mole per cent. *p*-dichlorobenzene, and with triphenylmethane a simple eutectic at 35.9° and 68.5 mole per cent. *p*-dichlorobenzene.

2. Solubilities, eutectic temperatures and eutectic compositions in each of the three binary systems are a close approach to those calculated for ideal solutions.

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[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

Equilibrium in the System, Lithium Phthalate–Phthalic Acid–Water

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Introduction

The use of acid phthalates as standards in volumetric analysis has become widespread during the past twenty years. Both the potassium and the sodium acid salts are used. Their use was first suggested by Dodge[1] and by Hendrixson.[2] A phase rule study of the system potassium phthalate, phthalic acid and water has been made by Smith,[3] and the system sodium phthalate, phthalic acid and water by Smith and Sturm.[4] It is possible that the acid phthalates of other alkali metals could be used for similar purposes and it is with this point in mind that an investigation of the solubility relations in the system lithium phthalate, phthalic acid and water has been undertaken.

Experimental Part

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

Lithium phthalate was prepared by neutralizing in aqueous solution an equivalent weight of phthalic acid with C. P. lithium carbonate. The resulting solution was boiled to drive off carbon dioxide, evaporated to a small volume and allowed to crystallize. The resultant crystals of lithium phthalate were filtered on a Büchner funnel and dried in the air. The composition of this salt was found by analysis to be $2Li_2C_8H_4O_4 \cdot 3H_2O$.

Lithium acid phthalate, while not a component of this system, appears as one of the important solid phases and is used in the preparation of mixtures for analysis. This salt as will be apparent later cannot be crystallized from aqueous solution at room temperature and was prepared by adding less than the equivalent weight of phthalic acid to each equivalent of lithium phthalate prepared as above, and allowing the acid salt to crystallize from a solution of lithium phthalate.

Solubilities were determined by analyzing solutions obtained by rotating for a minimum of twenty-four hours mixtures of the three components in an electrically controlled thermostat. At zero degrees 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. At elevated temperatures the pipet was previously warmed to prevent crystallization during the sampling. When necessary, to prevent entrance of solid phase into the pipet, a small plug of cotton was placed in a short length of rubber tubing slipped over the end of the pipet.

Phthalic acid was determined by titration with alkali using phenolphthalein as the indicator. Lithium phthalate was determined by conversion into lithium sulfate with sulfuric acid and evaporating to dryness. The excess sulfuric acid was removed by ignition in a stream of ammonia. Water was determined by difference.

In making up the original mixtures, wherever possible the salts were used which exist as solid phases after equilibrium has been reached. The composition of the solid phases was determined by the analysis of wet residues according to Schreinemakers.[5] Because of the viscosity of many of the solutions, no attempt was made to determine their density.

Experimental Results.—Isotherms at 0, 25 and 50° have been completed. Compound formation takes place at all these temperatures. The solubility isotherms at these temperatures 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 solutions. Inasmuch as no new solid phases appeared and the same solid phases remained at these three temperatures, no further isotherms were completed.

Experimental results are given in Table I. The symbol "P" is used here as in previous work to designate the phthalate radical, $C_8H_4O_4$. The figures representing the composition of the solutions at the isothermally invariant points are the average of several closely agreeing results.

The Acid Salt.—The composition of the acid salt, $LiHP \cdot 2H_2O$, is most important as it is this material that has possibilities as a standard in volumetric analysis. The composition of this salt has been determined both graphically and by analysis. The extrapolated tie lines at each

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[1] F. D. Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915).

[2] W. S. Hendrixson, THIS JOURNAL, **37**, 2352 (1915).

[3] S. B. Smith, *ibid.*, **53**, 3711 (1931).

[4] S. B. Smith and W. A. Sturm, *ibid.*, **55**, 2414 (1933).

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

temperature intersect at a point closely representing this composition. Calculating the composition of the solid phase by the algebraic extrapolation of tie lines according to Hill and Ricci,[6] it was found that in no case did the calculated composition vary from the theoretical by more than 0.72%, with an average deviation of 0.33%.

TABLE I

SOLUBILITY DATA

Point in figs.	Solution % H_2P	Solution % Li_2P	Wet residues % H_2P	Wet residues % Li_2P	Solid phases
			Temperature, 0°		
A	0.30	None	...	...	H_2P
	1.47	1.62	92.47	0.78	H_2P
	1.97	2.28	92.39	.43	H_2P
	2.63	3.41	95.10	.67	H_2P
	3.92	5.83	98.64	.48	H_2P
	5.58	11.06	88.13	1.86	H_2P
	7.45	16.55	92.74	2.18	H_2P
	8.67	20.39	94.29	1.89	H_2P
B	9.61	22.45	71.14	13.48	H_2P; $LiHP·2H_2O$
			39.65	32.39	H_2P; $LiHP·2H_2O$
	8.36	24.18	...	...	$LiHP·2H_2O$
	7.15	26.09	...	...	$LiHP·2H_2O$
	6.18	27.37	38.67	41.70	$LiHP·2H_2O$
	4.15	32.40	...	...	$LiHP·2H_2O$
	3.46	36.25	38.26	42.56	$LiHP·2H_2O$
	2.84	40.55	...	...	$LiHP·2H_2O$
	2.81	45.06	39.10	42.76	$LiHP·2H_2O$
C	2.81	45.75	20.96	63.08	$LiHP·2H_2O$; $2Li_2P·3H_2O$
	1.27	45.41	0.82	72.04	$2Li_2P·3H_2O$
D	None	45.37	...	...	$2Li_2P·3H_2O$
			Temperature, 25°		
E	0.68	None	...	...	H_2P
	3.34	3.22	83.43	0.69	H_2P
	4.59	5.07	66.61	1.31	H_2P
	6.97	8.87	...	...	H_2P
	8.15	10.55	73.25	3.78	H_2P
	10.56	14.56	76.21	4.35	H_2P
	11.38	16.10	71.54	4.99	H_2P
	13.32	19.39	75.56	5.76	H_2P
	15.85	23.40	88.87	4.32	H_2P
F	16.34	24.25	82.61	6.01	H_2P; $LiHP·2H_2O$
			53.53	28.73	H_2P; $LiHP·2H_2O$
	14.01	25.56	...	...	$LiHP·2H_2O$
	11.39	28.23	...	...	$LiHP·2H_2O$
	9.08	32.36	...	...	$LiHP·2H_2O$
	7.79	34.07	38.34	42.64	$LiHP·2H_2O$
	7.56	35.17	35.89	42.37	$LiHP·2H_2O$
	6.51	38.13	...	...	$LiHP·2H_2O$
	5.25	44.55	33.70	42.80	$LiHP·2H_2O$
G	5.20	45.19	26.00	50.70	$LiHP·2H_2O$; $2Li_2P·3H_2O$
			7.38	67.64	$LiHP·2H_2O$; $2Li_2P·3H_2O$
	3.60	45.15	0.99	76.24	$2Li_2P·3H_2O$
	2.38	45.17	0.48	75.01	$2Li_2P·3H_2O$
H	None	45.20	...	...	$2Li_2P·3H_2O$
			Temperature, 50°		
I	1.75	None	...	...	H_2P
	4.75	3.28	92.46	0.75	H_2P
	6.81	5.30	95.31	.70	H_2P
	11.48	10.80	87.16	.95	H_2P
	15.29	15.28	87.94	2.73	H_2P
	20.21	21.36	83.81	4.18	H_2P
J	24.00	26.69	70.87	17.79	H_2P; $LiHP·2H_2O$
			46.04	36.42	H_2P; $LiHP·2H_2O$
	21.78	28.29	38.07	40.50	$LiHP·2H_2O$
	18.92	30.05	...	...	$LiHP·2H_2O$
	16.47	32.57	35.92	41.00	$LiHP·2H_2O$
	15.07	34.77	...	...	$LiHP·2H_2O$
	12.42	39.32	34.21	42.45	$LiHP·2H_2O$
	10.51	44.10	34.17	42.49	$LiHP·2H_2O$
K	9.97	46.01	30.15	50.46	$LiHP·2H_2O$; $2Li_2P·3H_2O$
			13.97	71.20	$LiHP·2H_2O$; $2Li_2P·3H_2O$
	9.44	46.00	3.01	72.43	$2Li_2P·3H_2O$
	6.40	46.00	2.49	70.52	$2Li_2P·3H_2O$
	3.72	46.01	...	...	$2Li_2P·3H_2O$
L	None	46.08	...	...	$2Li_2P·3H_2O$

A sample of the acid salt was carefully prepared by adding solid lithium phthalate and phthalic acid to a solution of lithium phthalate, the proportions being arbitrarily selected, as will be apparent. The mixture was rotated in the thermostat at 25° for sixty hours and then allowed to settle. The composition of the liquid phase was found by analysis to be H_2P = 7.32% and Li_2P = 35.27%, represented by a point in approximately the middle of the line representing the composition of all solutions in equilibrium with the acid salt as solid phase. The residue was quickly centrifuged and analyzed, giving the data: H_2P = 39.22%, Li_2P = 43.80%, H_2O by difference = 16.98%. The percentage composition

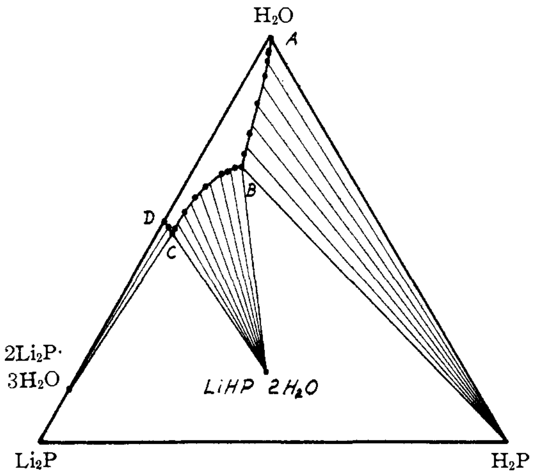

Fig. 1.—Temperature, 0°.

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

corresponding to the formula $LiHP\cdot 2H_2O$ is H_2P = 39.91%, Li_2P = 42.77%, H_2O = 17.32%.

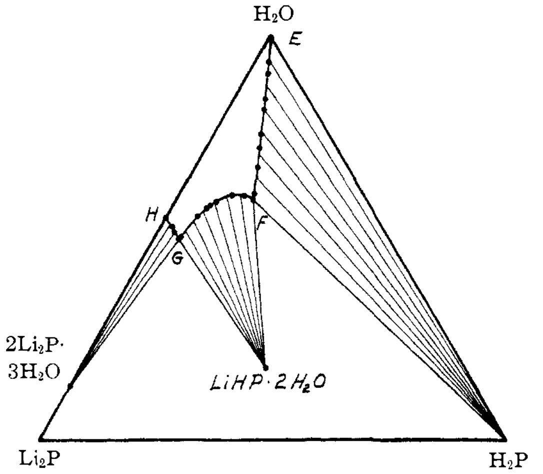

Fig. 2.—Temperature, 25°.

Discussion of Results

In order that a salt shall be crystallizable from aqueous solution at a given temperature, it is necessary that a straight line on the triangular diagram for that temperature, drawn from the apex, representing pure water, to that point on the diagram representing the composition of the salt in question, shall pass through the line representing the composition of all solutions in stable equilibrium with that salt as the solid phase.

Inspection of Fig. 3 shows that such a line would pass directly through the isothermally invariant point, "J." This means that at 50° lithium acid phthalate cannot be purified by crystallization from aqueous solution if the impurity is phthalic acid. Such procedure would result in the deposition of both salts. If the impurity were lithium phthalate, purification would result from recrystallization. At temperatures below 50°, Figs. 1 and 2, this reference line crosses the line representing the composition of all solutions in stable equilibrium with phthalic acid as the solid phase. Purification by recrystallization from aqueous solution at temperatures below 50° is obviously impossible.

It is apparent that the isothermally invariant point representing the composition of solutions in stable equilibrium with the two solid phases, phthalic acid and lithium acid phthalate, is working toward the right side of the diagram and approaches the above mentioned reference line as the temperature increases. In order to determine whether or not it has moved sufficiently so that our reference line crosses the line representing the composition of all solutions in stable equilibrium with lithium acid phthalate as the solid phase, a few experiments were carried out at 60°.

The composition of the solution in equilibrium with solid phthalic acid and solid lithium acid phthalate at this temperature was found to be H_2P = 27.31% and Li_2P = 28.05%. This point has now moved across our reference line, showing the acid salt, $LiHP\cdot 2H_2O$, to be crystallizable from aqueous solution at 60°.

Lithium acid phthalate might therefore be purified by recrystallization from aqueous solution for use as a volumetric standard provided the crystallization were carried out at a temperature not less than 60°. Owing to the high cost of lithium salts as well as to the fact that recrystallization must be carried out at a high temperature resulting in large losses, it is doubtful that lithium acid phthalate will be added to our list of volumetric standards.

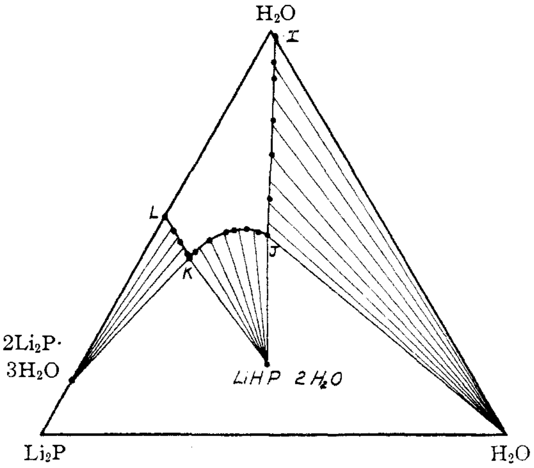

Fig. 3.—Temperature, 50°.

Summary

1. The solubility relations in the ternary system, lithium phthalate, phthalic acid and water at 0, 25 and 50° have been determined.

2. Compound formation has been found to take place at all of these temperatures.

3. The composition of this compound has been shown to be $LiHC_8H_4O_4\cdot 2H_2O$.

4. It has been shown that this acid salt is crystallizable from aqueous solution at temperatures not lower than 60°.

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