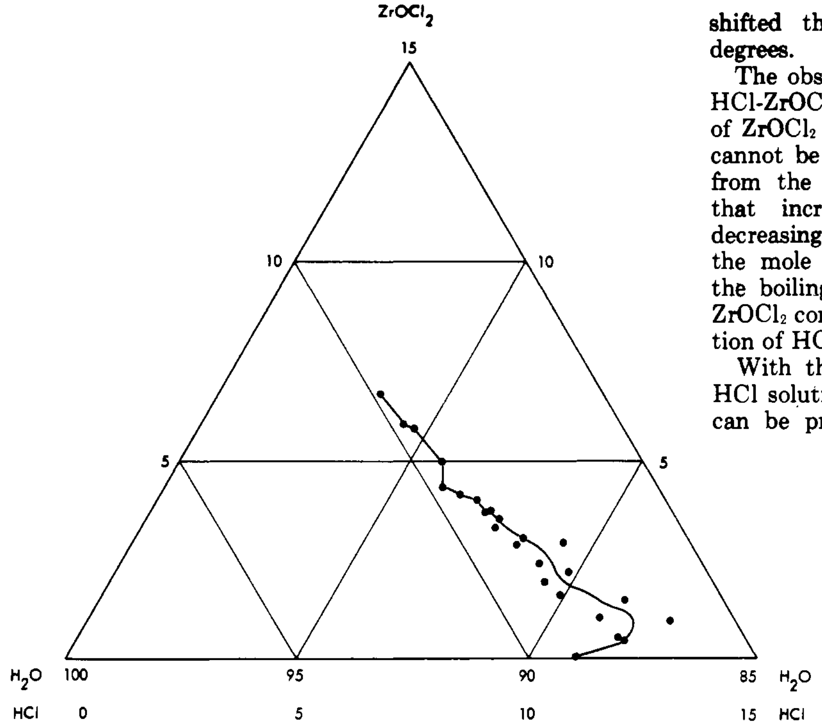


Figure 2. HCl-H_2O-$ZrOCl_2$ system at boiling points
In mole percentage

The reproducibility between runs, particularly in the temperature of incipient crystallization—see runs 5 and 8, for example—confirms that the measurements were indeed made on a reproducible azeotropic system, analogous to the two-component H_2O-HCl system, but containing a specific amount of a third component, $ZrOCl_2$. In experiments previous to those reported above, it was discovered that small deviations from the azeotropic HCl-H_2O ratio shifted the incipient-crystallization temperature several degrees.

The observation that the boiling point of the azeotropic HCl-$ZrOCl_2$ solutions was nearly constant over the range of $ZrOCl_2$ concentrations investigated was unexpected and cannot be fully explained at present. However, it is clear from the results, particularly as presented in Figure 2, that increasing $ZrOCl_2$ concentrations correspond to decreasing HCl concentrations and have little effect on the mole per cent of H_2O. Thus, the ionic strength of the boiling solutions must remain nearly constant as the $ZrOCl_2$ concentration increases. This is due to the volatilization of HCl.

With the aid of Figure 1, the properties of a $ZrOCl_2$-HCl solution that has been boiled at atmospheric pressure can be predicted at $ZrOCl_2$ concentrations up to 3.5*M*.

ACKNOWLEDGMENT

Chemical analyses were provided by the groups of G. R. Wilson and W. R. Laing, Oak Ridge National Laboratory, Analytical Chemistry Division.

RECEIVED for review January 24, 1966. Accepted August 29, 1966. Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

Acid Ionization Constants of Phenol and Some Hydroxymethylphenols between 20° and 60° C.

ANDREAS A. ZAVITSAS
Research Department, Plastic Products and Resins Division, Monsanto Co., Springfield, Mass.

The temperature dependence of the acid ionization constants of phenol and four hydroxymethylphenols has been determined between 20° and 60° C. The pK_a at an ionic strength of 0.1 at 60° C. and the quantity $d(pK_a)/d(1/T)$ are: phenol 9.49, 1046; 2-hydroxymethylphenol 9.42, 1182; 4-hydroxymethylphenol 9.39, 981; 2,4-dihydroxymethylphenol 9.31, 1072; and 2,4,6-trihydroxymethylphenol 9.10, 991.

THE industrial preparation of phenolic resins of the "resole" type is based on the hydroxymethylation of phenol by formaldehyde; relatively small amounts of base, of the order of 5 mole % on phenol, are used to catalyze the reaction, usually at temperatures in the vicinity of 60° C. The intermediate products are the hydroxymethylphenols, having the general formula $HOC_6H_{5-n}(CH_2OH)_n$ (n = 1, 2, or 3), which also react with formaldehyde when n = 1 or 2. The rates of these reactions are proportional to the anion concentration of each phenolic species, and an exact knowledge of the acid ionization constants is necessary to establish the distribution of the anion form among phenol and the five hydroxymethylphenols during any kinetic investigation of the system. Lack of this knowledge has been one of the factors that have hampered rigorous kinetic studies of the reaction.

The acid ionization constants have been determined at 25° C. for phenol and the hydroxymethylphenols (*13*); the temperature dependence of pK_a for phenol also has been determined (*2*, *4*). Comparisons between our data and those reported previously are given below.

Our method involved the determination of the pH of aqueous solutions of very nearly 0.1*M* in each acid and an exactly equivalent amount of its sodium salt. The pK_a

was determined by the usual relationship, Equation 1 (*8*),

$$pK_a = pH - \log \frac{[A^-]}{[AH]} \qquad (1)$$

where $[A^-]$ is the concentration of completely ionized salt, and $[AH]$ the concentration of the acid. Under the conditions of out experiments, $[A^-] = [AH]$ and, therefore, the logarithmic term is zero. The values thus obtained for phenol, 2-hydroxymethylphenol (2-HMP), 4-hydroxymethylphenol (4-HMP), 2,4-dihydroxymethylphenol (2,4-DHMP), and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) are shown graphically in Figure 1 plotted *vs.* $1/T°$ K.

Serious complications could arise from self-condensation reactions of the hydroxymethylphenols during the measurements as shown in Equation 2; this type of reaction is usually promoted by heat.

$$2\ HOC_6H_4CH_2OH \rightarrow HOC_6H_4CH_2C_6H_4OH + HCHO + H_2O \qquad (2)$$

In order to minimize and estimate the extent of the occurrence of self-condensations, the pH as a function of temperature was measured while the solutions were cooling after having been brought quickly to just over 60° C. The rate of cooling applied allowed sufficient temperature equilibration with the electrodes and relatively short times at the elevated temperatures. At 30° C. self-condensations are known to be relatively slow (*7*) compared to the time required for the pH measurements. The values obtained at 25° C. were then compared to those of Sprengling and Lewis (*13*), which were obtained by ultraviolet spectrophotometry at about the same ionic strength ($\mu \cong 0.1$); if reactions such as 2 had occurred to any significant extent while the solutions were warm, there would be disagreement between the two sets of values. Table I shows good agreement and indicates that the extent of self-condensations was insignificant for the purpose of these measurements.

The experimentally obtained data at $\mu \cong 0.1$ must be corrected by the Debye-Hückel relation for the ionic activity coefficient in order to be converted to the thermodynamic scale, denoted by pK_a° and defined in Equation 3.

$$pK_a^\circ = pK_a + \log \gamma_\mp \qquad (3)$$

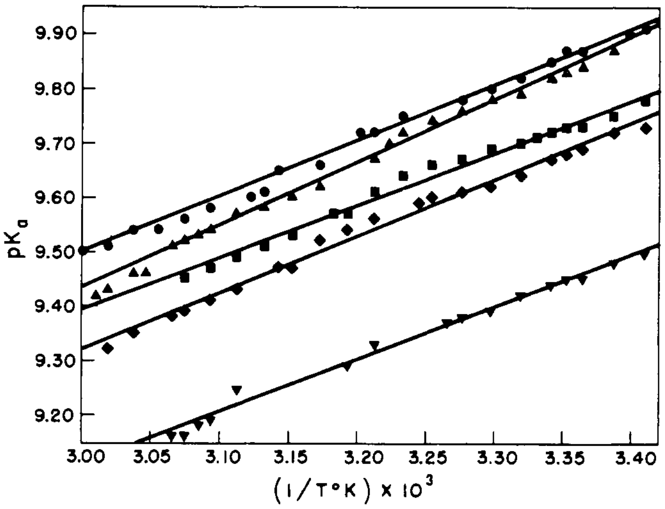


Figure 1. pK$_a$ Determined at μ = 0.1 *vs.* $1/T°$ K.

● Phenol
▲ 2-HMP
■ 4-HMP
◆ 2,4-DHMP
▼ 2,4,6-THMP

Table I. pK$_a$ Found at 25° C. at $\mu \cong 0.1$

Compound	This Work	Ref. (*13*)
Phenol	9.86	9.85
2-HMP	9.84	9.83
3-HMP		9.74
4-HMP	9.73	9.73
2,4-DHMP	9.68	9.68
2,6-DHMP		9.57
2,4,6-THMP	9.45	9.47

Within the accuracy of the measurements, the logarithm of the mean ionic activity coefficient can be obtained from Equation 3a,

$$\log \gamma_\mp = \frac{a\,(\mu)^{1/2}}{1 + (\mu)^{1/2}} = 0.11 \qquad (3a)$$

assuming an average 1 to 1 electrolyte behavior (*10*). The value of a has been taken as 0.5 throughout our temperature range, since, in the expression for a, the changes in temperature and dielectric constant of the solvent are nearly compensatory in this region, within the limits of error in the measurements.

Assuming a constant heat of reaction over this relatively small range of temperature, the integrated form of the van't Hoff equation (*8*), Expression 4,

$$\cdot \log \frac{K_2}{K_1} = \frac{-\Delta H}{4.576}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

requires that the experimental points as plotted on Figure 1 lie on a straight line. The lines shown on the figure are fitted to the points by a least-squares analysis performed on a digital computer. The least-squares smoothed values at nine temperatures are shown in Table II.

After correction to the thermodynamic scale, a least-squares fitting of the points gave the information tabulated in Table III, where $d(pK_a^\circ)/d(1/T)$ is the slope, and the heat of ionization is given by Equation 5.

$$\Delta H^\circ = -4.576\,\frac{d(pK_a^\circ)}{d(1/T)} \qquad (5)$$

The standard free energy change is given by Equation 6

$$\Delta G^\circ = 2.303\,R\,pK_a^\circ \qquad (6)$$

and the entropy of inoization is given by Equation 7 (*8*).

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad (7)$$

Table II. pK$_a$ at μ = 0.1 at Various Temperatures[a]

Temp., °C.	Phenol	2-HMP	4-HMP	2,4-DHMP	2,4,6-THMP
20	9.92	9.91	9.79	9.75	9.51
25	9.86	9.84	9.73	9.69	9.45
30	9.80	9.77	9.68	9.63	9.39
35	9.74	9.71	9.63	9.57	9.34
40	9.69	9.65	9.58	9.52	9.29
45	9.64	9.59	9.53	9.46	9.24
50	9.59	9.53	9.48	9.41	9.19
55	9.54	9.48	9.43	9.36	9.15
60	9.49	9.42	9.39	9.31	9.10

[a] Corresponding thermodynamic values can be obtained by adding 0.11 to above values (see text).

Table III. Thermodynamic Paramaters near 25° C.

Function	Phenol	2-HMP	4-HMP	2,4-DHMP	2,4,6-THMP
$d(\mathrm{p}K_a^\circ)/d(1/T)$	1047	1182	981	1072	991
ΔH°, kcal./mole	4.8	5.4	4.5	4.9	4.5
ΔG°, kcal./mole	13.6	13.6	13.4	13.4	13.1
ΔS°, cal./deg.mole	−29.6	−27.4	−30.0	−28.4	−28.6

Our value of $\mathrm{p}K_a^\circ = 9.97 \pm 0.03$ at 25° C. for phenol can be compared with previously reported values of 9.94 (*13*) by spectrophotometry, 9.97 (*2*) by buffered cells of the type

$$H_2|C_6H_5OH,\ C_6H_5ONa,\ NaCl|AgCl\text{-}Ag$$

9.98 used by Fernandez and Hepler (*5*), and a more recent value of 10.02 (*4*).

The uncertainty in the other derived parameters of Table III can be estimated at ±0.5 kcal. in ΔH°, ± 0.03 in ΔG°, and ± 1.3 cal./deg. mole in ΔS°, on the basis of errors of ±0.03 unit in the $\mathrm{p}K_a$ determinations (*12*). Our values for ΔH°, ΔG°, and ΔS° for phenol are, respectively, 4.8 ± 0.5, 13.61 ± 0.03, and -29.6 ± 1.3; these can be compared with reported values of 5.6 ± 0.4, 13.67 ± 0.02, and -26.9 ± 1.2 (*4*). The differences are not greater than about the sum of the experimental errors. Values for the heats of ionization for all the investigated hydroxymethylphenols range between 4.5 and 5.5 and are in line with the generalization that phenols have $\Delta H^\circ = 5 \pm 1$ kcal. (*12*).

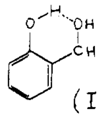
An application of the Hammett equation to the data can provide imformation regarding the extent of the electron-withdrawing capacity of the hydroxymethyl group (*9*).

Equation 8 is one form of the relationship (*1*); the value

$$\Delta\, \mathrm{p}K_a^\circ = -\rho\,\sigma \tag{8}$$

of rho, the reaction constant, is very nearly 2.2 (*1, 11*). The decrease of 0.13 $\mathrm{p}K_a$ unit with *p*-hydroxymethyl substitution leads to a substituent constant, $\sigma_p = 0.059$; it appears then that the $-CH_2OH$ group is only slightly electron-withdrawing, intermediate between $-CH_2Cl$ ($\sigma_p = 0.184$) and $-CH_2CN$ ($\sigma_p = 0.007$) and similar to $-F$ ($\sigma_p = 0.062$) (*11*).

Table I shows that substitution of hydroxymethyl in either the para or the meta position of phenol causes an increase in acidity reflected by a decrease of about 0.12 in the $\mathrm{p}K_a$ at 25° C. In the ortho isomer, however, the decrease is very small (0.02 $\mathrm{p}K_a$ unit). Apparently the increase in the acid strength expected from the inductive effect of the hydroxymethyl group is counteracted by a weakening of the strength of the acid because of intramolecular hydrogen bonding between the two hydroxyl groups, the phenolic hydroxy hydrogen serving to form the bridge. The introduction of a second hydroxymethyl group seems to reduce or completely destroy this hydrogen bonding; the average decrease in the $\mathrm{p}K_a$ caused by each hydroxymethyl substituent is 0.12 ± 0.02, derived from all the entries on Table I with the exception of those for 2-hydroxymethylphenol. This intramolecular hydrogen bonding leads to a six-membered ring (I); there is independent evidence that the phenolic rather than the alcoholic hydrogen is directly involved. In an NMR investigation of the hydrogen bonding between phenols and ethanol it was found that association of the phenolic -OH proton occurs with the alcohol, rather than the reverse (*14*).



(I)

The conclusion that intramolecular hydrogen bonding is significant only in the mono *o*-hydroxymethyl substitution is supported by the temperature dependence of the acid strengths. The increase in temperature results in a breakdown of this hydrogen bonding and a faster increase in the acid strength of 2-HMP; only this isomer shows a temperature effect significantly greater than that of phenol itself.

EXPERIMENTAL

Materials. Phenol was reagent grade material redistilled before use. 2-Hydroxymethylphenol and 4-hydroxymethylphenol were commercial reagent grade materials recrystallized from water-methanol mixtures with the first and the last 20% of the crop rejected. 2,4,6-Trihydroxymethylphenol was prepared as the sodium salt from phenol and formaldehyde according to the procedure of Freeman (*6*).

Equipment. The pH measurements were carried out with a Photovolt Model 125 meter standardized with the necessary buffers. The temperature corrections applied to the readings were checked by determining the known temperature dependence of the ionization constant of acetic acid by a procedure identical to that used for the phenols. Our results did not vary by more than the experimental error from those previously listed (*3*). The type of equipment and the standardization procedures used can be estimated to be capable of producing, in addition to random errors, systematic errors of about ±0.03 pH unit.

Procedure. The procedure followed for phenol, 2- and 4-hydroxymethylphenol, and 2,4-dihydroxymethylphenol was to dissolve 0.0200 equivalent of the acid and 0.0100 equivalent of sodium hydroxide (as 1.00*M* solution) in 35 ml. of distilled water and add 55 ml. of boiling distilled water to make approximately a 0.1*M* solution of the acid and its salt near 65° C. The electrodes were immersed in the stirred system and a mixture of ice and water was used to effect a cooling rate of about 3° C. per minute. pH readings were taken at intervals of a few degrees.

The procedure for 2,4,6-trihydroxymethylphenol was similar, except that 0.0200 equivalent of the sodium salt was mixed with 0.0100 equivalent of hydrochloric acid (as a 1.00*M* solution) in 100-ml. total volume.

ACKNOWLEDGMENT

We acknowledge the skillful technical assistance of K. Kozlowski.

LITERATURE CITED

(1) Biggs, A.I., Robinson, R.A., *J. Chem. Soc.* **1961**, 388.
(2) Binns, E.H., *Trans. Faraday Soc.* **55**, 1900 (1959).
(3) Chemical Rubber Publishing Co., Cleveland, Ohio, "Handbook of Chemistry and Physics," 44th ed., p. 1758, 1963.
(4) Chen, D.T.Y., Laidler, K.J., *Trans. Faraday Soc.* **58**, 480 (1962).
(5) Fernandez, L.P., Hepler, L.G., *J. Am. Chem. Soc.* **81**, 1783 (1959).
(6) Freeman, J.H., *Ibid.*, **74**, 6257 (1952).
(7) Freeman, J.H., Lewis, C.W., *Ibid.*, **76**, 2080 (1954).

(8) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., Van Nostrand, New York, 1946.
(9) Hammett, L.P., *Chem. Revs.* **17**, 125 (1935).
(10) Hammett, L.P., "Introduction to the Study of Physical Chemistry," p. 323, McGraw-Hill, New York, 1952.
(11) Jaffé, H.H., *Chem. Revs.* **53**, 191 (1953).
(12) King, E.J., "Acid-Base Equilibria," Chap. 7 and 8, Pergamon Press, New York, 1955.
(13) Sprengling, G.R., Lewis, C.W., *J. Am. Chem. Soc.* **75**, 5709 (1953).
(14) Somers, B.G., Gutowsky, H.S., *Ibid.*, **85**, 3065 (1963).

RECEIVED for review February 10, 1966. Accepted September 12, 1966.

Preparation and Single-Crystal Growth of Anhydrous $RbMnCl_3$ and $CsMnCl_3$

M. KESTIGIAN, W. J. CROFT, and F. D. LEIPZIGER
Sperry Rand Research Center, Sudbury, Mass.

The formation of anhydrous $RbMnCl_3$ and $CsMnCl_3$ was confirmed by chemical analysis. Large, optical-quality single crystals were prepared by the temperature gradient and vertical Bridgman methods by utilization of an evacuated sealed ampoule technique. X-ray powder diffraction data obtained at room temperature indicate $RbMnCl_3$ and $CsMnCl_3$ to exhibit hexagonal symmetry with $a = 7.164$, $c = 17.79_8$, and $a = 7.288$, $c = 27.44$ A., respectively.

THE existence of $RbMnCl_3$ was first reported by Natsvlishvili and Bergman (*3*), who examined the liquidus line of the $RbCl$-$MnCl_2$ system. Gramakov (*1*) investigated the $RbCl$-$MnCl_2$ system and presented data that did not agree with the previous research. A more recent study of the $RbCl$-$MnCl_2$ and $CsCl$-$MnCl_2$ systems reports the formation of compounds of molar ratios 1:1, 2:1, and 3:2; and 1:1, 2:1, 3:1, and 1:4, respectively (*2*). The single-crystal growth and characterization of the anhydrous compounds $RbMnCl_3$ and $CsMnCl_3$ have not been reported previously.

EXPERIMENTAL

Anhydrous $RbMnCl_3$ and $CsMnCl_3$ were prepared by heating an intimate equimolar mixture of the respective alkali metal chloride and manganous chloride tetrahydrate in an atmosphere of dry hydrogen chloride transported by purified argon carrier gas. The sample, contained in a platinum vessel, was heated slowly to above its melting point and the temperature maintained for 2 hours. Single crystals were prepared by the vertical Bridgman and temperature gradient methods utilizing an evacuated sealed ampoule technique. Nominally a 100° C. temperature gradient between the hot and cool temperature zone and a travel rate of 1.5 mm. per hour were used. The single crystals were program cooled 20° per hour to room temperature to eliminate or minimize thermal shock effects.

ANALYSIS

Samples were weighed and dissolved in water. The chlorine was precipitated as $AgCl$, dried at 110° C., and weighed. The alkali metal cations were precipitated with tetraphenylboron, dried, and weighed. The manganese was determined titrimetrically with permanganate. Analysis. Calculated for $RbMnCl_3$: Rb, 34.6; Mn, 22.2; Cl, 43.2. Found: Rb, 35.1; Mn, 22.3; Cl, 43.4. Calculated for $CsMnCl_3$: Cs, 45.1; Mn, 18.7; Cl, 36.2. Found: Cs, 44.7; Mn, 19.1; Cl, 36.2.

CRYSTALLOGRAPHY

Because of the extremely hygroscopic nature of these materials, x-ray diffraction data were obtained by loading the powdered sample into a capillary which was then sealed with paraffin. The powdered samples were prepared by carefully grinding single crystalline material. These procedures were carried out in a purified nitrogen dry box. The preliminary x-ray powder diffraction patterns were obtained using $CuK\alpha$ radiation and a 114.6-mm. Debye camera. The final data were taken with a Norelco high-angle diffractometer. The x-ray powder pattern for $RbMnCl_3$ was indexed on the basis of a hexagonal unit cell with $a = 7.164$ A. and $c = 17.79_8$ A. ($c/a = 2.484$). The density was measured in toluene on a modified Berman balance and found to be 3.10. The theoretical density of a hexagonal unit containing six units of $RbMnCl_3$ was calculated to be 3.107. The hexagonal unit cell parameters for $CsMnCl_3$ are: $a = 7.288$ A. and $c = 27.44$ A.

The density was measured to be 3.48 grams per cc., which agrees with the calculated density for 9 $CsMnCl_3$ units in the provisional cell. The x-ray powder diffraction data for $RbMnCl_3$ and $CsMnCl_3$ are presented in Table I. The data were indexed on the basis of the two proposed unit cells. These crystallographic results are tentative and require further investigation.

Melting point determinations were made by use of a polarizing microscope equipped with a heating stage. The heating chamber was flushed continuously with helium that had passed through a trap cooled with liquid nitrogen. Small (0.1-mm.) single crystalline samples were rested directly on a transparent fused silica disk which was heated from below by a platinum coil. A Pt-Pt-13% Rh thermocouple was placed in direct contact with the disk and was calibrated against substances of known melting points. A melting point of 571° ±5° C. was determined for $RbMnCl_3$, and a melting point of 617° ±5° C. was found for $CsMnCl_3$. These values are somewhat higher than the corresponding values reported by Markov and Chernov (*2*). A possible explanation of the higher melting points observed in this investigation is the purity of the respective alkali metal chlorides. The starting materials and final products were analyzed spectroscopically and found to be at least 99.9% pure. When small amounts of one alkali metal cation were substituted for another, the melting point of the product was lower than that observed for the pure compound. These experiments, together with the fact that the alkali metal raw materials obtained from several suppliers were analyzed and rejected because of the presence