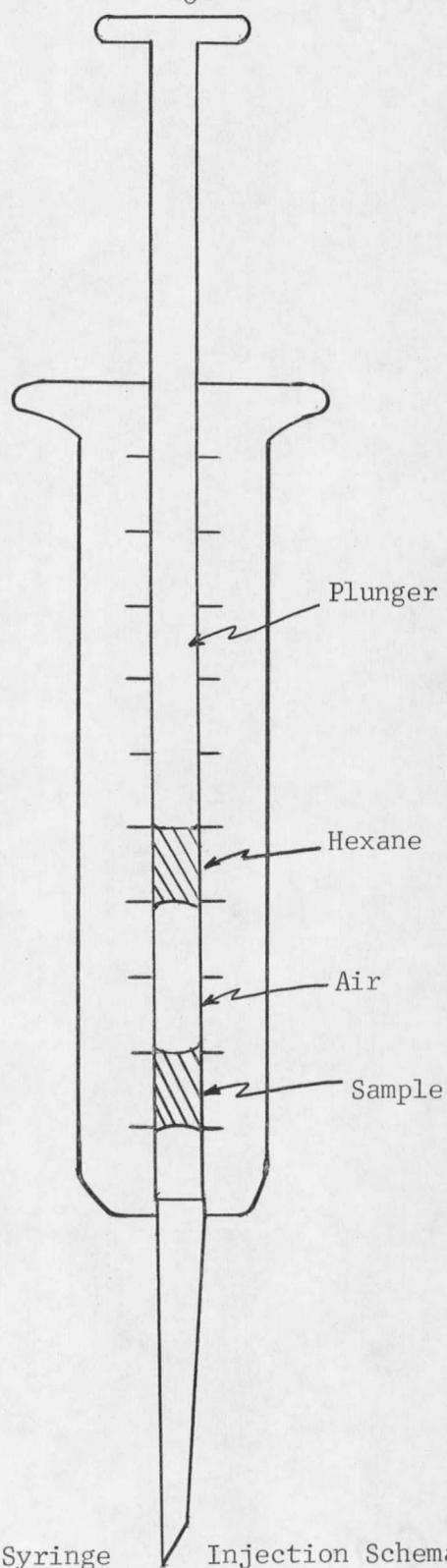


Figure 1. Syringe Injection Schematic

Two similar wood constant temperature boxes were used in the solubility determinations at 32, 43, and 45°C. One is shown in Figure 2. The heating elements are 110-120 volt infrared lamps and are controlled by a Fenwal Thermostat, catalog #17300-0, Fenwal Inc. Air is circulated throughout the box by a Delco Blower, Service No. 5062369, Delco Service Division, General Motors Corporation. The 61°C. studies were carried out in a Blue M oven, Model OV-480A, Blue M Electric Co., and the 4°C. studies in a cool room in the Montana State University Chemistry Department.

The following equipment was employed in various experimental situations: a Burrell Wrist Action Shaker, Model No. 00; a Blue M Constant Temperature Bath, Model MW-1172SS-A; Magnestirs, catalog #58945-1, Van Waters and Rogers, Inc; and Spinballs, Chemical Rubber Co.

Cleaning

Glassware was thoroughly cleaned in warm chromic acid, soaked in phosphoric acid to remove adsorbed chromium, rinsed extensively with distilled water until the rinse water was neutral, and dried in an oven at 110°C. (20). The teflon-lined Erlenmeyer flask caps were wiped thoroughly with lens tissue to remove dust, soaked in distilled water to dissolve soluble impurities, and dried at 110°C. before use.

Initial Solubility Experiments

The initial solubility experiments were conducted using a technique similar to that proposed by Noyes (21). A 3 mg. sample of hexadecanol was weighed into a 1 ml. beaker. The beaker and alcohol were then placed in a

