Equilibria in the Sodium Phthalate–Sodium Bromide–Water System

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PHASE RULE STUDIES of the solubilities in ternary systems involving phthalates have been carried out in this laboratory for several years. As a further step along this line, this investigation was undertaken.

EXPERIMENTAL

Materials and Methods. The sodium phthalate used in this investigation was prepared by neutralizing pure phthalic anhydride with pure sodium carbonate and recrystallizing the product from aqueous solution. The composition of the hydrate has been shown by Foote and Smith (*1*) to be $2Na_2C_8H_4O_4 \cdot 7H_2O$.

Hydrated sodium bromide was prepared by recrystallizing reagent grade sodium bromide in water below 51° C. Anhydrous sodium bromide was prepared by drying the recrystallized product at 110° C.

Solubilities were determined by analyzing solutions obtained by rotating mixtures of the three components in an electrically controlled thermostat until equilibrium was established. A minimum of 24 hours was allowed for the attainment of equilibrium. In some instances, at 0° C. and again where solid solution exists, three to four days were required. In preparing the original complexes, wherever possible the salts were used which exist as solid phases when equilibrium is reached. Temperature variations were within ±0.05° C.

Samples for analysis were obtained by allowing the equilibrium mixtures to settle and drawing off portions of the supernatant liquid by means of a pipet carrying a small cotton filter. Samples were weighed in a calibrated volumetric flask and aliquot portions used for analysis.

Sodium bromide was determined by precipitation as silver bromide with an excess of standard silver nitrate in acid solution and the excess titrated with standard thiocyanate solution. Total sodium was determined by acidifying a second aliquot portion with sulfuric acid and evaporating to dryness. Excess sulfuric acid was removed by ignition in a current of ammonia. From the weight of the resultant sodium sulfate and the sodium bromide previously determined, the percentage of sodium phthalate was calculated.

The wet residues were quickly dried between sheets of filter paper and analyzed by the same procedures. Their composition was determined by the graphic method of Schreinemakers (*2*).

Experimental Results. Isotherms at 0°, 25°, 35°, 45°, and 50° C. have been completed. At 0°, 25°, 35°, and 45° only two solid phases existed. The isotherms therefore consist of two isothermally univariant curves intersecting at an isothermally invariant point. At 50° C. two more solid phases appeared, so that this isotherm consists of four isothermally univariant curves and three isothermally invariant points.

Experimental results are given in Table I. P is used here as in previous work to designate the phthalate radical, $C_8H_4O_4$. Solid phases are represented as:

I. $2Na_2P \cdot 7H_2O$
II. $NaBr \cdot 2H_2O$
III. Solid solution
IV. NaBr

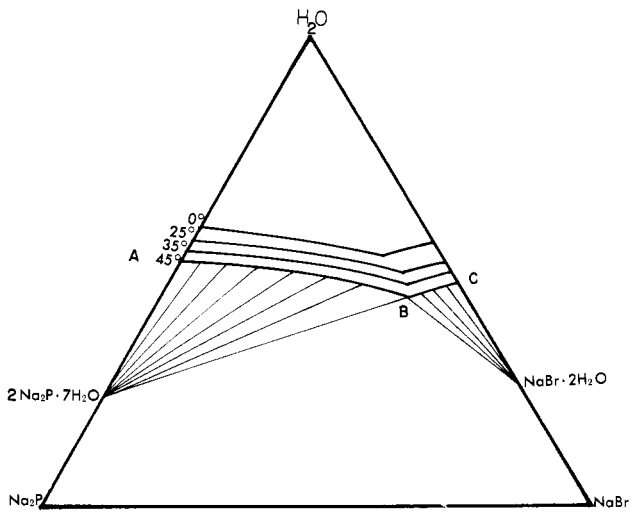

Figure 1. Solubility at 0°, 25°, 35°, and 45° C.

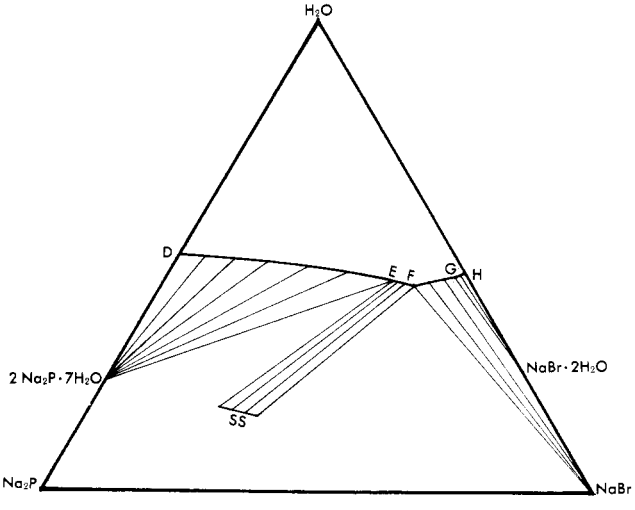

Figure 2. Solubility at 50° C.

Solid Solution. In the 50° C. isotherm two solid phases appear for the first time. One is the anhydrous sodium bromide, which is expected. Wholly unexpected is a solid solution of hydrated sodium phthalate and anhydrous sodium bromide. During a short interval, the solid phase in equilibrium with solutions whose composition is expressed along line *EF* showed a somewhat variable composition.

Experimental work in this region is extremely sensitive because the solid solution holds liquid mechanically and causes the whole mixture to become solid. To establish equilibrium it was necessary to keep the quantity of solid solution rather small and to rotate the samples from 72 to 96 hours.

Table I. Solubility Data

Point in Figure	Solution % Na_2P	Solution % NaBr	Residue % Na_2P	Residue % NaBr	Solid Phase
	Temperature, 0° C.				
A	40.60	...			I
	32.89	8.43	74.14	0.83	I
	27.36	15.12	73.47	1.22	I
	25.13	17.75	70.94	2.04	I
	22.08	21.34	72.13	1.83	I
	19.78	24.21	74.05	1.34	I
	15.33	30.03	73.12	1.95	I
B	10.68	36.34	49.69	21.40	I, II
	10.60	36.53	8.54	63.19	I, II
	5.73	39.81	0.60	70.62	II
C	...	44.46			II
	Temperature, 25° C.				
A	43.85	...			I
	39.56	4.27	74.19	0.37	I
	36.31	7.81	73.83	0.66	I
	32.49	12.00	72.62	1.10	I
	28.12	16.92	74.96	0.83	I
	22.99	22.97	74.78	0.67	I
	18.22	28.66	73.94	1.61	I
	14.49	33.69	72.60	2.33	I
B	9.17	41.71	65.99	9.30	I, II
	9.14	41.69	18.06	53.98	I, II
	6.78	43.47	1.01	71.62	II
	4.45	45.29	0.55	72.42	II
	0.84	48.04	0.88	72.17	II
C	...	48.63			II
	Temperature, 35° C.				
A	45.90				I
	41.39	4.61	75.99	0.17	I
	41.07	4.86	74.29	0.71	I
	35.16	11.14	72.68	0.89	I
	34.40	11.91	76.02	0.40	I
	28.24	18.54	75.28	0.99	I
	24.02	23.50	74.78	1.55	I
	22.68	25.18	75.21	0.87	I
	13.68	36.82	73.33	2.06	I
B	9.49	43.31	75.21	1.39	I, II
	9.52	43.32	12.27	61.37	I, II
	5.86	46.08	0.33	73.67	II
	3.44	47.76	0.15	73.14	II
C	...	50.49			II
	Temperature, 45° C.				
A	48.22	...			I
	42.15	6.05			I
	37.77	10.54	74.02	0.78	I
	24.05	25.85			I
	17.98	33.29	72.99	2.28	I
	11.61	43.07	71.32	3.57	I
B	10.88	44.45	43.24	31.61	I, II
	10.85	44.48	6.10	67.60	I, II
	7.49	46.93	0.18	74.47	II
C	...	52.49			II
	Temperature, 50° C.				
D	50.21	...			I
	44.25	5.95	73.33	0.76	I
	39.33	10.65	74.89	0.74	I
	32.52	17.90	73.01	1.25	I
	26.83	24.35	73.68	1.67	I
	26.35	24.84	73.36	1.80	I
	20.26	32.36	72.69	2.26	I
	16.67	37.50			I
	15.46	39.38	71.80	3.24	I
	14.23	41.23	73.61	2.00	I
E	14.04	41.68	54.92	18.43	I, III
	13.92	41.63	47.25	25.35	I, III
	13.00	42.76	38.21	31.72	III
	12.72	43.15	34.70	33.39	III
	12.04	43.98	39.85	32.22	III
	10.82	45.55	36.25	36.15	III
F	10.60	45.75	28.75	47.67	III, IV
	10.62	45.75	2.08	89.43	III, IV
	7.83	47.92	1.87	89.45	IV
	4.07	50.79	3.55	92.66	IV
G	2.54	52.01	1.00	74.20	IV, II
	2.51	52.01	0.90	74.70	IV, II
	0.98	52.69	0.56	73.31	II
H	...	53.74			II

Analyses showed composition of the solid solution varying from 36.25% Na_2P and 36.15% NaBr to 38.21% Na_2P and 31.72% NaBr.

Transition Points. The transition temperature of $NaBr \cdot 2H_2O$ to anhydrous NaBr is 50.2° C. (*3*). Addition of sodium phthalate to the saturated solution of $NaBr \cdot 2H_2O$ lowers this transition temperature. The limiting temperature is reached when the solution has become saturated with solid solution. This is a true invariant point, where the saturated solution is in equilibrium with three solid phases.

Attempts to determine this temperature by cooling and heating curves have been unsuccessful. This is probably due to the high solubility of the substances, giving viscous solutions with a great tendency for supersaturation, and to the small heat effect involved. When the three solid phases were placed in a vacuum-jacketed flask in presence of saturated solution, no constancy of temperature was obtained.

This transition temperature was determined by analyzing the residues of invariant point *G* at successively lower temperatures at intervals of 0.1° C. The lowest temperature at which anhydrous NaBr appeared in the solid phase was 49.0° C.

The transition temperature at which solid solution appeared was even more difficult, since analysis of the solid phase would prove nothing. Solutions were prepared of the composition of point *F* and were rotated in presence of excess sodium bromide and sodium phthalate for periods up to 4 days at intervals of 0.1° C. The appearance of solid solution was determined by visual examination both with and without the microscope.

The lowest temperature at which solid solution appeared was 47.3° C. No solid solution appeared at 47.2° C. after seeding with crystals of solid solution.

LITERATURE CITED

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