

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Solubility of Sodium Iodide in Sodium Hydroxide Solutions at 20°

BY RICHARD POMEROY AND H. DARWIN KIRSCHMAN

In a recent article¹ we have presented the results of a study of the solubility of potassium iodide in potassium hydroxide solutions at 20° over the range 0 to 14.35 *N* in alkali. The present paper extends the study to the iodide of sodium in solutions of sodium hydroxide from 0 to 15.21 *N*.

The results of our measurements are presented in Table I and Fig. 1.

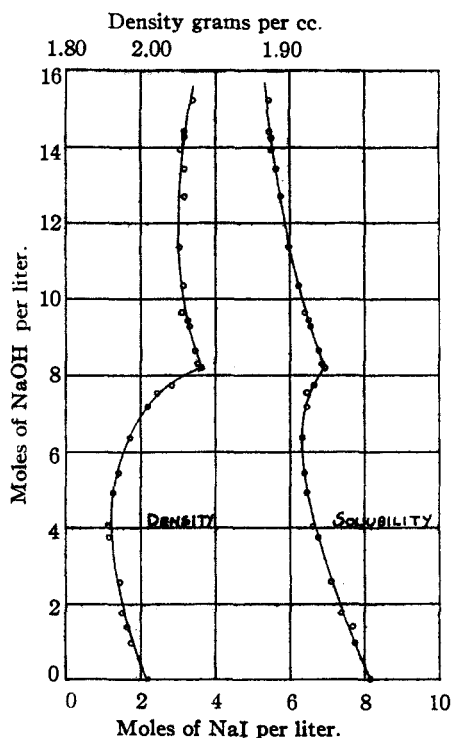


Fig. 1.

Experimental

Sodium iodide of c. p. grade was purified by recrystallization as the dihydrate. A highly concentrated solution of sodium hydroxide was prepared, filtered free from carbonate, and crystallized as the monohydrate by cooling. The bottle containing these crystals was warmed to produce a melt which was mixed with suitable amounts of water and sodium iodide crystals in the equilibrium bottles. These bottles were then immersed in a water-bath at 20° for from four to twelve days and shaken frequently. Portions were removed with pipets and diluted with water to suitable concentrations for analysis. The drainage error in the use of a pipet with these rather viscous solutions was corrected for by washing out and titrating the residual liquid in the pipet. The alkalinity was determined by titration with standard sulfuric acid solution using methyl orange indicator. The iodide content was determined gravimetrically as silver iodide. The density determination was made by weighing a 25-ml. sample of the saturated solution. These weighings were corrected for the buoyant effect of the air.

(1) Kirschman and Pomero, *This Journal*, 66, 1695 (1943).

TABLE I

SOLUBILITY AND DENSITY DATA AT 20°

NaOH moles/liter	NaI moles/liter	Density, g./ml.
0.00	8.14	1.910
0.97	7.74	1.888
1.40	7.69	1.881
1.76	7.40	1.876
1.77	7.34	1.871
2.62	7.11	1.872
3.72	6.76	1.860
3.78	6.72	1.856
4.04	6.63	1.856
4.90	6.48	1.865
4.93	6.43	1.858
4.94	6.54	1.870
5.45	6.40	1.870
6.38	6.36	1.885
7.10	6.44	1.905
7.16	6.45	1.908
7.19	6.42	1.912
7.24	6.41	1.908
7.27	6.56	1.919
7.54	6.49	1.922
7.74	6.66	1.942
8.20	6.92	1.981
8.30	6.88	1.977
8.66	6.76	1.972
9.29	6.54	1.965
9.44	6.50	1.962
9.61	6.47	1.962
9.70	6.34	1.948
10.36	6.24	1.956
11.38	5.99	1.952
12.71	5.76	1.958
13.41	5.62	1.957
13.49	5.64	1.958
13.95	5.50	1.953
14.24	5.52	1.959
14.41	5.45	1.959
15.21	5.42	1.970

Equilibrium seemed to be somewhat more slowly attained than in the experiments with potassium iodide in potassium hydroxide but a few trials employing mechanical stirring of the mixture for several hours showed satisfactory agreement with other methods of saturation. The density and solubility curves show a discontinuity at a point corresponding to 8.20 *N* in sodium hydroxide and 6.92 *N* in sodium iodide. The solid phase in the mixtures with hydroxide concentrations above 8.20 was identified as anhydrous, cubic, sodium iodide.

The accuracy of results is estimated to be 1%.

Summary

The solubility of sodium iodide at 20° was determined in sodium hydroxide solutions from 0 to 15.21 *N* in alkali. The density and solubility curves show a discontinuity at a point correspond-

ing to 8.20 *N* in sodium hydroxide and 6.92 *N* in sodium iodide, which point marks the transition

from the dihydrate to anhydrous sodium iodide. PASADENA, CALIF. RECEIVED OCTOBER 4, 1943

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The Density and Transition Points of the *n*-Paraffin Hydrocarbons

BY WM. F. SEYER, RALPH F. PATTERSON¹ AND JOHN L. KEAYS²

The density and transition point of dicetyl ($C_{32}H_{66}$) formed the subject matter of a previous communication to this Journal.³ Since then, all the even-numbered hydrocarbons, beginning with $C_{16}H_{34}$ and ending with $C_{34}H_{70}$, have been investigated, also $C_{29}H_{60}$ of the odd-numbered series.

Materials.—All of these hydrocarbons excepting $C_{16}H_{34}$ and $C_{29}H_{60}$ were synthesized in the laboratory. Samples of hexadecane were obtained from Messrs. Deanesly and Carleton of the Shell Oil Company, and Professor Parks of Stanford University. Both samples were from lots that had been carefully purified by the donors, but upon comparing the m. ps. of the two, it was found that the m. p. from the former had a slightly higher value than that from the latter. The m. p. of the best material was found to be 18.145 and its setting point 18.3.

The nonacosane was obtained from the Bureau of Standards through the efforts of Dr. B. J. Mair. It had an m. p. of 63.0° but as Piper and his co-workers⁴ gave a value of 63.4–6° it was recrystallized until the m. p. rose to 63.5°.

The method employed for synthesizing the desired hydrocarbons depended upon the nature of the material available. Where alcohols served as a starting point the Kraft procedure was followed and where acids, the Peterson electrolytic method was utilized. After the usual preliminary purification the hydrocarbons were treated with sulfuric acid until no color formed upon the addition of the acid. To remove it, the hydrocarbons were washed with hot water. They were then dried and recrystallized from five to twenty times until a constant m. p. and t. p. were obtained.

Tetratriacontane, the highest member so far synthesized, was prepared by the electrolysis of the corresponding acid which in this case was stearic. Considerable difficulty was encountered in the purification of this compound. It could not be obtained completely colorless although it was drastically treated with sulfuric acid and recrystallized from glacial acetic acid over forty times. The reason for this failure may lie in the following statement of Oldham and Ubbelohde.⁵ "Owing to the appreciable oxidation of certain liquid paraffins at 130°, it was advisable to hinder the circulation of air over the surface of the paraffin during the purification." It may be that this hydrocarbon was oxidized at the temperatures where purification was attempted.

Melting Points of the Normal Paraffin Hydrocarbons.—A knowledge of the melting points of the normal paraffin hydrocarbons was found to be essential for the present investigation. Piper,⁴ *et al.*, claim that the transition point is a more reliable index of purity than the melting point.⁴ This may be true for those hydrocarbons having more than twenty-six carbon atoms but for those below this in the series this cannot be so, because there is either no transition point or it is indistinct. As mentioned in

the previous article, the melting points, even when done by the method outlined by Piper, *et al.*, were affected by the rate of heating and the personal equation, but experience showed that the setting point was not. It could be reproduced by any worker in the Laboratory to within 0.2 to 0.1° for any one sample by observing the temperature when the first crystal formed upon slow cooling (temperature dropping less than 0.5° per minute). Hence, the setting point has been used in this Laboratory for the purpose of establishing the purity of the compounds under investigation. The observed setting points along with the melting and transition points are given in Table II, where *N* denotes the number of carbon atoms in the chain.

Equations have been developed by Moullin,⁶ Taskototos,⁷ and Garner⁸ for correlating the melting points with number of carbon atoms in the paraffin hydrocarbon chain. None of the equations was found to be satisfactory over the whole range of melting points. Moullin's equation, which is of the form $\log(N-2) = a + bt$, could be made to fit the curve of melting point against carbon number, if one assumed discontinuities at about $N = 16$ and $N = 33$. *N* here represents the number of carbon atoms in the chain and *a* and *b* are constants. There is also up to $C_{16}H_{34}$ one curve for the odd numbers and one for the even numbers. Above this member, melting points of the odd and even numbered paraffins fall on the same straight line.

The values of the constants, *a* and *b*, obtained by the method of least squares for different sections of the curve are given in Table I. Members lower than C_6H_{14} , for both the odd and even numbered compounds, are not included, as the deviations of observed from calculated m. ps. are too great. The recorded m. p. of $C_{11}H_{24}$ is also out of line.

TABLE I

VALUES OF CONSTANTS <i>a</i> AND <i>b</i>		<i>a</i>	<i>b</i>
No. of carbon atoms range:			
$C_6 \rightarrow C_{16}$ (even)		1.051	0.00481
C_7 C_{15} (odd)		1.067	.00410
C_{16} C_{34} (odd and even)		1.02	.0065
C_{33} C_{70}		0.08	.0006

In correlating the melting points of the normal paraffin series with numbers of carbon atoms in the chain, it was attempted insofar as possible to select values obtained by one set of workers. For as has been mentioned above, the m. ps. obtained depend not only upon the purity of the product but also upon the m. p. technique. Further, workers interested in a set of values are sure to develop laboratory methods and gain experience much broader in scope that those who accidentally are led to make measurements only on one compound. Consequently, we have used the selected values of Deanesly and Carleton⁹ for the range 6–18, and our own for the range 18–34.

For 40, 50, 60 and 70 we selected the melting point given by Carothers,¹⁰ and for 36, 52, 62 and 64 those of Gascard.¹¹

(1) Standard Oil Company of British Columbia Research Fellow, 1938–1939.

(2) Standard Oil Company of British Columbia Research Fellow, 1941–1942.

(3) Seyer and Morris, THIS JOURNAL, 61, 1114 (1939).

(4) Piper, *et al.*, *Biochem. J.*, 25, 2072 (1931).

(5) Oldham and Ubbelohde, *J. Chem. Soc.*, 200 (1938).

(6) Moullin, *Proc. Camb. Phil. Soc.*, 34, 459 (1938).

(7) Taskototos, *Compt. rend.*, 143, 1235 (1900).

(8) Garner, Van Bibber and King, *J. Chem. Soc.*, 1533 (1931).

(9) Deanesly and Carleton, *J. Phys. Chem.*, 46, 1104 (1941).

(10) Carothers, Hill, Kirby and Jacobson, THIS JOURNAL, 58, 5279 (1930).

(11) Gascard, *Ann. chim.*, 16, 332 (1921).