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Salt Hydrates: New Reversible Absorbents for Carbon Dioxide

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Abstract: Melts of salt hydrates such as tetramethylammonium fluoride tetrahydrate, $[(CH_3)_4N]F{\cdot}4H_2O$, and tetraethylammonium acetate tetrahydrate, $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$, have been found to exhibit unexpectedly large carbon dioxide absorption capacities. For example, $[(CH_3)_4N]F{\cdot}4H_2O$ at 50 °C and 100 kPa CO_2 absorbs 0.28 mol of gas/mol of salt corresponding to a CO_2 concentration of about 1.9 M. Absorption is fully reversible and gas is desorbed by reducing the CO_2 pressure above the melt. A survey of salt hydrates revealed that those which contain relatively basic anions, such as malonate or citrate, likewise exhibit relatively large CO_2 absorption capacities while those which contain relatively neutral anions, such as chloride, do not. Further, the CO_2 absorption capacity of salt hydrates is dependent on the water content of the salt and decreases with increasing water content. Characterization by NMR, FTIR, and Raman spectroscopy of $[(CH_3)_4N]F{\cdot}4H_2O$ containing absorbed CO_2 is consistent with the presence of bicarbonate and bifluoride ions in the melt. Exposure of $[(CH_3)_4N]F$ containing $H_2{}^{18}O$ to CO_2 resulted in incorporation of the label into the gas phase as $C^{18}O^{16}O$ and $C^{18}O_2$, implying that CO_2 reacts reversibly with the melt via a hydration reaction. Spectroscopic evidence suggests that carboxylate-containing salt hydrates also bind CO_2 as bicarbonate but the nature of the protonated anion species remains undetermined. However, modeling of isotherm data suggests a one-to-one salt hydrate-to-CO_2 reaction stoichiometry. In contrast, modeling of fluoride-containing salt hydrate isotherms supports a two-to-one salt hydrate-to-CO_2 reaction stoichiometry, which is consistent with spectroscopic and reactivity studies of the underlying chemistry. The heats of absorption of CO_2 by $[(CH_3)_4N]F{\cdot}4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ are relatively low, −4.5 and −8.4 kcal/mol, respectively, suggesting that these salts may be attractive, more energy efficient, alternatives to commercial amine based absorbents for the removal of CO_2 from process gas streams.

Introduction

As a result of concerns about global warming, there is currently a growing interest in new ways to recover and utilize carbon dioxide. The separation of carbon dioxide from other gases, such as H_2, CO, and CH_4, and from air has always been of considerable fundamental interest and industrial importance.[1] In general, CO_2 is removed from gas mixtures by the use of reversible absorption methods employing a variety of chemical or physical solvents.[1] The chemical solvents of choice are aqueous solutions of alkanolamines or of strongly alkaline salts such as K_2CO_3.[2,3] Our interest in the area of acid gas separations, particularly with regard to facilitated transport membranes,[4,5] has led to the identification of a new type of acid gas absorbent, salt hydrates.

Salt hydrates are simply salts that contain bound water. The melting points of salt hydrates are generally much lower than those of the anhydrous salts and the corresponding melts can often be obtained at near ambient temperatures. The resulting molten salt hydrates are not merely concentrated aqueous solutions; rather, they may be viewed as salts containing the minimum quantity of water necessary to fill the primary hydration spheres of the ions.[6] Since water in excess of the primary hydration spheres is absent, water−ion interactions dominate and, unlike in aqueous solutions, exclusive $H_2O{-}H_2O$ interactions are absent.[7] Such differences necessarily influence the chemical properties of both the salt and the bound water. Hence, the bulk water in an aqueous solution and the bound water in a molten salt hydrate are chemically quite different. Such differences are reflected in various thermodynamic and other properties such as enthalpy of evaporation, conductivity, and partial molar dilution enthalpy.[7−9]

We have found that certain salt hydrates and salts in the presence of limited amounts of water have the remarkable and previously unrecognized property of reversibly absorbing large amounts of CO_2.[10,11] Displaying this property are hydrates of various salts which contain fluoride or carboxylate ions. Two examples are tetramethylammonium fluoride tetrahydrate, $[(CH_3)_4N]F{\cdot}4H_2O$, and tetraethylammonium acetate tetrahydrate, $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$. In this paper we report on the reactivity of CO_2 with various salt hydrates and our attempts to understand the underlying chemistry.

Results and Discussion

CO_2−Salt Hydrate Reactivity. An examination of the reactivity of CO_2 with $[(CH_3)_4N]F{\cdot}4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ revealed unexpectedly large and reversible CO_2 absorption capacities. Molten $[(CH_3)_4N]F{\cdot}4H_2O$ (mp 39−42 °C) at 50 °C and 100 kPa absorbed 0.28 mol of CO_2 per mol of salt, which corresponds to a CO_2 concentration of about 1.9

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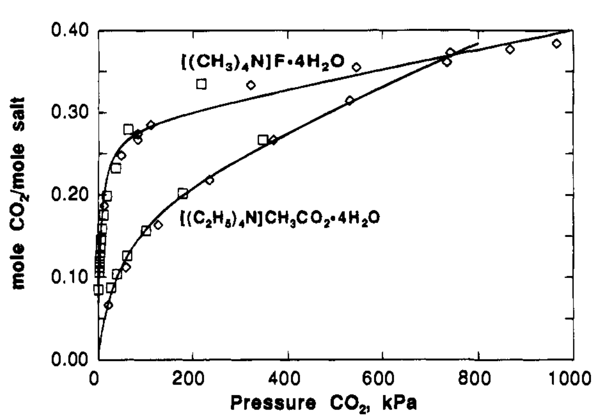

Figure 1. CO_2 absorption/desorption isotherms of $[(CH_3)_4N]F•4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2•4H_2O$ at 50 °C: squares, absorption; diamonds, desorption.

M.[12] The acetate salt $[(C_2H_5)_4N]CH_3CO_2•4H_2O$ (mp 45 °C) at 50 °C and 100 kPa absorbed 0.15 mol of CO_2 per mol of salt corresponding to a 0.64 M solution of CO_2. In contrast, the solubility of CO_2 in water at 50 °C and 101 kPa is approximately 0.02 M,[13] some two orders of magnitude less. Also, considering that CO_2 solubilities in aqueous salt solutions are generally less than that in pure water (e.g. 0.012 M CO_2 in 3.5 M NaCl at 100 kPa and 35 °C[14]) and that solubility decreases with increasing salt concentration,[14,15] the observed extent of dissolution of CO_2 in the above salt melts is even more striking.

The absorption/desorption isotherms of $[(CH_3)_4N]F•4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2•4H_2O$ were determined at 50 °C and are displayed in Figure 1 as moles of CO_2 absorbed per mole of salt versus CO_2 pressure. For both absorption and desorption, the experimental points lie along the same curve, demonstrating that CO_2 absorption is fully reversible. The isotherms clearly show a nonlinear dependence of absorption capacity on pressure. This isotherm shape, together with the magnitude of CO_2 absorbed, strongly suggest that CO_2 is absorbed by chemical reaction with the salt hydrates. The gradient of the isotherm at low pressures is related to the affinity of the salt for CO_2 with a steep rise in the isotherm being indicative of a high affinity for the gas. By this qualitative criterion, $[(CH_3)_4N]F•4H_2O$ clearly binds CO_2 more strongly than $[(C_2H_5)_4N]CH_3CO_2•4H_2O$. Such conclusions are borne out by a quantitative treatment of CO_2–salt hydrate reactivity (see below).

Evaluation of CO_2 absorption properties of other salt hydrates, compounds of general formula $A_x^{m+}B_y^{n-}•rH_2O$, or salts in the presence of limited water revealed that, in general, those consisting of monovalent cations (A^+) and fluoride or weak carboxylic acid anions (B^{n-}) reversibly absorb relatively large amounts of CO_2. Representative data are listed in Table 1. For example, the liquid consisting of CsF in the presence of 4 mol of water/mol of salt absorbed 0.16 mol CO_2/mol of salt at 40 °C and 100 kPa, suggesting that the presence of tetraalkylammonium cations is not required for high absorption capacities. The tetramethylammonium salts of propionic acid and of the di- or triprotic malonic or citric acids also have substantial absorption capacities as indicated in Table 1.

Table 1. CO_2 Absorption Capacities of Various Salt Hydrates at 50 °C and 100 kPa

		absorption capacity	
salt	mol of water/ mol of salt	mol of CO_2/ mol of salt	concn, M[b]
$[(CH_3)_4N]F$	4	0.28	1.91
CsF	4	0.16[a]	1.58
KF	4	0.20	
$[(C_4H_9)_4N]F$	3	0.63	
$[(C_2H_5)_4N]CH_3CO_2$	4	0.15	0.60
$[(C_2H_5)_4N]CH_3CO_2$	3	0.30	1.28
$[(CH_3)_4N]CH_3CH_2CO_2$	4	0.13	0.60
$[(C_2H_5)_4N]CH_3CH_2CO_2$	4	0.16	2.09
$[(CH_3)_4N]_2O_2CCH_2CO_2$	6.2	0.24	0.84
$[(CH_3)_4N]_2$maleate	6.8	0.56	1.56
$[(CH_3)_4N]_2$phthalate	6.1	0.25	
$[(CH_3)_4N]_3$citrate	10.1	0.48	0.91

[a] 40 °C. [b] Molar concentrations calculated as described in ref 12.

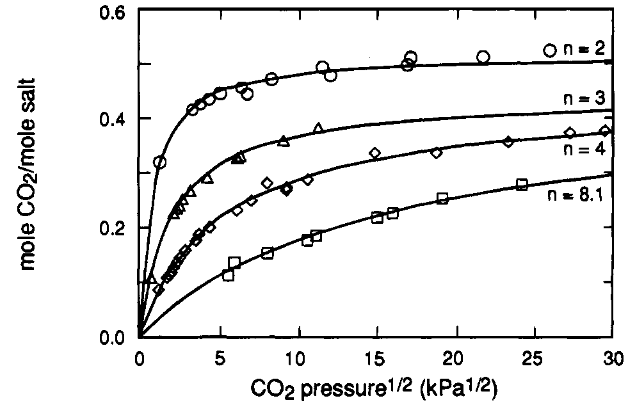

Figure 2. CO_2 absorption/desorption isotherms of $[(CH_3)_4N]F•nH_2O$ at 50 °C in terms of mol of CO_2/mol of salt versus the square root of the CO_2 pressure. Symbols are experimental data. Curves were calculated using eq 4 and the values of K and b listed in Table 4.

In addition to the nature of the anion, the CO_2 absorption capacity of a salt hydrate depends on the water content of the salt. In general, the less water present the greater is the CO_2 affinity and absorption capacity of the salt hydrate. This is clearly illustrated by the absorption/desorption isotherms for $[(CH_3)_4N]F$ containing 2–8.1 mol of water/mol of salt (Figure 2). With decreasing water content, the isotherms become steeper and at a given pressure more CO_2 is absorbed. Unlike the higher hydrates, the solid monohydrate $[(CH_3)_4N]F•H_2O$ apparently reacts irreversibly with CO_2. At pressures greater than 13 kPa, $[(CH_3)_4N]F•H_2O$ absorbed 0.5 mol of CO_2/mol of salt and no gas was desorbed upon reducing the pressure above the adduct.

Although salt hydrates such as $[(CH_3)_4N]F•4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2•4H_2O$ have been known for a long time, their reactivity with CO_2 has apparently been overlooked and we are aware of only a handful of relevant references. Belton et al.[16] reported that the reaction of CO_2 with solid $Na_3PO_4•11H_2O$ resulted in the (presumably) irreversible formation of solid $Na_2HPO_4•7H_2O$ and $NaHCO_3$. Lawlor and Passmore[17] described the reaction of $[(C_2H_5)_4N]F•2H_2O$ in acetonitrile with CO_2. Following exposure to the gas, the volatile components were condensed from the reaction mixture. The increase in weight of the remaining material corresponded to an irreversible absorption of 0.5 mol of CO_2/mol of salt, since the gas was apparently not removed along with other volatile components. Finally, an absorption of CO_2 by anhydrous KF has been claimed in a patent as a method to prevent clumping of the

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[12] Concentrations of CO_2 were calculated by assuming that the volume of the melt was unchanged upon CO_2 absorption and that the densities of the solid and liquid salt hydrates were the same: $[(CH_3)_4N]F•4H_2O$, 1.126 g/mL, ref 34; $[(C_2H_5)_4N]CH_3CO_2•4H_2O$, 1.086 g/mL, ref 35.

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salt.[18] Anhydrous KF reportedly took up 0.03−2.0 wt % CO_2 by an unknown mode of absorption. We have not observed any CO_2 absorption by anhydrous KF or other anhydrous fluoride or carboxylate salts. In related chemistry, the reaction of fluoride salts with SO_2 has been described.[19] Salts such as $[(CH_3)_4N]F$ and KF react with SO_2 to form stable adducts, for example, $KF{\cdot}0.85SO_2$, in which SO_2 is present as the fluorosulfinate ion, SO_2F^-. Addition of water results in formation of HF_2^- and HSO_3^-.

Characterization of CO_2−Salt Hydrate Adducts. The desorption of gas from the CO_2 adduct of $[(CH_3)_4N]F{\cdot}4H_2O$ at room temperature was sufficiently slow so that the collection of analytical and spectroscopic data was possible. The adduct is a colorless, slightly viscous liquid which contains about 0.3 mol of CO_2/mol of salt if prepared under about 100 kPa of the gas. Since solid $[(CH_3)_4N]F{\cdot}4H_2O$ (mp 39−42 °C) "liquefies" at room temperature in the presence of CO_2, the adduct can be prepared by exposing either the melt or the solid to carbon dioxide.

The ^{13}C NMR spectrum at 50 °C of $[(CH_3)_4N]F{\cdot}4H_2O$ containing 0.32 mol of CO_2/mol of salt displayed two resonances at 56.4 ppm (t, CH_3) and 160.8 ppm arising from absorbed CO_2. The ratio of the integrated areas of the two resonances was 13.3 to 1, consistent with the presence of 0.3 mol of CO_2/mol of salt. The spectrum of the adduct prepared using $^{13}CO_2$ showed an enhanced intensity of the signal at 160.8 ppm relative to the methyl resonance, confirming that the former is due to bound CO_2. In view of the literature ^{13}C chemical shift values for $CO_2(g)$ (124.5 ppm), $CO_2(aq)$ (125.9 ppm), $HCO_3^-(aq)$ (161.3 ppm), and $CO_3^{2-}(aq)$ (169.5 ppm),[20] the 160.8 ppm resonance can reasonably be assigned to bicarbonate. For comparison, $[(CH_3)_4N]HCO_3$ was prepared and its ^{13}C NMR spectrum (D_2O) recorded. It exhibited two resonances at 54.8 (t, CH_3) and 161.0 ppm (HCO_3^-). The ^1H NMR of the CO_2 adduct exhibited resonances only at 5.75 (H_2O) and 3.00 ppm from the methyl groups of the cation. A resonance due to HCO_3^- was not observed because of exchange with water protons.

The above CO_2 adduct of $[(CH_3)_4N]F{\cdot}4H_2O$ was further characterized by FTIR using attenuated total reflectance techniques. The spectrum (below 2000 cm^{-1}) of the parent compound (Figure 3) displays three major bands: two bands at 1490 and 952 cm^{-1} associated with the cation, and a band due to water at 1664 cm^{-1}.[21] Reaction with CO_2 resulted in the appearance of several new bands: 1620 (sh), 1384, 1336, 1240, 992, and 841 cm^{-1} (Figure 3). With the exception of the 1240 cm^{-1} band (vide infra), there is virtually a one-to-one correspondence between these new absorptions and those of $[(CH_3)_4N]HCO_3$ in water. However, there is not such a coincidence between the spectrum of $[(CH_3)_4N]_2CO_3$ in water and that of the CO_2 adduct. Table 2 summarizes the IR absorption frequencies for the CO_2 adduct of $[(CH_3)_4N]F{\cdot}4H_2O$ and their assignments from a comparison with literature data for bicarbonate.[22] The assignment of frequencies for the bicarbonate ion is further supported by IR data for the CO_2 adduct prepared using $^{13}CO_2$ and for the salt containing D_2O in place of H_2O (Table 2). The assignment of the 1384-cm^{-1} band of the CO_2 adduct remains unclear.

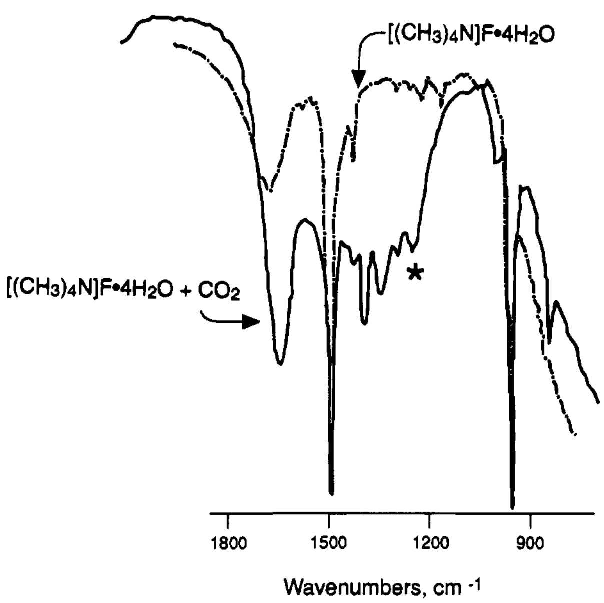

Figure 3. FTIR spectra at 50 °C of $[(CH_3)_4N]F{\cdot}4H_2O$ and of $[(CH_3)_4N]F{\cdot}4H_2O$ containing 0.32 mol of CO_2/mol of salt. The 1240 cm^{-1} band tentatively assigned to HF_2^- is marked with an asterisk.

The ^{19}F NMR spectrum of neat $[(CH_3)_4N]F{\cdot}4H_2O$ at 55 °C exhibited one, sharp resonance at −113.7 ppm while that of the CO_2 adduct showed a broad resonance at −133.3 ppm, suggestive of exchange between two fluorine-containing species. Since fixation of CO_2 as HCO_3^- requires generation of a proton, formation of a protonated fluoride-containing species is expected. Average values of ^{19}F resonances for various fluoride and bifluoride salts and hydrogen fluoride in various solvents are as follows: F^-, −124 ppm; HF, −183 ppm; HF_2^-, −153 ppm.[23-26] That the resonance due to the adduct lies between those of F^- and HF_2^- suggests that both ions are present and are in chemical exchange. In fact, a liquid sample at 50 °C containing a 1.6:1.0 molar ratio of $[(CH_3)_4N]F{\cdot}4H_2O$ to $[(CH_3)_4N]HF_2$ gave a single broad resonance centered at −128 ppm in the ^{19}F NMR. Similar NMR results have been reported for aqueous solutions containing both NaF and $NaHF_2$.[27]

Some additional support for the presence of bifluoride in the CO_2 adduct was derived from a comparison of the IR spectrum of the adduct and that of $[(CH_3)_4N]HF_2$. The literature spectrum of solid $[(CH_3)_4N]HF_2$ has absorption bands at 1376 cm^{-1} (FHF stretch) and 1264−1255 cm^{-1} (FHF bend).[28] The IR of aqueous $[(CH_3)_4N]HF_2$, however, exhibited a strong, broad band at 1480 cm^{-1} (overlapping a cation band at 1490 cm^{-1}) and another band at 1218 cm^{-1}, both attributable to the HF_2^- anion. The IR of the CO_2 adduct of $[(CH_3)_4N]F{\cdot}4H_2O$ exhibited a band at 1240 cm^{-1} which apparently is not assignable to bicarbonate, water, or the cation and tentatively can be assigned to a HF_2^- bend (ν_2). We looked for a shift of the 1240 cm^{-1} band upon deuteration. The 1240 cm^{-1} band did not appear in the spectrum of the CO_2 adduct of $[(CH_3)_4N]F{\cdot}H_2O{\cdot}3D_2O$, but because of strong background absorptions, it was not possible to clearly

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(26) It should be noted that the positions of the ^{19}F NMR resonance for anhydrous fluoride salts in aprotic solvents are quite different from these values. See ref 27.

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Table 2. Infrared Data (cm^{-1}) and Vibrational Assignments for the CO_2 Adduct of $[(CH_3)_4N]F{\cdot}4H_2O$, Its Isotopic Analogs, and Various Bicarbonate Salts[a]

$[(CH_3)_4N]F{\cdot}4H_2O/CO_2$ adduct			$[(CH_3)_4N]HCO_3$		HCO_3^-		
with $H_2O/^{12}CO_2$	with $H_2O/^{13}CO_2$	with $D_2O/^{12}CO_2$	in H_2O	in D_2O	aqueous[b]	in KBr[c]	assignments for HCO_3^- ($C_s(\sigma_h)$)[b]
1620	1589	1623	1616	1620	1620	1697	ν_2 (A′) CO asym stretch
1384	1364	1376	1386				
1336	1306	1342	1348	1355	1335	1338	ν_3 (A′) CO sym stretch
1288	1286	1015	1288	1300	1300	1211	ν_4 (A′) COH bend
1240[d]	1239[d]						
992	992	890	1006	1000	1000	960	ν_5 (A′) C−OH stretch
841	813	844	844	840	840	835	ν_8 (A″) CO_3 out-of-plane deformation

[a] Absorptions due to cations or water are not included. [b] Reference 22a. [c] Reference 22b; monomeric bicarbonate at liquid N_2 temperatures. [d] Tentatively assigned to HF_2^-; see text.

discern the expected bands for DF_2^- at 977 and 900 cm^{-1} as in the literature spectrum of $[(CH_3)_4N]DF_2$.[28]

Characterization of the CO_2 adduct of $[(CH_3)_4N]F{\cdot}4H_2O$ by Raman spectroscopy proved to be more informative. Multiple scans of the liquid revealed a very weak, but clearly discernable, band at 609 cm^{-1}, which is close to the 596 cm^{-1} symmetric stretching frequency reported for solid $[(CH_3)_4N]HF_2$.[29] For comparison, it was found that the Raman spectrum of $[(CH_3)_4N]HF_2$ in water (1:4 molar ratio) exhibited a slightly stronger, but still quite weak, band at 607 cm^{-1}.[30] A weak Raman absorption at 609 cm^{-1} was also observed for a liquid sample containing $[(CH_3)_4N]F$, $[(CH_3)_4N]HF_2$, and water in a 0.4:0.3:4.0 molar ratio.

The various data cited above suggest that the reaction of CO_2 with $[(CH_3)_4N]F{\cdot}4H_2O$ yields bicarbonate and bifluoride as represented by reaction 1, where *n* is the number of moles of bound water per mole of fluoride ion. In actuality, the situation is more complex and likely involves clusters of hydrated anions as will be described below.

$$2F^-{\cdot}nH_2O + CO_2 = HCO_3^- + HF_2^-{\cdot}(2n - 1)H_2O \quad (1)$$

Reaction 1 requires that chemical exchange of oxygen atoms occurs between CO_2 and H_2O. Thus, reaction of $[(CH_3)_4N]F{\cdot}4H_2O$ containing ^{18}O labeled water should result in an incorporation of the label into CO_2 gas that is in equilibrium with the melt. At the time of this study, preparation of $[(CH_3)_4N]F{\cdot}4H_2{}^{18}O$ was not convenient since anhydrous $[(CH_3)_4N]F$ could not be prepared without some decomposition.[31,32] However, addition of 3 equiv of $H_2{}^{18}O$ to $[(CH_3)_4N]F{\cdot}H_2O$ gave a tetrahydrate containing three labeled waters. This salt was exposed to CO_2 at room temperature for an extended period and the contents of the gas phase were analyzed by mass spectrometry. The isotopically labeled carbon dioxides, $C^{16}O_2$, $C^{18}O^{16}O$, and $C^{18}O_2$ (1.0 to 2.3 to 1.8 ratio), were found in the gas phase, consistent with reaction 1.

Attempts to characterize the CO_2 adduct of $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ were not successful,[33] but ^{13}C NMR data were obtained for the CO_2 adducts of two other salt hydrates, tetraethylammonium propionate tetrahydrate, $[(C_2H_5)_4N]CH_3CH_2CO_2{\cdot}4H_2O$, and tetramethylammonium malonate, $[(CH_3)_4N]_2O_2CCH_2CO_2$, in the presence of 6.4 mol of water/mol of salt. Liquid $[(C_2H_5)_4N]CH_3CH_2CO_2{\cdot}4H_2O$ at 25 °C and 100 kPa absorbed 0.21 mol of CO_2/mol of salt. The ^{13}C NMR spectrum of the liquid adduct exhibited resonances at 7.1, 10.6, 30.3, and 179.4 ppm due to the salt and a resonance at 159.8 ppm assignable to CO_2 absorbed as HCO_3^- and which integrated for 0.2 mol of C/mol of salt. No resonances attributable to protonated propionate species were apparent in the spectrum of the CO_2 adduct. Similar spectroscopic results were obtained for $[(CH_3)_4N]_2O_2CCH_2CO_2$ in the presence of 6.4 mol of water/mol of salt and containing 0.30 mol of CO_2/mol of salt. The ^{13}C NMR spectra of the salt and its CO_2 adduct were almost identical with the exception of an additional resonance at 159.1 ppm due to HCO_3^- (integrated for 0.26 mol of C/mol of salt). Again, no other resonances which might indicate the presence of protonated malonate species were seen in the ^{13}C NMR spectrum of the adduct. Thus, it appears that carboxylate-containing salt hydrates bind CO_2 as HCO_3^- but the identity of the resulting protonated carboxylate species remains unknown. Based on modeling of absorption data of various carboxylate salt hydrates (described below), the most reasonable stoichiometry involves reaction of 1 mol of salt for each mole of CO_2 absorbed, as in reaction 2.

$$RCO_2^-{\cdot}nH_2O + CO_2 = HCO_3^- + RCO_2H{\cdot}(n - 1)H_2O \quad (2)$$

The above representations are admittedly oversimplifications. Salt hydrates do not contain discrete, separate water molecules or ions. Rather, water molecules are coordinated to the anions through relatively strong hydrogen bonds, a fact well established by X-ray crystallography. Solid $[(CH_3)_4N]F{\cdot}4H_2O$, for example, consists of cations interspersed between layers of hydrogen bonded fluoride ions and water molecules.[34] The fluoride ions adopt an approximately square planar coordination environment and each water is hydrogen bonded to two other waters and one F^- in a trigonal planar arrangement. Similarly, $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ consists of hydrogen bonded layers of water and acetate ions with cations located between the layers.[35] Each acetate is hydrogen bonded to four water molecules. Much of the ordered structure of solid salt hydrates is apparently retained in the liquid state. The similarity of the IR spectra of solid and liquid $[(CH_3)_4N]F{\cdot}4H_2O$ led Harmon et al.[36] to propose that there is no appreciable gain in hydrogen bonding energy upon crystallization. This evidence, coupled with additional IR and NMR results for other hydrates, suggests that there is significant order in liquid salt hydrates.[36] Hence, the reaction of CO_2 with $[(CH_3)_4N]F{\cdot}4H_2O$ or $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ involves hydrated anions in an ordered liquid, rather than the simple, but useful, schemes represented by reactions 1 and 2.

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(30) It is unclear why the symmetric stretch of aqueous HF_2^- is so weak in the Raman. However, similar results have been reported for aqueous KHF_2 for which the Raman bands due to H_2O bend and HF_2^- stretch vibrations are of comparable intensities. See: Giguere, P. A.; Turrell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5473−5477.

(31) Harmon, K. M.; Gennick, I. *Inorg. Chem.* **1975**, *14*, 1840−1845.

(32) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990**, *112*, 7619−7625.

(33) As will be described in a future report (to be published in *Sep. Sci. Technol.*), this is due to an unusual and unexpected desorption of CO_2 upon solidification of the melt.

(34) McLean, W. J.; Jeffrey, G. A. *J. Chem. Phys.* **1967**, *47*, 414−417.

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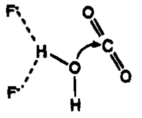
Table 3. CO_2 Absorption Capacities of Various Salt Hydrates as a Function of the pK_a of the Conjugate Acid of the Salt Anion

salt[a]	pK_a	$P(CO_2)$ (kPa)	[CO_2] (M)
$[(CH_3)_4N]Cl$	−8	100	0.01
$[(CH_3)_4N]CF_3CO_2$	0.23	133	0.05
$[(CH_3)_4N]F$[b]	3.45	100	1.9
$[(CH_3)_4N]HCO_2$	3.75	131	0.08
$[(CH_3)_4N]C_6H_5CO_2$	4.19	125	0.17
$[(C_2H_5)_4N]CH_3CO_2$[b]	4.75	103	0.64
$[(CH_3)_4N]CH_3CH_2CO_2$	4.87	101	0.65

[a] All salts in the presence of 4 mol of water/mol of salt at 30 °C. [b] 50 °C.

The hydrated anions, fluoride or carboxylate, as discussed above, are strongly hydrogen bonded to the limited amount of water present in the salt hydrates. As pictured below, this results in water molecules of enhanced basicity which can react with carbon dioxide.



We have no evidence for the presence of "free" hydroxide ions in $[(CH_3)_4N]F{\cdot}4H_2O$. Hydroxide ions would be expected to react irreversibly with CO_2 as is observed for its reaction with the salt hydrate $[(CH_3)_4N]OH{\cdot}5H_2O$. The resulting bicarbonate salt, $[(CH_3)_4N]HCO_3$, was stable (i.e. no desorption of CO_2) when the pressure above the salt was reduced to less than 0.1 mmHg at 25 °C.

Survey of CO_2 Reactivity of Salt Hydrates. The CO_2 affinities of $[(CH_3)_4N]F{\cdot}4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ depend ultimately on the effective basicity of the fluoride and carboxylate anions. A survey of the reactivity of salt hydrates with CO_2 reveals that, in general, absorption capacities are inversely related to the basicity of the salt anion as measured by the pK_a of its conjugate acid in dilute aqueous solutions. Representative data for various salt hydrates containing 4 mol of water/mol of salt listed in Table 3 illustrate such a qualitative relationship between absorption capacity and pK_a. For example, the CO_2 absorption capacity of $[(CH_3)_4N]HCO_2{\cdot}4H_2O$ (pK_a HCO_2H, 3.75[37]) is 0.08 M at 130 kPa while that of $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ is 0.60 M (pK_a CH_3CO_2H, 4.75[37]) at 100 kPa. Salts containing anions from strong acids such as $[(CH_3)_4N]Cl$ (pK_a HCl, −8[38]) in the presence of 4 mol of water/mol of salt exhibit "normal" CO_2 capacities, 0.01 M at 50 °C and 100 kPa.

The CO_2 absorption capacity of $[(CH_3)_4N]F{\cdot}4H_2O$ is significantly higher, 1.9 M CO_2 at 100 kPa, than would be predicted by the pK_a of HF, 3.45.[37] As has been pointed out in the literature, but often unappreciated, fluoride ion in the presence of limited water is a very powerful base. In the extreme, anhydrous fluoride salts are comparable in basicity to organolithium reagents and can deprotonate such weak acids as dimethyl sulfoxide, acetonitrile, and nitromethane.[39] Tetraalkylammonium fluorides, with some notable exceptions,[32] are generally unstable in the absence of water or other protic material and decompose by a Hofmann elimination reaction which is initiated by abstraction of a β proton by F^-.[40]

The basicity of F^- decreases markedly in the presence of water or other protic material.[39] In dilute water or alcoholic solution, the enhanced basicity of F^- is nearly completely masked. Studies involving $[(C_6H_{13})_4N]F{\cdot}nH_2O$ have revealed a seven order of magnitude decrease in the rate of Hofmann elimination in low polarity solvents as n was varied from 0 to 4.6.[41] Similarly, the CO_2 affinities of fluoride-containing salt hydrates depend on the quantity of water present (see Figure 2). For low water content salts, the relatively high basicity of F^- results in large CO_2 absorption capacities. Conversely, F^- in the presence of relatively large quantities of water will display normal basicity and, hence, a "normal" CO_2 absorption capacity. That the CO_2 adduct of $[(CH_3)_4N]F{\cdot}4H_2O$ liberates CO_2 gas upon the addition of excess water illustrates the dependence of absorption capacity on water concentration. The resulting dilute solution of $[(CH_3)_4N]F{\cdot}4H_2O$ has a CO_2 absorption capacity about 1/100th of that of $[(CH_3)_4N]F{\cdot}4H_2O$. Some of these effects of anion hydration on CO_2 affinity have been quantified in the following modeling studies of CO_2 absorption by salt hydrates.

Modeling of CO_2−Salt Hydrate Reactivity. Various reaction schemes involving absorption of CO_2 by salt hydrates were used to generate equilibrium constant expressions to which CO_2 absorption/desorption data could be fitted. In each case, it was assumed that the physical solubility of CO_2 in the salt hydrate melt was negligible compared with its chemical solubility. Comparison of the physical and chemical solubilities of CO_2 in $[(CH_3)_4N]F{\cdot}4H_2O$ at 100 kPa, less than 0.01 M[42] and about 1.9 M, respectively, suggest that this assumption is reasonable. The results of these modeling efforts imply that the stoichiometry of CO_2 absorption is different for fluoride- and carboxylate-containing salt hydrates.

The CO_2 isotherms of fluoride-containing salt hydrates are best fit by assuming the stoichiometry of reaction 1 above. Setting the initial concentration of $F^-{\cdot}nH_2O$ to a, the equilibrium concentration of HCO_3^- to c, and the equilibrium CO_2 pressure to P, eq 3 can be obtained where K is the equilibrium constant for reaction 1.

$$c/a = \frac{K^{1/2}P^{1/2}}{(1 + 2K^{1/2}P^{1/2})} \qquad (3)$$

For infinite pressures, c/a is equal to 0.5, which is the maximum CO_2 absorption capacity permitted by the stoichiometry of reaction 1. If instead of fixing a maximum capacity of 0.5 mol of CO_2/mol of salt and slight perturbations of eq 3 are permitted, the factor 2 can be replaced by b, where $1/b$ is equal to the maximum CO_2 absorption capacity. Making this substitution and rearranging gives eq 4.

$$1/(c/a) = \frac{1}{(K^{1/2}P^{1/2})} + b \qquad (4)$$

Thus, if the stoichiometry of reaction 1 is appropriate, a plot of the inverse of absorption capacity ($1/(c/a)$) versus $1/P^{1/2}$ should result in a straight line with a slope of $1/K^{1/2}$ and an intercept of b. As listed in Table 4, such plots for $[(CH_3)_4N]F$ in the presence of various water concentrations gave excellent linear fits with intercepts between 0.44 and 0.52, consistent with the reaction stoichiometry described above. The model represented by eq 4 was used to calculate the CO_2 isotherm curves

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[42] The physical solubility of CO_2 in $[(CH_3)_4N]F{\cdot}4H_2O$ could not be determined experimentally. Instead, the CO_2 solubility in $[(CH_3)_4N]Cl{\cdot}4H_2O$ was determined and assumed to be equal to that of the fluoride salt.

Table 4. Equilibrium Constants for the Reaction of CO_2 with Fluoride-Containing Salt Hydrates

$$2F^-{\cdot}nH_2O + CO_2 = HCO_3^- + HF_2^-{\cdot}(2n-1)H_2O$$

salt	mol of water/ mol of salt	T (°C)	10^3K (kPa^{-1})	max capacity, $1/b$ (mol of CO_2/mol of salt)	R^2 of plot[b]
$[(CH_3)_4N]F$	8.1	50	0.86 (4)[a]	0.45 (4)[a]	0.9835
	6.3	50	1.69(5)	0.50 (3)	0.9900
	4.0	50	7.22 (6)	0.436 (6)	0.9987
	3.0	50	45.2 (8)	0.442 (5)	0.9976
	2.0	50	430 (20)	0.519 (5)	0.9715
CsF	4.0	40	1.02 (4)	0.36 (4)	0.9905
	2.65	40	3.41 (6)	0.329 (9)	0.9979
	1.65	40	44.4 (1)	0.422 (6)	0.9866
KF	4.0	40	3.4 (3)	0.30 (4)	0.9347

[a] Numbers in parentheses are estimated errors of the least significant figure. [b] R^2 of plot as described in the text, eq 4.

Table 5. Equilibrium Constants for the Reaction of CO_2 with Carboxylate-Containing Salt Hydrates at 50 °C

$$RCO_2^-{\cdot}nH_2O + CO_2 = HCO_3^- + RCO_2H{\cdot}(n-1)H_2O$$

salt	mol of water/ mol of salt	10^3K (mol of CO_2/ mol of salt kPa^{-1})	R^2 of plot[b]
$[(C_2H_5)_4N]CH_3CO_2$	4.0	0.276 (4)[a]	0.9978
	3.0	1.03 (2)	0.9968
$[(C_2H_5)_4N]CH_3CH_2CO_2$	4.0	0.35 (2)	0.9848
$[(CH_3)_4N]CH_3CH_2CO_2$	4.0	0.190 (6)	0.9912
$[(CH_3)_4N]_2O_2CCH_2CO_2$	6.1	0.77 (1)	0.9964
$[(CH_3)_4N]_2$maleate	6.8	5.75 (6)	0.9991
$[(CH_3)_4N]_2$phthalate	6.1	0.68 (2)	0.9953

[a] Numbers in parentheses are estimated errors of the least significant figure. [b] R^2 of plot as described in the text.

for $[(CH_3)_4N]F{\cdot}nH_2O$ that are displayed in Figure 2. As is evident, there is an excellent fit to the experimental data. The equilibrium constant increases with decreasing water concentration, as expected, and ranges from $0.86 \times 10^{-3}\ kPa^{-1}$ ($[(CH_3)_4N]F{\cdot}8.1H_2O$) to $430 \times 10^{-3}\ kPa^{-1}$ ($[(CH_3)_4N]F{\cdot}2H_2O$). The model provides good fits for CsF but the results for KF are less reliable. For both CsF and KF, values of $1/b$ are significantly less than 0.5. This may be ascribed to a greater degree of ion pairing than for $[(CH_3)_4N]F{\cdot}nH_2O$ salts. Data for some fluoride salts, such as $[(C_4H_9)_4N]F{\cdot}3H_2O$, could not be satisfactorily fitted to the above model.

Plots of the inverse of capacity versus $1/P^{1/2}$ gave poor linear fits for carboxylate salt hydrates, suggesting that absorption of CO_2 does not occur by the stoichiometry of reaction 1. Alternatively, it was found that more reasonable agreement was obtained when a one-to-one stoichiometry was assumed as in reaction 2. For various carboxylate salt hydrates, plotting of $c^2/(a-c)$ versus P gave straight lines for which the slope is equal to K for reaction 2 (Table 5). It appears that salt hydrates containing either monovalent or divalent carboxylate anions follow the stoichiometry of reaction 2. However, absorption data for the trivalent citrate anion was not consistent with this stoichiometry. Limited data for carboxylate salt hydrates suggest that decreasing water content results in increased values of K, as it does for fluoride-containing salt hydrates. Of the carboxylate salt hydrates in Table 5, tetramethylammonium maleate is notable for its large equilibrium constant with respect to the other carboxylate salts. This is more striking when compared to K for tetramethylammonium malonate, since the pK_a values for the second ionization of maleic (6.07)[37] and malonic acid (5.69)[37] are comparable. Perhaps maleate appears "more basic" in a salt hydrate since it has a fixed geometry which permits chelation of a proton.

Heats of CO_2 Absorption. The heats of absorption of CO_2 by molten $[(CH_3)_4N]F{\cdot}4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ were determined at 50 °C and at CO_2 pressures to 300 kPa by calorimetric methods (see Experimental Section). For $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$, a value of -8.40 kcal/mol of CO_2 was obtained over the pressure range investigated. In contrast, heats for $[(CH_3)_4N]F{\cdot}4H_2O$ exhibited a pressure dependence. At CO_2 loadings of less than 0.25 mol/mol of salt, the heat was -4.49 kcal/mol of CO_2, while above 0.25 mol/mol of salt, the heat decreased to -3.4 kcal/mol.

It is interesting, and at first apparently contradictory, that $[(CH_3)_4N]F{\cdot}4H_2O$ has a higher CO_2 absorption capacity than $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ in spite of its lower heat of absorption. It is believed that this arises from the relative strength of fluoride and acetate hydrogen bonding. As described above, $[(CH_3)_4N]F{\cdot}4H_2O$ consists of sheets of fluoride ions and water molecules held together by hydrogen bonds. It is reasonable that reaction with CO_2 requires some disruption of this hydrogen bonded network. Hence, the net heat of reaction can be viewed as the sum of the exothermic reaction of CO_2 with the salt hydrate and the endothermic disruption of the $F^- {-} H_2O$ hydrogen bonds. Apparently, the stronger $F^- {-} H_2O$ hydrogen bonds of $[(CH_3)_4N]F{\cdot}4H_2O$ require more heat to disrupt than do the acetate−water hydrogen bonds of $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ resulting in a smaller net heat of absorption. It is likely that the endothermic disruption of the hydrogen bonding structure of the salt hydrate is the key to the relatively low heats of absorption of $[(CH_3)_4N]F{\cdot}4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ as compared to those of commonly used chemical solvents for CO_2, 15−20 kcal/mol for primary and secondary alkanolamines and 10−12 kcal/mol for tertiary alkanolamines.[2] Thus, $[(CH_3)_4N]F{\cdot}4H_2O$ or $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ may be attractive alternatives to amine-based absorbents due to the lower heats required to regenerate the gas-free absorbent.

Experimental Section

General Methods. Water contents were determined using an Aquastar V1B volumetric titrator. FTIR and Raman spectra were obtained using a Nicolet 20 DXB spectrometer or an Instruments SA S3000 spectrometer, respectively. NMR spectra were recorded using an IBM SY-200 or a Bruker ACP-300 spectrometer; ^{19}F chemical shifts are reported relative to $CFCl_3$. NMR spectra were routinely obtained using glass NMR tubes. Spectra were recorded immediately after sample preparation. In one case, the ^{13}C and ^{19}F NMR spectra of molten $[(CH_3)_4N]F{\cdot}4H_2O$ containing absorbed CO_2 were recorded using a Teflon lined tube. Results obtained using glass or Teflon lined tubes were identical.

Absorption/Desorption Isotherms. The CO_2 absorption/desorption isotherms and CO_2 absorption capacities were determined using standard manometric techniques. A known quantity of the salt of interest was added to a stainless steel reaction vessel and attached to a manifold of known volume. The reaction vessel was maintained at a constant temperature and the salt melt was stirred. In-line pressure transducers were used to determine pressures. The volume of the system available to gas was determined by expansion of helium from the manifold at known pressure into the reaction vessel. The water vapor pressure of the salt hydrate was determined by exposing the melt to a static vacuum and allowing the pressure to reach its equilibrium value. It was assumed that the vapor pressure remained constant throughout the experiment and subsequent CO_2 pressures were corrected accordingly. Quantities of CO_2 in the gas phase were calculated using a one-term virial equation of the form $PV = nRT(1 + Bn/V)$. Values of B were obtained by interpolation of literature data.[43]

Heats of Absorption. Measurements were performed by W.W.Y. Eng, H. L. Wilson, W. V. Wilding, and G. M. Wilson of Wiltec Research Co. Provo, UT, using a calorimetric apparatus. The calorimeter cell was constructed from a 470 cm^3 stainless steel vacuum flask, in which a heater and a calibrated Pt resistance probe were installed. The cell was equipped for loading with gases under pressure and was contained in a thermostated water bath. The heat of absorption was measured directly at 50 °C from an energy balance calculation for the calorimeter.

Materials. The salts $[(CH_3)_4N]F\cdot4H_2O$, $[(C_2H_5)_4N]CH_3CO_2\cdot4H_2O$, CsF, $[(CH_3)_4N]Cl$, $[(CH_3)_4N]HF_2$, $[(C_4H_9)_4N]F\cdot3H_2O$, and $[(CH_3)_4N]OH\cdot5H_2O$ were obtained commercially (Aldrich) and were used without further purification. $[(CH_3)_4N]F\cdot4H_2O$ and $[(C_2H_5)_4N]CH_3CO_2\cdot4H_2O$ were protected from atmospheric moisture and their water contents were checked periodically. The synthesis of $[(C_2H_5)_4N]CH_3CO_2\cdot3H_2O$ will be described elsewhere.

The monohydrate $[(CH_3)_4N]F\cdot H_2O$ was prepared by drying $[(CH_3)_4N]F\cdot4H_2O$ under vacuum at 65 °C for 7 days.[31] ^{1}H NMR revealed that the product contained 1.06 mol of water/mol of salt.

Tetramethylammonium fluoride dihydrate $[(CH_3)_4N]F\cdot2H_2O$ was prepared by the addition of 1 mol of water/mol of salt to $[(CH_3)_4N]F\cdot H_2O$. All the added water was absorbed and no liquid was formed. Heating to 80 °C under N_2 led to a solid/liquid mixture.

Tetramethylammonium fluoride trihydrate $[(CH_3)_4N]F\cdot3H_2O$ was prepared by the addition of 2 mol of water/mol of salt to $[(CH_3)_4N]F\cdot H_2O$ under N_2. Stirring and gentle heating resulted in formation of a liquid which was solidified by cooling in liquid N_2. The water content by Karl Fischer titration was 3.09 mol of water/mol of salt.

Isotopically labeled $[(CH_3)_4N]F\cdot H_2O\cdot3D_2O$ was prepared by stirring $[(CH_3)_4N]F\cdot H_2O$ with 3 equiv of D_2O under N_2. The resulting liquid solidified upon standing at room temperature (mp 47–50 °C). $[(CH_3)_4N]F\cdot H_2O\cdot3H_2{}^{18}O$ was synthesized by addition of three equiv of $H_2{}^{18}O$ to solid $[(CH_3)_4N]F\cdot H_2O$. Stirring the components at room temperature gave a liquid with evolution of considerable heat. The supercooled liquid was crystallized by cooling briefly in liquid N_2.

Tetramethylammonium formate, $[(CH_3)_4N]HCO_2$, was synthesized by neutralization of $[(CH_3)_4N]OH\cdot5H_2O$ in methanol with 91% formic acid. Removal of the alcohol under vacuum gave a liquid. Continued drying overnight afforded a solid which was dissolved in a minimum of ethanol. Addition of acetone and cooling in ice water led to a white solid which was collected by filtration, washed with acetone, and vacuum dried. IR(KBr): υ_{CO} 1600 cm^{-1}. ^{1}H NMR: 2.7 ppm (12H, CH_3), 7.95 ppm (1H, HCO_2).

Tetramethylammonium propionate was synthesized by the metathesis reaction of sodium propionate and tetramethylammonium chloride in methanol. The NaCl precipitate was removed by filtration and the solvent was removed from the filtrate under vacuum. The solid was dissolved in hot acetone with a minimum of added ethanol. Cooling resulted in precipitation of a white solid which was collected by filtration, washed with acetone, and dried under vacuum overnight. IR(KBr): υ_{CO} 1580 cm^{-1}. ^{1}H NMR (D_2O): 2.7 ppm (12H), 0.50 ppm (t, 3H), 1.65 ppm (q, 2H).

Tetraethylammonium propionate was prepared by neutralization of $[(C_2H_5)_4N]OH$ in water with propionic acid. Drying under vacuum at room temperature resulted in a liquid which contained 3.9 mol of water/mol of salt as determined by Karl Fischer analysis. ^{1}H NMR (neat liquid): 0.55 ppm (t, 3H), 0.81 ppm (t, 12H), 1.60 ppm (q, 2H), 2.86 ppm (q, 8H), 4.6 ppm (H_2O).

Tetramethylammonium malonate was synthesized by reaction of $[(CH_3)_4N]OH\cdot5H_2O$ and malonic acid in water in a 2:1 molar ratio. Following filtration, much of the water was removed under vacuum. The resulting solid was dissolved in a minimum of hot methanol and filtered. Addition of acetone resulted in precipitation of a white solid which was washed with acetone and dried under vacuum overnight. IR (KBr): υ_{CO} 1560 cm^{-1}. ^{1}H NMR (D_2O): 2.55 ppm (24H), 2.3 ppm (2H), 4.8 ppm (H_2O). 1.9 mol of water/mol of salt by Karl Fischer analysis.

Tetramethylammonium maleate was prepared by reaction of maleic acid with 2 equiv of $[(CH_3)_4N]OH\cdot5H_2O$ in methanol. Removal of the solvent under vacuum gave a white solid which was redissolved in methanol and precipitated by addition of acetone. The resulting solid was dried under vacuum overnight. IR (KBr): υ_{CO} 1570 cm^{-1}. ^{1}H NMR (D_2O): 5.2 ppm (2H), 2.6 ppm (24H), 4.6 ppm, (H_2O); 2.0 mol of water/mol of salt by Karl Fischer analysis.

Tetramethylammonium phthalate was prepared by the reaction of phthalic acid with 2 equiv of $[(CH_3)_4N]OH\cdot5H_2O$ in ethanol. The product was recrystallized from methanol/acetone. After being dried under vacuum at room temperature, the solid was found to contain 0.1 mol of water/mol of salt. IR (KBr): υ_{CO} 1580 cm^{-1}. ^{1}H NMR (D_2O): 6.8, 6.7 ppm (4H), 2.4 (24H).

Tetramethylammonium citrate was prepared by reaction of citric acid with 3 equiv of $[(CH_3)_4N]OH\cdot5H_2O$ in methanol. Removal of the solvent under vacuum gave a white solid which was dissolved in methanol and precipitated by addition of acetone. The resulting solid was dried under vacuum overnight. IR (KBr): υ_{CO} 1570 cm^{-1}. ^{1}H NMR (D_2O): 2.65 ppm (36H), 2.00 ppm (4H), 4.7 ppm (H_2O); 4.5 mol of water/mol of salt by Karl Fischer analysis.

Tetramethylammonium carbonate $[(CH_3)_4N]_2CO_3$ was prepared by a literature method.[44] A sample of 3.37 g of $[(CH_3)_4N]OH\cdot2H_2O$ was exposed to CO_2 in a reactor for several hours and about 0.5 mol of CO_2/mol of salt were absorbed. The solid was dried under vacuum at 82 °C overnight. Anal. Calcd for $C_9H_{24}N_2O_3$: C, 51.90; H, 11.61; N, 13.45; $CO_3{}^{2-}$, 28.81. Found: C, 46.46; H, 10.71; N, 11.77; $CO_3{}^{2-}$, 19.86. Hence, the salt is best described as a mixture of carbonate and bicarbonate.

Tetramethylammonium bicarbonate $[(CH_3)_4N]HCO_3$ was obtained by reaction of the corresponding hydroxide with CO_2. A Schlenk tube containing 2.5 g of $[(CH_3)_4N]OH\cdot5H_2O$ was purged with CO_2 for 1 h. The resulting liquid was filtered in air and dried under vacuum for 1 week at room temperature. Anal. Calcd for $C_5H_{13}NO_3$: C, 44.4; H, 9.69; N, 10.36; $HCO_3{}^-$, 45.14. Found: C, 44.17; H, 9.92; N, 10.44; $HCO_3{}^-$, 39.6.

The salt $[(CH_3)_4N]OH\cdot2H_2O$ was prepared[45] by drying $[(CH_3)_4N]OH\cdot5H_2O$ for 2 days at 82 °C under vacuum. Anal. Calcd for $C_4H_{17}NO_3$: C, 37.78; H, 13.47; N, 11.01; H_2O, 28.33. Found: C, 38.21; H, 13.42; N, 11.71; H_2O, 31.30.

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