eral hours. However, the value of $\epsilon_{\max.}$ of iodine in unpurified acetone dropped rapidly, two-thirds of the iodine having reacted in fifteen minutes. We suggest, therefore, that Getman had not purified his acetone sufficiently to remove the impurity that catalyzes the reaction between iodine and acetone.

Acknowledgment.—We wish to express our appreciation to the Office of Naval Research for financial support of this research, and to the American Chemical Society for the post-doctoral fellowship held by the junior author during part of the period spent upon this research.

Summary

The absorption spectra of iodine in trifluoromethylbenzene, benzene, toluene, *o*- and *p*-xylene and mesitylene have been measured in the region 270–700 mμ. In the visible region, the absorption peaks of these solutions showed moderate shifts toward shorter wave lengths in the order listed above. With the exception of iodine in trifluoromethylbenzene, each of the aromatic hydrocarbon solutions had an intense absorption band in the ultraviolet region which we have shown to be characteristic of a complex containing one iodine and one aromatic hydrocarbon molecule.

The equilibrium between iodine and the aromatic hydrocarbons has been investigated in the neutral solvents, carbon tetrachloride and *n*-heptane, and the results show that the iodine–mesitylene complex is more stable than the iodine–benzene complex. These findings are strong evidence for an acid–base interaction between iodine and aromatic hydrocarbons.

Absorption measurements have also been made of iodine in carbon tetrachloride, carbon disulfide, *n*-heptane, ethyl ether, acetone and 1,1-dichloroethane. No absorption bands analogous to those of the aromatic hydrocarbon solutions were found in the region 270–400 mμ.

BERKELEY 4, CALIF. RECEIVED FEBRUARY 23, 1949

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Effect of Sodium Iodide on the Phase Separation in the System Sodium–Ammonia

BY M. J. SIENKO

Kraus[1] has shown that solutions of sodium in liquid ammonia separate into two liquid phases which have an upper critical temperature of $-41.6°$.[2] Similar behavior is observed in lithium and potassium solutions.[3] In a report prepared for the Office of Naval Research Ogg suggests[4] that the separation of these alkali metal–liquid ammonia solutions into two liquid phases that are both *dilute* solutions of metal in ammonia indicates an origin for the phase separation different from that of other liquid phase separations, such as that in the system water–phenol, where one of the conjugate solutions is rich in one component and the other, rich in the other component. The present investigation was undertaken to determine the effect of a dissolved salt, sodium iodide, on the phase separation in the system sodium–ammonia and to determine the distribution of sodium iodide between the two phases. Sodium iodide was selected since it is sensibly inert with respect to the two components of the system and has an appreciable solubility even in the concentrated solutions.

The temperature of phase separation for the system sodium–ammonia in the presence of sodium iodide was investigated by the method of Kraus and Lucasse,[2] in which the resistance of a given solution of sodium in ammonia was determined as a function of decreasing temperature. The discontinuity in the slope of the resistance–temperature curve corresponds to the temperature at which phase separation occurs.

Experimental Procedure

The conductance cell is shown in Fig. 1. M indicates a thin-walled capillary of 1.5 mm. inner diameter across which the resistance is measured by means of tungsten electrodes in mercury-filled wells K and L. In order to check the apparatus and the possibility that the substitution of tungsten electrodes for platinum electrodes may have an effect on the temperature of phase separation, solutions were also prepared without any sodium iodide. The observed temperatures of phase separation were in excellent agreement with the results reported by Kraus and Lucasse.

The solutions were prepared by introducing into arm H 0.50 ml. of an aqueous solution of sodium iodide (containing 0.52 millimole per ml. of solution) from a graduated 1-ml. pipet. With stopcocks G closed and F open, the solution was rinsed down into the cell with a few ml. of distilled water. H was sealed and the water pumped off by gradual evacuation of the cell through A. The sodium iodide deposited in the capillary was degassed for twenty-four hours at a pressure of 5×10^{-6} mm. and a temperature of about 80°. Ammonia, stored over sodium in B, was allowed to diffuse through the cell while H was opened and a section of glass tubing containing approximately the desired weight of sodium was introduced. H was resealed and the cell re-evacuated and degassed for another twenty-four hours. Heat was subsequently supplied from a spiral heater around H to just melt the sodium which flows through constriction J into the cell. (Experiments in which sodium was actually distilled into the cell from a horizontal arm H without constriction J proved to be rather lengthy and did not affect the reproducibility of the final results.) J was heated with the tip of an oxygen flame and H pulled off. Copper wires were introduced

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[1] C. A. Kraus, THIS JOURNAL, **29**, 1565 (1907)

[2] C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1949 (1922).

[3] D. Loeffler, M. J. Sienko and R. A. Ogg, Jr., unpublished.

[4] R. A. Ogg, Jr., mimeographed report dated at Stanford University on April 11, 1947.

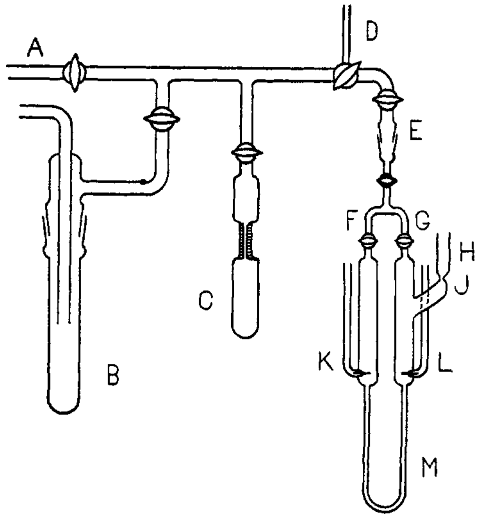

Fig. 1.—Conductance cell.

into K and L and two iron–constantan thermocouples were securely attached to the cell—one next to the electrode in the left arm and the other at the bottom of the capillary loop. A bath of precooled acetone in a Dewar flask was brought up around the cell and dry ammonia, previously distilled from B into measuring bulb C, was condensed in the cell. Thorough mixing of the solution was achieved by alternately increasing the pressure in the arms of the cell by proper manipulation of F and G. Finally, in order to reduce the formation of bubbles of ammonia vapor in the capillary,[5] the cell was filled with electrolytic hydrogen which was first passed through a vapor trap immersed in liquid nitrogen and then introduced through D.

The resistance of the more concentrated solutions was measured with a Wheatstone bridge; that of the dilute solutions, with an a. c. bridge. For a given solution resistances measured with the a. c. bridge were somewhat lower (about eight per cent. for a solution containing 2.6 atomic per cent. sodium) than those obtained with the Wheatstone bridge, but the break in the resistance–temperature curve occurred at the same temperature. The temperature of the solution was reduced from −35 to −58° by dropping bits of Dry Ice into the acetone bath which was vigorously stirred throughout each experiment. The average rate of cooling was about half a degree per minute and thermal equilibrium was attained in a matter of seconds. The iron–constantan thermocouples were standardized with melting ice, freezing and melting mercury, and solid carbon dioxide at one atmosphere pressure. Reference junctions were kept at 0°. The two thermocouples agreed to a hundredth of a degree, indicating no appreciable thermal gradient over the capillary length. The resistance–temperature curve was determined three times for each solution. The maximum deviation in the temperature at which phase separation occurs for a given solution was 0.3° but the average deviation was less than 0.1°. Typical data for one solution are shown in Fig. 2.

At the conclusion of each experiment, the solution was analyzed by evaporating off the ammonia through D through a mercury valve and absorbing it in 5.985 *N* sulfuric acid. Traces of ammonia were flushed out of the cell with hydrogen. Sodium content was determined by adding methyl alcohol to the cell and titrating the resulting solution with dilute standard sulfuric acid using methyl red as indicator. Sodium iodide content was determined by adding 25.0 ml. of 0.0508 *N* potassium iodate solution and 10.0 ml. of 5.985 *N* sulfuric acid to the solution resulting from the sodium analysis. Iodine was boiled off, the solution cooled, excess potassium iodide added, and the iodine liberated was immediately titrated with 0.0536 *N* sodium thiosulfate. In a typical experiment, a solution which contained 5.20 ± 0.02 atomic per cent. sodium had 0.388 ± 0.001 mole of ammonia, 0.0213 ± 0.0001 gram atom of sodium, and 0.29 ± 0.01 millimole of sodium iodide.

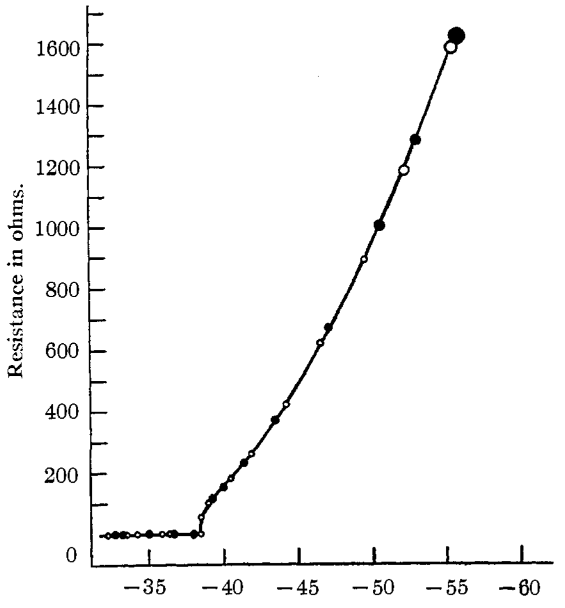

Fig. 2.—Resistance of a Na–NaI–NH_3 solution containing 5.20 atomic % Na: ●, first run; ○, second run.

All chemicals were C.P. obtained from Baker and Adamson except the hydrogen and liquid ammonia which were obtained from the Matheson Company.

The distribution of sodium iodide between the conjugate solutions was determined by preparing a solution in the apparatus shown in Fig. 3. The two phases were separated by lowering the collector A and slightly diminishing the pressure in A so that the bronze upper layer flowed from B into A. A surprisingly clean-cut separation can be achieved by gradually lowering A until most of the bronze phase has been removed. The temperature was kept constant in these experiments at −43.3 ± 0.1°. After the phases have been separated, collector A was raised and the entire apparatus immersed in liquid nitrogen. A and B can now be parted and analyzed by use of the procedure outlined above.

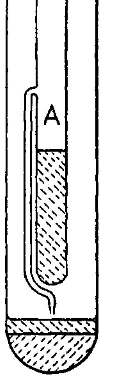

Fig. 3.—Distribution cell.

Results.—The temperatures of phase separation in the presence of sodium iodide are shown in tabular form in Table I and compared graphically in Fig. 4 with the results reported by Kraus and Lucasse[2] for the system sodium–ammonia. It must be emphasized that, although the curve of Kraus and Lucasse shows the proportion of sodium and ammonia of *coexisting* solutions at various temperatures, such is not the case for the results of this investigation. The addition of sodium iodide to the sodium–ammonia system in-

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[5] C. A. Kraus and W. W. Lucasse, This Journal, **44**, 1942 (1922).

TABLE I

TEMPERATURE OF PHASE SEPARATION AT DIFFERENT CONCENTRATIONS OF SODIUM

(0.28 millimole of NaI per 0.385 mole of NH_3)

At. % Na	Temp., °C.	At. % Na	Temp., °C.
1.93	−49.7	5.20	−38.5
2.61	−42.4	5.76	−40.0
2.69	−42.2	6.72	−43.6
3.52	−38.9	7.21	−44.9
3.85	−38.4	5.20[a]	−43.2
4.20	−38.1	3.38[a]	−42.2
4.53	−37.9	5.41[b]	−40.9
4.91	−38.2	5.60[c]	−40.1

[a] Contains no sodium iodide. [b] Contains 0.16 millimole of NaI per 0.385 mole NH_3. [c] Contains 0.28 millimoles of NaI per 0.503 mole NH_3.

creases the number of components and therefore introduces an additional degree of freedom in the system.

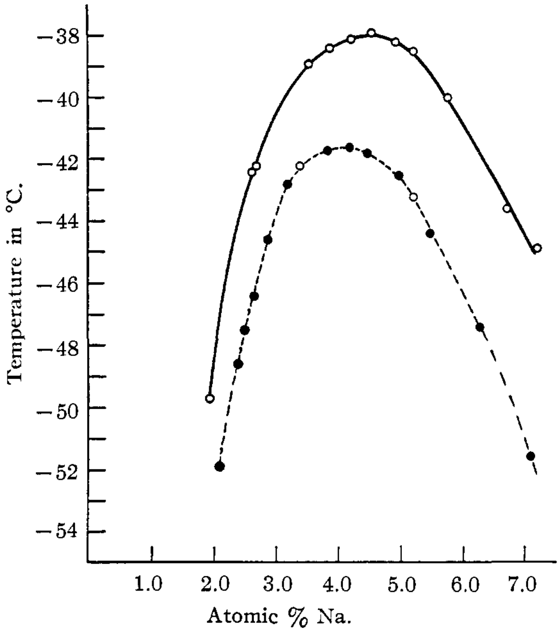

Fig. 4.—Temperature of phase separation of Na-NH_3 solutions: solid curve, with 0.28 millimole of NaI per 0.385 mole of NH_3; dashed curve, without NaI; ●, Kraus and Lucasse; ○, this investigation.

The distribution of sodium iodide between the conjugate solutions at −43.3° is shown in Table II with the data presented graphically in Fig. 5 which shows an isothermal section through the region of immiscibility. The two points showing 0.07 millimole of sodium iodide per mole of ammonia are estimated from the curve of Fig. 4. In Fig. 5 the field partly encircled by the solid curves corresponds to equilibrium between two liquid phases. The dotted lines are the usual tie-lines joining conjugate solutions of compositions indicated by the solid curves.

TABLE II

COMPOSITION OF CONJUGATE SOLUTIONS (AT −43.3°)

Added NaI	At. % of Na		Millimoles of NaI per mole of NH_3	
	Blue phase[a]	Bronze	Blue	Bronze
None	3.25	5.25	..	...
0.28 milimole in 0.385 mole NH_3	2.65	6.65	1.2	0.36
0.15 millimole in 0.388 mole NH_3	2.80	6.30	0.55	0.20
0.15 millimole in 0.380 mole NH_3	..	6.90[b]	..	0.42[b]

[a] Probably high because removal of bronze layer is not complete. [b] Sufficiently concentrated so no phase separation occurs at −43.3°. Samples from top and bottom show same concentration indicating that all of the sodium iodide has dissolved.

Discussion.—The discontinuity in the slope of the resistance–temperature curve typified in Fig. 2 is apparently due to an actual separation into two layers—the more dense, blue, less concentrated phase remains at the bottom and fills the capillary. From −35° to the temperature of phase separation, the slight increase in resistance (almost negligible for the more concentrated solutions) with falling temperature is similar to that found for solutions of electrolytes in water. At the temperature of phase separation and below, the dilute phase fills the capillary and progressively becomes more dilute as the more concentrated phase continues to separate and rise to the top out of that portion of the circuit for which the resistance is being determined. The resistance of these solutions increases greatly with decreasing concentration of sodium.

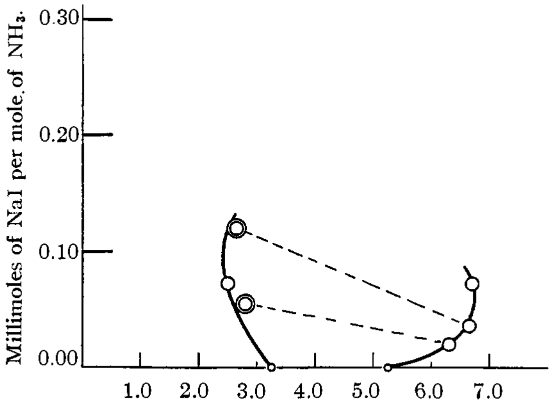

Fig. 5.—Equilibrium composition of phases in system Na-NaI-NH_3 at −43.3°: ◎, doubtful because of incomplete separation of phases.

The fact that the resistances measured with the a.c. bridge are somewhat lower than those measured with the Wheatstone bridge is probably due to polarization at the electrodes. This polarization is negligible in the more concentrated solutions as is shown by the identity of resistances for solutions more concentrated than 3.0 atomic per cent. sodium.

Summary

The general effect of adding sodium iodide to a solution of sodium in liquid ammonia is a decrease in the miscibility over the range of sodium iodide concentration studied. The sodium iodide is found to be more soluble in the conjugate solution having a lower concentration of sodium. A portion of the phase diagram for the ternary system Na–NaI–NH_3 is given.

ITHACA, N. Y. RECEIVED MARCH 12, 1949

[CONTRIBUTION FROM THE CHEMICAL RESEARCH SECTION, CHEMICAL ENGINEERING DIVISION, TENNESSEE VALLEY AUTHORITY]

Thermodynamics of Aqueous Hydrogen Fluoride at 25°

BY KELLY L. ELMORE, JOHN D. HATFIELD, CHARLES M. MASON[1] AND ARTHUR D. JONES

In research on the recovery of by-product hydrogen fluoride from the processing of phosphate rock, a need arose for certain calculations that could be made only through a knowledge of the thermodynamic properties of hydrogen fluoride in aqueous solution. The present paper describes the calculation of the activity, free energy, enthalpy, entropy and molal heat capacity of the system hydrogen fluoride–water at 25°.

Activity in Dilute Solution

Hydrofluoric acid is a weak electrolyte which exists in simultaneous equilibrium with ions and "triple ions"[2,3] as shown by the relations

$$HF = H^+ + F^-;$$

$$K_1 = a_{H^+}a_{F^-}/a_u = m_{H^+}m_{F^-}\gamma_{H^+}\gamma_{F^-}/m_u\gamma_u \qquad (1)$$

$$HF + F^- = HF_2^-;$$

$$K_2 = a_{HF_2^-}/a_u a_{F^-} = m_{HF_2^-}\gamma_{HF_2^-}/m_u m_{F^-}\gamma_u\gamma_{F^-} \qquad (2)$$

where a, m and γ represent the activity, molality and practical activity coefficient, respectively, of the designated ions or the undissociated acid, u. Wooster[2] has applied the principle of "unilateral triple ion formation," as developed by Fuoss and Kraus,[3] to the conductance data of Deussen[4] for aqueous hydrogen fluoride, and the same treatment was used as a basis for the present calculations in the dilute range.

In Table I the values of m_{F^-}/m and $m_{HF_2^-}/m$, where m is the total molality, at the concentrations given by Deussen[4] were calculated through the constants of Wooster[2] ($K_1 = 6.89 \times 10^{-4}$ and $K_2 = 2.695$), the activity coefficients of Kielland[5] for γ_{H^+} and γ_{F^-} (assuming that $\gamma_{HF_2^-} = \gamma_{F^-}$), the determination of m_{H^+}/m by means of the Shedlovsky[6] refinement, the elimination of γ_u and m_u by taking the ratio K_1/K_2, and the solution of the resulting quadratic for m_{F^-}/m. Subtraction of m_{F^-}/m from m_{H^+}/m gives $m_{HF_2^-}/m$.

TABLE I

VALUES OF COMPUTED FUNCTIONS FOR HYDROGEN FLUORIDE SOLUTIONS

C	m	γ_{H^+}	γ_{F^-}	m_{F^-}/m	$m_{HF_2^-}/m$
1.0	1.0158	0.8332	0.7744	0.01655	0.04987
0.5	0.50466	.8618	.8272	.02872	.04061
.25	.25153	.8847	.8650	.04628	.03156
.125	.12557	.9066	.8910	.07031	.02297
.0625	.062733	.9213	.9104	.1024	.0161
.03125	.031355	.9326	.9269	.1438	.0106
.01563	.015674	.9447	.9392	.1972	.0068
.007813	.0078367	.9540	.9499	.2646	.0041
.003906	.0039177	.9614	.9579	.3510	.0024
.001953	.0019588	.9682	.9660	.4530	.0013
.0009766	.00097948	.9730	.9730	.5736	.0008

The quantity $a_{H^+}a_{F^-}$ was calculated from the values in Table I and compared with the values calculated from the e.m.f. measurements of Broene and DeVries[7] as shown in Fig. 1. Whereas the two sets of calculated values are in substantial agreement at the higher concentrations, there is a marked difference in very dilute solutions, possibly because of the inherent lack of reliability of e.m.f. measurements in very dilute solutions.

Equations for the Activities of Hydrogen Fluoride and Water in Dilute Solution.—The molar concentrations given by Deussen[4] were converted to molal concentration by means of an equation that was derived from the density of hydrogen fluoride solutions as given in the "International Critical Tables."[8] Where necessary data at other temperatures were extrapolated to 25°. The equation

$$\rho = 0.99707 + 0.00369\,w \qquad (3)$$

where ρ is the density and w is the percentage of hydrogen fluoride by weight, proved applicable at values of w from 0 to 10%. Table I shows the molar and molal concentrations.

Values of a_u, calculated from equation 1 and the conductance data of Deussen[4] by means of values in Table I, were expressed as a function of m over

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[1] Present address: Explosives Branch, Bureau of Mines, U. S. Department of the Interior, Bruceton, Pennsylvania.

[2] C. B. Wooster, THIS JOURNAL, **60**, 1609-1613 (1938).

[3] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387-2399 (1933).

[4] E. Deussen, *Z. anorg. Chem.*, **44**, 303-331 (1905).

[5] J. Kielland, THIS JOURNAL, **59**, 1675-1678 (1937).

[6] T. Shedlovsky, *J. Franklin Institute*, **225**, 739-743 (1938). The constants calculated by Wooster were obtained from the conductance data of Deussen by means of a derived equation in which it was assumed that the undissociated fraction of HF in solution was represented by $1 - \Lambda/\Lambda_0$. The Shedlovsky refinement for evaluating m_{H^+}/m, when applied to a calculation of K_1 and K_2, gives values which agree with those of Wooster within experimental error, and it is concluded that no significant error is introduced by using the refinement in the calculation of m_{F^-}/m and $m_{HF_2^-}/m$.

[7] H. H. Broene and T. DeVries, THIS JOURNAL, **69**, 1644-1646 (1947).

[8] "International Critical Tables," Vol. III, p. 54.