p-Methylphenylaminotriphenylmethyl Perchlorate.—Two methods were used in this preparation as far as the carbinol. Thereafter the same method was used in both cases. In the first method the previously described procedure was used, except that *p*-methylphenylaminobenzophenone was substituted for *p*-dimethylaminobenzophenone. The resulting carbinol did not crystallize. The oily product was dissolved in ether and added to a 1 *M* aqueous solution of perchloric acid. On standing a brick-red precipitate was formed. This precipitate was dissolved in acetone converted to the carbinol, which came out of the acetone solution as an oil by addition of water. This was again transformed to the perchlorate, as described above. The perchlorate came out as brick-red needles. The perchlorate was recrystallized from chloroform–ether mixtures, and acetone–petroleum ether mixtures.

Anal. Calcd. for $C_{26}H_{22}O_4NCl$: C, 69.9; H, 4.95; N, 3.16; Cl, 7.92. Found: C, 69.8; H, 5.03; N, 3.22; Cl, 7.97.

This substance was also prepared by a different method. Since the same method was used in the last three preparations, we shall refer to it later as method 2. The general principle of this method is to condense α,β-dichlorodiphenylmethane with an aromatic amine by a procedure that keeps an excess of the aromatic amine during the reaction.

A solution of α,α-dichlorodiphenylmethane dissolved in carbon disulfide (0.1 mole in 100 ml.) was slowly added to a boiling solution of excess of methyldiphenylamine (0.2 mole) in 100 ml. of carbon disulfide and 0.2 mole of aluminum chloride. Constant stirring was maintained during the addition, which took about an hour and a half. Boiling and stirring were continued for about two hours after the addition. While warm, the reaction mixture was poured slowly onto cracked ice and perchloric acid. The salt was taken up in chloroform and precipitated with ether. The perchlorate was changed to the carbinol from an acetone solution as in the first method. Purification failed to crystallize the carbinol.

The carbinol was again changed to the perchlorate and recrystallized as in the first method. The perchlorate prepared by this method gave the same spectrum as that prepared by the previous one.

n-Phenylaminotriphenylmethyl Methyl Ether.—The perchlorate of this color base was prepared by method 2, using diphenylamine instead of methyldiphenylamine. The crystals were blue and the solution red. The perchlorate was dissolved in hot methanol, and a dilute solution of sodium methylate in methanol was added until the solution was colorless. The methanol was evaporated off, and the residue was extracted with ether. After removal of the ether, the residual solid was recrystallized several times with methanol. The final product was in the form of colorless prisms melting at 127–128°. This compound had been previously prepared by Baeyer and Villiger,[6] who obtained a melting point of 127°.

n-Diphenylaminotriphenylcarbinol.—This compound was prepared by method 2, except that longer times and room temperature were used, and the chloride instead of the perchlorate was made. The chloride was changed to the carbinol, and the chloride reformed from the carbinol in carbon tetrachloride with dry hydrochloric acid gas. After two such transformations, the carbinol was taken up in ether. The ether solution was dried and treated with charcoal. After filtration the ether was evaporated off, and the resulting residue repeatedly crystallized from acetone–water mixtures. Colorless prisms, m.p. 141–142°, were obtained.

Anal. Calcd. for $C_{31}H_{25}NO$: C, 87.1; H, 5.89; N, 3.26. Found: C, 86.7; H, 5.87; N, 3.15.

3-Carbazyldiphenylcarbinol.—This color base was made by method 2, using about a threefold excess of carbazole. The perchlorate was obtained by addition of the reaction product to 6 *M* perchloric acid. The salt was extracted with chloroform, from which it was precipitated with ether. This was dissolved in acetone, and the carbinol precipitated with water. This carbinol is so weak a base that no alkali is needed to obtain it from its salts. The carbinol was dissolved in acetone and treated with charcoal. The solution was filtered and petroleum ether was added. The resulting precipitate was crystallized several times from benzene, and finally from an acetone–petroleum ether mixture. The final product was obtained as colorless prisms, m.p. 217°.

Anal. Calcd. for $C_{25}H_{14}ON$: C, 86.1; H, 5.48; N, 4.01. Found: C, 86.1; H, 5.72; N, 3.81.

In general the salts of these compounds are soluble in acetone, methanol and chloroform, and insoluble in ether, carbon tetrachloride, benzene, petroleum ether and water. The color bases are soluble in acetone, chloroform, carbon tetrachloride, benzene and ether, somewhat less soluble in methanol, and insoluble in petroleum ether and water. The carbinol of the carbazyl compound is anomalous in that it is difficultly soluble in benzene and chloroform. Its solubility in carbon tetrachloride was not tried; but it was freely soluble in acetone, and fairly soluble in ether.

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(6) A. Baeyer and V. Villiger, *Ber.*, **37**, 2837 (1904).

BERKELEY, CALIF. RECEIVED JANUARY 2, 1951

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

The Vapor Pressure of Water over Phosphoric Acids

BY B. J. FONTANA

The vapor pressure of water over phosphoric acids has been measured over a range of compositions representing from 86.5% orthophosphoric acid to almost pure pyrophosphoric acid. Temperature dependence of the vapor pressure measured in the region of about 35 to 280° can be expressed in the usual form of $\log P = -A/T + B$. The variation in heat of vaporization calculated from the vapor pressures appears to agree qualitatively with analytical and phase studies of the composition of phosphoric acids.

Phosphoric acid is used as a polymerization catalyst at compositions in the region of, and exceeding, that corresponding to 100% orthophosphoric acid.[1] Process control requires appropriate data on the variation of water partial pressure as a function of temperature and phosphoric acid composition.

The old data of Balareff[2] on the "formation temperatures" of pyro- and metaphosphoric acids should correspond to the water partial pressures over the pure ortho- and pyrophosphoric acids, respectively. However, the values thus obtained are completely erroneous.

The only data in the literature in the region of interest are those correlated by Striplin.[3] This author found the available data, consisting of (1) a nomograph by Perry and Duus[4] covering the range of 75 to 95% orthophosphoric acid at temperatures between 25 and 35°, (2) data by Kablukov and Zagvozdkin[5] up to a maximum composition of 87.1% orthophosphoric acid and

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(1) G. E. Langlois and J. E. Walkey, presented before the Third World Petroleum Congress, The Hague, May 28–June 6, 1951.

(2) D. Balareff, *Z. anorg. Chem.*, **67**, 234 (1910).

(3) M. Striplin, Jr., *Ind. Eng. Chem.*, **33**, 910 (1941).

(4) J. H. Perry and H. C. Duus, *Chem. Met. Eng.*, **41**, 74 (1934).

(5) I. A. Kablukov and K. I. Zagvozdkin, *Z. anorg. Chem.*, **224**, 315 (1935).

temperature of 80° and (3) "unpublished TVA data," to be discordant as to the effect of composition on the vapor pressure. However, Striplin combined these data and measurements of his own on 95 and 99% orthophosphoric acid in the range of 30 to 150° (experimental data not given) to yield a correlation in the form of a plot covering the range of 50 to 100% orthophosphoric acid from 20 to 150°.

The data obtained in the present work cover the range of compositions from 86.5% orthophosphoric acid (H_3PO_4) to that corresponding almost to pure pyrophosphoric acid ($H_4P_2O_7$) at maximum temperatures of about 110 to 280°, respectively.

Vapor Pressure Measurement.—The dynamic "air saturation" method was used for the experimental measurements of the water vapor pressure. The experimental setup and method of calculation of the vapor pressures were strictly analogous to those used by Thomas and Barker[6] for water partial pressure measurements over concentrated sulfuric acid. In the present work the entering air was dried over concentrated sulfuric acid and Drierite, and the water vapor from the phosphoric acid sample was collected, for weighing, over Drierite. Enough phosphoric acid was used in every case (210 to 260 g.) so that concentration changes produced by removal of water could ordinarily be neglected. Duplicate runs with from two- to fivefold air flow rate increases revealed no systematic differences, indicating that equilibrium was attained at the flow rates used.

Constant temperatures were maintained to at least ±0.1° with appropriate vapor baths. Temperatures were measured with an accuracy of ±0.1° with a copper–constantan thermocouple (calibrated against a N.B.S. certified platinum resistance thermometer). The volume of air passed through the acid sample was measured with a wet test meter (0.1 cu. ft. full-scale, ±0.5% accuracy).

Preparation and Analysis of Phosphoric Acid.—The phosphoric acid preparations were made, in every case, by heating C.P. grade 85% orthophosphoric acid to drive off the water. It is notable that in two of the three previous publications on phosphoric acid vapor pressure measurements,[4,5] no mention is made of the analytical methods used to determine the phosphoric acid composition (Striplin[3] presumably used density measurements). This may be a contributing factor to the disagreement observed in the vapor pressure measurements.

The method of analysis used in the present work was that of titration of the diluted acid with 0.5 normal sodium hydroxide, following the course of the titration with a *p*H meter. Inflection points obtained from plots at about 0.1-cc. intervals yielded results differing usually by ±0.1–0.2% and never more than ±0.3% for duplicate determinations. The first hydrogen of orthophosphoric acid shows the sharpest inflection, but whenever both the first and second hydrogens were titrated, good agreement was observed.

Discussion of Results

It should first be noted that separate experiments established that no appreciable amounts of acid were present in the vapor phase over even the most concentrated acid at the highest temperatures employed. The measurements correspond then only to the vapor pressure of water over phosphoric acid.

The experimental data were found to be represented adequately by equations of the usual form: $\log P = A/-T + B$. The parameters of this equation (where P = mm. and T = °K.) are given in Table I for each experimental phosphoric acid composition. The composition is tabulated as the per cent. orthophosphoric acid (or "apparent per cent." for over 100%) and as the equivalent per cent. of phosphorus pentoxide. Pure pyrophosphoric acid ($H_4P_2O_7$) would correspond to 110.1 apparent per cent. orthophosphoric acid.

TABLE I

THE VAPOR PRESSURE OF PHOSPHORIC ACID

$\log P = -A/T + B$

C, % H_3PO_4	P_2O_5, %	A	B	$\Delta A/\Delta C$
86.5	62.7	2430	8.455	17
96.2	69.7	2586	8.210	126
100.1	72.5	3065	8.626	136
102.8	74.5	3433	8.992	148
109.9	79.6	4486	9.757	

The actual experimental data are shown in Table II along with values calculated from the equations of Table I. The average difference between the observed and calculated values at any given concentration varies from 1 to 5%, which is probably representative of the over-all accuracy of the data. The agreement with data from Striplin's correlation[3] (estimated by that author to be accurate to ±10%) is poor.

TABLE II

EXPERIMENTAL AND CALCULATED VALUES OF THE VAPOR PRESSURE OF PHOSPHORIC ACID

H_3PO_4, %	t, °C.	P. obsd.	P. calcd.	Av. difference, %	P[a]
86.5	34.7	3.53	3.63		
	56.5	12.55	12.08		
	109.9[b]	124.6	128.8	±3.3	
96.2	56.0	2.26	2.24		
	80.0	7.63	7.69		
	110.2	29.7	29.0		
	122.4	47.7	47.1		
	155.1[b]	152.1	152.1	±1.1	
100.1	79.1	0.81	0.84		1.3
	110.2	4.23	4.26		5.4
	138.7	16.3	15.3		18.0
	219.8	246.2	255.3	±3.6	
102.8	109.8[b]	1.00	1.06		
	138.9	4.63	4.57		
	182.9[b]	30.0	29.0		
	238.7	174.6	192.3	±4.9	
109.9	221.3	4.91	4.81		
	240.0	10.27	10.33		
	276.5	38.8	39.1	±1.2	

[a] Data from reference 3. [b] Duplicate runs made at different air flow rates.

It is of interest to note the behavior of the heat of vaporization as a function of concentration as indicated by the values of the parameter A ($= \Delta H_v/R$) in the vapor pressure equation. The heat of vaporization starts to rise very sharply and uniformly with composition (see the values of $\Delta A/\Delta C$ in Table I) at about 96% orthophosphoric acid. It is evident then, that new equilibria governing the release of water apply at compositions appreciably below 100% orthophosphoric acid. This conclusion is in qualitative agreement with studies of the composition and phase behavior of phosphoric acid. The recent analytical work of Bell[7] indicates that phosphoric acids other than H_3PO_4 are probably present at and below the composition corresponding to "100% H_3PO_4,"

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(6) Thomas and Barker, *J. Chem. Soc.*, **127**, 2820 (1925).

(7) R. N. Bell, *Ind. Eng. Chem.*, **40**, 1464 (1948).

a result not apparent in earlier studies.[8] The hydrate $(H_3PO_4)_2 \cdot H_2O$, corresponding to 91.5% H_3PO_4, has been reported by Ross and Jones[9] and earlier workers. The premature formation of $H_4P_2O_7$, for example, at compositions below "100% H_3PO_4" can be accounted for then if the above hydrate persists in the liquid phase at compositions up to, and then necessarily also slightly exceeding, that corresponding to pure orthophosphoric acid.

The value of "*A*" at 86.5% orthophosphoric acid is in agreement with the more or less constant values observed by Kablukov and Zagvozdkin[5] for acid concentrations ranging from about 6 to 82%.

RICHMOND, CALIF. RECEIVED DECEMBER 15, 1950

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[8] J. H. Lum, J. E. Malowan and C. B. Durgin, *Chem. Met. Eng.*, **44**, 721 (1937).

[9] W. H. Ross and R. M. Jones, THIS JOURNAL, **47**, 2165 (1925); earlier references to the semi-hydrate are given in this article.

[CONTRIBUTION FROM THE RESEARCH DIVISION OF ARMOUR AND COMPANY]

The Binary Systems of Water with Dodecylammonium Chloride and Its N-Methyl Derivatives[1]

BY F. K. BROOME, C. W. HOERR AND H. J. HARWOOD

The systems of dodecylammonium chloride and its N-methyl, dimethyl and trimethyl derivatives with water have been investigated over the entire range of concentration. Each of these systems is characterized by the formation of a hydrate which forms a simple eutectic with water and possesses an incongruent melting point. Superimposed upon these systems are mesomorphic regions indicative of various liquid crystalline orientations. In the primary and secondary salt systems the liquidus curve in dilute solution is altered abruptly by the occurrence of the so-called "Krafft effect" in the region of micelle formation. The liquidus curve of the primary salt is further interrupted by a crystalline transformation at 57.5°, unstable crystal forms have been observed in all four systems. The similarity of these diagrams with those of the soap–water systems has been mentioned.

Recent reports on the influence of N-methylation on the physical properties of dodecylammonium chloride have included studies of solubilities in hexane, benzene and ethanol[2] and electrical conductances in aqueous solution.[3] Since much of the interest in these materials centers in their colloidal and colloidal–electrolytic nature, the studies have been extended to include their binary systems with water. This paper presents the phase diagrams with water of dodecylammonium chloride and methyl-, dimethyl- and trimethyldodecylammonium chlorides.

Experimental

Preparation of Materials.—The salts used in this study are identical with those of the earlier study,[2] in the report of which their preparations have been sufficiently described. The extremely hygroscopic quaternary ammonium chloride was dried *in vacuo* over phosphorus pentoxide and stored in a dry atmosphere. An infrared spectrogram of this salt in chloroform solution showed no absorption in the 3 and 6 μ regions, demonstrating the absence of water.

In the primary and quaternary salt studies, two preparations of each of these salts were used in several instances. In all these cases, duplicate concentrations gave reproducibility of the observed phase changes within ±0.1°.

Freshly prepared conductivity water was used in this investigation.

Procedures.—Most of the data reported herein were obtained on known mixtures of a salt and water sealed into glass tubes. These tubes, by procedure already described extensively,[4,5,6] were examined visually during heating and cooling. Visible phase changes were observed at all the points plotted on the diagrams. The lines and curves connecting these points represent true reversible equilibria, observable both upon raising and upon lowering the temperature. In general, the transition temperatures of the crystalline phases were reproducible to within ±0.1° below 100° and ±0.2° above this temperature, with the exception of the metastable equilibria of the secondary and tertiary salt systems which are probably accurate only to ±0.5°. The curves representing the unstable systems were obtained by lowering the temperature of a mixture until crystals appeared and then raising the temperature until solution occurred. Maintaining the temperature for a time just below the precipitation point resulted in transformation to the stable form and re-solution only at the higher temperature. In the case of quaternary salt mixtures in the neighborhood of the eutectic composition, the transformation was exceedingly slow, extreme conditions such as Dry Ice temperatures overnight being used to effect the transformation. Phase boundaries among the liquid–crystalline phase were reproducible within about ±0.2° below 100° and ±0.5° above this temperature.

At high salt concentrations, particularly in the case of trimethyldodecylammonium chloride, the high temperatures necessary to produce isotropic solutions result in excessive decomposition. Therefore, in some cases it was impossible to obtain perfect homogenization of the tube contents before observations were made. Satisfactory mixing, as judged by the reproducibility and reasonableness of results, was obtained by subjecting the tubes and contents to ultrasonic vibrations.

The liquidus and solidus curves of the crystalline systems at concentrations below those of the eutectics were verified by means of cooling and heating curves. These curves were obtained with a platinum resistance thermometer in conjunction with a Mueller bridge (Leeds and Northrup). The temperatures at which ice or the eutectic mixtures froze and melted agreed within ±0.05° and were reproducible well within these limits.

A number of mixtures of amine salt with water were examined on an electrically heated stage under a polarizing microscope (×420). Concentrations of amine salt were so chosen that all the regions observed macroscopically below 100° could be verified microscopically upon heating and cooling. The existence of the various regions was further proved by allowing dilute solutions to evaporate at constant temperature, thereby traversing the various regions of the diagrams isothermally. The decomposition temperature of the hydrate of dodecylammonium chloride was established microscopically within ±0.1°.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society, September, 1950.

[2] F. K. Broome and H. J. Harwood, THIS JOURNAL, **72**, 3257 (1950).

[3] A. W. Ralston, F. K. Broome and H. J. Harwood, *ibid.*, **71**, 671 (1949).

[4] A. W. Ralston, E. J. Hoffman, C. W. Hoerr and W. M. Selby, *ibid.*, **63**, 1598 (1941).

[5] H. J. Harwood, A. W. Ralston, W. M. Selby, *ibid.*, **63**, 1916 (1941).

[6] C. W. Hoerr and A. W. Ralston, *ibid.*, **64**, 2824 (1942).