

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of Some Unsaturated Alcohols

BY P. M. GINNINGS, ELEANOR HERRING AND DORIS COLTRANE

Previous investigations¹ of the relationships between molecular structure and aqueous solubility of some saturated alcohols suggested a similar study of some unsaturated alcohols, since only approximate values for the latter are given in the literature. Theory seems to indicate that introduction of a semi-polar unsaturated group into the alcohol molecule should cause an increase in the aqueous solubility. Our experimental results confirm this, as every one of the seven unsaturated alcohols investigated is more soluble than the analogous saturated alcohol. This is also in agreement with a related study of some ternary systems of allyl alcohol,² where it was found that allyl alcohol is more difficult to salt out than the saturated analog—*n*-propyl alcohol. Diallyl ether is also much more soluble than di-*n*-propyl ether.³ Our results also reveal that maximum solubility is obtained when both the unsaturated and hydroxyl groups are located close to the center of the molecule (nos. 2, 3 and 4; also 5 and 7). As in the saturated alcohols, the more compact molecule is more soluble (nos. 6 and 7) and the solubility in all cases decreases with increasing molecular weight and temperature.

Experimental

Syntheses which used saturated alkylmagnesium halides in reaction with unsaturated aldehydes in the usual Grignard procedure gave much better yields of the desired unsaturated alcohols than the use of allylmagnesium bromide with various saturated aldehydes and ketones; so the latter method was discontinued. No. 4 was prepared by the unusual reaction of Paul⁴ from tetrahydrofurfuryl alcohol. The bromide was first prepared from the alcohol by treatment with phosphorus tribromide and pyridine. Action of magnesium on the tetrahydrofurfuryl bromide gave the Grignard reagent which was then decomposed with ice to give no. 4. As pointed out by Paul, this product probably contained some cyclopentanol which is difficult to remove completely on account of the closely adjacent boiling points of the two alcohols. Presence of the cyclopentanol probably caused the solubility data for no. 4 to be slightly higher than if it were absent. The following specific reagents were used in the preparation

(1) (Pentanol) Ginnings and Baum, *THIS JOURNAL*, **59**, 1111 (1937); (hexanol) Ginnings and Webb, *ibid.*, **60**, 1388 (1938); (heptanol) Ginnings and Hauser, *ibid.*, **60**, 2581 (1938); (octanol) Ginnings and Coltrane, *ibid.*, **61**, 525 (1939).

(2) Ginnings and Dees, *ibid.*, **57**, 1038 (1935).

(3) Bennett and Philip, *J. Chem. Soc.*, 1930 (1928).

(4) Paul, *Compt. rend.*, **195**, 1289-1291 (1932).

TABLE I

No.	d_{25}^{25} of pure alc. and b. p. °C. (760 mm.)	Temp., °C.	Wt. % alc.	d_4 of liquid phase Alc. rich	Water rich
Buten-3-ol-2					
1	0.8350 96.0-97.0	20	Soluble in all proportions		
		25	Soluble in all proportions		
		30	Soluble in all proportions		
Penten-3-ol-2					
2	0.8328 121.7-124.2	20	9.46 87.71	0.8602	0.9874
		25	8.92 87.65	.8560	.9862
		30	8.48 87.57	.8534	.9851
Penten-4-ol-3					
3	0.8347 114.0-114.6	20	8.72 87.12	0.8617	0.9896
		25	8.20 86.88	.8586	.9887
		30	7.74 86.68	.8550	.9876
Penten-4-ol-1					
4	0.8578 138.8-139.3	20	5.89 86.83	0.8755	0.9942
		25	5.70 86.57	.8722	.9933
		30	5.56 86.19	.8690	.9919
Hexen-4-ol-3					
5	0.8415 133.8-136.2	20	4.06 96.07	0.8559	0.9936
		25	3.81 95.85	.8524	.9928
		30	3.58 95.74	.8480	.9917
2-Methylpenten-4-ol-3					
6	0.8364 125.1-126.1	20	3.29 94.16	0.8535	0.9947
		25	3.06 94.10	.8494	.9938
		30	2.89 93.97	.8451	.9926
Hexen-1-ol-3					
7	0.8318 133.5-134.0	20	2.72 94.12	0.8466	0.9953
		25	2.52 93.92	.8430	.9944
		30	2.36 93.90	.8376	.9936

of the other alcohols: no. 1 from methylmagnesium iodide and acrolein; no. 2 from methylmagnesium iodide and crotonaldehyde; no. 3 from ethylmagnesium bromide and acrolein; no. 5 from ethylmagnesium bromide and crotonaldehyde; no. 6 from *i*-propylmagnesium bromide and acrolein; no. 7 from *n*-propylmagnesium bromide and acrolein. The usual Grignard procedure was followed except only that finely crushed ice was used to decompose the Grignard complex. Products were purified by fractional distillation through a 1-meter column and the solubilities determined by the same method as for the saturated alcohols. With the possible exception of no. 4, the authors feel that these data are valid to within 0.3 weight per cent.

Summary

Aqueous solubilities of seven unsaturated alcohols have been determined for 20, 25 and 30°. Each of these is more soluble than the analogous

saturated alcohol. Maximum solubility seems to be obtained with both the unsaturated and hydroxyl groups close to the center of a compact

molecule. The solubility also decreases with increasing molecular weight and temperature.

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Successive Phases in the Transformation of Anhydrous Sodium Palmitate from Crystal to Liquid¹

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The purpose of this paper is to present the evidence for the existence of several new soap phases, to discuss the possibility that all are mesomorphic, and to indicate the nature of the extensions which these new phases make necessary in the technically important phase rule diagrams of systems of water and soap. Although the present work involves only anhydrous sodium palmitate, preliminary experiments on anhydrous sodium laurate, sodium stearate and sodium oleate (undertaken by Mr. Macomber) and on aqueous systems of sodium palmitate and sodium oleate show that also in these cases a larger number of phases exist in the concentrated systems than were previously suspected.

Simple crystals in which the binding forces are essentially isotropic melt at a single temperature, which provides a qualitative indication of the strength of the bonds. However, many more complex substances form crystals in which the binding forces are markedly anisotropic. Some of these compounds do not change directly from crystal to isotropic liquid, but instead pass through one or more distinct, stable intermediate phases, the liquid crystalline states.

Bernal and Crowfoot² have summarized the molecular characteristics favorable to liquid crystal formation: (1) the molecule must be anisometric, either rod-shaped or flat, lath-shaped; (2) it must contain not more than one highly polar group but may contain additional mildly polar groups such as $-\text{C}-\text{O}-\text{C}-$ or $-\text{CH}=\text{N}-$. These authors also discuss the relation of the po-

(1) This investigation was begun in collaboration with Dr. R. H. Ferguson and Dr. F. B. Rosevear in consultation with Dr. A. S. Richardson at the Procter and Gamble Company, Ivorydale, Ohio, primarily in connection with phase rule studies of soap-salt-water systems. A preliminary account of the discovery of two of the new soap phases, to be published in *Oil and Soap*, was presented at the Chicago meeting of the Oil Chemists' Association, October, 1938. The more thorough investigation discussed in this paper was carried out subsequently at Stanford University.

(2) J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933).

sition of the active group in the molecule to the type of liquid crystal formed.

The alkali salts of the *n*-fatty acids (the soaps) conform to the general conditions summarized by Bernal and Crowfoot. Correspondingly, it has been long accepted that these substances undergo "double melting."^{3,4} However, the temperatures that have been reported for the transition from crystalline curd fibers to liquid crystal, and from liquid crystal to isotropic liquid, vary widely. Visual and microscopic observations³⁻⁵ of the temperature of liquid crystal formation have led to values in the neighborhood of 215-220° for the first melting point of sodium palmitate. However, McBain, Lazarus and Pitter⁶ give 134° for this point, based partly on visual observations and partly on extrapolation of phase boundaries determined in the sodium palmitate-water system. They also noticed that incipient transition sometimes occurred at 114-121°. More recently Lawrence⁷ has given the value 150-155° for this transition temperature. Visual and microscopic determinations of the temperature of formation of isotropic liquid from liquid crystal have led to the values 265°,³ 291°^{6,7} and 316°,³ while a method based on apparent viscosity led to 259°.⁷

The measurements of specific volume as a function of temperature, reported in this paper, show that this galaxy of values arises from the existence of at least six phases of sodium palmitate between 70 and 320°, instead of the three heretofore recognized. Microscopic examination, together with

(3) D. Vorländer, *Ber.*, **43**, 3120 (1910).

(4) J. W. McBain, in Alexander's "Colloid Chemistry," Vol. 1, Chapter V, 1926.

(5) J. W. McBain and M. C. Field, *J. Chem. Soc.*, 921 (1933).

(6) J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik. Chem.*, **A147**, 87 (1930).

(7) A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938).

The figures given in Table V of this author's paper purport to refer to sodium palmitate monohydrate. The inference is that the samples were prepared by drying the soap to constant weight at temperatures just above 100°. It has been shown, however,²⁰ that such a procedure results in essentially anhydrous soap.