[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of Some Isomeric Hexanols

BY P. M. GINNINGS AND RUTH WEBB

Aqueous solubilities of the eight isomeric pentanols were determined in a previous investigation[1] and a similar investigation of ten isomeric hexanols has just been concluded. These ten isomers include the three tertiary, the six secondary and the most compact primary isomer.

TABLE I

No.	Compound	Temp., °C.	Wt. % alc.		d^{25}_4 pure alc.	B. p. (760 mm.), °C.	d_4 liq. phases	
							Alc. rich	Water rich
1	Diethylmethylcarbinol	20	4.82	89.53	0.8242	122.6–122.8	0.8498	0.9933
		25	4.26	89.64			.8454	.9926
		30	3.81	89.76			.8410	.9919
2	Dimethyl-*i*-propylcarbinol	20	4.65	89.06	.8118	118.0–118.8	.8464	.9934
		25	4.18	89.12			.8421	.9929
		30	3.76	89.26			.8372	.9910
3	Dimethyl-*n*-propylcarbinol	20	3.63	89.87	.8053	122.4–122.6	.8321	.9935
		25	3.24	89.95			.8280	.9929
		30	2.96	89.99			.8237	.9921
4	*t*-Butylmethylcarbinol	20	2.64	92.74	.8157	119.9–120.9	.8356	.9955
		25	2.43	92.71			.8313	.9946
		30	2.26	92.67			.8272	.9936
5	*i*-Propylethylcarbinol	20	2.24	94.97	.8186	126.3–127.3	.8323	.9950
		25	2.01	94.89			.8288	.9941
		30	1.82	94.72			.8249	.9940
6	*s*-Butylmethylcarbinol	20	2.09	93.43	.8231	133.5–134.5	.8390	.9960
		25	1.94	93.32			.8356	.9950
		30	1.79	93.21			.8316	.9939
7	*i*-Butylmethylcarbinol	20	1.79	93.79	.8034	131.6–131.8	.8186	.9956
		25	1.64	93.65			.8149	.9948
		30	1.52	93.45			.8114	.9939
8	*n*-Propylethylcarbinol	20	1.75	95.34	.8143	134.5–135.0	.8264	.9952
		25	1.61	95.14			.8225	.9951
		30	1.49	94.93			.8190	.9939
9	*n*-Butylmethylcarbinol	20	1.51	93.50	.8108	139.0–140.0	.8264	.9965
		25	1.37	93.38			.8231	.9954
		30	1.28	93.25			.8194	.9942
10	*t*-Pentylcarbinol	20	0.82	98.28	.8498	136.9–137.9	.8598	.9971
		25	.76	98.21			.8551	.9963
		30	.71	98.16			.8511	.9951

For a study of the relationships between molecular structure and aqueous solubility, these ten seemed of greatest interest, although a total of seventeen isomers exists. Apparently the aqueous solubility of only one hexanol has been determined accurately. Butler[2] using an interferometric method found 0.624 weight per cent. at 25° for normal hexanol. This is undoubtedly the minimum aqueous solubility of any of the hexanols at that temperature. Results of our determinations are given in the table. As in the case of the pentanols, the tertiary isomers are more soluble than any of the secondary isomers and these in turn are more soluble than the one primary isomer that was measured. The latter compound, having the most compact structure of any of the eight primary isomers, should have the greatest solubility of the eight. This assumption seems reasonable from a consideration of the four primary pentanols in the previous paper. Of some interest is the fact that water is most soluble in the tertiary hexanols, less in the secondary and least in the primary. However, the order of the individual compounds in each group does not correspond exactly with the reverse solubilities of the alcohols in water.

---

(1) Ginnings and Baum, THIS JOURNAL, **59**, 1111 (1937).

(2) Butler, Thomson and Maclennan, *J. Chem. Soc.*, 674 (1933).

It is quite obvious that the character of the alpha carbon atom in the hexanol (whether primary, secondary or tertiary) separates the isomers into three distinct groups. Also it is evident that further comparisons must be limited to compounds within these groups. Maximum solubility should exist in that isomer which has the most compact structure and which has the hydroxy group located as close to the center of the molecule as possible. In the tertiary group, the latter factor seems to dominate slightly (nos. 1 and 2). But in the secondary group, the former factor—compact structure—seems to prevail (nos. 4 and 5). Two of the isomers have almost identical solubilities of the alcohol in water (nos. 7 and 8) but even here the factor of compact structure seems to prevail slightly. In the two secondary isomers where the carbon chain remains constant (nos. 8 and 9), the solubility increases as the hydroxyl group is moved toward the center of the molecule, which is perfectly analogous to the behavior of the pentanols. Solubilities of all ten isomeric hexanols decrease as the temperature increases from 20 to 30°.

Experimental

All compounds were fractionally distilled from calcium oxide. Numbers 3 and 9 were Eastman best grade and were distilled using a short column. Number 7 was purified from Eastman practical grade by careful fractionation through a 1-m. column with a reflux ratio of about 10:1. All of the other compounds were prepared by some modification of the Grignard reaction with the usual procedure, and fractionally distilled through the 1-m. column. The following specific reagents were used: no. 1 from ethylmagnesium bromide and ethyl acetate; no. 2 from methylmagnesium iodide and *i*-propyl methyl ketone; no. 4 from *t*-butylmagnesium chloride and acetaldehyde; no. 5 from ethylmagnesium bromide and *i*-butyraldehyde; no. 6 from *s*-butylmagnesium bromide and acetaldehyde; no. 7 from *i*-butylmagnesium bromide and acetaldehyde; no. 8 from ethylmagnesium bromide and *n*-butyraldehyde; no. 10 from *t*-pentylmagnesium chloride and ethyl formate.

The procedure used for the measurement of the solubilities was essentially the same as that used in the work on pentanols. Any changes made were in the nature of slight refinements in technique. If details are desired, reference should be made to the article on pentanols. The results seem reliable to better than 0.1 weight per cent. and the authors feel that the validity of the results will approach this limit.

Summary

Aqueous solubilities of ten isomeric hexanols have been determined for 20, 25 and 30°. The three tertiary isomers are more soluble than any of the six secondary isomers which in turn are more soluble than the most compact primary isomer. Maximum solubility is obtained by having the hydroxyl group as close as possible to the center of a compact molecule. The solubility of all ten isomers decreases as the temperature increases from 20 to 30°.

GREENSBORO, N. C. RECEIVED MARCH 26, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Sulfur Dioxide. The Heat Capacity of Solid and Liquid. Vapor Pressure. Heat of Vaporization. The Entropy Values from Thermal and Molecular Data

BY W. F. GIAUQUE AND C. C. STEPHENSON[1]

This paper presents the results of a low temperature investigation on sulfur dioxide. The data and the third law of thermodynamics have been used to calculate the entropy of sulfur dioxide gas. Cross[2] has calculated the entropy from molecular data and, while these data are not as complete as is desirable, it is possible to show that the entropy of crystalline sulfur dioxide does approach zero at the absolute zero of temperature.

The apparatus and methods used in this investigation are similar to those of previous investigations on condensed gases in this Laboratory. The calorimeter used has been referred to previously[3] as Gold Calorimeter II. A full description of a similar calorimeter has been given by Giauque and Egan.[4] The most recent calibration of the standard thermocouple has been described by Stephenson and Giauque.[5]

Preparation and Purity of Sulfur Dioxide.—The sulfur dioxide was prepared by the action of concentrated sulfuric acid on sodium sulfite. The evolved gas was bubbled through water to remove any traces of sulfur trioxide and then

---

[1] Charles A. Coffin Fellow, Academic year 1934–1935.

[2] Cross, *J. Chem. Phys.*, **3**, 825 (1935).

[3] (a) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) Blue and Giauque, *ibid.*, **57**, 991 (1935).

[4] Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[5] Stephenson and Giauque, *ibid.*, **5**, 149 (1937).