Conclusions

The shape of binodal curves (Figures 1 and 2) resembles that of an asymmetric parabola. The asymmetry is likely to be due to differences in solubility of the acids in water and in HMDS.

The two-phase systems (lower area of the triangular diagram) separated into two layers. The upper one contained mostly HMDS, a small amount of the acid, and a very small amount of water, whereas the lower one comprised water as the main component, followed by the acid and a very small amount of HMDS.

In this work, the suitability of the cross-section method (Figure 3) has been demonstrated for determining tie lines of conjugated systems. The lines intersect at one point lying on the extension of one side of a triangle representing the composition of immiscible components.

Results of analyses of the conjugated layers allowed us to determine partition coefficients of the acids between the aqueous and HMDS phases. Their mean values were 2.21 and 0.913 for the acetic and propionic acid, respectively, at 20° ± 1°C.

Literature Cited

(1) Bancroft, W. D., *Phys. Rev.*, **3**, 21 (1896).
(2) Daudt, W. H., U.S. Patent 2,386,441; *Chem. Abstr.*, **40**, 348 (1946).
(3) Francis A., "Liquid-Liquid Equilibrium," Interscience, New York, N.Y., 1963.
(4) Hyde, J. F., Johanson, O. K., Daudt, W. H., Fleming, R. F., Laudenslager, H. B., Roche, M. P., *J. Amer. Chem. Soc.*, **75**, 5615 (1953).
(5) Killgore, A. Ch., Chew, W. W., Orr, V., *J. Chem. Eng. Data*, **4**, 535 (1966).
(6) Nikurashina, N. I., Mertslin, R. V., Komarova, T. M., *Zh. Obshch. Khim. (Moscow)*, **29**, 345 (1959).
(7) Sauer, R. O., *J. Amer. Chem. Soc.*, **66**, 1707 (1944).

Received for review June 11, 1974. Accepted December 12, 1974.

---

pH Dependence on Composition of Aqueous Solution Saturated with Sodium Phosphate, Sodium Chloride, and Sodium 5′-Inosinate

Yoshihisa Suzuki
Central Research Laboratories, Ajinomoto Co., Inc., Kawasaki, Japan

The composition data of the aqueous solution saturated with sodium phosphate, sodium chloride, and sodium 5′-inosinate were obtained between pH 2 and 11 at 10° and 30°C, respectively. Those in the absence of sodium chloride were also obtained. The salting-out effect of sodium phosphate on sodium chloride or on sodium 5′-inosinate is clearly demonstrated. Sodium chloride also showed a salting-out effect on disodium 5′-inosinate.

For the industrial production of disodium 5′-inosinate (disodium inosine-5′-monophosphate, 5′-IMP·Na_2), an excellent flavor enhancer, phosphorylation of inosine with an excess of phosphoryl chloride is eminently useful (*6*, *7*). In this reaction, however, a by-product of phosphoric acid and hydrochloric acid is inevitable as shown in the following equation:

$$\text{Inosine} + n\cdot POCl_3 + [2 + 3(n-1)]\cdot H_2O \rightarrow 5'\text{-IMP}\cdot H_2 + (n-1)\cdot H_3PO_4 + 3n\cdot HCl$$

where $n > 1$. After neutralization with sodium hydroxide to various pH values, crystallization of sodium 5′-inosinate can be performed in the presence of sodium phosphate and sodium chloride.

This paper describes the pH dependence on the composition of the aqueous solution saturated with sodium phosphate, sodium chloride, and sodium 5′-inosinate at 10° and 30°C, respectively. No data have been previously reported involving these systems.

Experimental

Disodium 5′-inosinate octahydrate (5′-IMP·Na_2·$8H_2O$) was obtained through recrystallization of commercial "IN" (Ajinomoto Co., Inc.) in water. The melting point was 118–120°C (rapid heating in a capillary, uncorrected). The water content by Karl Fischer method (3), 26.5%: Calcd for $8H_2O$, 26.9%. The molar extinction coefficient at 250 nm in 0.1*N* HCl, 11,500.

Monosodium 5′-inosinate tetrahydrate (5′-IMP·NaH·$4H_2O$) was prepared according to Suzuki et al. (*5*). The melting point was 108–111°C (rapid heating in a capillary, uncorrected). The water content by Karl Fischer method (*3*), 16.3%: Calcd for $4H_2O$, 16.3%. The molar extinction coefficient at 250 nm in 0.1*N* HCl, 11,500. Other materials were obtained commercially (GR reagent grade). 5′-Inosinic acid was determined by measurement of the ultraviolet absorbance at 250 nm in 0.1*N* HCl, using the tentative molar extinction coefficient of 11,500. Phosphoric acid was determined by a phosphovanadomolybdate method (*2*). Sodium chloride was determined by the Volhard method (*1*).

Samples were allowed to reach equilibrium in a constant-temperature bath maintained at ±0.5°C. The pH of the solutions was measured by a Toa Dempa pH meter Model HM-5A. The electrode was standardized with two buffer solutions. In the acidic pH measurement a phosphate buffer solution (pH 6.86) and a phthalate buffer solution (pH 4.01) were adopted, whereas in the alkaline pH measurement a phosphate buffer solution (pH 6.86) and a borate buffer solution (pH 9.18) were used.

Several kinds of the materials were added to water to make a slurry in a tightly capped glass bottle. The cap was also made of glass. Dissolution and equilibration were achieved by tumbling the bottles for at least 16 hr at 10° or 30°C. No indications of bacterial growth were found at 30°C/16 hr, probably because the concentration of the solution was too high. After equilibration the pH of the solution was measured, and the liquid phase was separated from the solid phase by filtration. Each portion of the filtrates and the wet residues was sampled, diluted, and analyzed, respectively.

The method of slurry making was as follows: In a region below pH 4.0, an excess amount of 5′-IMP·NaH·

Table I. pH Dependence on Composition of Aqueous Solution Saturated with Both Sodium Phosphate and Sodium 5′-Inosinate

pH	Composition, w/w %	
	5′-IMP·H_2	H_3PO_4
	10°C	
2.02	1.39	40.0
2.52	0.77	36.5
2.96	0.62	35.7
3.29	0.51	34.6
3.66	0.50	33.3
4.02	0.50	34.9
4.90	0.26	38.7
5.30	1.97	25.5
5.70	8.85	7.55
5.78	11.2	8.03
5.98	7.92	4.48
6.40	6.70	4.35
6.79	6.32	3.51
7.59	6.08	2.03
8.12	6.35	1.93
8.91	8.96	1.62
9.59	15.4	1.01
10.24	22.2	0.86
10.48	30.2	1.04
10.73	42.3	0.69
	30°C	
2.05	1.64	44.7
2.46	1.05	43.1
3.10	0.70	42.2
3.73	0.44	43.5
4.29	0.26	45.1
4.63	0.13	48.2
5.00	0.19	45.2
5.40	1.01	34.7
5.62	0.41	36.1
5.90	1.45	27.2
6.34	1.87	22.7
7.00	3.32	14.5
7.40	4.43	12.5
7.80	5.09	11.2
8.45	7.29	10.3
8.60	7.32	10.0
9.48	14.8	7.86
9.99	30.7	7.64
10.45	43.9	2.25

Table II. pH Dependence on Composition of Aqueous Solution Saturated with Sodium Phosphate, Sodium Chloride, and Sodium 5′-Inosinate

pH	Composition, w/w %		
	5′-IMP·H_2	H_3PO_4	NaCl
	10°C		
2.05	1.15	13.1	19.1
2.52	0.80	12.7	19.3
3.12	0.66	11.5	19.8
3.60	0.70	11.3	19.3
4.08	0.72	16.6	16.5
4.52	0.67	23.8	12.2
4.82	0.62	29.9	8.42
5.30	1.07	4.07	23.1
5.78	0.87	3.69	23.8
6.20	0.61	1.98	25.1
6.58	0.53	1.26	25.2
7.00	0.56	1.35	25.1
8.68	0.87	1.43	24.8
9.15	2.01	1.65	23.8
9.40	2.90	1.40	23.6
9.60	4.28	2.15	22.2
10.04	24.3	0.62	14.1
10.32	26.5	0.59	12.7
10.69	38.6	0.32	7.98
	30°C		
1.70	4.43	37.5	6.66
2.18	2.43	31.2	9.56
3.02	1.44	25.8	11.7
3.72	1.05	31.5	8.88
4.08	0.72	36.7	5.89
4.60	0.27	44.7	2.57
5.05	0.35	42.6	2.81
5.30	1.25	30.0	7.69
5.38	1.78	21.8	12.2
6.00	1.00	17.0	14.8
6.20	1.10	12.1	17.7
6.40	1.03	9.58	19.4
7.10	0.98	6.98	20.9
7.30	1.03	6.64	21.1
8.10	1.35	6.14	21.6
8.42	1.67	6.39	20.9
8.89	2.49	7.02	20.5
9.15	7.95	7.31	17.0
9.50	10.4	6.05	16.8
9.80	22.1	2.64	13.3
10.81	39.1	0.53	4.36

$4H_2O$ was added to an aqueous solution of H_3PO_4 having a definite concentration, followed by an addition with an excess amount of NaCl and $NaH_2PO_4·2H_2O$. In a region between pH 4.0 and pH 7.0, an excess amount of two or three salts with or without a small amount of other salts, selected from among 5′-IMP·NaH·$4H_2O$, 5′-IMP·$Na_2·8H_2O$, $NaH_2PO_4·2H_2O$, $Na_2HPO_4·12H_2O$, Na_2HPO_4, and NaCl, was added to water. The pH of the mixture was adjusted with either concentrated HCl or concentrated NaOH if necessary. In a region over pH 7.0, an excess amount of 5′-IMP·$Na_2·8H_2O$ (dehydrated or nondehydrated) was added to aqueous NaOH having a definite concentration, followed by the addition of an excess amount of NaCl and $Na_2HPO_4·12H_2O$ and/or $Na_3PO_4·12H_2O$.

The composition of the saturated solution was determined by the results of the analysis. The Volhard method gave the amount of Cl ion in the saturated solution, and the analytical data thus obtained were converted to those of NaCl by the calculation using the molecular weight. The phosphovanadomolybdate method gave the amount of PO_4 ion in the saturated solution, and the analytical data were converted to those of H_3PO_4 same as above. The measurement of ultraviolet absorbance gave the mole amount of 5′-inosinic acid, and the data were converted to the weight percent. Accordingly, the solubility of the salts of phosphoric acid ($NaH_2PO_4·2H_2O$, $Na_2HPO_4·12H_2O$, or $Na_3PO_4·12H_2O$) or those of 5′-inosinic acid (5′-IMP·NaH·$4H_2O$ or 5′-IMP·$Na_2·8H_2O$) in this study is expressed in terms of, not the individual salt form, but the free acid over the whole pH range. This expression must be noted in the data reading.

Results and Discussion

The experimental data for the systems investigated are presented in Tables I–II. The compositions of the solution

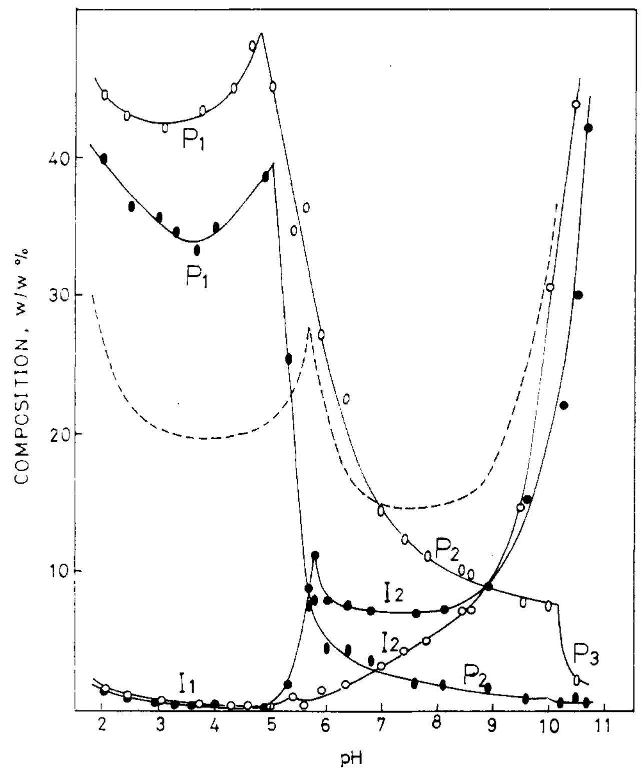

Figure 1. pH dependence on composition of aqueous solution saturated with both sodium phosphate and sodium 5′-inosinate at 10° and 30°C. [- - - Sodium 5′-inosinate alone at 30°C (2)]

▮ Phosphoric acid at 10°C
o Phosphoric acid at 30°C
● 5′-inosinic acid at 10°C
○ 5′-inosinic acid at 30°C
Residues: P_1 = $NaH_2PO_4 \cdot 2H_2O$
P_2 = $Na_2HPO_4 \cdot 12H_2O$
P_3 = $Na_3PO_4 \cdot 12H_2O$
I_1 = $5'\text{-IMP} \cdot NaH \cdot 4H_2O$
I_2 = $5'\text{-IMP} \cdot Na_2 \cdot 8H_2O$

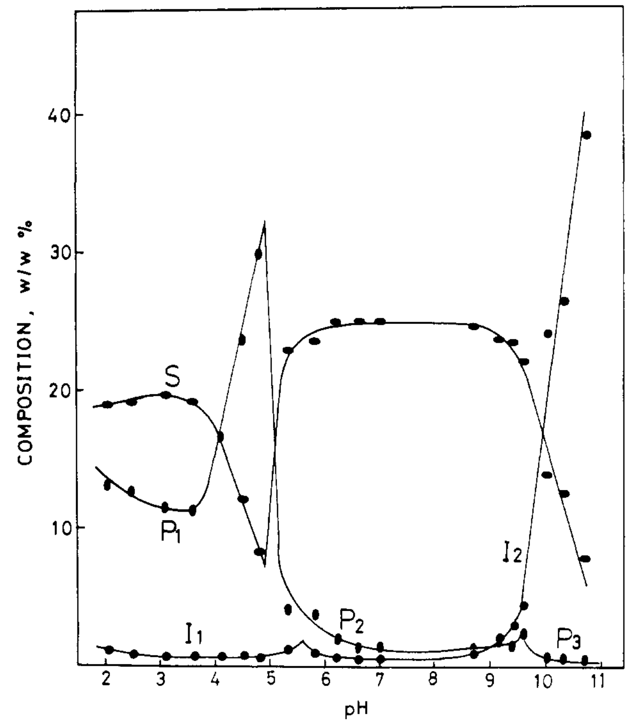

Figure 2. pH dependence on composition of aqueous solution saturated with sodium phosphate, sodium chloride, and sodium 5′-inosinate at 10°C

▮ Phosphoric acid
▬ Sodium chloride
● 5′-inosinic acid
Residues: P_1 = $NaH_2PO_4 \cdot 2H_2O$
P_2 = $Na_2HPO_4 \cdot 12H_2O$
P_3 = $Na_3PO_4 \cdot 12H_2O$
S = NaCl
I_1 = $5'\text{-IMP} \cdot NaH \cdot 4H_2O$
I_2 = $5'\text{-IMP} \cdot Na_2 \cdot 8H_2O$

shown in terms of phosphoric acid and 5′-inosinic acid with or without sodium chloride are convenient to obtain a continuous solubility curve over the complete pH range, whereas the residues are varied along with the pH ($NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$ or $Na_3PO_4 \cdot 12H_2O$, and $5'\text{-IMP} \cdot NaH \cdot 4H_2O$ or $5'\text{-IMP} \cdot Na_2 \cdot 8H_2O$). The composition data of the wet residue used for the conformation of the saturation are omitted here.

Figures 1–3 are illustrations of the data in Tables I–II. The differences between the residues are clearly demonstrated as the breaks of the curves forming cusps for phosphoric acid and 5′-inosinic acid. However, sodium chloride in the residues is invariable at both sides of the breaks of the curve. The solubility curve of 5′-inosinic acid in water at 30°C (*4*) is also exhibited for comparison.

It is of interest that the solubility of sodium 5′-inosinate (pH 5.0–9.0) at 10°C, in the presence of sodium phosphate, is higher than that at 30°C (Figure 1). This is probably because of the high solubility (accordingly indicating the strong salting-out effect) of disodium hydrogen phosphate at 30°C. Also, sodium chloride is more soluble at 10°C than at 30°C (Figures 2 and 3, pH 2.0–9.5) owing to the strong salting-out effect of sodium phosphate at 30°C.

The presence of sodium chloride notably decreases the solubility of disodium 5′-inosinate (Figures 1 and 2, pH 6.0–9.0). In the high pH region over 9.5, the solubility

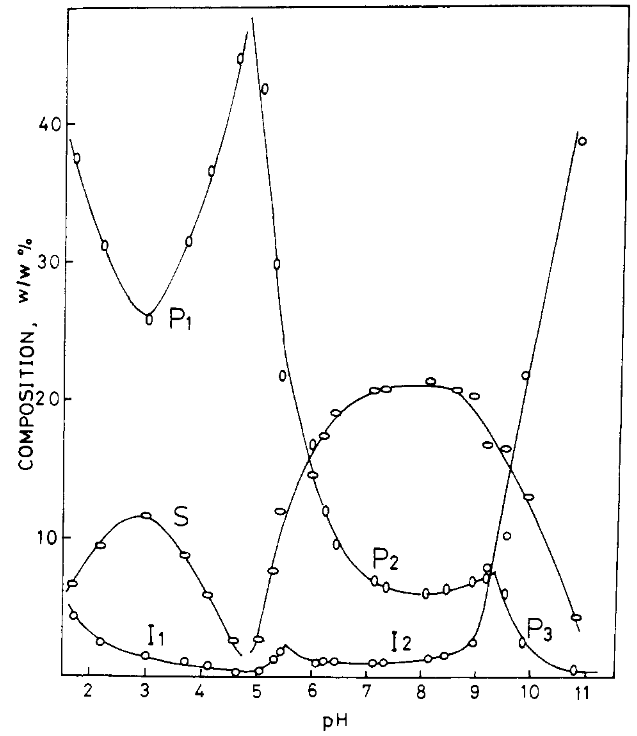

Figure 3. pH dependence on composition of aqueous solution saturated with sodium phosphate, sodium chloride, and sodium 5′-inosinate at 30°C. (Representation of symbol letters same as Figure 2)

o Phosphoric acid
▭ Sodium chloride
○ 5′-inosinic acid

of disodium 5'-inosinate increases, resulting in a decrease of the solubility of the other two inorganic salts (sodium chloride and trisodium phosphate), whereas the solubility of 5'-inosinate is suppressed by the high solubility of the inorganic salts in the lower pH region (pH 2.0–9.5).

Acknowledgment

The author thanks Tadashi Nakamura, Director of the Process Engineering Laboratories, for his encouragement and also the late Toshihiro Kikuchi for his technical assistance.

Literature Cited

(1) Caldwell, J. R., Moyer, H. V., *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).
(2) Chem. Soc. Japan, Ed., "Jikken kagaku kôza," 15-II, p 374, Maruzen, Tokyo, Japan, 1963.
(3) Japanese Union of Food Additives Association, Japanese Standards of Food Additives, 3rd ed., p 434, 1974.
(4) Kobayashi, H., Suzuki, Y., Hirahara, T., Nakamura, T., Div. of Phys. Chem., Annual Meeting, Agri. Chem. Soc. Japan, Sapporo, Japan, July 1964.
(5) Suzuki, Y., Satô, N., Kobayashi, H., Nakamura, T., (to Ajinomoto Co., Inc.), Japan Patent 43-20157 (Aug. 29, 1968).
(6) Yoshikawa, M., Katô, T., *Bull. Chem. Soc. Jap.*, **40**, 2849 (1967).
(7) Yoshikawa, M., Katô, T., Takenishi, T., *ibid.*, **42**, 3505 (1969).

Received for review June 17, 1974. Accepted November 4, 1974.

Vapor-Liquid Equilibria in System Carbon Tetrachloride-Acetic Acid

Jaime Wisniak[1] and Abraham Tamir
Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel

Vapor-liquid equilibrium data are determined for the system carbon tetrachloride–acetic acid at 760 and 417 mm Hg. The system presents strong positive deviations from the ideal solution and at 76.17°C and 760 mm Hg exhibits an azeotrope with 94.0 mol % carbon tetrachloride. The experimental results are thermodynamically consistent only when association effects are taken into account.

The association in a phase is usually described quantitatively by the proper equilibrium constant, assuming no interaction between the different chemical species present. The experimental evidence indicates that association increases with dilution and that the main species present are the monomer and dimer (*1*), although Ritter and Simons (*12*) claim that the tetramer is also significant. The system acetic acid–carbon tetrachloride provides a good example of an associating substance mixed with a nonpolar solvent that affects the dimerization phenomena.

The general problem of association has been thermodynamically analyzed by Marek and Standart (*6, 7*), Sebastiani and Lacquaniti (*13*), and Ratkovics (*11*) by different approaches. Very few data are available on the vapor-liquid equilibrium data for the system examined. Miksch et al. (*8*) and Ratkovics (*11*) measured the total vapor pressure of acetic acid–carbon tetrachloride mixtures at 20°, 32.28°, and 40°C and reported data at 740 mm without indicating the values of the equilibrium temperatures and the activity coefficients. Houghton (*3*) studied the variation in acetic acid composition of the azeotrope and found that it dropped from 1.54 wt % at 760 mm and 76°C to 1.00 wt % at 530 mm and 64.6°C. Kenney (*4*) determined the total pressure of the binary at 25°C.

It is our purpose to provide complete vapor-liquid equilibrium data for the system acetic acid–carbon tetrachloride and to analyze the effect of association and dilution of the thermodynamic consistency of the data obtained.

Experimental

Purity of materials. Analytical-grade reagents purchased from Merck and Frutarom were employed without further purification after gas chromatographic analysis failed to show any significant impurities. Physical properties of the pure compounds appear in Table I.

Apparatus and procedure. An all-glass modified Dvorak and Boublik recirculation still (*2*) was used in the equilibrium determinations. The original apparatus was further modified after pressure equalization problems were encountered when working at temperatures above 90°C. Recirculation of the condensed vapor phase was substantially improved by providing a connection between the entrance to the vapor condenser and the condensed vapor reservoir. A vacuum system controlled by a cartesian manostat connected the vapor condenser with a Swietoslawski ebulliometer and allowed total pressure regulation. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebulliometer. Temperatures were measured with a Hewlett-Packard quartz thermometer, Model 2801A, with an accuracy of ±0.005°C, so that the accuracy of the pressure measurements was better than 0.1 mm Hg. Several 1-ml samples were taken during each run until no significant changes in the refractive index and temperature were detected. The time required for reaching equilibrium varied between 2 hr for low-temperature determinations, to 4 hr for high-temperature levels.

Analyses of the samples were made at 25°C with a Bausch & Lomb Abbe-3L precision refractometer which gave direct readings to four significant figures and estimated values reproducibly to the nearest 0.00025. The calibration data appear in Table II. These data could be represented by two straight lines with slopes dn/dx 0.0990 in the range $0 \leq x_1 \leq 0.29$ and 0.0841 in the range $0.29 \leq x_1 \leq 1.0$. The accuracy of the concentration data can thus be estimated to be at least 0.003 concentration units.

Table I. Physical Constants of Compounds at 20°C

Compound	Density	Refractive index
Carbon tetrachloride	1.5940	1.4600
	1.5940 (*15*)	1.4601 (*15*)
Acetic acid	1.0493	1.3717
	1.0492 (*15*)	1.3716 (*15*)

---

[1] To whom correspondence should be addressed.