described a chromatographic method for the separation of carotene from cryptoxanthol. Their losses averaged 3%; in 10% of their columns it was 10–18%.

The degree of the separation as shown in Table III is of the order that would be expected from the relative values of the distribution coefficients. Error in quantitative analysis caused by the incomplete separation would be nearly compensated when the two pigments are present in corn in approximately equal proportions.

Summary

1. A quantitative study was made of the distribution of β-carotene, cryptoxanthol, and zeaxanthol between hexane and various aqueous solutions of three alcohols—methanol, diacetone alcohol, and 2-methyl-2,4-pentanediol.

2. In the absence of monohydroxycarotene, partition of carotene–dihydroxycarotene mixtures between hexane and diacetone alcohol solutions (94.5 to 77.0% diacetone alcohol by volume) should be satisfactory for the separation of these two classes of pigment.

3. In the presence of cryptoxanthol, extraction by 78.5% diacetone alcohol gives satisfactory separation of the carotene plus cryptoxanthol from the dihydroxycarotenes.

4. Extraction of a hexane solution by a 92.0% solution of 2-methyl-2,4-pentanediol in water gives fair separation of cryptoxanthol from carotene, as shown by analysis of corn grain pigments.

The Temperature–Composition Relations of the Binary System Manganous Nitrate–Water

BY WARREN W. EWING AND HERBERT E. RASMUSSEN

This article and the succeeding one[1] are continuations of the series of studies that have been made in this Laboratory on the thermodynamic properties of concentrated solutions. The nitrates of certain bivalent metals have been chosen for these studies because very concentrated solutions can be made from them, particularly so since the supersaturated solutions in the concentrated range are quite stable. Supersaturated solutions of the present system, manganous nitrate–water, up to 24 m, can be prepared and worked with at room temperature without too much difficulty.

It was necessary to establish the temperature–composition equilibria in order to facilitate the vapor pressure and calorimetric studies.[1] Various hydrates have been reported in the literature. Mellor[2] mentions a hexahydrate, a tetrahydrate, a trihydrate, a hemipentahydrate, and a monohydrate. The solubility data of Funk[3] seem to be erroneous especially in the more concentrated range. Ewing and Glick[4] found the hexahydrate, tetrahydrate, dihydrate, sesquihydrate, monohydrate, and hemihydrate existing in the ternary

system, manganous nitrate–nitric acid–water, at 20°. They also prepared the anhydride.

It seemed probable that all these forms did not exist in the manganous nitrate–water system. This present investigation indicates that only the hexahydrate, the tetrahydrate, the dihydrate, and the monohydrate are in stable equilibrium with water in the temperature range 10 to 75°.

Experimental

The preparation and analysis of solutions of manganous nitrate have been described elsewhere.[4]

The freezing point method employed in previous work[5] was used for concentrations up to 75%. It was found that for concentrations greater than this, the extreme viscosity and the slow attainment of equilibrium made the freezing point method unfeasible. Consequently, a solubility method was used on the more viscous solutions.

In the solubility method crystals of the desired concentration were melted and then cooled to just below the freezing temperature in a tube that was placed in a constant temperature bath ($\pm0.02°$). A seed crystal was added and the mixture was stirred until equilibrium was attained between the crystals and the solution. Due precautions were

(1) Ewing, Glick and Rasmussen, THIS JOURNAL, 64, 1445 (1942).
(2) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XII, Longmans, Green and Co., London, 1932, p. 440.
(3) "International Critical Tables," Vol. IV, 1930, p. 224.
(4) Ewing and Glick, THIS JOURNAL, 62, 2174 (1940).
(5) Ewing, Krey, Law and Lang, ibid., 49, 1958 (1927).

taken to protect the hygroscopic mixture from the surroundings. The liquid was then filtered from the viscous slurry through glass wool packed in a small bell-shaped glass tube that was attached to the tip of a small pipet by means of a ground glass joint. Suction was applied to fill the pipet. The filtered solution obtained in this manner was then analyzed. The attainment of equilibrium, which usually took about four hours, was ascertained by analyzing a sample of the liquid phase every hour until the concentration remained constant.
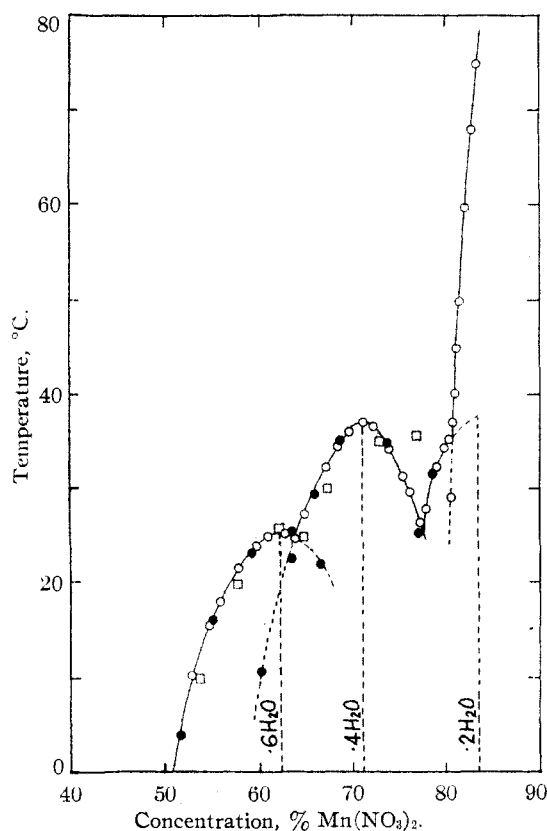

Fig. 1.—Freezing point–composition diagram of the system manganous nitrate–water: ●, vapor pressure data; □, "I. C. T." data.

Equilibrium was approached also from the opposite direction. The cooled mixture was warmed up to the desired temperature and stirred the required length of time. The two methods gave concordant results. A check on the relative reliability of the two methods was obtained by determining the equilibrium conditions on solutions between 70 and 75% and for a few of the more dilute solutions by both methods. The results were concordant.

Results

The data obtained are tabulated in Table I and are plotted in Fig. 1. Also appearing in Fig. 1 are the data (indicated by solid circles) obtained from vapor pressure measurements.[1] Solubility data obtained in this manner extend the phase diagram to the metastable region of supersaturated solutions (dotted lines). The data of Funk from "International Critical Tables" are also plotted (squares) for comparison.

TABLE I

FREEZING POINT-COMPOSITION DATA

The entries under "solid phase" are the numbers of molecules of water of hydration per molecule of manganous nitrate.

% $Mn(NO_3)_2$	F. p., °C.	Solid phase	% $Mn(NO_3)_2$	F. p., °C.	Solid phase
52.9	10.3	6	73.9	34.2	4
54.8	15.5	6	75.4	31.3	4
56.0	18.1	6	75.3	31.0	4
57.8	21.7	6	76.1	29.7	4
59.8	24.0	6	76.9	28.4	4
61.1	25.0	6	77.2	26.5	4
62.1	25.2	6	77.9	28.0	2
62.4	25.3	6[a]	78.5	30.0	2
62.5	25.3	6	79.2	32.2	2
62.7	25.3	6	79.8	34.3	2
63.8	24.9	6	80.3	35.2	2
64.0	24.7	6–4[b]	80.6	29.0	1
64.9	27.3	4	80.9	37.0	1
67.2	32.3	4	81.0	40.1	1
68.4	34.5	4	81.2	45.0	1
69.7	36.2	4	81.6	50.0	1
71.3	37.1	4[c]	82.1	59.9	1
71.5	37.0	4	82.8	68.1	1
71.7	36.8	4	83.3	75.0	1
72.2	36.6	4			

[a] Freezing point of hexahydrate.   [b] Eutectic point.
[c] Freezing point of tetrahydrate.

Figure 1 shows that the hexahydrate, f. p. 25.3°, and the tetrahydrate, f. p. 37.1°, are stable at their melting points and that there is an eutectic point between them. There is also an eutectic point between the tetrahydrate and the dihydrate. The dihydrate is not stable at its melting point, but there is a transition from dihydrate to monohydrate at 36.0°. The existence of the monohydrate cannot be confirmed from the diagram. The steep curve might indicate equilibrium between solution and any hydrate having less than two molecules of water of hydration or even the anhydride. That this equilibrium salt was the monohydrate was confirmed by analyzing the crystals. A sample of the wet crystals was placed in a small glass tube and centrifuged, keeping the temperature between 40 and 50°. The bottom of

the tube containing the solid phase was then cut off and the crystals analyzed. Analysis showed 90.3% manganous nitrate. Theoretically, the monohydrate contains 90.86% manganous nitrate.

It is estimated that the results are accurate to 0.1% up to concentration of about 78%. For concentrations higher than this the accuracy is not quite so good since these very concentrated solutions decompose slowly at their melting points.

The sesquihydrate and the hemihydrate which appear as stable forms in the ternary system manganous nitrate–nitric acid–water at 20°[4] do not appear in the binary system. Existence of stable hydrates in equilibrium with concentrated nitric acid solutions does not indicate that they are in stable equilibrium with their saturated water solutions. Also the data for the ternary system were at 20°, and the sesquihydrate curve, if this hydrate were in stable equilibrium with its saturated water solution, would be in the 35° temperature region and similarly the hemihydrate curve somewhere around 75°. This latter temperature is in the range where manganous nitrate is decomposing quite rapidly. However, it is not even necessary that a stable form appear in both systems. The anhydride appeared in neither system. It was prepared only by dehydrating the dry solid hydrates in vacuum. It should be possible to prepare the sesquihydrate and the hemihydrate in a similar manner, taking due precaution to keep the vapor pressure above the salt in the equilibrium pressure range corresponding to the hydrate desired. The trihydrate reported by Funk[3] failed to appear in the binary system in any of the three methods used, solubility, freezing point, or vapor pressure, nor did it appear in the ternary system.

Summary

The solubility temperature relations for the system manganous nitrate–water over the temperature range 5 to 75° and the concentration range 50 to 84% have been investigated.

The existence of the hexahydrate, the tetrahydrate, the dihydrate, and the monohydrate in equilibrium with water solutions has been established.

No evidence of the existence of the trihydrate, which is reported in the literature, has been found.

Vapor Pressure–Temperature Relations and Heats of Solution and Dilution of the Binary System Manganous Nitrate–Water

By Warren W. Ewing, Charles F. Glick and Herbert E. Rasmussen

The manganous nitrate–water system is well adapted to a physical chemical study of concentrated solutions because its anhydride is very soluble in water and the concentrated solutions can be supercooled to room temperatures. Solutions up to 24 m can thus be obtained. These desirable characteristics are counterbalanced to some extent by the tendency for the solute to decompose slowly, especially in the concentrated range at higher temperatures.

Vapor pressure data from 20 to 40° and from 5 to 24 m for solutions, saturated solutions, and supersaturated solutions and calorimetric data on heats of solution and dilution of the anhydride are reported in this article. Only fragmentary data on these systems are found in the literature.

Vapor Pressure Part.—The methods used in preparing and analyzing the materials have been reported[1] and the apparatus and technique for measuring vapor pressures have been described[2] previously.

In Table I are tabulated vapor pressure data of the solution phase for the temperature range 20 to 40°. The measured data have been corrected to whole degrees by means of the equation

$$\ln p = A/T + B \qquad (1)$$

The constants A and B were determined for each solution by the method of least squares. The temperature correction was never more than 0.1°.

The difficulty experienced in supercooling the 66.18% solution was overcome by filtering the melted solution through sintered glass and warming to 60° to destroy any crystalline nuclei present.

(1) Ewing and Glick, This Journal, 62, 2174 (1940).
(2) Ewing and Fisher, ibid., 59, 1046 (1937).