part, of insoluble orthophosphates. In the presence of large excess of phosphate ions the precipitate is converted entirely to the insoluble orthophosphate. This is a flocculent gelatinous precipitate in contrast to the finely divided oxide precipitate.

The precipitated niobium (or tantalum) orthophosphate is hydrated and amorphous. Upon ignition it loses water and becomes crystalline.

The hydrated orthophosphate hydrolyzes readily in solution, reverting partially to the oxide. It is stable only in the presence of a large excess of phosphoric acid. Hydrolysis is never complete, however, and repeated washings do not remove the phosphoric acid completely. The ignited compound does not hydrolyze as readily as the hydrated form.

Analytical Applications.—Attempts were made to remove phosphate ions from solutions by adding a large excess of potassium niobate (or tantalate). Complete removal was never achieved. Hence this method cannot be employed as a method of eliminating phosphate ions from solutions. Studies are being made to find if niobium and tantalum might be separated and determined as phosphates.

Acknowledgments.—The author wishes to thank Mr. R. M. Steele for his aid in the X-ray diffraction studies and Mr. C. Feldman for the spectrographic analyses.

OAK RIDGE, TENN. RECEIVED MARCH 5, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA]

Dielectric Properties of Sodium, Potassium and Ammonium Bicarbonates[1]

BY CHESTER T. O'KONSKI

The dielectric properties of these bicarbonates, determined from measurements on fine crystalline powders, indicate that the protons do not have the freedom postulated for certain other hydrogen-bonded solids. The effects of humidity are accounted for in the measurements and are attributed to formation of electrically conducting surface films by the adsorption of water.

Introduction

This work is related to a study of the dielectric properties of hydrogen-bonded solids. The high dielectric constant and the dielectric relaxation effects in ice and the behavior of certain of the piezoelectric and ferroelectric crystals have been attributed to proton transfer over, or tunneling through, a potential energy barrier along the O—H···O bonds.[2,2a,3] The ferroelectric state, with its spontaneously polarized domains, enormous dielectric constant and electric hysteresis, is believed to result when the dipole orientations are closely coupled within the crystal lattice. Since there are no reliable criteria for *a priori* predictions of this type of behavior, it is of interest to examine the dielectric properties of hydrogen-bonded solids in which conditions appear favorable for proton transfer.

The shortest O—H···O distances found in the literature are those for KH_2PO_4, 2.54 Å.,[4] and $NaHCO_3$, 2.55 Å.[5,6] It therefore is of special interest to compare $NaHCO_3$ and other bicarbonates with KH_2PO_4, a ferroelectric substance which has been extensively studied.

Experimental

Method.—Attempts were made to grow large single crystals of $NaHCO_3$ for dielectric measurements along the different crystallographic directions. Even under carefully controlled conditions (CO_2 atmosphere, slow cooling) crystal growth on visually perfect seeds was slow and overgrowths always resulted. Measurements were therefore made on fine crystalline powders, following the method of Böttcher.[7]

Materials.—Reagent-grade crystalline powders were sieved, and only the fractions passing a U.S. Series 200 mesh sieve (hole size 74 microns) were used. Several samples were recrystallized and gave the same results, indicating that impurities were unimportant.

Cell.—The condenser consisted of two carefully machined flat brass electrodes which were cleaned before each set of measurements. One electrode was secured in a machined Mycalex[8] block and the outer removable electrode was bolted directly on the machined supporting rim, as illustrated in Fig. 1. The area of the inner region containing the powder was 112.7 cm.^{2} and the plate separation was normally 0.10 cm. For purposes of equilibration and to evaluate the effect of possible decomposition, carbon dioxide of controlled humidity was passed through the cell by means of two tubes push-fitted into holes in the outer electrode and capped by fine wire gauze flush with the inner surface. The cell was loaded with just enough powder, estimated from a density measurement on the sample, to fill it uniformly without excessive pressure.

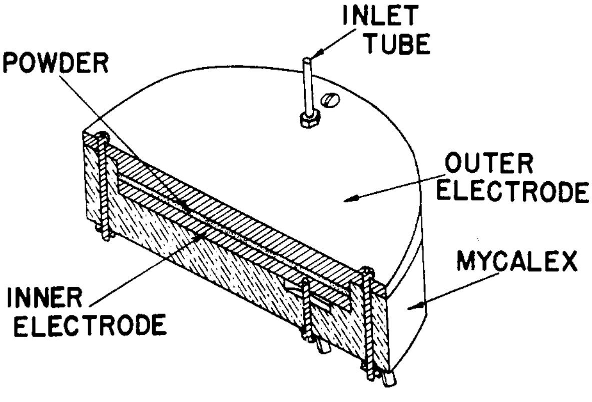

Fig. 1.—Dielectric cell for powders.

Bridge.—A shielded 1:1 ratio-arm bridge, operable over the range 20 c.p.s. to 200 kc., was used for the measurements. It consisted of the circuit shown in Fig. 2. An appropriate transformer T_1 was selected by means of a straightforward switching arrangement not shown in the diagram. With Sw_4 open, the bridge was balanced capacitively at any selected frequency by means of C_1 and C_2, and resistively by means of the network, R_1–R_4, using the oscilloscope as a null indicator. The capacity-arm switch

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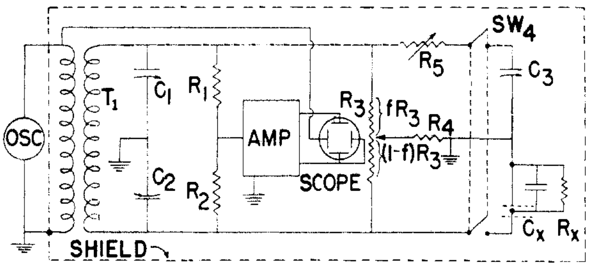

Fig. 2.—Variable frequency bridge: The oscillator was a Hewlett-Packard Model 200C giving 10 r.m.s. volts from 20 c.p.s. to 200 kc. T_1 = General Radio 578-B or 578-C. C_1 = 15 $\mu\mu$fd., max.; C_2 = 100 $\mu\mu$fd., max.; $R_1 = R_2$ = 10,000 ohm, non-inductively wire-wound resistors. Amplifier was an R-C coupled 6AK5 pentode, and the oscilloscope a Waterman "Pocketscope," Model 511-A. R_5 = 0–100,000 ohm non-inductive decade resistance box, C_3 = 1000 $\mu\mu$fd. max., vernier-scale. The network R_3–R_4 is thoroughly discussed by R. H. Cole and P. M. Gross, Jr.[9]

Sw_4 was then closed, and the bridge was rebalanced with the calibrated condenser C_3 and either the combination R_3–R_4, or the non-inductive decade resistance box R_5. Capacity and a.c. resistance values in the measuring arm, C_x and R_x, were calculated on the basis of the usual assumption that the dielectric could be represented by a parallel combination of the two. For convenience in calculations, resistive balance was generally obtained by means of the network[9] R_3–R_4. This allows capacity values to be read directly from the calibration curve for the variable condenser, C_3.

The chief advantages of the arrangement described are that one of the terminals of the cell, the standard condenser, and the preamplifier is always at ground potential and successive adjustments of a conventional grounding arrangement are not necessary for final balance. Another feature, the use of the oscillator to provide the horizontal sweep on the oscilloscope, provides very convenient indication of phase and amplitude balance, and has been in use in these laboratories for a number of years.[10]

Calibration of Bridge and Cell.—The condenser C_3 was calibrated in terms of capacity added to the bridge terminal by placing a factory-calibrated variable precision air condenser across the output lead. Precision was well within the rated 0.1% of full scale (1000 $\mu\mu$fd.) of the factory standard from 200 to 50,000 c.p.s. and slightly less at the extreme frequencies. The main sources of error in determination of the dielectric constant were in the measurements of the plate spacing and the packing fraction of the powder. It is estimated that absolute values of the dielectric constant are reliable within about 2% whereas relative values in the frequency range from 200 to 50,000 c.p.s. are precise within 1%.

The cell was calibrated by measurements on benzene and aniline, using the relation

$$C_f - C_e = C_o(\epsilon - 1) \qquad (1)$$

where the subscripts f and e refer to capacity values, including parasitics, for the filled and empty cell, C_o is the capacity between the electrodes in vacuum, and ϵ is the dielectric constant. The spacing s between the electrodes was calculated from the relation $C_o = 0.0885\,A/s$, where A is the area of the plates, 112.7 cm.². The results were C_o = 103 $\mu\mu$fd. ± 1% and s = 0.097 cm. The value of s determined from micrometer measurements checked this value within the experimental error of the former. The more accurate electrical value was used in calculating the volume, 10.9 cc., and the weight of the powder. Equation (1) with C_o evaluated, was subsequently used to calculate the dielectric constants of the powders. Fringing errors were estimated below 1% and are largely compensated by the above calibration.

Results

Data for the three bicarbonates at 25° and low humidities are shown in Table I. All results were obtained at 10,000 c.p.s. Here δ is the volume fraction of crystals in the powder, x_{H_2O} is the relative pressure of water vapor in the gas stream with which the powder was equilibrated, ϵ_p is the dielectric constant of the powder, and $\bar{\epsilon}$ is the mean dielectric constant of the bulk crystals, calculated from Böttcher's equation[7]

$$\frac{\epsilon_p - 1}{3\epsilon_p} = \delta\,\frac{\bar{\epsilon} - 1}{\bar{\epsilon} + 2\epsilon_p} \qquad (2)$$

which is readily solved for $\bar{\epsilon}$.

TABLE I

Compound	δ	x_{H_2O}	ϵ_p	
$NaHCO_3$	0.512	0.16	2.49	4.82
	.486	.03	2.22	4.29
	.478	.00	2.20	4.35
	.497	.00	2.30	4.42
	.520	.00	2.38	4.41
			Average of last three =	4.39 ± 0.04
$KHCO_3$	0.503	0.10	2.26	4.23
	.494	.00	2.26	4.32
	.481	.00	2.20	4.28
	.468	.00	2.17	4.32
			Average of last three =	4.31 ± 0.03
NH_4HCO_3	0.512	0.12	2.46	4.72
	.525	.00	2.46	4.58
			Average =	4.65 ± 0.07

In the averages, only the last three results for $NaHCO_3$ and $KHCO_3$ were taken because the other samples had been previously equilibrated at higher humidities and such samples consistently gave higher results when re-equilibrated, probably because of sintering of the powder. In the runs for which x_{H_2O} = 0.00, the CO_2 stream was dried with phosphorus pentoxide. The trend of the data clearly indicates that possible partial decomposition at the surface of the crystals does not affect the results. The uncertainty of the data for NH_4HCO_3 is slightly greater because of the greater volatility of the powder. The effects of higher humidities are discussed below.

Discussion

Results obtained by the powder method raise the questions of the validity of Böttcher's equation and of the possible effect of the state of subdivision on the dielectric properties of a material. The equation assumes randomly oriented particles which may be anisotropic. In a fine powder such as used here this condition is believed fulfilled. The equation has been carefully checked for NaCl and KCl and gives results accurate within 0.5% for these isotropic crystals in powdered form.[11] In addition, measurements on anisotropic KH_2PO_4 and $NH_4H_2PO_4$ powders in connection with this work gave the same values for the mean dielectric constants of these crystals as those calculated from the measured dielectric constants of single crystals,[12,13] within experimental error, which here would be around 10% for substances with bulk dielectric constants around 40. These rough checks indicate that no serious difficulties arise from anisotropy or state of subdivision.

The molecular polarizabilities of these compounds are listed in Table II, together with the ionic polarizabilities for HCO_3^- in $NaHCO_3$ and $KHCO_3$,

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which are based upon the values for Na^+ and K^+ given by Roberts.[14] It is of interest to note that the values for HCO_3^- agree within experimental error and fall within the range of values given by Roberts for $CO_3^=$. This indicates that the atomic polarization of the hydrogen is small. This type of calculation is of course open to the usual questions regarding internal fields.[14]

TABLE II

MOLECULAR AND IONIC POLARIZABILITIES

Compound	V	α_m	$\alpha_{HCO_3^-}$
$NaHCO_3$	63.4(D)	100.7	80.5
	64.0(X)	101.7	81.5
$KHCO_3$	76.5(D)	120.4	78.1
	76.0(X)	119.8	77.5
NH_4HCO_3	83.5(D)	137.6	..
	86.1(X)	141.9	..

V = molecular volume, in Å.^{3}; α_m = molecular polarizability in Å.^{3}; $\alpha_{HCO_3^-}$ = polarizability of the bicarbonate ion. Calculated from the equation $\alpha_m = 3V(\bar{\epsilon} - 1)/(\bar{\epsilon} + 2) = \Sigma\alpha_i$. (D) refers to molecular volumes calculated from bulk density measurements, and (X) from X-ray data.

Measurements on $NaHCO_3$ from −78 to 50° indicated negligible temperature dependence. All observed frequency dependence and dielectric losses are attributed to the humidity effects discussed below. These observations, together with the low values of the dielectric constants and the polarizability of HCO_3^-, contrast sharply with those for KH_2PO_4. It is evident that the protons in the bicarbonates do not enjoy the type of freedom found in ice and KH_2PO_4. This might be explained by the supposition that each proton is midway between two oxygens in a single potential energy well, as has been postulated by Westrum and Pitzer for the bifluoride ion on the basis of thermodynamic, spectroscopic and dielectric data for KHF_2.[15]

It is of interest to note that Zachariasen[5] came to a similar conclusion from X-ray diffraction studies. The evidence in this case is indirect as the hydrogens give no diffraction lines. Moreover, a similar conclusion by West[4] for KH_2PO_4 appears invalid in the face of the success of Slater's theory.[2a,3,13] An alternative explanation to the one involving a single potential energy well is that a special type of crystal symmetry is required before proton displacements will cause an appreciable change in dielectric properties. A striking difference between the structure of KH_2PO_4 and $NaHCO_3$ is that the former has a symmetry which will permit displacements of protons in all three directions of space, whereas the latter allows displacements in only one direction through the crystal. It is not difficult to see how such considerations would affect any dielectric properties involving coöperative proton transfer.

Humidity Effects.—Preliminary studies of $NaHCO_3$, undertaken without any special precautions in handling the powder, indicated high dielectric losses at audio frequencies. The dielectric constants increased with decreasing frequency. Subsequent studies under conditions of controlled humidity at 25° gave results as shown in Figs. 3, 4 and 5. Note particularly that KCl shows the same type of behavior as the bicarbonates. In

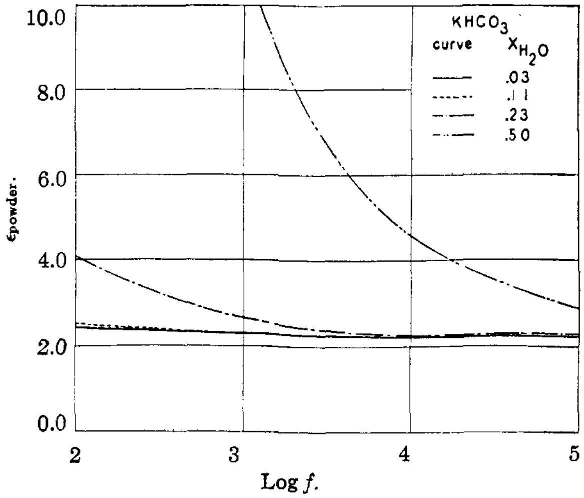

Fig. 3.—Dielectric constant of $KHCO_3$ powder. Here x_{H_2O} is the relative pressure of the water vapor and f is the frequency in cycles per second.

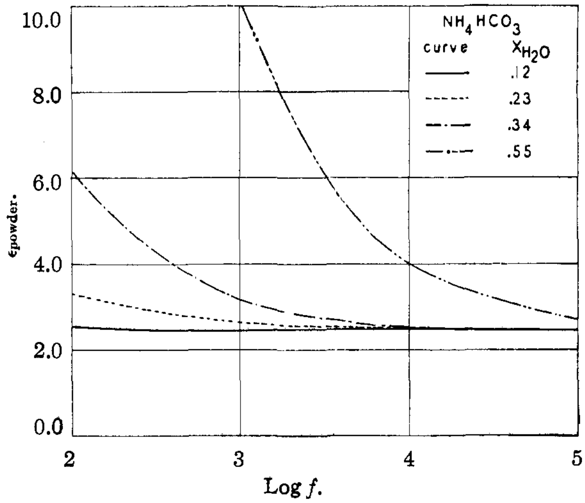

Fig. 4.—Dielectric constant of NH_4HCO_3 powder. Curves for $NaHCO_3$ resemble these very closely.

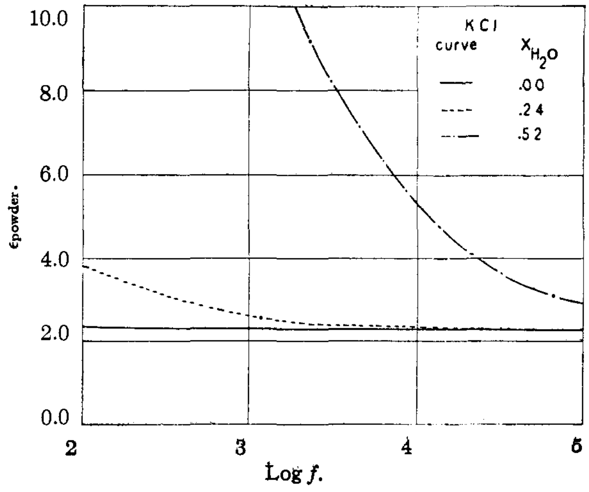

Fig. 5.—Dielectric constant of KCl powder.

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(14) S. Roberts, *Phys. Rev.*, **76**, 1215 (1949).

(15) E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, **71**, 1940 (1949).

each case measurements at low humidities approached a constant value for high frequencies, and in the case of KCl the correct value for the dielectric constant is obtained under these conditions. Cooling the samples below 0° virtually eliminated all dielectric losses. Also the dielectric constant became frequency-independent and equal to the limiting high-frequency value. Attempts to measure the water uptake by the powders showed less than 0.1% by weight in $NaHCO_3$ for x_{H_2O} = 0.50 at 25°. It is concluded that the observed effects are due to the formation of electrically conducting films by the adsorption of water vapor. Further studies of the electrical properties of such films under more precisely defined experimental conditions should be of considerable interest in surface chemistry.

Acknowledgments.—I wish to acknowledge the stimulating discussions of my colleagues, particularly Professor W. M. Latimer, who pointed out the interest in this study, and the assistance of W. J. Potts, Fred Andrews, Floyd Momyer and David Schwartz in some of the preliminary studies.

BERKELEY, CALIF. RECEIVED MARCH 23, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

A Study of the Hydrogen Chloride–Aluminum Chloride System

BY RYDEN L. RICHARDSON[1] AND SIDNEY W. BENSON

The hydrogen chloride–aluminum chloride system has been examined over a wide range of conditions by use of varied techniques. Pressure–composition isotherms at −78, 0 and 25° gave negative results as to formation of $HAlCl_4$. Weak physical adsorption and extremely low conductivity were noted. At 195° and ~1500 mm. deviations of all-vapor system from ideal behavior were so slight as to be questionable. Complete exchange of $^{36}_{17}Cl$ occurred at similarly elevated conditions but no exchange was detected at room temperature.

Introduction

Although the complex compound $HAlCl_4$ has been cited in proposed mechanisms for certain Friedel–Crafts reactions, the existence of this complex has never been experimentally verified. Several investigators[2,3,4] have found that aluminum chloride and hydrogen chloride decidedly resist combination. Fairly recent studies[5,6] have cast doubt upon a kinetic investigation[7] which appeared to substantiate existence of the bromine analog, $HAlBr_4$.

The present paper describes several experiments designed to detect either complex formation or intermolecular attraction within the hydrogen chloride–aluminum chloride system. Accordingly, measurements have been devoted to phase equilibria, solubility, conductivity, *P–V–T* behavior and isotope exchange. The data collectively apply to a temperature range of −80 to 220° and a pressure range of 0 to 1200 mm.

Experimental

Materials.—Reagent-grade anhydrous aluminum chloride was further purified by fractionation in an all-Pyrex system pressured to 1.2 atm. with dry nitrogen. Three samplings of product, sealed in evacuated capillary tubes, had an average m.p. of 193.7 ± 0.1° within 0.8° range (reported,[8] 192.6°).

Hydrogen chloride from a commercial cylinder was purified by repeated batch-wise fractionation in a U-tube train. Purity of four samples was checked by vapor pressure measurements in −110 to 86° range; these measurements had a mean deviation of < 2% from data cited in Landolt–Börnstein.[9]

Radioactive hydrogen chloride was generated by a mixture of C.P. concentrated sulfuric acid and radio-potassium chloride ($^{36}_{17}Cl$, Oak Ridge Laboratories). Purification of the evolved gas was carried out in essentially the same manner and degree as described for unactive species.

Phase Equilibrium.—Data for pressure *vs.* composition isotherms at −78, 0 and 25° were obtained by contacting 0.4–0.6 g. of anhydrous aluminum chloride with hydrogen chloride in a conventional adsorption apparatus.[10] Temperature measurements with a toluene thermometer were occasionally checked by ammonia or carbon dioxide vapor pressure thermometers; mixtures of Dry Ice–acetone or water–ice served as cooling baths. Pressure equilibrium was instantaneously attained and no hysteresis was observed. The amount of aluminum chloride was volumetrically determined at the end of each run series by use of silver nitrate and dichlorofluorescein.

Solubility.—During phase equilibrium measurements at −78°, hydrogen chloride was condensed to give 2–4 ml. of liquid in contact with excess of solid aluminum chloride. Six observations on two different samples indicated a lowering of vapor pressure. Temperatures were checked with ammonia and carbon dioxide vapor pressure thermometers. A third sample, also used for conductivity measurements, was equilibrated for 24 hours at −81° with occasional agitation; vapor pressure lowering of the same magnitude was observed. Flaming and sustained evacuation prior to introduction of materials precluded water as the cause of such an effect.

Conductivity.—With exception of platinum electrodes and tungsten leads, the conductivity cell was of all-Pyrex construction. Cell contents were magnetically stirred and occasionally lead shields from the cell were flamed to prevent moisture condensation. A Jones bridge[11] measured the resistance at 1000 cycles/sec. No frequency effects (400 cycles/sec.) were noted.

Oven Bulb Apparatus.—This apparatus included an air-bath, oven-bulb (600 ml.), null-detector,[12] mercury manometer, three copper–constantan thermocouples and a L. & N. potentiometer (Model #8662). Materials sealed in the oven-bulb system contacted Pyrex surfaces only. Upon

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