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Ion Exchange Resins as Reversible Acid Gas Absorbents

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ABSTRACT

Strongly basic anion exchange resins containing quaternary ammonium functionality and fluoride or acetate anions were found to remove carbon dioxide and hydrogen sulfide from gas streams. The absorption/desorption isotherms, heats of absorption, and gas separation properties were determined for a series of such resins. The fluoride form of Amberlyst® A-26, for example, absorbed CO_2 and H_2S reversibly, 0.23 mol CO_2/mol F^- and 0.24 mol H_2S/mol F^- at 100 kPa and 22 and 30°C, respectively. Absorption of CO_2 was fast compared to its desorption. Characterization by NMR indicated that bicarbonate was formed by reaction of CO_2 with F^- containing resins. Heats of CO_2 absorption by F^- Amberlyst® A-26 were pressure dependent and ranged from -5.0 to -3.2 kcal/mole CO_2 for pressures of 50 to 1000 kPa. The fluoride and acetate containing resins were effective for removal of CO_2 and H_2S from gas mixtures. Passage of a gas mixture containing 1% CO_2 or 5% H_2S through a packed column of F^-

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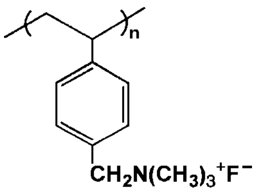
Amberlyst® A-26 at 22°C reduced the CO_2 or H_2S concentration to less than 25 ppm. Regeneration of the absorbents was accomplished by purging with inert gas at 50°C. Removal of CO_2 from gas streams containing substantial water vapor concentrations was achieved using F^- Amberlyst® A-26 resin.

Key Words: Ion exchange resins; Carbon dioxide; Hydrogen sulfide; Absorption.

INTRODUCTION

In a series of publications and patents,[1–7] we described the development of new membranes that selectively permeate carbon dioxide or hydrogen sulfide from gas mixtures. Acid gas permeation in these membranes occur by a facilitated transport mechanism resulting from a reversible reaction between the gas and the membrane material. Active membrane materials were fluoride- or acetate ion-containing molten salt hydrates or polyelectrolytes. Examples of such materials are the salt hydrate tetramethylammonium fluoride tetrahydrate, $[(CH_3)_4N]F{\cdot}4H_2O$, and the polyelectrolyte poly(vinylbenzyltrimethylammonium fluoride) (PVBTAF, see structure below). These facilitated transport membranes exhibited exceptional permselective properties—high CO_2/H_2 selectivities along with modest CO_2 permeances. Using polyelectrolytes such as PVBTAF, practical membranes can be fabricated. As for other facilitated transport membranes, however, these membranes have limitations as described elsewhere.[5,8]



PVBTAF

Absorption technology offers an alternative to facilitated transport membranes for acid gas removal. Certain fluoride containing salt hydrates have relatively large CO_2 absorption capacities and can function as reversible CO_2 or H_2S absorbents.[9,10] Similarly, polyelectrolytes, such as PVBTAF, absorb CO_2 reversibly but since these materials lack high surface area and porosity, gas absorption and desorption are quite slow.[4] The high water affinity of PVBTAF also presents difficulties. Under high gaseous water pressure,

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the polymer tends to swell or gel, further reducing surface area. In the absence of water vapor, the structure of the polyelectrolytes becomes such that CO_2 absorption is extremely slow.

Limitations of polyelectrolytes can be overcome by the use of structurally comparable ion exchange resins. The commercially available Amberlyst® A-26 has essentially the same structure as PVBTAF, except that it is crosslinked. With this similarity of structures in mind, an investigation of the acid gas sorption properties of Amberlyst® A-26 and related ion exchange resins was initiated.[11] The resins evaluated in this study are referred to as macroreticular "strongly basic" anion exchange resins.[12] These resins have relatively high porosity and surface area, thus permitting exposure of the resin active sites to gas.[13] Because of crosslinking, usually with divinylbenzene, the resins are water insoluble and undergo no visual swelling in the presence of liquid or gaseous water, which is often present in acid gas containing streams.

"Strongly basic" anion exchange resins consist of a polymer with pendant cationic groups, most often quaternary ammonium moieties. Associated with the cationic groups are anions, usually chloride. The anions of the resin, as the name implies, can be readily exchanged by washing with an excess of an aqueous solution of another anion. Based on the presence of quaternary ammonium groups and chloride ions, the term "strongly basic" would seem inappropriate since neither ion is even slightly basic. The term was derived from the hydroxide form of the resins where OH^- ions are associated with the pendant cationic groups. Two types of strongly basic anion exchange resins are commercially available. Type I resins contain trialkylammonium groups, usually $-N(CH_3)_3$. Amberlyst® A-26, Dowex® MSA-1, and a resin from Scientific Polymer Products designated SP2-722 are the type I resins examined in the current work. The structures of the Dowex® MSA-1 and SP2 722 resins are similar to that of Amberlyst® A-26. Type II resins contain dimethylethanolammonium groups, $(CH_3)_2NCH_2CH_2OH$. Examined in this work were the type II resins Amberlite® IRA 910 and Diaion PA408.

EXPERIMENTAL

Materials

The chloride and fluoride forms of Amberlyst A-26 were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). The fluoride forms of Amberlyst A-26 was also prepared as described below. Dowex MSA-1 and Diaion PA408 were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Amberlite IRA 910 was obtained from ICN Biochemicals, Inc. (Cleveland, OH, USA). The resin

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designated as SP2-722 was obtained from Scientific Polymer Products, Inc. (Ontario, NY, USA). under the name "polystyrene, crosslinked, quaternary ammonium chloride form," catalog #722.

Preparation of Resins

The fluoride and acetate forms of the various resins used in this study were prepared by a common procedure.[14] Details for the preparation of F^- and acetate (OAc^-) Amberlyst A-26 are presented as examples. As received Cl^- Amberlyst A-26, 102 g, was placed in a 250 mL Nalgene separatory funnel. The resin was washed repeatedly with 1 M NaOH until the washings were nearly Cl^- free as judged by addition of aqueous $HNO_3/AgNO_3$. About 10 L of solution were required. The resin was washed with deionized water until the washing were near neutral, with 1 M HF (about 1 L) until acidic, and water again until neutral. Following a final wash with 800 mL of acetone and 250 mL of ether, the resin was air dried for several hours and under vacuum overnight. Analysis by ion selective electrodes (Cl^-, F^-) indicated 97.6 mole% conversion to the fluoride form. For OAc^- Amberlyst A-26, Cl^- Amberlyst A-26 was washed with 1 M NaOH until the washings were almost Cl^- free. Following repeated washing with water, the resin was washed with 1 M acetic acid until the pH of the washings were 2.8 (the same as 1 M acetic acid). The resin was washed with water until the washings were neutral. Following washing with acetone, the resin was dried overnight under vacuum at room temperature. Water contents of the resins were determined using Karl Fischer (KF) analysis.

The F^- and OAc^- Amberlyst A-26 resins of lower water contents were prepared as follows. Resins were washed with 500 mL methanol. Following filtration, each sample was dried under vacuum at 50°C for 3 h and overnight at room temperature. Karl Fischer analysis indicated the following water content: F^-, 0.99% water, 0.12 mol H_2O/mol F^-; OAc^-, 0.55% water, 0.08 mol H_2O/mol OAc^-. The methanol content of the resins were not determined but methanol was detected (gas chromatography) when the resin was purged with helium at room temperature.

Prior to evaluation, as received Cl^- Amberlyst A-26 (100 g) was washed with 500 mL water followed by 500 mL 0.8 M HCl to ensure complete conversion to the Cl^- form. The resin was washed repeatedly with water until the washings were neutral and then with 750 mL acetone. Following air drying for several hours, the resin was dried under vacuum at room temperature for 2 days and at 60°C for 3 h. Water content by KF analysis was 8.75%, or 1.2 mol H_2O/mol Cl^-. A portion of the resin was further dried by washing with

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methanol and drying under vacuum for 3 h at 50°C and overnight at room temperature, resulting in a water content of 0.49%, or 0.062 mol H_2O/mol Cl^-.

A sample of OH^- Amberlyst A-26 resin was prepared by washing Cl^- Amberlyst A-26 with 1 M NaOH until the washings were almost Cl^- free (by $HNO_3/AgNO_3$). The resin was washed repeatedly with water until the washings were near neutral, followed by 200 mL acetone. The resin was dried under vacuum overnight at room temperature, resulting in a color change to gray and a strong odor of ammonia or amine, indicating that some decomposition of the resin had occurred. Water content by KF analysis was 30.8%, or 5.7 mol H_2O/mol OH^-.

Determination of CO_2 and H_2S Isotherms

Carbon dioxide and hydrogen sulfide absorption/desorption data were obtained by methods described previously.[9,10] The procedure involved exposing a known quantity of resin to a pressure of CO_2 or H_2S. After waiting until no measurable change in pressure was observed, usually 24 h, the quantity of gas absorbed was determined from the change in gas pressure. Determination of desorption data required the removal of a known quantity of gas from the system and waiting until a constant pressure was achieved. Isotherms were determined at 23 or 50°C for CO_2 and 30°C for H_2S.

Determination of Gas Separation Properties

Evaluation of the CO_2 and H_2S separation properties of the various resins was performed using small test columns of resins at 23°C. The columns consisted of a 6 in. long by 0.5 in. outer diameter stainless steel tubing packed with the resin of interest. Routinely, each column was purged with helium for 2 to 18 h at 23°C prior to the experiment. A feed gas consisting of 1% CO_2 and 1% CH_4 in helium (11.9 sccm) or 5.0% H_2S in CH_4 (10.0 sccm) at 101.3 kPa was passed through the test column. Gases exiting the column were analyzed by gas chromatography (GC) at regular intervals. Feed gas flow was continued until CO_2 or H_2S were detected in the exiting gases. The time to CO_2 or H_2S breakthrough was used along with the feed gas flow rate to calculate the amount of gas absorbed by the resin. The GC limits of detection were about 25 ppm for both CO_2 and H_2S. Regeneration of the column was accomplished at 50°C by purging with helium (10 sccm). Humidified feed gases, when used, were generated by passage of the premixed feed gas

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through a series of water bubblers maintained at 5 or 20°C, thus yielding gas mixtures with water vapor partial pressures of 0.87 and 2.34 kPa, respectively. Since the resin test column was maintained at 23°C, these water vapor pressures correspond to relative humidities of 31% and 83%.

Other Methods

Thermogravimetric analysis (TGA) experiments were conducted using a Perkin Elmer TGA 7 (Perkin Elmer, Inc., Shelton, CT, USA). Gases to the balance head and furnace sidearm were supplied by Tylan mass flow controllers. To minimize weight changes due to water loss, samples were purged with N_2 (25 sccm) at 30°C until a constant weight was obtained. The sample was then exposed to a 25 sccm flow of CO_2 (absorption) for 4 min followed by N_2 (desorption), 25 sccm, for 6 min. Absorption/desorption cycles were then repeated as desired.

The water absorption isotherm of F^- Amberlyst A-26 was determined at 20 and 40°C using a McBain balance. Prior to evaluation, a Karl Fischer titration showed that the sample contained 25.8% by weight H_2O, or 4.07 mole H_2O/mole F^-, and absorption data were corrected for this initial water content.

RESULTS AND DISCUSSION

Most strongly basic anion exchange resins are commercially available in the chloride form, i.e., with Cl^- as the counterion. Such materials are expected to be nonreactive with respect to acid gases because neither the anion nor the polymer backbone has any basic character. Resins containing the more basic fluoride or acetate anions can interact more strongly with acid gases. When this work was conducted, only the fluoride form of Amberlyst A-26 was commercially available but the fluoride or acetate forms can be prepared by a straightforward, published procedure.[14] This method, described in detail in the experimental section, involves ion exchange of the Cl^- form to the hydroxide by washing with aqueous base followed by neutralization with the appropriate aqueous acid, either hydrofluoric acid, HF, or acetic acid, HOAc. The F^- or OAc^- forms of five different resins were prepared and some properties are listed in Table 1. Physical properties, such as porosity and surface area, were not determined during this study but these are generally available. For example, product literature for Amberlyst A-26 resin lists the following properties: porosity, 0.30 cc/g; surface area, 30 m^2/g; average pore diameter, 40 nm.[15]

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Table 1. Exchange capacities and water contents of the resins evaluated.

Resin	Resin type	X^-	Exchange capacity[a] (meq/g)	Water content Weight %	Water content mol H_2O/mol X^-
Amberlyst A-26	I	F^-	4.7	27.6	4.5
		OAc^-	4.0	8.23	1.25
Dowex MSA-1	I	F^-	4.3	17.0	2.65
SP2 722	I	F^-	4.7	19.2	2.8
		OAc^-	4.0	10.2	1.6
Amberlite IRA-910	II	F^-	4.1	12.3	1.9
		OAc^-	3.5	10.8	1.9
Diaion PA408	II	F^-	3.5	25.5	5.5
		OAc^-	3.1	15.8	3.4

[a] Exchange capacity based on dry resin and complete conversion to the X^- form.

CO_2 Absorption Properties

The carbon dioxide absorption/desorption isotherms for the various resins in the F^- and OAc^- forms were determined and those for Amberlyst A-26 are illustrated in Figs. 1 and 2. Anion exchange resins containing the basic F^- or OAc^- ions reversibly absorbed relatively large amounts of CO_2. Replacing F^- or OAc^- with a strongly basic anion, such as hydroxide, resulted in a near irreversible absorption of CO_2. At 195.8 kPa and 22°C, OH^- Amberlyst A-26 absorbed 0.720 mol CO_2/mol OH^-. Lowering the CO_2 pressure above the resin to 61.0 kPa resulted in desorption of only 0.008 mol CO_2/mol OH^-. For comparison, the absorption/desorption isotherms of the chloride ion form of Amberlyst A-26 is shown in Fig. 3. Chloride ion is only very weakly basic as shown by the pK_a of its conjugate acid HCl, -8.[16] At 100 kPa CO_2, Cl^- Amberlyst A-26 absorbed 0.090 mol CO_2/mol Cl^-, while the absorption capacity of F^- Amberlyst A-26 was 2.6-fold greater at the same pressure. The differences in capacities were still greater at lower pressures. For example, at 10 kPa, the capacity of the F^- resin was 4.3 times that of the Cl^- form. The differences in capacities are small, however, when compared with those of the analogous salt hydrates or polyelectrolytes,[5,9] as illustrated by the 190-fold greater CO_2 capacity of $[(CH_3)_4N]F\cdot 4H_2O$ (0.3 mol/mol at 100 kPa) relative to $[(CH_3)_4N]Cl\cdot 4H_2O$.[9]

Absorption/desorption isotherm data for F^- containing resins can be modeled using a two-term capacity expression: a Henry's law term accounting

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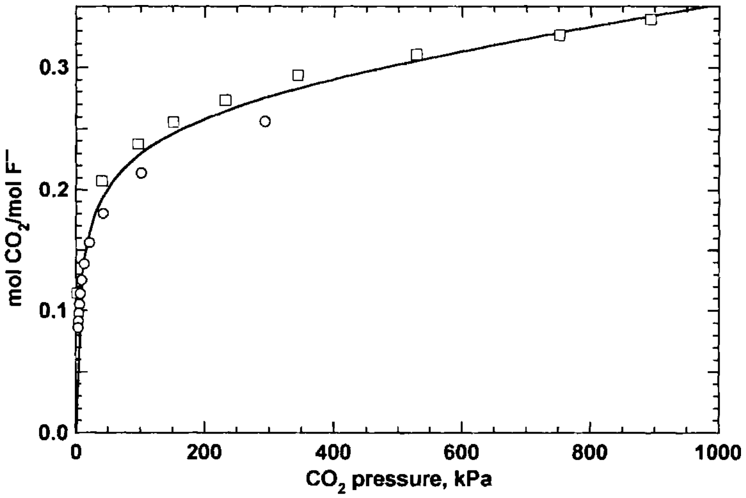

Figure 1. CO_2 isotherm of F^- Amberlyst A-26 at 22°C: squares = absorption; circles = desorption.

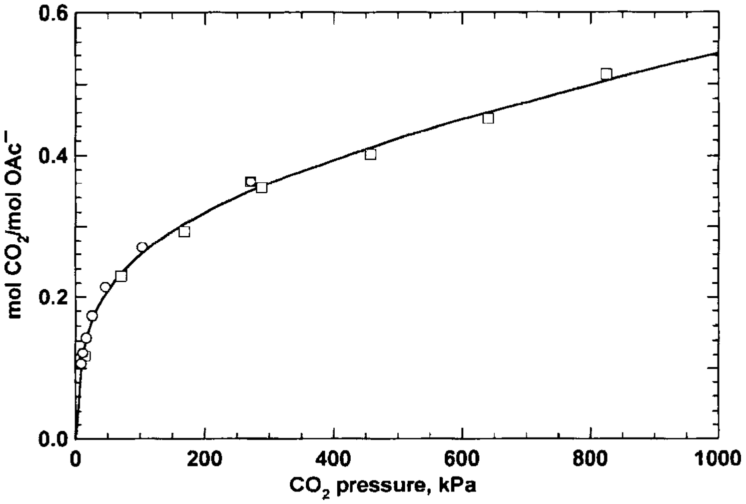

Figure 2. CO_2 isotherm of OAc^- Amberlyst A-26 at 22°C: squares = absorption; circles = desorption.

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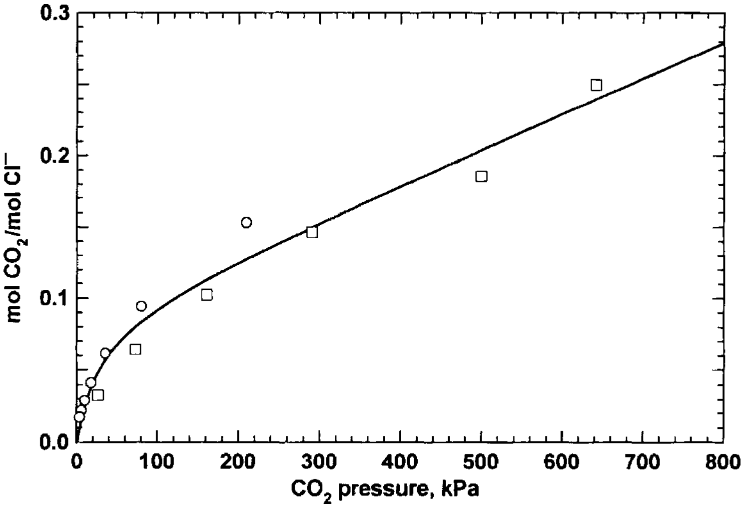

Figure 3. CO_2 isotherm of Cl^- Amberlyst A-26 at 22°C: squares = absorption; circles = desorption.

for physically absorbed CO_2 and a second term resulting from chemically absorbed CO_2. Reasonable reactions for chemical absorption involve one or two moles of hydrated F^- for each mole of CO_2. Fits using either stoichiometry were not completely satisfactory; however, one-to-one stoichiometry gave completely unreasonable fits and could be excluded. An approximation of the two-to-one stoichiometry of reaction 1 resulted in reasonable fits using Eq. (2) for the total CO_2 absorption capacity. In Eq. (2), k is a Henry's law constant and K is the equilibrium constant for reaction 1. The parameter b is the number of moles of F^- ions required for reaction with each mole of CO_2; b = 2 for reaction 1. Best fit values of k, b, and K are listed in Table 2. As shown by Figs. 1 and 2, the data are fit reasonably well. The curves in these figures were generated using Eq. (2) and the best values. The average value of b for F^- containing resins is about 3, implying that closer to 3 moles of F^- were consumed for each mole of chemically bound CO_2.

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

$$\text{capacity} = kP + [K^{1/2}P^{1/2}/(1 + bK^{1/2}P^{1/2})] \qquad (2)$$

The reactivity of F^- containing resins is similar to that of F^- containing salt hydrates,[9] for which each mole of CO_2 reacts with two moles of hydrated F^-

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Table 2. Fitting parameters for the CO_2 and H_2S absorption/desorption isotherms of F^- and OAc^- containing ion exchange resins.

	k, b, and K_{eq} [Eq. (2)]						
Resin	Resin type	T (°C)	Gas	$k \times 10^4$ (equiv/kPa)[a]	$K_{eq} \times 10^3$ (kPa^{-1})	b (equiv)	Capacity at 100 kPa
F^- Amberlyst A-26	I	22	CO_2	0.7 (2)[b]	5.5 (9)	3.1 (2)	0.230
F^- Amberlyst A-26	I	50	CO_2	0.3 (3)	3.0 (6)	3.0 (3)	0.210
F^- Amberlyst A-26	I	30	H_2S	4 (1)	1.3 (7)	2.4 (9)	0.237
F^- SP2 722	I	22	CO_2	1.60 (9)	67.3 (7)	3.45 (5)	0.277
F^- Dowex MSA-1	I	22	CO_2	1.51 (7)	107 (8)	2.81 (2)	0.336
F^- Amberlite IRA-910	II	22	CO_2	1.2 (5)	20 (4)	2.8 (1)	0.301
F^- Diaion PA408	II	22	CO_2	0.9 (3)	1.3 (3)	3.2 (5)	0.178
OAc^- Amberlyst A-26	I	22	CO_2	1.8 (3)	2.4 (3)	2.1 (2)	0.260
OAc^- Amberlyst A-26 (dried)	I	22	CO_2	1.2 (6)	2.4 (7)	2.2 (4)	0.248
OAc^- Amberlyst A-26	I	30	H_2S	10 (2)	1 (1)	2 (2)	0.297
OAc^- SP2 722	I	22	CO_2	1.3 (2)	1.8 (1)	2.1 (2)	0.240
OAc^- Amberlite IRA-910	II	22	CO_2	1.0 (4)	0.48 (7)	1.9 (4)	0.165

	k, b, C from dual mode fit: capacity = kP + [bCP/(1 + bP)]						
Resin	Resin type	T (°C)	Gas	$k \times 10^4$ (equiv/kPa)[a]	b (kPa^{-1})	C (equiv)	Capacity at 100 kPa
F^- Amberlyst A-26 (dried)	I	22	CO_2	2.2 (2)	1.4 (2)	0.39 (1)	0.409
OAc^- Amberlyst A-26	I	50	CO_2	1.8 (1)	0.02 (2)	0.19 (1)	0.143
OAc^- Amberlyst A-26	I	30	H_2S	11.4 (1)	0.041(9)	0.23 (2)	0.297
Cl^- Amberlyst A-26	I	22	CO_2	2.6 (4)	0.04 (2)	0.08 (2)	0.090
Cl^- Amberlyst A-26 (dried)	I	22	CO_2	1.0 (8)	0.003 (1)	0.29 (9)	0.077

[a] Equiv = mol CO_2 or H_2S/mol F^- or OAc^-.

[b] Numbers in parentheses are the estimated errors of the least significant figure.

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ions. However, the physical solubility of CO_2 in the analogous salt hydrates is much less than for the F^- containing resins, a property attributable to the resin structure. A fairly wide range of equilibrium constant values, 1.3×10^{-3} to $107 \times 10^{-3}\,kPa^{-1}$, were obtained for the resins examined. Henry's law constant varied from 0.7×10^{-4} to 1.6×10^{-4} equiv-kPa^{-1} (equiv = mole absorbed species/mole anion).

The chemistry of reaction 1 is further supported by solid state NMR identification of bicarbonate. The ^{13}C MAS NMR spectrum of F^- Amberlyst A-26 was consistent with its structure with resonances at 140 to 120 ppm (aromatic) and 50 ppm ($N\text{-}CH_3$). The one-pulse NMR spectrum of the resin containing absorbed CO_2 exhibited resonances at 52 ppm ($N\text{-}CH_3$) and 162 ppm, assigned to CO_2 bound as HCO_3^-. Surprisingly, none of the ^{19}F NMR spectra of F^- containing resins in the presence or absence of CO_2 exhibited the expected sharp resonances near -115 ppm attributable to fluoride ion, perhaps due to exchange broadening.

Previous studies involving F^- containing salt hydrates had shown that CO_2 absorption affinity and the degree of anion hydration were inversely related.[9] Similar results were obtained for F^- containing resins. A comparison of the CO_2 isotherms of F^- Amberlyst A-26 resin containing 0.12 mol H_2O/mol F^- with that of the resin containing 4.5 mol H_2O/mol F^- clearly shows a higher CO_2 affinity for the resin of lower water content. For example, absorption capacities at 100 kPa were 0.409 mol CO_2/mol F^- for the drier resin vs 0.230 for the resin containing 4.5 mol H_2O/mol F^-. Unfortunately, data for F^- Amberlyst A-26 containing 0.12 mol H_2O/mol F^- could not be fitted to Eq. (2) so a direct comparison of equilibrium constants was not possible. However, for the purpose of reconstructing data, dried F^- Amberlyst A-26 isotherm data was fit to a dual mode model[17] and fitting parameters are listed in Table 2. Also included are results for other resins, for which only the dual mode model provided a satisfactory fit of absorption/desorption data.

The CO_2 reactivity of acetate-containing resins were best modeled by the two-to-one reaction stoichiometry of reaction 3, where bicarbonate formation is accompanied by formation of biacetate ion (analogous to bifluoride). Fits based on a one-to-one reaction stoichiometry were poor, which is surprising considering that acetate-containing salt hydrates react in this fashion.[9] Values of k, b, K_{eq} were obtained from best fits to Eq. (2) (see Table 2). All b values were very near 2, in agreement with the stoichiometry of reaction 3. Equilibrium constants ranged from 0.48×10^{-3} to $2.4 \times 10^{-3}\,kPa^{-1}$. The equilibrium constant for CO_2 absorption by OAc^- Amberlyst A-26 was, as expected, about half that of the fluoride-containing resin.

$$2CH_3CO_2^- \cdot nH_2O + CO_2 = HCO_3^- + (CH_3CO_2)_2H^- \cdot (n-1)H_2O \qquad (3)$$

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Heats of CO_2 absorption were determined from isotherm data at 22 and 50°C using the equation $\ln(P_2/P_1) = -(\Delta H/R)(1/T_2 - 1/T_1)$, where P_1 and P_2 are pressures for identical absorption capacities at T_1 and T_2. For both F^- and OAc^- Amberlyst A-26, heats appear to be pressure dependent and become more negative with decreasing pressure, as illustrated by representative data in Table 3. Heats for the OAc^- Amberlyst A-26 were significantly more negative than those of the F^- form. Heats for both resins were comparable to those for the analogous fluoride and acetate containing salt hydrates: $[(CH_3)_4N]F{\cdot}4H_2O$, −-4.49 kcal/mol; $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$, −8.40 kcal/mol.[9]

The use of anion exchange resins as CO_2 absorbents has been reported but none offer the combination of reversibility and capacity of the fluoride and acetate resins just described. For example, the strongly basic anion exchange resin Amberlyst XN-1002, after conversion to its reactive form by treatment with aqueous strong base (i.e., OH^- as the anion), reportedly absorbs CO_2. Absorption occurs via bicarbonate formation with regeneration accomplished by purging with hot, humid, inert gas streams.[18] Weakly basic anion exchange resins containing amino groups in the free base form have been shown to absorb CO_2. Dowex MWA-1, for example, absorbs 24 mg CO_2/g resin at 35°C and 100 kPa.[19] This can be compared with the capacity of F^- Amberlyst A-26, 44 mg CO_2/g at the same pressure. There are also several reports of CO_2 absorption by uncrosslinked polymer. For example, copolymers of vinylbenzene and vinylbenzylchloride functionalized by reaction with various amines reportedly absorb CO_2 by reaction with the pendant amino group forming a zwitterionic carbamate. Sorption capacities in mole of CO_2 per mole of amino nitrogen atoms were 0.18 for primary amines, 0.07 for secondary amines, and 0.02 for tertiary amines. Regeneration was accomplished by heating to 105°C.[20]

Table 3. Heats of CO_2 absorption by F^- and OAc^- Amberlyst A-26.

F^- Amberlyst A-26		OAc^- Amberlyst A-26	
Pressure (kPa) at 22°C	Heat of absorption kcal/mol CO_2	Pressure (kPa) at 22°C	Heat of absorption kcal/mol CO_2
23.7	−5.03	29.2	−13.0
46.1	−5.22	43.1	−13.1
96.9	−4.88	60.9	−12.7
285.8	−3.77	116.5	−11.0
485.0	−3.37	203.5	−9.22
618.5	−3.24	312.5	−7.84

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H_2S Absorption Properties

Hydrogen sulfide absorption and desorption data were collected for F^- and OAc^- Amberlyst A-26 at 30°C. As shown in Figs. 4 and 5, absorption was fully reversible. The H_2S capacities of both resins were comparable to those for CO_2 at pressures below 200 kPa but H_2S capacities were substantially greater at higher pressures (Figs. 6 and 7). Fits of absorption/desorption data to the model for CO_2 were consistent with the two-to-one reaction stoichiometry of reactions 4 and 5, although the fits were less than ideal. As detailed in Table 2, errors in k, b, and K_{eq} were substantial.

$$2F^-\cdot nH_2O + H_2S = HS^- + HF_2{}^-\cdot 2nH_2O \tag{4}$$

$$2CH_3CO_2{}^- nH_2O + H_2S = HS^- + (CH_3CO_2)_2H^-\cdot 2nH_2O \tag{5}$$

As for CO_2, strongly basic anion exchange resins in the OH^- or Cl^- form have been used to separate H_2S from gas mixtures. The OH^- form of Amberlite IRA-410, for example, absorbs 102 mg H_2S/g resin. Regeneration requires washing with aqueous base.[21] Other similar resins in the OH^- form reportedly have capacities of 70 to 74 mg H_2S/g resin but, again, regeneration required washing the resin with aqueous 5% NaOH.[22] Not unexpectedly,

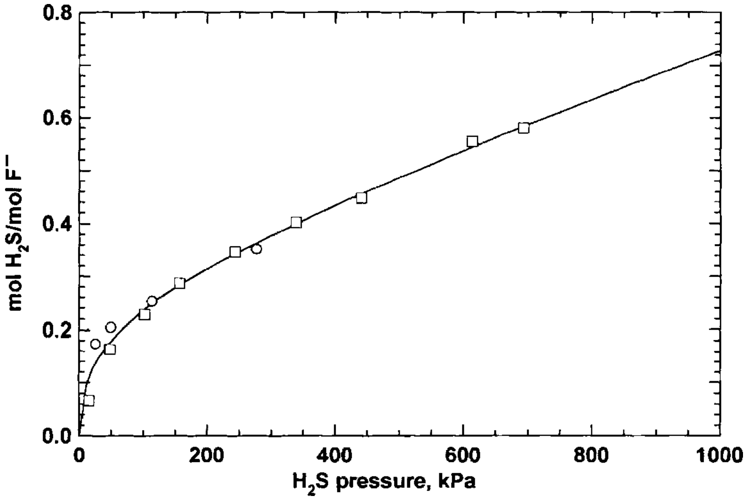

Figure 4. H_2S isotherm of F^- Amberlyst A-26 at 30°C: squares = absorption; circles = desorption.

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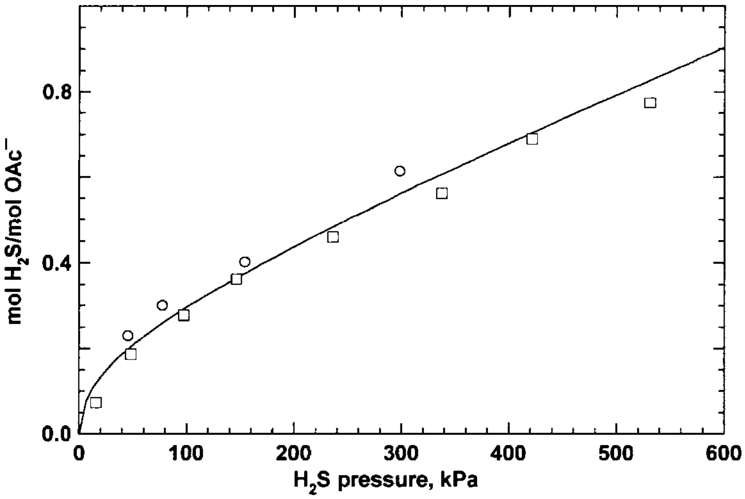

Figure 5. H_2S isotherm of OAc^- Amberlyst A-26 at 30°C: squares = absorption; circles = desorption.

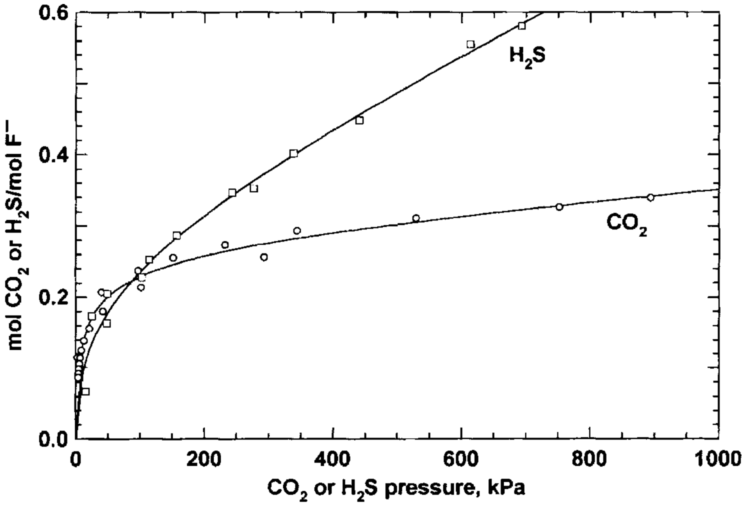

Figure 6. A comparison of the CO_2 and H_2S isotherms of F^- Amberlyst A-26.

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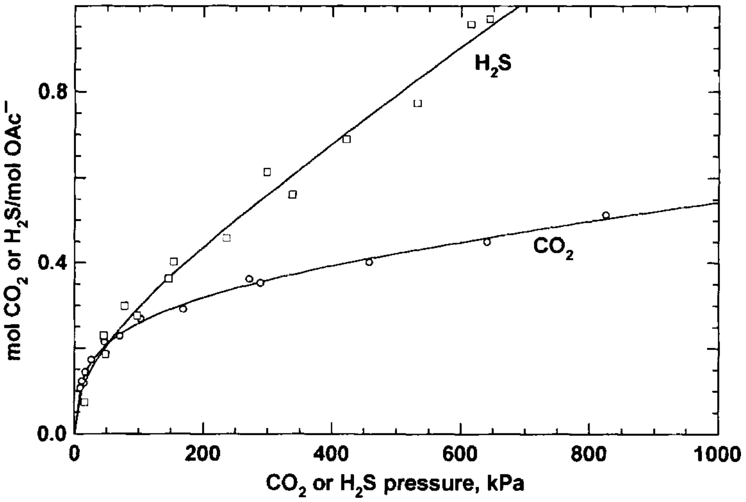

Figure 7. A comparison of the CO_2 and H_2S isotherms of OAc^- Amberlyst A-26.

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the H_2S capacities of F^- and OAc^- Amberlyst A-26 were lower, 38 and 40.4 mg H_2S/g at 100 kPa, but treatment with aqueous base is not required for regeneration.

The Cl^- form of various strongly basic anion exchange resins have lower H_2S affinities and, consequently, are more readily regenerated. For example, Amberlyst A-27 absorbs 20 to 24 mg H_2S/g resin and regeneration was accomplished under a N_2 purge at 100 to 110°C.[23] The chloride form of Amberlyst A-26 resin reportedly absorbs 470 mg H_2S/g resin at 0.526 kPa and 25°C and about 70 mg H_2S/g resin at 0.013 kPa. Absorption rates were very slow, with some times greater than 8 days to reach equilibrium.[24] The reported Cl^- Amberlyst A-26 H_2S capacities are very large compared to those for the F^- form of the resin, perhaps because it was assumed in the current work that equilibrium was achieved after 24 h of gas exposure.

H_2O Absorption Properties

The water absorption isotherm of F^- Amberlyst A-26 was determined at 20°C and 40°C between 0.2 to 1.6 kPa. Over this narrow pressure range, capacity increased linearly with pressure. Henry's law constants were 1.88 equiv/kPa and 0.911 equiv/kPa (equiv = mole H_2O/mole F^-) at 20 and

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40°C, respectively. The heat of absorption was −6.0 kcal/mol based on absorption data at the two temperatures.

CO Absorption Properties

The CO absorption capacities of F^- Amberlyst A-26 were, as expected, quite low. At 26°C, capacity was fairly linear with respect to pressure over the pressure range examined, 0 to 100 kPa, with a Henry's law constant of 1.8×10^{-5} equiv/kPa or a capacity of 1.8 mmol CO/mol resin (0.0085 mmol CO/g) at 100 kPa. The CO_2 absorption capacity of F^- Amberlyst A-26 is nearly 120-fold greater under the same conditions. Thus, F^- containing resins offer the potential advantage of lower product loss when applied to a CO_2/CO separation. By analogy, a similar lower product loss could be expected for CO_2/N_2, CO_2/O_2, and CO_2/CH_4 separations.

Rates of CO_2 Absorption and Desorption

In addition to the quantities of gas absorbed, the rate of absorption and desorption are critical to an absorbent's performance. A qualitative comparison of such rates was obtained using thermogravimetric analysis. Samples at 30°C were exposed alternately to CO_2 (absorption) and N_2

Table 4. CO_2 absorption and desorption by F^- and Cl^- Amberlyst A-26 at 30°C as determined by TGA.[a]

Absorption cycle	Change wt%	Equiv CO_2 absorbed	Desorption cycle	Change wt%	Equiv CO_2 desorbed
F^- Amberlyst A-26					
1	2.74	0.131	1	1.13	0.054
2	1.21	0.058	2	1.15	0.055
3	1.26	0.060	3	1.17	0.056
4	1.21	0.058	4	1.11	0.053
5	1.13	0.054	5	1.05	0.050
Cl^- Amberlyst A-26					
1	0.788	0.0382	1	0.782	0.0379
2	0.812	0.0393	2	0.758	0.0367
3	0.800	0.0388			

[a] Conditions: absorption cycle, 4 min, CO_2/N_2 feed; desorption cycle, 6 min, N_2 feed.

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(desorption) and the resulting weight changes are detailed in Table 4. As shown in Fig. 8, the initial quantity of CO_2 absorbed by F^- Amberlyst A-26 was larger than for subsequent cycles. Absorption was rapid with, for example, 90% occurring during the first 1 minute of the second cycle. Desorption was significantly slower and a complete conversion to the gas-free absorbent was not achieved during the brief N_2 purge. Results for other F^- and OAc^- containing resins were qualitatively similar to those for F^- Amberlyst A-26. For each sample, the initial exposure to CO_2 gave the largest increase in weight. Type II resins absorbed CO_2 more slowly than did type I resins, as

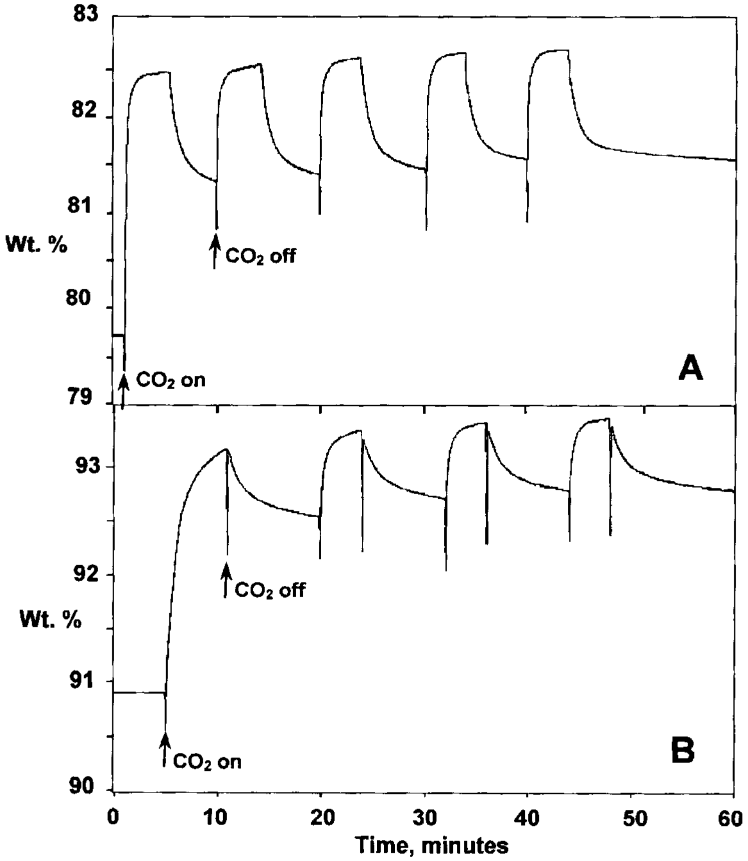

Figure 8. TGA traces at 30°C; absorption cycle, 4 min CO_2/N_2; desorption cycle, 6 min N_2. A. F^- Amberlyst A-26. B. F^- Amberlite IRA-910.

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shown by the TGA traces of F^- Amberlyst A-26 (type I) and F^- Amberlite IRA910 (type II) (see Fig. 8). All attempts to fit TGA data to absorption or desorption rate expressions were unsuccessful. This may be related to the surprising results obtained for Cl^- Amberlyst A-26 (see Table 4), which showed a relatively large weight increase upon exposure to CO_2 even though the resin has a lower CO_2 affinity. Desorption of CO_2 from the resin was rapid and nearly complete regeneration of the gas-free absorbent was achieved.

CO_2 Separation Properties

The utility of various ion exchange resins for removal of CO_2 from gas mixtures was investigated using packed columns of resin at 23°C exposed to a gas mixture consisting of 1 vol% CO_2 and CH_4 in helium at 101.3 kPa. The time to CO_2 breakthrough along with the feed gas flow rate were used to calculate the quantity of CO_2 removed by the resin. Following each feed gas cycle, the resin was regenerated by purging with helium. An initial experiment at 23°C indicated that desorption was relatively slow and unfavorable. A slight increase in temperature from 23 to 50°C significantly improved the extent of regeneration achievable because of increased desorption rates and the more favorable thermodynamics of desorption at the higher temperature. Long regeneration times, often greater than a day, were used in an attempt to achieve maximum desorption of bound CO_2. In practice, much shorter regeneration periods would be used to achieve an acceptable working capacity.

For fluoride-containing resins (Table 5), CO_2 removal capacities were generally lower after the first feed cycle, implying that regeneration to a CO_2 free resin did not occur. Quantities of CO_2 removed were much lower for the type II resins Amberlite IRA-910 and Diaion PA408 than for type I resins even though the equilibrium absorption capacities of all F^- resins were comparable. The poor performance of type II resins is likely due to the slow reaction of such resins with CO_2 as described above. A dried F^- Amberlyst A-26 containing 0.12 mol H_2O/mol F^- exhibited the largest CO_2 removal capacity, about twice that of the resin containing 2.9 mol H_2O/mol F^-. However, quantities of CO_2 removed during successive feed gas cycles were much lower, implying that only a small fraction of gas was desorbed during regeneration; that is, absorption was largely irreversible.

Results for acetate containing resins are also listed in Table 5. The quantities of CO_2 removed were consistently lower than those of the fluoride containing resins. For example, the CO_2 removal capacity of OAc^- Amberlyst A-26 was about 60% that of the F^- containing resin. However, regeneration of the absorbent was more facile and, generally, no decline in removal capacity

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Table 5. CO_2 separation properties of anion exchange resins at 23°C.[a]

	Removal capacity (equiv CO_2) for indicated feed cycle			
Resin	1	2	3	4
F^- Amberlyst A-26	0.117	0.231	0.146	0.121
Dried F^- Amberlyst A-26[b]	0.392	0.060	0.057	0.049
F^- SP2 722	0.168	0.181	—	—
F^- Dowex MSA-1	0.262	0.181	—	—
F^- Amberlite IRA 910	0.107	0.106	0.092	—
F^- Diaion PA408	0.029	0.021	—	—
OAc^- Amberlyst A-26	0.069	0.070	0.081	0.085
Dried OAc^- Amberlyst A-26[c]	0.065	0.057	0.039	—
OAc^- SP2 722	0.043	0.055	0.062	0.062
OAc^- Amberlite IRA910	0.021	0.027	—	—
OAc^- Diaion PA408	0.010	0.003	—	—
Cl^- Amberlyst A-26	<0.007	—	—	—
OH^- Amberlyst A-26	0.737	0.037	0.013	

[a] Conditions: feed, 1% CO_2, 1% CH_4 in He; regeneration: He, 10 sccm at 50°C.
[b] 0.12 mole H_2O/mol F^-.
[c] 0.08 mole H_2O/mol OAc^-.

with successive regenerations was observed. Once again, the capacities of type II resins were significantly lower. A sample of dried OAc^- Amberlyst A-26 resin, unlike the analogous fluoride resin, exhibited no improvement in CO_2 removal properties.

For comparative purposes, the CO_2 removal properties of Cl^- Amberlyst A-26 and OH^- Amberlyst A-26 were determined (see Table 5). For the Cl^- form, less than 0.0071 mol CO_2/mol Cl^- were removed from the feed gas, or about 1/27 the capacity of the F^- form. Desorption of CO_2 occurred very readily when the column was purged with helium at 23°C. These results imply that, as expected, the Cl^- form of Amberlyst A-26 is nearly inert with respect to CO_2. The OH^- form of the resin removed 0.737 mol CO_2/mol OH^- during the first feed gas cycle. Successive cycles resulted in much lower quantities absorbed, implying that regeneration was largely ineffective. This is expected for the near irreversible formation of bicarbonate by reaction with hydroxide.

Since industrial CO_2-containing streams often contain water, the effects of water vapor on the CO_2 separation properties of F^- Amberlyst A-26 resin at 23°C were evaluated. For feed relative humidities of 31% and 83% (see Experimental), the CO_2 removal capacities were 0.151 and

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0.144 mol CO_2/mol mol F^-, respectively, vs 0.214 mol CO/mol F^- for an anhydrous feed. Thus, the CO_2 removal capacities decreased with increasing feed humidities, consistent with the reported decrease in CO_2 affinity of salt hydrates with increasing degree of hydration.[9] Nonetheless, even at 83% relative humidity, substantial quantities of CO_2 were removed. This is unusual. Conventional absorbents, such as molecular sieves, usually absorb more H_2O than CO_2 and a gas drying step prior to CO_2 removal is generally required. F^- Amberlyst A-26 and related resins, however, offer the possibility of separating CO_2 prior to drying. Concurrently with CO_2 removal, the resin also removed H_2O from the feed gas. At 31% feed relative humidity, approximately 50 to 75% of the water in the feed was removed along with CO_2. Following CO_2 breakthrough, 30 to 50% of the feed water was removed.

H_2S Separation Properties

Fluoride and acetate containing ion exchange resins were also effective for removal of H_2S from gas streams. Removal capacities were obtained using a feed gas consisting of 5.0% H_2S in CH_4 (Table 6). Contrary to results for CO_2, there were no significant differences between the H_2S removal capacities of type I and II resins. The largest H_2S removal capacity was that for F^- Amberlyst A-26, 0.22 to 0.25 mol H_2S/mol F^-. Regeneration at 50°C by purging with helium resulted in no decrease in the removal capacity with

Table 6. H_2S separation properties of anion exchange resins at 23°C.

	Removal capacity (equiv H_2S) for indicated feed cycle		
Resin	1	2	3
F^- Amberlyst A-26	0.215	0.215	0.254
F^- SP2 722	0.140	0.100	0.060
F^- Dowex MSA-1	0.184	0.102	0.102
F^- Amberlite IRA-910	0.169	0.072	0.072
OAc^- Amberlyst A-26	0.273	0.273	0.212
OAc^- SP2 722	0.215	0.236	0.408
Cl^- Amberlyst A-26	0.128	0.077	0.077
OH^- Amberlyst A-26	0.676	0.023	0.023

Conditions: feed, 5% H_2S in CH_4; regeneration, He, 10 sccm at 50°C.

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successive feed cycles. The other three resins, however, showed a significant drop-off in H_2S removal capacity after the first feed gas cycle. The acetate containing resins, Amberlyst A-26 and SP2 722, exhibited removal capacities comparable to those for F^- containing resins.

For comparative purposes, the H_2S removal properties of Cl^- and OH^- Amberlyst A-26 were determined (see Table 6). The first feed cycle for Cl^- Amberlyst A-26 resulted in removal of 0.13 mole H_2S/mole Cl^-, a value about 60% and 48% those of the analogous F^- and OAc^- resins, respectively. The removal capacities were lower in successive feed cycles. The time required for regeneration of the gas free Cl^- form was significantly shorter than for F^- or OAc^- consistent with a lack of chemical interaction between H_2S and the resin. As expected, OH^- Amberlyst A-26 absorbed a large quantity of H_2S, 0.68 mol H_2S/mol OH^- but absorption was largely irreversible, as shown by the very low capacities for successive feed gas cycles.

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CONCLUSION

Strongly basic anion exchange resins containing quaternary ammonium functionality and fluoride or acetate anions can quantitatively remove CO_2 and H_2S from gas mixtures. Removal occurs via the chemical absorption of either gas by an acid–base reaction resulting in bicarbonate or bisulfide. Regeneration of the resins containing absorbed CO_2 or H_2S can be accomplished by purging with inert gas. Carbon dioxide removal is effective even in the presence of substantial water vapor pressures.

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