[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of Some Isomeric Heptanols

BY P. M. GINNINGS AND MARY HAUSER

Aqueous solubilities of the pentanols[1] and some hexanols[2] have been determined in previous investigations. This is a similar investigation of nine heptanols that seemed of greatest interest. These nine include the seven tertiary and the two secondary isomers of most compact structure. Apparently the solubility of only one heptanol has been determined precisely. Butler[3] using an interferometric method found a value of 0.180 weight per cent. at 25° for normal heptanol.

The results of our determinations, which are given in the table, seem to be in accord with the theory outlined in previous investigations. As in the lower alcohols, the seven tertiary isomers are more soluble than the two secondary isomers of most compact structure, and increase of temperature is always accompanied by a decrease in solubility. Six of the seven tertiary heptanols can be considered as being derived from the six secondary hexanols by addition of a methyl group to the alpha carbon atom. It is noteworthy that the *relative* solubilities of the resulting six heptanols remain in the same order as in the hexanols. In the case of compound no. 1, the measurement of the solubility at the usual temperatures of the others was prevented by separation of the solid phase of the crystalline hydrate of the alcohol. However, determination of the solubility of the next alcohol (no. 2) at 40° also supplied a definite basis for comparison with the rest of the isomers. The importance of the compact molecule is easily noticed by a comparison of the solubilities of compounds nos. 1 and 2, where the former has a much more compact molecule than the latter. In the case of the two secondary isomers (nos. 8 and 9), the asymmetrical molecule containing the tertiary butyl group seems to dominate slightly the symmetrical molecule of no. 9.

TABLE I

No.	d^{25}_4 of pure alc. and b. p., °C. (760 mm.)	Temp., °C.	Wt. % alc.		d_4 of liquid phase	
					Alc. rich	Water rich
	2,3,3-Trimethylbutanol-2					
1	0.8380	40	2.20	94.72	0.8352	0.9902
	130.3–130.8					
	3-Ethylpentanol-3					
2	0.8402	20	1.91	94.25	.8541	.9964
	143.1–	25	1.68	94.24	.8502	.9957
	143.2	30	1.50	94.21	.8457	.9945
		40	1.26	94.31	.8366	.9921
	2,3-Dimethylpentanol-3					
3	0.8365	20	1.87	94.11	.8513	.9965
	139.6–	25	1.64	94.12	.8470	.9961
	139.8	30	1.43	94.12	.8430	.9945
	2,3-Dimethylpentanol-2					
4	0.8307	20	1.69	93.69	.8477	.9964
	138.5–	25	1.54	93.69	.8441	.9955
	139.5	30	1.40	93.71	.8404	.9943
	2,4-Dimethylpentanol-2					
5	0.8100	20	1.50	93.49	.8279	.9962
	132.5–	25	1.34	93.48	.8240	.9954
	133.5	30	1.22	93.49	.8199	.9943
	3-Methylhexanol-3					
6	0.8202	20	1.35	94.77	.8348	.9965
	142.7–	25	1.19	94.75	.8312	.9958
	142.9	30	1.07	94.73	.8272	.9946
	2-Methylhexanol-2					
7	0.8093	20	1.08	93.77	.8268	.9967
	143.0–	25	0.97	93.65	.8233	.9958
	143.2	30	.87	93.56	.8199	.9946
	2,2-Dimethylpentanol-3					
8	0.8224	20	.88	97.00	.8329	.9971
	134.7–	25	.82	96.94	.8289	.9962
	135.1	30	.79	96.88	.8253	.9950
	2,4-Dimethylpentanol-3					
9	0.8254	20	.78	96.79	.8351	.9974
	138.4–	25	.70	96.68	.8315	.9965
	138.9	30	.67	96.56	.8271	.9955

Experimental

All compounds were prepared by some modification of the Grignard reaction with the usual procedure and purified by careful fractionation through a 1-meter column with a reflux ratio of about 10:1. Usually calcium oxide was also used in the distillation. The following specific reagents were used: no. 1 from *t*-butylmagnesium chloride and acetone; no. 2 from ethylmagnesium bromide and ethyl propionate; no. 3 from ethylmagnesium bromide and *i*-propyl methyl ketone; no. 4 from *s*-butylmagnesium bromide and acetone; no. 5 from *i*-butylmagnesium bromide and acetone; no. 6 from *n*-propylmagnesium bromide and methyl ethyl ketone; no. 7 from *n*-butylmagnesium bromide and acetone; no. 8 from *t*-butylmagnesium chloride and propionaldehyde; no. 9 from *i*-propylmagnesium chloride and *i*-butyraldehyde.

The procedure used for the measurement of the solubilities was essentially identical with that used in the work on

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

(2) Ginnings and Webb, *ibid.*, **60**, 1388 (1938).

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

pentanols and hexanols. 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 eight isomeric heptanols have been determined for 20, 25 and 30° and one for 40°. The seven tertiary isomers are more soluble than the two most compact secondary isomers. Maximum solubility is obtained by having the hydroxyl group as close as possible to the center of a compact tertiary molecule. Solubility of the isomers decreases as the temperature increases from 20 to 30°.

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The Densities of Aqueous Solutions of Urea at 25 and 30° and the Apparent Molal Volume of Urea[1]

BY FRANK T. GUCKER, JR., FRED W. GAGE AND CHARLES E. MOSER

Introduction

In 1929 Masson[2] showed that the apparent molal volume of an electrolyte is a linear function of the square root of the concentration, while that of a weak electrolyte or a non-electrolyte is a linear function of a higher power of the concentration. The relationship for electrolytes has been confirmed by numerous investigators. In reviewing this and other properties of electrolytic solutions, one of us[3] pointed out that the data of Perman and Urry[4] for the apparent molal volumes and compressibilities of sucrose and of urea also might be represented as linear functions of the square root of the concentration. Redlich and Klinger[5] subsequently proved from more accurate density data that the change of the apparent molal volume of sucrose was much more nearly linear with the first power than with the square root of the concentration. We then found that the data of Perman and Urry could be represented equally well by either plot, within the limit of 0.1% to which their data were tabulated. The present work was undertaken to determine the apparent molal volumes of urea in aqueous solutions with high enough precision to determine whether it was also a linear function of the concentration—like sucrose.

Experimental Methods.—In order to attain an accuracy of a few parts per million (p. p. m.) the densities were measured differentially, using three pycnometers of about 60-ml. capacity. Two of them were filled with solution and the third with water. After all three had come to equilibrium in a thermostat and the volumes were adjusted in the capillaries, the pycnometers containing solution were weighed successively against the water-filled tare. Such a differential arrangement minimizes errors due to changes in the temperature of the thermostat, and also decreases the errors due to adsorption of moisture on the surface of the pycnometers and the correction required in reducing the weights to the vacuum standard.

In adjusting the pycnometers, they were placed in a thermostat holding 36 liters of water. The bottom and sides of the thermostat were protected by a 5-cm. layer of magnesia insulation and the top was covered with a wooden lid, in the center of which was a glass panel, through which the capillaries of the pycnometers were read.

The thermostat was equipped with an adequate stirrer and heated by means of three coils of bare nichrome wire connected to the lighting circuit through a thyratron relay. During the first series of measurements (made by F. W. G.) the relay was actuated by a large ether-filled regulator with mercury contact, which kept the temperature constant to ±0.002° under most conditions and to ±0.005° at all times. The temperature throughout the bath was found to be uniform to 0.001°. These temperatures were measured with a calibrated Beckmann thermometer. During the second series of measurements (made by C. E. M.) the regulator consisted of a pair of 100-ohm nickel resistance thermometers, connected in opposite arms of a Wheatstone bridge, equipped with a sensitive galvanometer. The light from the galvanometer mirror actuated a photoelectric cell which controlled the relay. This system gave more rapid response and kept the temperature constant to ±0.0004°, as measured by a platinum resistance thermometer. This regulator has the added advantage of great flexibility and instant response at any desired temperature.

The pycnometers were constructed of Pyrex glass, which has the advantage of chemical inertness but the disadvantage of changing volume appreciably with time. The body of each pycnometer was made from 2-cm. tubing bent into a U which was 6 cm. in total width and about 13 cm. high.

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[1] Part of this paper was presented before the Symposium on "The Electrochemistry of Solutions" held by the Division of Physical and Analytical Chemistry at the Kansas City meeting of The American Chemical Society, April, 1936.

[2] Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

[3] Gucker, *Chem. Rev.*, **13**, 111 (1933).

[4] Perman and Urry, *Proc. Roy. Soc.* (London), **A126**, **44** (1929).

[5] Redlich and Klinger, *Sitzb. Akad. Wiss. Wien*, Abt. IIb, **143**, 489 (1934); *Monatsh.*, **65**, 137 (1934).