NOTE ON THE SYSTEM SODIUM IODIDE–WATER

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In the course of a phase rule study of the system sodium iodide–iodine–water, now nearing completion in this laboratory, we have had occasion to construct the temperature–composition diagram of the system sodium iodide–water. On assembling the available published data, however, we discovered that a few additional measurements were needed, especially at the lower temperatures, before the diagram could be drawn with the desired accuracy and completeness. A brief special investigation was accordingly carried out, the results of which are presented here in the form of a separate communication.[1]

As is well known, the solid phases encountered in the binary system are NaI, $NaI \cdot 2H_2O$, $NaI \cdot 5H_2O$, and ice. The solubilities of the anhydrous salt and dihydrate have been accurately determined over a wide range of temperatures by Kremers (8), de Coppet (2), Brønsted (1) (at 100°C.), Scott and Frazier (15) (at 25°C.), Scott and Durham (14), Hill, Wilson, and Bishop (4) (at 8°, 25°, and 40°C.), and Ricci (11) (at 25° and 40°C.). According to Scott and Durham the $NaI \cdot 2H_2O$–NaI transition temperature, as estimated from the point of intersection of the respective solubility curves, is 68.1°C.

We have been unable to find, however, more than two points on the solubility curve of the pentahydrate,—one of these having been determined by Étard (3) (51.5 per cent sodium iodide at −20°C.) and the other by de Coppet (2) (56.93 per cent sodium iodide at −15.2°C.). We have also been unable to find any exact determination of the pentahydrate–dihydrate transition temperature, though Panfilow (10) reports that it is about −10°C.

Freezing-point determinations up to moderate concentrations of sodium iodide have been made by Rüdorff (12), and these were later extended almost to the eutectic point by Jones and his associates (7). According to Meyerhoffer (9), the eutectic temperature is −31.5°C. and the eutectic composition is 39 per cent sodium iodide. It should be pointed out here, however, that the latter value is entirely inconsistent with the data of Jones and his coworkers, whose work was very carefully done.

Boiling-point determinations have been made by Schlamp (13), Johnston (6), and Jablczynski and Kon (5). Johnston's measurements are the most comprehensive, extending as they do to solutions containing up to 60 per cent sodium iodide. According to Kremers (8), the saturated solution boils at 141°C.

[1] The ternary system will be presented in a later paper.

EXPERIMENTAL

A number of carefully prepared mixtures of sodium iodide and water, designed so as to include the region of the pentahydrate, were subjected to thermal analysis in air-jacketed tubes held in a well-stirred cooling bath

TABLE 1

Temperature arrests

SERIAL NO.	NaI	FIRST ARREST	SECOND ARREST
	per cent	°C.	°C.
1	18.7	−5.6	Not determined
2	37.2	−17.8	Not determined
3	41.9	−23.5	−31.7
4	44.2	−26.8	−31.2
5	46.5	−30.6	−31.5
6	49.0	−36.1	−31.6
7	53.3	−24.8 ?	−31.5
8	57.2	−17.3 ?	−31.8
9	61.0	−12.2	−31.8
10	64.0	−12.4	None
11	77.5	68.0	Not determined
12	82.4	68.0	Not determined

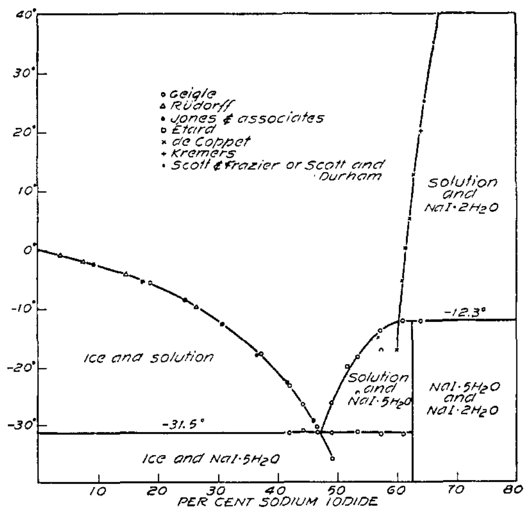

FIG. 1. Water and sodium iodide

with a 10-degree temperature differential. The mixtures were agitated by means of a magnetic stirrer and all thermometers were especially calibrated by means of a number of standard fixed temperatures.

The temperature arrests are presented in table 1. They have been designed as "first" and "second" arrests only as a matter of convenience in showing the order in which they were obtained.

These arrests (excepting Nos. 11 and 12) have been plotted in figure 1. Extreme undercooling with respect to the pentahydrate occurred in the case of Nos. 6, 7, and 8, so that the attempt to obtain points on the solubility curve of the pentahydrate was not successful. With No. 6, for example, the first arrest at −36.1°C. proved to be a point on the metastable extension of the ice line below the eutectic temperature, and the second arrest at −31.6°C. appeared only after the pentahydrate had actually begun to form. In the case of Nos. 7 and 8 the pentahydrate made its appearance before the eutectic temperature was reached; but there was still much undercooling, and the arrests (shown in figure 1 as half-circles) were indefinite and much too low. Accordingly, heating

TABLE 2

Boiling points of solutions of sodium iodide

NaI	BOILING POINT
per cent	*°C.*
37.2	104.8
44.2	107.0
53.3	113.0
57.2	117.4
64.0	121.6
70.0	131.8
75.0	142.0
76.2 (saturated)	142.4

curves were run after each mixture had been cooled to the second (i.e., eutectic) arrest, with the following results (three points on the pentahydrate solubility curve):

SERIAL NO.	NaI	TEMPERATURE
	per cent	*°C.*
6	49.0	−26.5
7	53.3	−18.5
8	57.2	−14.0

According to figure 1, the eutectic point lies at −31.5°C. and 47.1 per cent sodium iodide. Meyerhoffer's value for the temperature is thus satisfactorily confirmed but not his value for the composition, which is found to be seriously in error, as had been suspected from the first. The pentahydrate–dihydrate transition temperature is found to be −12.3°C., at which point the solution contains 60.2 per cent sodium iodide. The dihydrate–anhydrous sodium iodide transition temperature (68.0°C.) is given by the "first" arrests of Nos. 11 and 12 in table 1; it is in good agreement with the value (68.1°C.) obtained by Scott and Durham. At this transition point the solution contains 74.8 per cent sodium iodide.

TABLE 3

Temperature–composition data

TEMPERATURE	NaI	SOURCE	TEMPERATURE	NaI	SOURCE
Solution and ice			Solution and vapor		
°C.	*per cent by weight*		°C.	*per cent by weight*	
−0.85	3.74	(12)	101.1	13.40	(6)
−1.9	7.48	(12)	102.4	24.03	(6)
−2.44	9.34	(7)	103.4	29.23	(6)
−4.25	14.59	(12)	104.8	35.30	(6)
−5.37	17.44	(7)	104.8	37.2	*
−5.6	18.7	*	106.7	41.38	(6)
−8.70	24.55	(7)	107.0	44.2	*
−9.75	26.50	(12)	108.3	45.41	(6)
−12.72	30.84	(7)	110.1	48.28	(6)
−17.8	37.2	*	111.6	50.72	(6)
−18.0	36.46	(7)	113.0	53.3	*
−23.0	41.55	(7)	113.3	53.31	(6)
−23.5	41.9	*	114.4	54.71	(6)
−26.8	44.2	*	116.2	57.64	(6)
−29.5	46.00	(7)	117.2	58.75	(6)
−30.6	46.5	*	117.4	57.2	*
−31.5 E	47.1	*	118.2	59.56	(6)
−36.1 m	49.0	*	118.6	60.31	(6)
Solution and NaI·5Aq			121.6	64.0	*
			131.8	70.0	*
−26.5	49.0	*	142.0	75.0	*
−20	51.5	(3)	142.4 S	76.2	*
−18.5	53.3	*	141 S	76.2	(8)
−15.2	56.93	(2)			
−14.0	57.2	*			
−12.3 U 2Aq	60.2	*			

* Briggs and Geigle; E, eutectic point; m, metastable; U, transition point; S, saturated.

A few determinations (probably accurate to ±0.5°C.) were also made in order to follow the boiling-point line to its point of saturation with the anhydrous salt. Precautions were taken to minimize superheating and to promote steady ebullition; the atmospheric pressure was about 745 mm. The results, which are fairly concordant with those of Johnston, are given in table 2.

In conclusion, the data which are now available for the construction of the freezing-point, boiling-point, and pentahydrate solubility curves have been assembled in table 3. All compositions are in percentages by weight.

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THE PHYSICAL PROPERTIES OF THE TERNARY SYSTEM BUTYL ALCOHOL-ETHYL ACETATE-TOLUENE

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INTRODUCTION

This and two previous investigations (5, 6) were carried out to obtain physical data for use in chemical engineering design studies. The densities, viscosities, surface tensions, refractive indices, and boiling points of the ternary system butyl alcohol-ethyl acetate-toluene were determined and are reported in this paper.

EXPERIMENTAL

Materials

Normal C.P. butyl alcohol was treated as described in the paper of Ernst, Litkenhous, and Spanyer (5). The C.P. ethyl acetate was repeatedly distilled in a specially constructed long glass rectifying column,