[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary System $NaCl-NaI-H_2O$

BY JOHN E. RICCI AND NICHOLAS S. YANICK

The purpose of studying the system $NaCl-NaI-H_2O$ was two-fold: first, to obtain solubility data for the pair of salts in water; and, second, to investigate the behavior of the binary system NaCl–NaI at the temperatures reported. The binary system NaCl–NaI is described in the "International Critical Tables"[1] as giving the two solid phases solid solution of sodium chloride in sodium iodide (from 0 to 24 mol % of sodium chloride), and pure sodium chloride; this, of course, refers to the system studied at the melting point temperatures. In the original paper on the system, however, by Amadori, 1912,[2] the second phase is stated to be a second series of solid solutions, containing from 0 to 3 or 4 mol % of sodium iodide in sodium chloride, although the evidence for this appears to be not very conclusive—simply the failure to observe any eutectic arrest in the cooling curve for mixtures in that range of composition. Since the eutectic arrests for the rest of the system are given in whole tens of seconds, 10, 20, 30, etc., which indicates perhaps a lack of great precision in their measurement, it seems not unlikely that small arrests might have been overlooked by the experimenter. Such evidence points only to a possibility of the existence of a solid solution as the second phase, but cannot be accepted as conclusive or positive proof. The interest in the possibility of the occurrence of such a combination of phases in a binary system as a single solid solution and a pure component, lies in the problem of the place of such a type of system in the familiar Roozeboom classification of the "possible" types of solid solutions, a classification which does not provide for this case.[3]

The work of Amadori on the system covers only the crystallization curve, giving no information as to the equilibrium between the two salts in the solid state. This type of binary equilibrium between solids, however, can be studied quite easily with the aid of a ternary system involving the two salts and water, over the range of temperatures in which solubility measurements can be made with the solution. The present system was investigated, therefore, with this purpose in mind, to see whether the mutual solubility of the two salts increased or decreased with the drop in temperature from the melting points to the temperatures here reported. The results obtained show, within the limits of the experimental error (which is very small in this type of work), no formation of solid solutions of sodium chloride and sodium iodide whatever between 10 and 100°. The solubility of sodium chloride in sodium iodide, therefore, which is as high as 26 mol % at 578°, has fallen off to zero or practically zero, at 100°, while the solubility of sodium iodide in sodium chloride, if such solid solution actually exists at 578°, has also disappeared at the lower temperatures.

Experimental Method

The experimental procedure for the solubility measurements on the ternary system was the same as that described for previous similar investigations;[4] for the determinations at 75 and 100° the thermostat and experimental procedure have been described.[5] The time of stirring allowed for the attainment of equilibrium was from two to three days at 100°, to ten to fourteen days at 10°. For the analysis of the solutions, the sodium iodide was determined volumetrically by Andrews'[6] method for iodide in the presence of chloride, the total solid was determined by evaporation to dryness at 100° followed by 250°, and the sodium chloride was then calculated by difference. The procedure usually described for Andrews' method[7] is for the titration of relatively small amounts of iodide, using 10 cc. of 0.05 M potassium iodate. For the sake of precision in the present work, it was found advisable to use quantities of iodide requiring 40 cc. of potassium iodate solution of the same strength (0.05 M) to ensure the same sharp end-point for the titration. Since this involves the temporary formation of a considerable amount of free iodine during the titration, the determination must be carried out with certain special precautions. The pro-

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[1] "International Critical Tables," Vol. IV, p. 68, 1928.

[2] Amadori, *Atti accad. Lincei.* [I] **21**, 467 (1912).

[3] Ricci, THIS JOURNAL, **57**, 805 (1935).

[4] Ricci, *ibid.*, **56**, 290 (1934).

[5] Hill and Yanick, *ibid.*, **57**, 645 (1935).

[6] Andrews, *ibid.*, **25**, 756 (1903).

[7] Kolthoff and Furman, "Volumetric Analysis," New York, N. Y., 1929, Vol. II, p. 456.

cedure used was therefore as follows. To the sample, containing about 0.65 g. of sodium iodide, and diluted to about 25 cc. in a glass-stoppered Erlenmeyer flask, were added 5 cc. of carbon tetrachloride and 25 cc. of concd. hydrochloric acid. Standard 0.05 *M* potassium iodate solution was then added, from a buret, rapidly and with no stirring, to about 1 or 2 cc. from the end-point. After the addition of 25 cc. more of concd. hydrochloric acid, the flask was stoppered and the contents shaken under cold water; the titration was then completed, drop by drop, to the end-point, with very vigorous shaking after the addition of each drop. The results so obtained are very precise and accurate. The solubility of sodium iodide at 75°, determined gravimetrically by direct evaporation, was 74.71%; volumetrically, 74.73% (both determinations in triplicate). The accuracy of the analysis for the ternary system is further shown by the results of the algebraic extrapolation of the tie-lines passing through the composition of the original complex and that of the saturated solution to the composition of the solid phase known and seen to be in equilibrium with the given solution (sodium chloride, in all the cases extrapolated). The average deviation of the extrapolated point from the point representing 100% sodium chloride, was 0.17% for 26 cases covering all five temperatures studied. Densities, calculated from the weight delivered by a volumetric pipet calibrated for delivery, were determined only at 25°, the results being listed in the Table. Finally, the solubilities of the pure salts reported below agree very closely with values recently appearing in the literature.

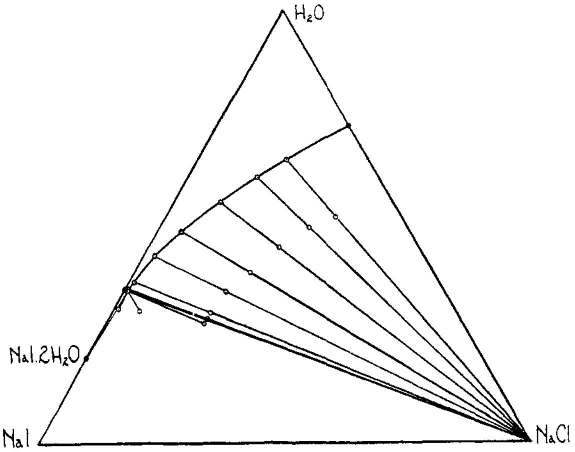

Fig. 1.—25° Isotherm: NaCl–NaI–H_2O.

The experimental data for the five temperatures studied are presented in Table I. The solid phases are NaCl and $NaI\cdot2H_2O$ at 10, 25 and 50°, while at the higher temperatures, 75 and 100°, both salts are anhydrous. The isotherm for 25° is shown graphically in Fig. 1, the curves for the other temperatures being very similar to this.

TABLE I

SOLUBILITIES FOR THE SYSTEM NaCl–NaI–H_2O

Temp., °C.	Original complex, Weight per cent NaCl	NaI	Saturated solution, Weight per cent NaCl	NaI	Solid phase	Density of satd. soln.
10	...	0.00	26.36	0.00	NaCl	
	31.59	10.82	19.91	12.67	NaCl	
	29.69	25.39	10.43	32.36	NaCl	
	29.87	35.33	3.86	48.45	NaCl	
	20.01	44.85	2.02	54.91	NaCl	
	17.41	57.90	0.62	62.03	NaCl + $NaI\cdot2H_2O$	
	9.28	63.82	.67	62.00	NaCl + $NaI\cdot2H_2O$	
	Average (of 5)		.67	61.99	NaCl + $NaI\cdot2H_2O$	
	0.00	...	.00	62.78	$NaI\cdot2H_2O$	
25	...	0.00	26.46	0.00	NaCl	1.195
	34.51	13.25	18.02	16.61	NaCl	1.304
	30.46	19.97	14.04	24.72	NaCl	1.367
	26.52	28.47	9.14	35.24	NaCl	1.464
	23.46	37.26	4.59	46.48	NaCl	1.593
	20.93	44.27	2.06	54.84	NaCl	1.714
	19.96	49.52	0.72	61.43	NaCl	1.836
	20.00	51.30	.45	63.97	NaCl	1.887
	19.98	52.23	.39	64.35	NaCl + $NaI\cdot2H_2O$	1.899
	0.79	67.04	.43	64.29	NaCl + $NaI\cdot2H_2O$	1.903
	Average (of 6)		.40	64.33	NaCl + $NaI\cdot2H_2O$	1.904
	0.00	...	.00	64.71	$NaI\cdot2H_2O$	1.904
50	...	0.00	26.83	0.00	NaCl	
	30.04	10.03	21.25	11.20	NaCl	
	32.02	18.29	15.37	22.75	NaCl	
	31.60	31.65	5.97	43.49	NaCl	
	21.46	44.35	2.21	55.21	NaCl	
	19.63	54.56	0.42	67.59	NaCl	
	17.94	57.43	.37	69.05	NaCl + $NaI\cdot2H_2O$	
	3.01	72.99	.17	68.96	NaCl + $NaI\cdot2H_2O$	
	Average (of 4)		.26	69.00	NaCl + $NaI\cdot2H_2O$	
	0.00	...	.00	69.34	$NaI\cdot2H_2O$	
75	...	0.00	27.44	0.00	NaCl	
	32.23	18.03	15.88	22.37	NaCl	
	31.98	31.76	6.32	43.66	NaCl	
	22.08	44.82	2.36	56.10	NaCl	
	20.13	54.85	1.17	67.78	NaCl	
	18.90	59.39	0.40	72.91	NaCl	
	9.36	72.67	.25	74.55	NaCl + NaI	
	1.00	80.84	.22	74.48	NaCl + NaI	
	Average (of 4)		.18	74.45	NaCl + NaI	
	0.00	...	.00	74.72	NaI	
100	...	0.00	28.05	0.00	NaCl	
	32.55	17.87	16.70	22.18	NaCl	
	32.00	31.50	7.05	42.93	NaCl	
	19.42	45.98	2.80	55.50	NaCl	
	19.21	54.75	0.78	67.29	NaCl	
	19.53	58.71	.45	72.63	NaCl	
	9.40	72.53	.50	74.66	NaCl + NaI	
	1.98	80.39	.45	74.76	NaCl + NaI	
	Average (of 4)		.39	74.70	NaCl + NaI	
	0.00	...	.00	75.14	NaI	

Summary

Solubility measurements are given for the system NaCl–NaI–H_2O at 10, 25, 50, 75 and 100°;

although the salt pair sodium chloride and sodium iodide is known to form solid solutions at the temperatures of the melting points, the system is found to form neither double salts nor solid solutions at the temperatures here reported.

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The Determination of Bound Water by Means of the Ultracentrifuge

BY JAMES W. MCBAIN

A considerable literature has accumulated around the problem, fundamental in physical chemistry and even more in biology, as to the amount of solvent which may be considered as existing as such in a solution, as distinguished from the solvent which is chemically or otherwise combined with the dissolved substance. Most methods are forced to rely either upon an interpretation of an observed deviation from ideal behavior or upon the assumption that a particular reference substance does not dissolve in, or in any way react with, the dissolved substance or its water of hydration. We have elsewhere[1] suggested, without elaboration, that the ultracentrifuge affords a new and sometimes more certain method of determining bound water. It is the purpose of this communication to discuss the theory of the new method.

That the subject has not been clearly understood is illustrated by the following quotation:[2] "Solvation is another factor affecting molecular weight determinations in various ways. In the case of osmotic pressure measurements in dilute solutions, solvation to the extent of 100 per cent. or so has a negligible effect on the calculated molecular weight. The same is true for ultracentrifuge determinations unless the partial specific volumes of the solvated and unsolvated molecules differ, whereupon there is a corresponding error in the calculated molecular weight. For cellulose esters and ethers in organic solvents, the effect is probably not marked." Evidently it has been overlooked that whenever sedimentation is observed the partial specific volumes of solvated and unsolvated molecules must differ significantly (see below and Fig. 1).

The best known discussion of the methods of deriving partial specific volumes is that of Lewis and Randall, who give four methods of calculating them from the observed densities of a binary system.[3] We shall therefore first discuss partial specific volumes in a binary system as illustrated by their "Method IV (graphical, method of intercepts)" in Fig. 1.

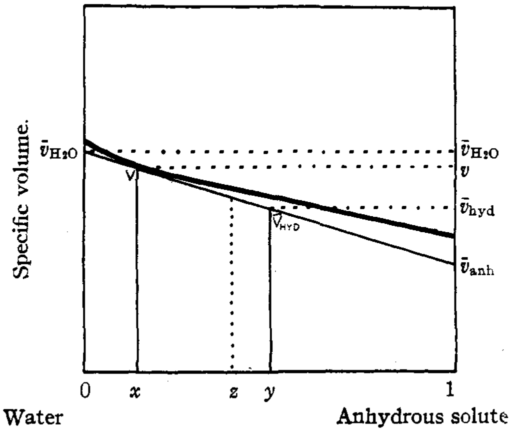

Fig. 1.—The relation between partial specific volumes of hydrated and anhydrous solute.

In Fig. 1, the reciprocal of the density, or the specific volume v, for a range of solutions is plotted against composition, from pure water on the left to anhydrous solute on the right. The particular solution under observation is taken as containing x grams of anhydrous solute and $1 - x$ grams of water and having the specific volume v. The partial specific volumes of the pure constituents are designated as $\bar{v}_{H_2O}$ and $\bar{v}_{anh}$, respectively, at the ends of the tangent. $\bar{v}_{hyd}$ is therefore the partial specific volume of the hydrate referred to in the quotation above. It is at once evident from inspection that $\bar{v}_{hyd}$ for the case quoted must lie closer to the value v than to the value $\bar{v}_{anh}$. In the extreme case where $x = 0$ it will lie exactly half way between.

This is of essential importance because the very occurrence of any kind of sedimentation depends

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[1] J. W. McBain, *Nature*, **135**, 831 (1935).

[2] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 165 (1935).

[3] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 33–41.