cooling crystals were obtained which had the characteristics of tetrabromothiophene. The mother liquor was carefully concentrated. When cooled in a freezing mixture, white, shiny crystals were formed which melted at 55–65°; weight less than 1 g. It was recrystallized from petroleum ether, then distilled with steam and the solid distillate was again crystallized from the same solvent. The final product melted at 61°. Analysis showed that the compound was 2,5-dibromo-3-nitrothiophene.[10]

Anal. Calcd. for $C_4HS(NO_2)Br_2$: S, 11.17; Br, 55.70. Found: S, 10.90; Br, 56.16.

Summary

In the vapor phase and at room temperature a limited quantity of bromine converts ordinary nitrothiophene into 2-bromo-5-nitrothiophene, 2,3-dibromo-5-nitrothiophene, 2,5-dibromo-3-nitrothiophene and tetrabromothiophene.

Qualitative tests also indicate the formation in traces of one other brominated derivative of thiophene.

The reaction confirms the heretofore assumed structural formula of bromonitrothiophene.

The reaction leads to the inference that in 2-nitrothiophene the nitro group resists replacement by bromine during the entry of the first atom of halogen into the thiophene nucleus; but this group is considerably loosened after the entry of the second bromine atom.

BETHLEHEM, PENNA. RECEIVED SEPTEMBER 12, 1938

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[10] The same compound had been produced by the direct bromination of 3-nitrothiophene,[1b] p. 161.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

Ternary Systems. V. Phthalic Acid, Magnesium Phthalate and Water. VI. Magnesium Phthalate, Lithium Phthalate and Water

BY STERLING B. SMITH AND EDWARD C. ELY[1]

Introduction

A number of phase rule studies of ternary systems involving phthalates and acid phthalates, particularly of the alkalies, have been made in this Laboratory. It is for the purpose of gaining further information regarding the solubilities of these salts that this investigation has been undertaken.

Experimental Part

Materials and Methods.—The phthalic acid used was prepared by crystallizing from aqueous solution sublimed phthalic anhydride obtained from the Eastman Kodak Company.

Magnesium phthalate was prepared by adding to an aqueous solution of phthalic acid an excess of magnesium carbonate, A. R. The solution was boiled to drive off carbon dioxide and filtered hot to remove the insoluble magnesium carbonate. The filtrate was evaporated to a small volume and allowed to stand several days while the magnesium phthalate crystallized out. The salt was filtered on a Büchner funnel and allowed to dry in the air. The composition of this salt was found by analysis to be $2MgC_8H_4O_4 \cdot 11H_2O$. Air dried samples heated to constant weight in an electric oven at 120° lost weight corresponding to 34.72, 34.60, 34.58, 34.45, 34.27 and 34.23% of water. The theoretical value for the per cent. of water in $2MgC_8H_4O_4 \cdot 11H_2O$ is 34.47%.

Lithium phthalate, $2Li_2C_8H_4O_4 \cdot 3H_2O$, was prepared as described in a previous publication.[2]

Magnesium acid phthalate, while not a component of either of these systems, appears as one of the solid phases and is used in the preparation of mixtures for analysis. It was prepared by adding slightly more than one-half the equivalent weight of magnesium carbonate to an aqueous solution containing the equivalent weight of phthalic acid, boiling off the carbon dioxide and evaporating to crystallization.

Solubilities were determined by analyzing solutions obtained by rotating mixtures of the three components in an electrically controlled thermostat for a minimum of twenty-four hours. In making up the mixtures, as far as possible the salts were used which exist as solid phases after equilibrium has been reached. At 0° the temperature was maintained constant by the use of ice and a small amount of salt. Temperature variations were within ±0.1°. When equilibrium was attained, the mixtures were allowed to settle and samples for analysis removed from the clear supernatant liquid by means of a pipet. When necessary to ensure a clear solution, a small plug of cotton or glass wool was inserted in a short piece of rubber tubing and slipped over the end of the pipet. Due to the viscosity of many of these solutions, density determinations were not attempted.

The composition of the solid phases was determined by the analysis of wet residues according to Schreinemakers.[3]

In the system phthalic acid, magnesium phthalate and water, phthalic acid was determined by titration with standard alkali. Magnesium phthalate was determined by precipitation of the magnesium as magnesium am-

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[1] The material for this paper was taken from a thesis of Mr. Edward C. Ely presented to the Graduate Committee of Trinity College in partial fulfilment of the requirements for the Master of Science degree. Original manuscript received February 15, 1938.

[2] Smith, Sturm and Ely, THIS JOURNAL, **57**, 2406 (1935).

[3] Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

monium phosphate followed by ignition to the pyrophosphate. Water was determined by difference.

In the system magnesium phthalate, lithium phthalate and water, water was determined as loss in weight when a sample was heated to constant weight in a platinum dish in an electric oven at 180°. Magnesium phthalate was determined in the same sample by the pyrophosphate method and lithium phthalate determined by difference. Solutions saturated with both lithium phthalate and magnesium phthalate were so viscous and so dense that a week was required for the solid phase to settle. Even then these solutions were slightly turbid after passing through glass wool. No improvement was found after centrifuging. Solubility determinations, therefore, in this system near its univariant point may be off as much as 0.5%.

Experimental Results.—Isotherms at 0, 25 and 50° have been completed for the system phthalic acid, magnesium phthalate and water. Compound formation takes place at all three temperatures. The solubility isotherms, therefore, consist of three intersecting curves representing isothermally univariant equilibrium between the solutions and one solid phase, and two isothermally invariant points where two solid phases are in equilibrium with the solution.

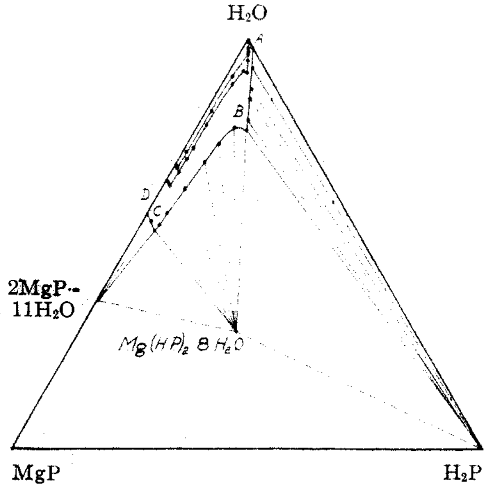

Fig. 1.—Temperatures, 0, 25, 50°.

One isotherm at 25° has been completed for the system magnesium phthalate, lithium phthalate and water. A second isotherm at 50° was undertaken but due to the extreme viscosity of the solutions at the higher concentrations, no conclusive results were obtained near the invariant point and further experiments abandoned. The 25° isotherm shows no evidence of compound formation. The isotherm consists of two intersecting curves representing isothermally univariant equilibrium between the solutions and one solid phase, and one isothermally invariant point at which the solution is in equilibrium with two solid phases. The portion of the 50° isotherm which is reported is similar. It is possible that compound formation or solid solution may occur in that region where unsatisfactory non-reproducible results were obtained.

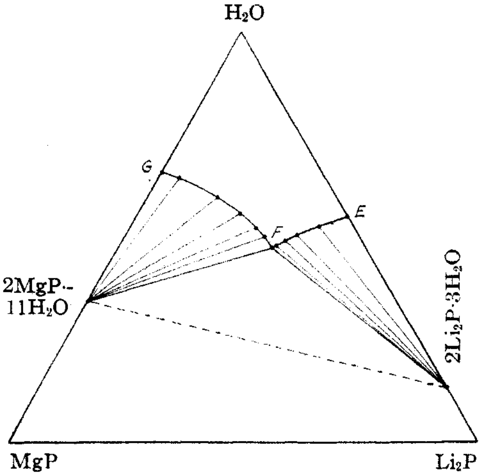

Fig. 2.—Temperature, 25°.

Experimental results are given in Tables I and II. The symbol "P" is used here as in previous work to designate the phthalate radical, $C_8H_4O_4$.

TABLE I

SOLUBILITY DATA: THE SYSTEM H_2P, MgP, H_2O

Point in Fig.	Solution % H_2P	Solution % MgP	Wet residues % H_2P	Wet residues % MgP	Solid phases
			Temperature, 0°		
A	0.29	None	...	...	H_2P
	1.00	0.99	83.34	...	H_2P
B	1.58	1.93	66.55	8.32	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	1.58	1.95	53.17	18.52	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	1.59	1.95	46.41	28.57	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	1.06	7.69	29.43	34.47	$Mg(HP)_2 \cdot 8H_2O$
	.76	16.20	28.80	34.71	$Mg(HP)_2 \cdot 8H_2O$
	.47	26.58	27.30	36.09	$Mg(HP)_2 \cdot 8H_2O$
C	.39	30.76	15.05	48.66	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
	.39	30.80	23.43	43.34	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
D	None	30.63	...	...	$2MgP \cdot 11H_2O$
			Temperature, 25°		
A	0.69	None	...	...	H_2P
	1.69	1.27	79.12	0.28	H_2P
	2.70	2.66	81.91	0.56	H_2P
B	3.61	4.16	48.66	20.50	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	3.62	4.18	29.64	28.56	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	3.60	4.14	58.50	9.98	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	3.23	4.71	24.96	28.39	$Mg(HP)_2 \cdot 8H_2O$
	2.33	8.92	28.12	31.48	$Mg(HP)_2 \cdot 8H_2O$
	1.79	19.17	23.07	31.97	$Mg(HP)_2 \cdot 8H_2O$
	1.72	20.46	22.74	32.54	$Mg(HP)_2 \cdot 8H_2O$
	1.60	22.75	25.70	33.87	$Mg(HP)_2 \cdot 8H_2O$
	1.54	23.49	29.61	35.95	$Mg(HP)_2 \cdot 8H_2O$
	1.36	27.49	...	...	$Mg(HP)_2 \cdot 8H_2O$
	1.30	30.98	27.03	36.72	$Mg(HP)_2 \cdot 8H_2O$
	1.21	32.26	26.86	36.18	$Mg(HP)_2 \cdot 8H_2O$

TABLE I (*Concluded*)

Point in Fig.	Solution % H_2P	Solution % MgP	Wet residues % H_2P	Wet residues % MgP	Solid phases
C	1.16	34.42	27.32	39.32	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
	1.17	34.38	10.05	55.37	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
	1.03	34.26	0.85	58.39	$2MgP \cdot 11H_2O$
	0.47	34.16	.56	60.80	$2MgP \cdot 11H_2O$
D	None	34.11	...	...	$2MgP \cdot 11H_2O$
			Temperature, 50°		
A	1.72	None	...	...	H_2P
	4.13	2.85	95.22	...	H_2P
	6.15	5.36	...	...	H_2P
	7.43	6.95	...	...	H_2P
	9.47	9.95	74.86	3.20	H_2P
B	10.18	11.22	49.49	22.21	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	10.23	11.16	52.68	19.79	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	10.23	11.20	33.98	29.33	H_2P; $Mg(HP)_2 \cdot 8H_2O$
	7.95	13.68	29.61	34.15	$Mg(HP)_2 \cdot 8H_2O$
	6.56	18.72	...	...	$Mg(HP)_2 \cdot 8H_2O$
	5.52	24.20	27.92	35.73	$Mg(HP)_2 \cdot 8H_2O$
	4.64	31.51	26.07	35.85	$Mg(HP)_2 \cdot 8H_2O$
	3.88	38.25	28.22	38.11	$Mg(HP)_2 \cdot 8H_2O$
	3.67	41.19	...	...	$Mg(HP)_2 \cdot 8H_2O$
C	3.54	42.85	16.31	49.81	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
	3.56	42.75	15.32	48.39	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
	3.49	42.79	14.88	49.39	$Mg(HP)_2 \cdot 8H_2O$; $2MgP \cdot 11H_2O$
	3.12	42.71	0.75	60.43	$2MgP \cdot 11H_2O$
D	None	42.28	...	...	$2MgP \cdot 11H_2O$

TABLE II

SOLUBILITY DATA: THE SYSTEM MgP, Li_2P, H_2O

Point in Fig.	Solution % Li_2P	Solution % MgP	Wet residues % Li_2P	Wet residues % MgP	Solid phases
			Temperature, 25°		
E	45.24	None	...	...	$2Li_2P \cdot 3H_2O$
	41.12	7.52	78.94	2.39	$2Li_2P \cdot 3H_2O$
	36.72	12.98	80.93	2.40	$2Li_2P \cdot 3H_2O$
	34.50	16.39	81.47	2.66	$2Li_2P \cdot 3H_2O$
	33.05	19.27	74.92	5.13	$2Li_2P \cdot 3H_2O$
F	32.50	19.98	34.51	34.49	$2Li_2P \cdot 3H_2O$; $2MgP \cdot 11H_2O$
	32.50	19.97	35.51	33.65	$2Li_2P \cdot 3H_2O$; $2MgP \cdot 11H_2O$
	32.51	19.96	17.70	47.85	$2Li_2P \cdot 3H_2O$; $2MgP \cdot 11H_2O$
	29.53	20.43	7.67	54.70	$2MgP \cdot 11H_2O$
	26.88	20.96	7.14	54.28	$2MgP \cdot 11H_2O$
	21.78	22.40	6.25	55.58	$2MgP \cdot 11H_2O$
	19.63	23.06	4.25	55.43	$2MgP \cdot 11H_2O$
	14.86	25.31	3.88	56.37	$2MgP \cdot 11H_2O$
	4.55	31.09	1.12	58.71	$2MgP \cdot 11H_2O$
G	None	34.14	...	...	$2MgP \cdot 11H_2O$

Temperature, 50°

Solution % Li_2P	Solution % MgP	Solid phases
46.01	None	$2Li_2P \cdot 3H_2O$
41.76	6.97	$2Li_2P \cdot 3H_2O$
35.22	18.32	$2Li_2P \cdot 3H_2O$
31.05	26.06	$2Li_2P \cdot 3H_2O$
...	...	......
...	...	......
...	...	......
17.49	34.75	$2MgP \cdot 11H_2O$
11.78	36.10	$2MgP \cdot 11H_2O$
3.18	40.31	$2MgP \cdot 11H_2O$
None	42.28	$2MgP \cdot 11H_2O$

The Acid Salt.—The composition of the acid salt, $Mg(HP)_2 \cdot 8H_2O$, was determined by the extrapolation of tie lines which intersect at a point in the isotherms representing a composition which agrees very closely with this. The algebraic extrapolation of the tie lines as shown by Hill and Ricci[4] gives values for the composition which agree closely with the theoretical value of 28.91% water. The maximum deviation in this case was 0.90% with an average deviation of 0.10%. When samples of the hydrated acid salt were dried in an electric oven for twenty-four hours at 110°, percentages of water were found ranging from 28.71 to 29.12. Analyses of the hydrated acid salt for magnesium phthalate and phthalic acid gave an average value for water by difference of 29.08%. The octahydrate was kept in a desiccator over anhydrous magnesium acid phthalate for a prolonged period without loss in weight, giving no evidence of a lower hydrate.

The acid salt, $Mg(HP)_2 \cdot 8H_2O$, is congruently soluble only at 50°, for the three temperatures studied.

Summary

1. The solubility relations in the ternary system phthalic acid, magnesium phthalate and water at 0, 25 and 50° have been determined.
2. Compound formation has been found to take place in this system at all of these temperatures.
3. The composition of this compound has been shown to be $MgC_8H_4O_4 \cdot H_2C_8H_4O_4 \cdot 8H_2O$.
4. This acid salt is crystallizable from aqueous solution at temperatures of 50° and above.
5. When crystallized from water solution at room temperature, magnesium phthalate has the formula, $2MgC_8H_4O_4 \cdot 11H_2O$.
6. An isotherm showing the solubility relations in the ternary system magnesium phthalate, lithium phthalate and water at 25° has been completed. A 50° isotherm is incomplete.
7. No evidence of double salt formation in this system has been established.

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[4] Hill and Ricci, THIS JOURNAL, 53, 4306 (1931).