WATER SOLUBILITIES OF TETRADECANOL AND HEXADECANOL

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INTRODUCTION

Since monolayers of long-chain alcohols are capable of reducing water evaporation from ponds and reservoirs[1,2], questions concerning their ultimate fate are important from a conservation standpoint. Reliable estimates of alcohol loss through solubilization depend in part on accurate solubility data, which have been virtually nonexistent until recently.

The equation of KINOSHITA *et al.*[3]

$$\ln c = -1.39n + 5.53 \tag{1}$$

where c is the solubility in moles/l of a normal primary alcohol with n carbon atoms, can be used to estimate the 25° solubility of a long-chain alcohol. Such estimates, however, may not be reliable, as equation (1) holds strictly for alcohols with 10 or less carbons. These compounds are liquids at 25°. Long-chain alcohols with 14 or more carbons are solids at this temperature. The temperature dependence of the solubility of a substance may change appreciably as its melting point is passed. Hence, accurate solubilities of long-chain alcohols require direct determination.

KRAUSE AND LANGE[4] recently measured the water solubilities of *n*-dodecanol, *n*-hexadecanol, and *n*-octadecanol by a radiotracer technique. We herein describe a gas chromatographic procedure and its application to the determination of the solubilities of *n*-tetradecanol and *n*-hexadecanol.

EXPERIMENTAL

Preparation of saturated solutions

In the initial attempts to prepare saturated solutions, hexadecanol powder was shaken with water for periods up to three weeks and the resulting mixtures were then filtered through Millipore filters with pore diameter of 0.45 μ. Hexadecanol concentrations in the filtrates were found to be about 25 times larger than the solubility calculated from equation (1). An examination of one of the filtrates by light scattering indicated the presence of colloidal particles with weights in excess of $4.5 \cdot 10^9$ g/mole. The ratio of intensity of light scattered at an angle of 45° to that scattered at 135° was in the neighborhood of 6, thus confirming the existence of large particles.

Saturated solutions free of colloidal particles were eventually prepared by a procedure based on that of KRAUSE AND LANGE[4]. Solubilization was carried out in

2,000 ml Pyrex, round bottom, glass stoppered flasks. A 2.0 to 2.5 cm fluted glass nipple with a 3 mm opening was attached to each flask, the point of attachment being approximately 5 cm on an arc from the intersection of the vertical axis of the flask and its bottom. To each nipple was affixed *ca.* 5 cm of 1/4 in. tygon tubing. A pinch clamp sealed the tubing.

After a magnetic stirrer (1/2 in. ellipsoidal bar or a 5/8 in. spinball) and 1,000 ml of 50 p.p.b. aqueous silver nitrate (to prevent certain common bacteria, *e.g. Pseudomonas,* from ingesting the alcohol) had been placed in a flask, a 1 to 25 mg alcohol sample was introduced at the air–water interface with minimum agitation. The flask was stoppered and the solution stirred slowly. The magnetic stirrer was activated by a Magnestir set to operate at its slowest rate.

In the 32°, 43°, and 45° studies, flasks were kept in wooden chambers, heat being supplied by thermoregulated infrared lamps. The air in each of the two chambers used was continuously circulated by a blower. In the 61° work, flasks were housed in a large oven. For the 4° studies, a cold room was used.

Alcohol analyses

A solution was withdrawn from a flask by removing the stopper and opening the pinch clamp. The first 10 to 20 ml of a solution were discarded. The next portion was retained and weighed. For tetradecanol 10 to 12 ml aliquots and for hexadecanol 80 ml aliquots were collected. Five ml of hexane were added to each tetradecanol aliquot and 20 ml to a hexadecanol aliquot. Each aliquot was shaken with the hexane for 18 h in a Burrell Wrist Action Shaker. The hexane layer was then evaporated, 1 ml at a time, in a 1 ml centrifuge tube. This operation, carried out with the centrifuge tube immersed in an ice–water slurry and with the aid of a stream of nitrogen, left the alcohol as a deposit in the tube's tip. The tube was then sealed and refrigerated until its contents could be analyzed.

Analyses were carried out with an F & M Biomedical Model No. 400 analytical gas chromatograph equipped with a flame ionization detector. The glass column, 122 cm × 6 mm, contained 1% SE-30 on 80/100 Chromosorb W. It was operated at 120° for tetradecanol and at 140° for hexadecanol. The carrier gas consisted of helium, 75 ml/min; hydrogen, 35 ml/min; and air, 475 ml/min.

The alcohol residue in the centrifuge tube was dissolved *in situ* with 25 to 200 μl of hexane before injection into the gas chromatograph. The volume of hexane added to an unknown was always such that the peak area obtained for a 1 μl injection would fall within the range covered by the regression plots obtained for standard solutions. Thus, the weight of alcohol in 1 μl of solution was determined. Since the volume of hexane added to the centrifuge tube was known, the weight of soluble alcohol in the aqueous silver nitrate aliquot could be calculated.

Materials

Hexadecanol from Applied Science Laboratory was checked by thin layer and gas–liquid chromatography and found to be 99.8+% pure. Tetradecanol, 99.5+%, from Matheson, Coleman & Bell was further purified by preparative gas chromatography (Wilkens Aerograph Autoprep No. A-700). Water was doubly distilled, the second distillation being carried out over alkaline potassium permanganate. Baker and Adamson reagent grade silver nitrate was used as received to prepare all silver nitrate

solutions. Eighty-five mole percent minimum hexane from the Phillips Petroleum Company was 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.

Procedure checks

Possible sources of error in the extraction procedure include alcohol adsorption on container surfaces, alcohol evaporation during hexane removal, and incomplete recovery of the solubilized alcohol from the aqueous phase in the one-step extraction process. In order to determine whether or not the above possibilities and any others which might cause error were significant, the hexane extraction procedure was tested with tetradecanol–water systems of known composition.

Twenty-five μl samples of a $5 \cdot 10^{-8}$ g/μl solution of tetradecanol in hexane, which served as a standard, were injected separately into 5 dram vials containing 10 ml of 50 p.p.b. aqueous silver nitrate (test No. 1) and into empty 5 dram vials (test No. 2). The hexane was evaporated from each vial by a stream of nitrogen. Five ml of hexane were added to each vial containing aqueous silver nitrate and tetradecanol. To each vial containing only tetradecanol were added 10 ml of the aqueous silver nitrate solution and 5 ml of hexane. The extraction, evaporation of the hexane layers, and concentration of the alcohol were then carried out as previously described. Twenty-five μl of hexane were added to each of the centrifuge tube tips and 1 μl of each resulting solution was injected into the gas chromatograph.

Duplicate runs of tests No. 1 and No. 2 demonstrated that recovery of tetradecanol from aliquots was essentially quantitative. Peak areas for extracted tetradecanol were 96% or more of the areas obtained from 1 μl injections of the standard. Significant adsorption of alcohol on the walls of a glass vessel should have become apparent in test No. 2 had it occurred since at one point in the procedure only the alcohol was in the vial. The recovery of essentially all of the alcohol showed that adsorption presents no problems. The tests also showed that any errors arising from alcohol evaporation during extraction and from incompleteness of the one-step extraction are negligible.

The extraction of hexadecanol from aqueous silver nitrate with hexane (20 ml hexane added to 80 ml of the aqueous mixture) was checked with known mixtures in a manner similar to that used for tetradecanol. Again, the extraction removed essentially all of the alcohol from the aqueous phase.

The extraction scheme used in the present work is somewhat simpler than that used by KRAUSE AND LANGE[4], which involved the addition of ethanol to the aqueous phase before the addition of hexane. This step can be omitted.

RESULTS AND DISCUSSION

The results of a typical solubility determination are shown in Fig. 1A. Data for the upper curve were obtained from a solution supersaturated with tetradecanol. It was prepared by agitating for one day alcohol and solvent at 80° and them cooling to 32°, the temperature of the determination. The lower curve was obtained with a solution initially unsaturated. The results of a second run at the same temperature with larger initial tetradecanol charges are shown in Fig. 1B. Since the upper and

lower curves in each plot eventually level off and merge and since there is no detectable effect caused by the size of initial tetradecanol charge, equilibrium between solute and solvent was most likely achieved.

That saturation is not achieved almost instantaneously in an initially unsaturated solution—an impression that might be gained from Fig. 1—is demonstrated in Fig. 2. It presents the results of two short runs at 45° in which sampling was started in each case almost immediately after tetradecanol was placed on the surface of the solvent.

Equilibrium between a solution supersaturated with tetradecanol and solid tetradecanol was never reached at 4°, as indicated in Fig. 3, although sampling was
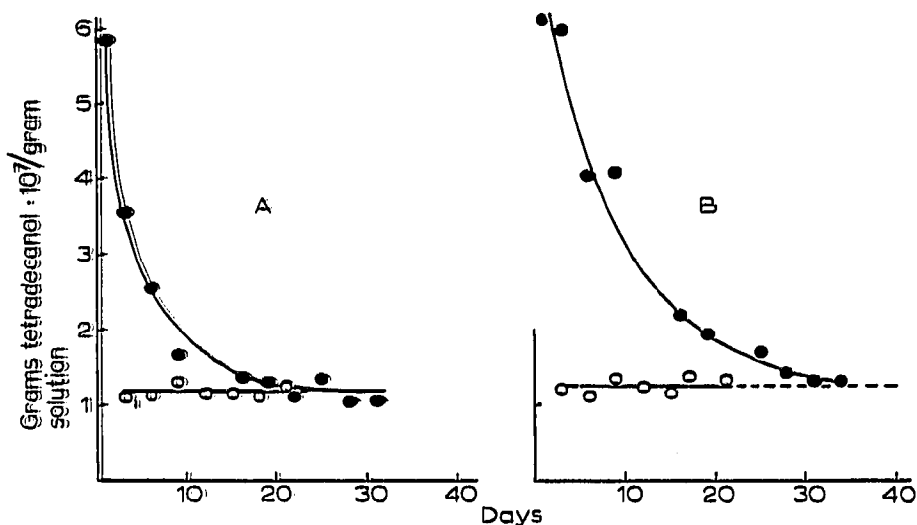

Fig. 1. Tetradecanol concentration vs. time plots at 32° ± 1°. Weights of alcohol samples used in run A were 3.9 mg for the initially unsaturated solution (O), and 4.2 mg for the initially supersaturated solution (●). The corresponding sample weights for run B were 5.4 and 5.9 mg.
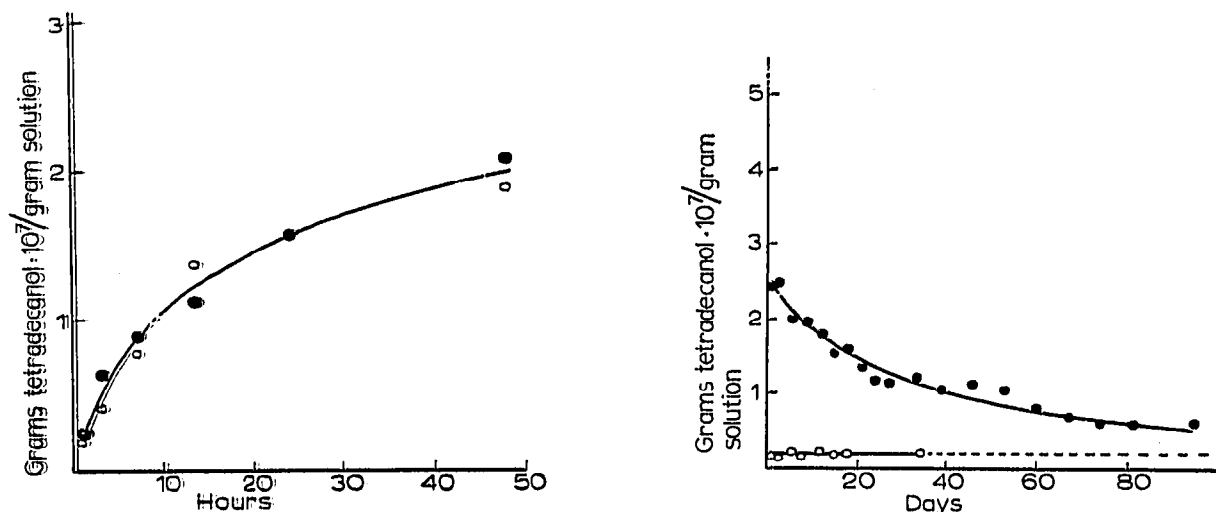

Fig. 2. Tetradecanol concentration vs. time plot for run at 45° ± 1.5°. Alcohol sample weights were 8.5 mg (O), and 2.7 mg (●).

Fig. 3. Tetradecanol concentration vs. time plots at 4° ± 1°. Alcohol sample weights were 2.0 mg for the initially unsaturated solution (O), and 0.9 mg for the initially supersaturated solution (●). The supersaturated solution was prepared at 40°.

continued for 95 days. The concentration level achieved by the initially unsaturated solution was taken as the solubility of the alcohol.

Hexadecanol solubilities were measured at 43° and 61°. Only initially unsaturated solutions were used in the determinations, which are summarized in Fig. 4.

Experimental solubilities, x and the 95% confidence intervals, L_1 and L_2, for the true population means are recorded in Table I. For purposes of comparison, KRAUSE AND LANGE's hexadecanol solubilities, which have an estimated experimental error of $\pm$ 10%, are included. The two sets of experimental values seem to mesh satisfactorily. The 25° solubilities calculated from equation (1) are also given. They are appreciably higher than the values obtained by extrapolating the present experimental data to 25°.

TABLE I

TETRADECANOL AND HEXADECANOL SOLUBILITIES

Alcohol	Temp. (°C)	x (10^{-6} g/100 ml)	L_1 (10^{-6} g/100 ml)	L_2 (10^{-6} g/100 ml)
Tetradecanol	4	1.94	1.77	2.11
Tetradecanol	32	12.3	11.6	13.0
Tetradecanol	45	23.7	22.8	24.6
Tetradecanol	61	44.9	43.6	46.2
Hexadecanol	61	4.06	3.86	4.26
Hexadecanol	43	1.55	1.48	1.62
Hexadecanol[a]	34	0.80		
Hexadecanol[a]	55	3.08		
Tetradecanol[b]	25	19.1		
Hexadecanol[b]	25	1.34		

[a] Data from KRAUSE AND LANGE[4].
[b] Calculated from eqn. (1).

Heats of solution

For a saturated solution of a sparingly soluble, pure solute, either liquid, l or solid, s, we may write[5]

$$(\delta \ln X/\delta T)_P = (\bar{H} - H)/RT^2 \tag{2}$$

Here H is the molar enthalpy of the pure solute, $\bar{H}$ is its partial molar enthalpy, X its mole fraction in the saturated solution, T the temperature, P the pressure, and R the gas constant. The quantity $\bar{H} - H$ is a differential heat of solution and for dilute solutions is not appreciably different from an integral heat of solution. When $\bar{H} - H$ is not greatly dependent on temperature, it may be estimated as $-2.303 R$ times the slope of a log X *vs.* $1/T$ plot. Fig. 5 is such a plot for tetradecanol. $\bar{H} - H_l$ and $\bar{H} - H_s$, as computed from the slopes above and below the melting point of the alcohol, are 8.5 and 11.1 kcal/mole, respectively. Although these values are probably of the correct magnitude, they should not be taken too seriously, as the data upon which they are based are meager. The temperature spread for each pair of points is perhaps too large to expect a constant heat of solution over the interval.

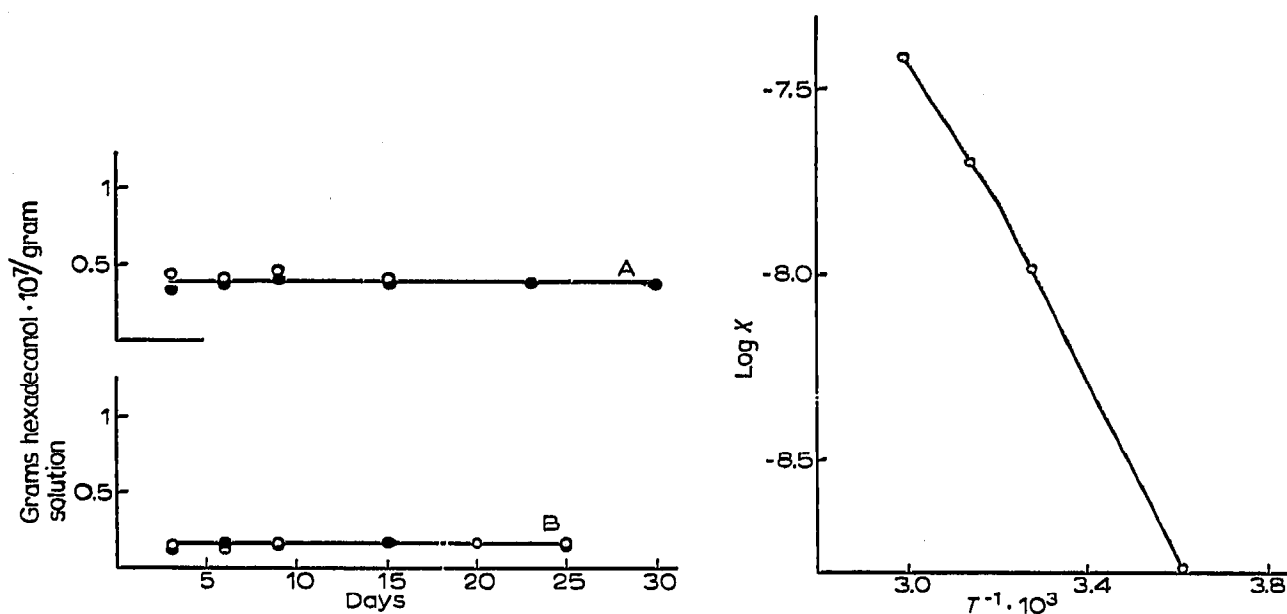There is a more compelling reason for not putting too much faith in the above

Fig. 4. Hexadecanol concentration *vs.* time plots at 61° ± 1.0°, curve A, and at 43° ± 1.5°, curve B. All starting solutions were initially unsaturated. Alcohol sample weights were 6.0 mg (O) and 3.4 mg (●) in A and 2.6 mg (O) and 1.0 mg (●) in B.

Fig. 5. Log X *vs.* $1/T$ plot for tetradecanol. X is the mole fraction of alcohol in a saturated solution at the temperature $T°K$.

values. If all assumptions made were valid, the difference between the two heats, *i.e.*, 2.6 kcal/mole, would be the heat of fusion of tetradecanol. DAVIES AND KYBETT[6] experimentally found the heat of fusion to be 9.5 kcal/mole. One possible explanation for the difference is that the tetradecanol introduced into the system takes on water of crystallization as a solid and dissolves more than an infinitesimal amount of water as a liquid. LAWRENCE *et al.*[7] found evidence for the formation of solid solutions of alkanols and water. They have also shown that liquid dodecanol can solubilize up to 3% water, *i.e.*, one molecule of water per three molecules of dodecanol. If this is also the case for tetradecanol, it is not surprising that our calculated heat of fusion is in considerable error. The solubility of water in liquid tetradecanol should be determined and the extent of hydration of solid tetradecanol investigated.

Both tetradecanol and hexadecanol exist in three polymorphic forms: α, β and γ. DAVIES AND KYBETT[8] have shown that the heats of solution of the three forms in benzene are significantly different. This would also be expected in the case for water. However, since the metastable α and β forms rearrange to the stable γ form in a relatively short time[6], polymorphism probably is not involved in an explanation of the error in our calculated heat of fusion. KRAUSE AND LANGE[4] have also ruled out polymorphism as a factor in their solubility measurements.

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SUMMARY

The solubilities of tetradecanol and hexadecanol in water were measured at several temperatures by gas–liquid chromatography. The 25° solubilities are smaller than values obtained by extrapolating data for lower homologs. Estimation of the heat of solution of tetradecanol in water from the temperature dependence of the solubility suggests that the amount of water in the alcohol rich phase in equilibrium with the water rich phase is not negligible.

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