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Ion Exchange Reactions of Quaternary Ammonium Halides with Wheat Straw. Preparation of Oil-Absorbents

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SUMMARY

Products useful for removing emulsified oil from water were prepared by first heating wheat straw with sodium hydroxide solution and then subjecting the resulting product to an ion exchange reaction with hexadecyltrimethylammonium bromide (CTAB). Comparison of sodium hydroxide solutions of varying concentrations showed that sufficient NaOH is needed to disrupt straw particles and produce a high surface area product; however, NaOH concentration must not be so high as to remove large amounts of hemicellulose, since the uronic acid substituents of hemicellulose are responsible for much of the ion exchange capacity of straw. Infrared spectroscopy of a typical straw-CTAB adduct indicated a C_{16} *quaternary ammonium cation content of 3·9% by weight (13·7 meq per 100 g of adduct).*

INTRODUCTION

Agricultural products and residues, such as kapok fiber (Kobayashi, 1978), cotton (Johnson *et al.*, 1973; Meenaghan *et al.*, 1976), rice hulls (Bertram, 1975), corncob meal (VanderHooven & VanderHooven, 1971), bagasse fibers (Fischer, 1979), and peat moss (Hennezel & Coupal, 1972) have been used to absorb oil, and these materials have the advantage of being inexpensive and readily available. Mats and column packings for oil removal have also been prepared by mixing cellulosic fibers with synthetic fibers, e.g. polyethylene (Wiegand *et al.*, 1978) or polypropylene-polyethylene-nylon blend (Ohkita *et al.*, 1974).

Cellulosics have also been mixed with inorganic materials, such as clay (Suzuki *et al.*, 1976), magnesium hydroxide, and alumina (Sato *et al.*, 1977) to give oil-absorbent compositions.

The hydrophobicity of cellulosic materials (and thus their affinity for oil) has been increased by reaction with organic isocyanates (Holst *et al.*, 1975) and with fatty acid derivatives, such as anhydrides (Ball, 1973) and acid chlorides (Teng & Stubits, 1975). Also, an oil-absorbing cellulose–polystyrene composite was prepared by immersing a cellulose sponge into styrene–benzoyl peroxide and then heating the mixture to 100°C (Marx, 1972). Coating cellulosics with hydrophobic compounds, such as paraffin wax (Peterson & Palkie, 1971; Orth, 1973; Matsuda *et al.*, 1977), insoluble fatty acid salts (Aoso, 1974), or low melting polymers such as polyolefins (Kunitomo *et al.*, 1977; Saida *et al.*, 1978), is another technique used to increase the affinity of fibers for oil. Some polymers (e.g. ethylene–vinyl acetate copolymer) also have been deposited onto fibers from aqueous emulsions (Sato & Itani, 1977; Sato & Oriya, 1977).

Recent studies from our Center (Fanta & Doane, 1985; Fanta *et al.*, 1985) describe low add-on graft polymerization of acrylic acid onto bleached softwood pulp followed by ion exchange reactions with hexadecyltrimethylammonium bromide (CTAB) (Fig. 1). The hydrophobic nature of C_{16} quaternary ammonium substituents conferred oil-absorbing properties on final products, and adducts of this type readily absorbed oil from aqueous dispersions to give clear supernatants. Carboxylmethyl derivatives of softwood pulp were also prepared by reaction with chloroacetic acid under alkaline conditions, and products of this type functioned in a similar manner (Fanta & Doane, 1985). Since straw already has ion exchange properties without the need for further derivatization (Larsen & Schierup, 1981; Shet & Zeronian, 1984), we

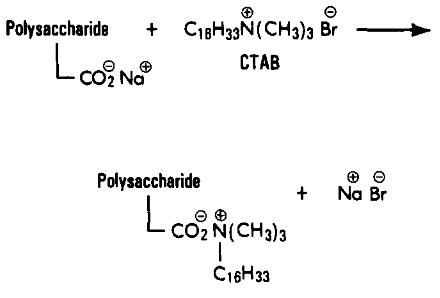

Fig. 1. Ion exchange reaction of carboxyl-containing polysaccharides with hexadecyltrimethylammonium bromide (CTAB).

have examined reactions between CTAB and alkali-treated wheat straw and have found that products with good absorbent properties can be easily prepared from this inexpensive and readily available agricultural residue (Fanta & Doane, 1985). In this report we will examine a number of variables in the wheat straw–CTAB reaction and will consider reasons for the observed behavior of straw under different experimental conditions.

EXPERIMENTAL

Materials

Straw of soft winter wheat (*Triticum aestivum* L.), variety 'Arthur', from central Illinois, was freed of heads, roots and leaves and was ground in a Wiley mill (screen with 2 mm diameter openings). Ground straw was washed eight times with water at room temperature (100 g straw in 3 liters) and was allowed to air-dry to a moisture content of about 8%. Weight loss (due to water solubles) was about 15%. Nitrogen analysis of washed straw was 0·2%. Technical grade CTAB was from Eastman Kodak Company.

Reaction of straw with sodium hydroxide and CTAB

To determine the amount of sodium hydroxide consumed by straw, 1·000 g (dry basis) of ground straw was blended with 5·6 ml of sodium hydroxide solution of varying concentration, and the mixture (in a saran-covered 25 ml erlenmeyer flask) was placed in a 100°C oven for 2 h. The mixture was washed onto a sintered glass funnel with water, and the supernatant was separated by filtration. The solid was washed three times with water, and the combined filtrate and washings (about 100 ml) were titrated with 0·116 N HCl. The endpoint was determined from a titration curve of pH versus ml of HCl solution. The solid was further extracted by stirring overnight with 50 ml of water followed by filtration, washing, and titration of the filtrate as described above. The total amount of 0·116 N HCl needed to titrate unreacted NaOH was used to calculate meq NaOH consumed per gram of straw.

For a typical reaction with CTAB, 5·00 g (dry basis) of straw was blended with 28 ml of sodium hydroxide solution (0·12–0·96 N), and the mixture was heated in a 100°C oven for 2 h, washed into a Waring blender with 250 ml of water, and stirred at high speed for 2 min. Temperature and pH of the dispersion were then measured. The solid was separated by filtration, washed three times with water, and stored as a wet solid. Water content was determined by vacuum drying at 100°C over P_2O_5. A solution of 2·00 g of CTAB in 40 ml of water was then added to 3·28 g of straw (dry basis), and the resulting mixture was allowed to stand at room temperature with periodic stirring for 2 h. The solid was separated by filtration and washed once with water and four times with 1:1 (v/v) ethanol–water. The solid was further extracted for 24 h with 95% ethanol in a Soxhlet apparatus. The extracted solid was finally washed four times with water (to remove ethanol) and was stored as a wet filter cake. Reaction times and oven temperature were arbitrarily chosen, since a study of the combined effects of these variables on oil-absorbent properties of final products is beyond the scope of this preliminary study. We did establish, however, that room temperature reaction with sodium hydroxide solution produced an inferior absorbent.

Test for oil absorption

A dispersion (emulsion) was prepared by adding 21 drops (0·47–0·50 g) of oil (white paraffin oil, Saybolt viscosity 125/135, Fisher Scientific Co.) to a solution of 0·100 g of dodecylbenzene sodium sufonate in 200 ml of water and stirring the resulting mixture for 2 min at high speed in a Waring blender. Ten milliliters of oil dispersion and sufficient straw–CTAB adduct to give 0·50 g on a dry basis were shaken together in a 50 ml screw cap bottle, allowed to stand for 2·5 min, shaken again, and allowed to stand for an additional 2·5 min. Supernatant was separated by screening through a small Buchner funnel containing no filter paper. Although the first few drops of supernatant contained some suspended solid, remaining supernatant was clear due to filtration through a settled layer of straw–CTAB adduct. Per cent transmission (%T) of the supernatant at 650 nm was then determined in a 1 cm ultraviolet cell. Supernatant and solid were returned to the 50 ml bottle, and an additional 5 ml of oil dispersion was added. The mixture was shaken and %T of the supernatant was again determined. This procedure was repeated with 5 ml increments of oil dispersion until %T dropped to about 10 or less; %T was then plotted against total volume of oil dispersion added.

Microscopy

Freeze-dried solids were mounted on aluminum stubs with double-sided tape and were coated with a 200 Å layer of gold–palladium (60–40) alloy. Samples were then examined and photographed at 50× in a Hitachi ISI scanning electron microscope.

Infrared analysis of straw–CTAB adduct

Accurately weighed samples of freeze-dried wheat straw (previously treated with 0·24 N NaOH, blended at high speed, and washed according to the above procedure) were first moistened with aqueous CTAB solutions of known concentrations and then freeze-dried to give mixtures containing 2·0, 3·5, and 6·4% CTAB, by weight. Potassium bromide disks (1·3 cm diameter) were prepared by pulverizing (Wig-L-Bug mixer) 13·0 mg ± 1% of each dry sample with 187 mg ± 1% of KBr (Barns Analytical) under nitrogen and then diluting 10 mg of each mixture with 290 mg of KBr. Spectra obtained with a Mattson Cygnus 25 FTIR with a water-cooled source and a DTGS detector showed over 88% T at 4000 cm^{-1}, over 94% T at 2000 cm^{-1}, and transmittance minima of 40–60% in regions where major absorptions occurred. Spectra of the same material obtained at different times by this method were superimposable.

One hundred scans of each sample were compared to 100 scans of a background disk prepared from 300 mg of KBr (total scan time was 132 s per sample), and Mattson Starlab software programs were used to correct the baseline of the absorbance spectra. Subtracting a spectrum of NaOH-treated straw from the spectra of straw–CTAB mixtures (subtraction factor = 1·0) showed C-H absorption for CTAB at 2925 and 2854 cm^{-1} (asymmetric and symmetric methylene stretching). Straight line plots of absorbance for these two bands versus weight per cent CTAB in the mixtures were used to determine concentration of C_{16} quaternary ammonium groups in a straw–CTAB adduct of unknown composition.

RESULTS AND DISCUSSION

Wheat straw is a composite polymer containing cellulose, hemicellulose, and lignin as major components, and the hemicellulose fraction is made up largely of β-(1→4) linked D-xylopyranose units with side chains containing L-arabinofuranose, D-glucuronic acid, and 4-*o*-methyl-D-glucuronic acid residues (Aspinall & Meek, 1956; Ghali *et al.*, 1974). A significant number of hemicellulose hydroxyls are either acetylated or (to a lesser extent) esterified with phenolic acid substituents (Evans, 1979; Chesson *et al.*, 1983). Inorganic material (largely silica) is also present in straw (Harbers *et al.*, 1982; Reddy *et al.*, 1983) in addition to a number of minor components, including pectin (Adams & Castagne, 1949; Harbers *et al.*, 1982), and protein (Anderson & Anderson, 1980). Uronic acids constitute roughly 4% of the total weight of straw (Miron & Ben-Ghedalia, 1982) and some carboxylic acid groups in these uronic acid units may be either esterified (Anderson & Anderson, 1980; Chesson *et al.*, 1983) or in the form of inorganic salts (e.g. Ca and Mg) (Shet & Zeronian, 1984). These carboxylic acid substituents in hemicellulose and pectin are probably the major reason for the ion exchange properties observed for straw, although the protein component of straw (Cornfield, 1960) and the phenolic groups present in lignin may also make some contribution to total ion exchange capacity.

Before reaction with CTAB, wheat straw was heated with NaOH solution to ensure that uronic acid esters were hydrolyzed and that carboxylate groups were converted into the sodium salts necessary for the subsequent ion exchange reaction. The normality of NaOH was varied from 0·12 to 0·96, and a control reaction was also run in which water alone was used (Table 1). The amount of NaOH consumed by the various components of straw under our pretreatment conditions increased sharply with normality at the low alkali concentrations, probably because milliequivalents of alkali added were less than theoretical at low normalities (Fig. 2). At higher normalities, however, alkali consumption leveled off to a maximum value of about 1·4 meq per gram of straw. Based on infrared analysis, little or no ester carbonyl remains in straw after treatment with 0·24 N NaOH. Calculations showed that more

TABLE 1

Reaction of Wheat Straw with Sodium Hydroxide[a]

Normality of NaOH	*NaOH consumed (meq per gram straw)*[b]	*Final pH*[c]	*Weight loss of straw (%)*
(H_2O)	—	4·2	4
0·12	0·59	8·4	8
0·24	0·94	9·8	20
0·48	1·21	10·6	34
0·96	1·36	11·3	41

[a] 5·00 g (dry basis) of wheat straw + 28 ml of sodium hydroxide solution (or water) heated for 2 h in a 100°C oven and then blended with 250 ml of water. Solid separated by filtration and water-washed.

[b] Determined by titration in a separate experiment.

[c] After blending with 250 ml of water.

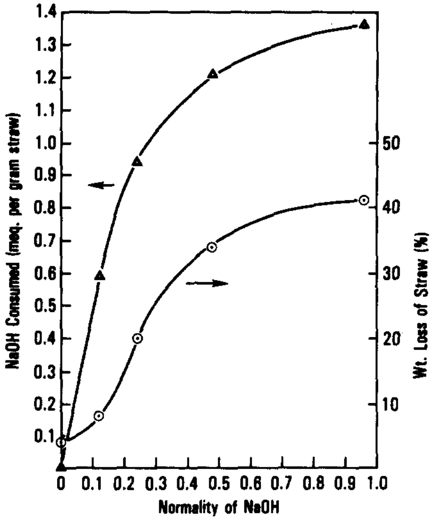

Fig. 2. Effect of initial NaOH normality on: △——△ consumption of NaOH by straw (meq NaOH per gram straw); ⊙——⊙ weight loss of straw (%).

NaOH is consumed by straw than can be accounted for by neutralization of uronic acids and by saponification of ester substituents. This additional consumption of alkali could be due to a number of factors, such as (1) neutralization of phenolic groups in lignin; (2) endwise depolymerization of polysaccharides (Meller, 1965); (3) cleavage of alkyl aryl ethers in lignin (Wallis, 1971); and (4) conversion of silica to sodium silicate.

Treatment of straw with aqueous alkali followed by high speed blending and water washing results in loss of a portion of the straw as water solubles (Table 1). Weight loss was less than 10% at or below 0·12 N but increased rapidly at higher alkalinity, leveling off to about 41% with 0·96 N NaOH (Fig. 2). Increased solubility under more alkaline conditions is largely due to solution of the hemicellulose and, to a lesser extent, of the lignin. The combination of alkaline treatment and blending at high speed also caused disruption and separation of straw into smaller particles and fibers, as shown by scanning electron microscopy of freeze-dried samples (Fig. 3). Whereas treatment with 0·12 N NaOH gave a product similar in appearance to that resulting from treatment with water alone, higher NaOH concentrations led to greater disruption of straw, a significant change in appearance being observed between 0·12 N and 0·24 N NaOH.

Alkali-treated straw samples were stirred with a water solution of CTAB to yield ion exchanged products, and unreacted CTAB was then

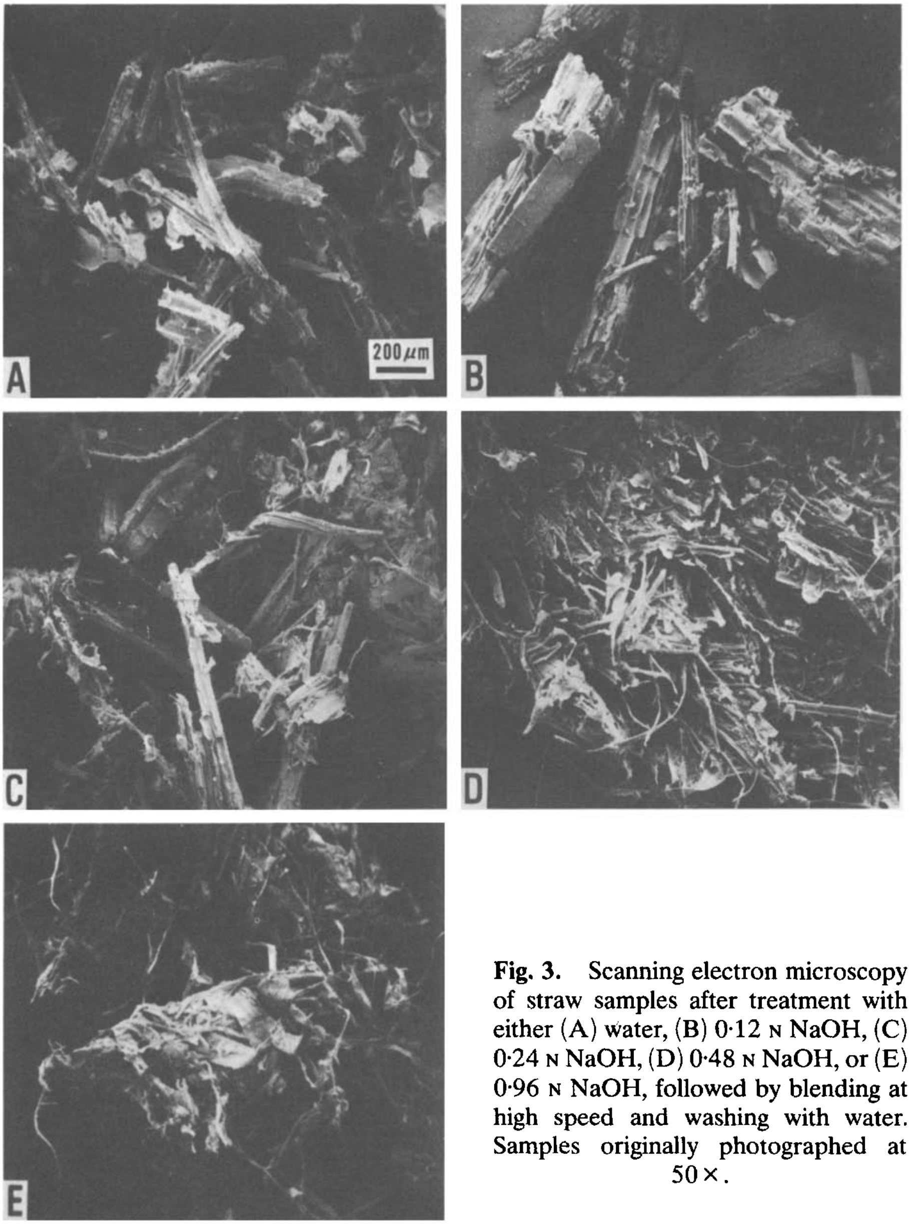

Fig. 3. Scanning electron microscopy of straw samples after treatment with either (A) water, (B) 0·12 N NaOH, (C) 0·24 N NaOH, (D) 0·48 N NaOH, or (E) 0·96 N NaOH, followed by blending at high speed and washing with water. Samples originally photographed at 50×.

removed by washing and by continuous extraction with 95% ethanol. Final products were water-washed to remove ethanol and were stored as wet solids. To test the ability of these products to absorb oil from water, a dispersion (emulsion) of paraffin oil in distilled water was added in 5 ml increments to 0·5 g of straw–CTAB adduct. Mixtures were shaken after each addition, and the presence of unabsorbed oil was then detected by the appearance of turbidity in the supernatant, as measured by %T at 650 nm. Values for %T were then plotted against total volume of oil dispersion added.

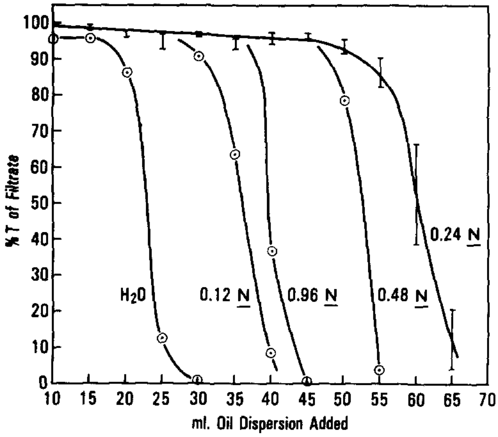

Fig. 4. Effect of NaOH concentration, used for the initial treatment of straw, on the oil absorbency properties of straw–CTAB adducts. Amount of CTAB used: 2·00 g for 3·28 g of treated straw.

Our first series of experiments (Fig. 4) was carried out to show how oil absorption of straw–CTAB adducts varies with the normality of NaOH used for the initial treatment of straw. Figure 4 shows successive increases in oil-absorbing ability when water, 0·12 N NaOH, and 0·24 N NaOH were used for initial treatments; however, treatment of straw with 0·48 N and 0·96 N NaOH resulted in products that were progressively poorer absorbents. Vertical bars for the experiment with 0·24 N NaOH show the degree of reproducibility found in three separate determinations (two different reactions of wheat straw with NaOH and CTAB and one repeat oil absorption test). Oil absorbency is obviously a direct result of CTAB treatment as evidenced by testing NaOH-treated straw before and after reaction with CTAB. Prior to CTAB treatment, no absorption of oil was observed.

The dependence of oil absorption on ion content of the aqueous oil dispersion used for testing was also investigated. Although absorption was not diminished (but was actually improved) when a tap water–oil dispersion was used (as opposed to oil dispersed in distilled water), straw–CTAB adducts did not function as absorbents for oil dispersed in

3% sodium chloride solution, possibly because of displacement of C_{16} quaternary ammonium substituents by an ion exchange mechanism. Use of these products is, therefore, limited to fresh water as opposed to sea water applications.

From the data presented, we can gain some insight into the factors responsible for variations in oil-absorbing ability. Figure 4 shows that the best absorbent is one resulting from treatment of straw with approximately 0·24 N NaOH. Since significant disruption of straw particles into fibers begins at this same normality (Fig. 3), high surface area is apparently a prerequisite for good oil absorbency. This was further shown by an experiment in which straw was treated with 0·24 N NaOH but was not blended at high speed prior to treatment with CTAB. Oil absorbency of this product was greatly reduced. Sufficient NaOH and blending are thus necessary not only for conversion of carboxylic acids and their derivatives into sodium carboxylate substituents necessary for ion exchange with CTAB, but also for disruption of the straw matrix. Although high alkali concentrations (0·48 N and 0·96 N) are more effective at disrupting straw, they also dissolve hemicellulose and will therefore deplete ion exchange capacity by removal of uronic acids. Conditions, therefore, need to be carefully balanced. Sufficient NaOH is needed to give high surface-area straw with all carboxyls in the sodium salt form but not so much as to remove large amounts of hemicellulose.

The importance of the hemicellulose in conferring ion exchange properties on straw was confirmed by removing hemicellulose from straw by selective hydrolysis with 1 N trifluoroacetic acid (Fanta *et al.*, 1984) before treatment with 0·24 N NaOH and CTAB. Oil-absorbent properties of the resulting straw–CTAB adduct were greatly diminished. Prior delignification of straw with sodium chlorite (Adams, 1965), however, did not reduce oil absorbency of the final straw–CTAB adduct, suggesting that lignin is not a major contributor to total ion exchange capacity.

Since any reduction in the amount of CTAB used in these reactions would improve the economics of a commercial process, we reduced CTAB by factors of 2, 4, and 10 and examined the effects of these reductions on oil-absorbent properties (Fig. 5). Straw was treated with 0·24 N NaOH, and the initial amount of CTAB used was the same as for Fig. 4 (2·00 g CTAB for 3·28 g of NaOH-treated straw). Figure 5 shows that reducing CTAB by a factor of 2 results in no significant change in oil absorption, while reduction by a factor of 4 causes a minor loss of absorption properties. A 10-fold reduction in CTAB, however, severely limits the ability of these adducts to absorb oil. Figure 5 also shows the detrimental effect of drying on properties of the straw–CTAB adduct.

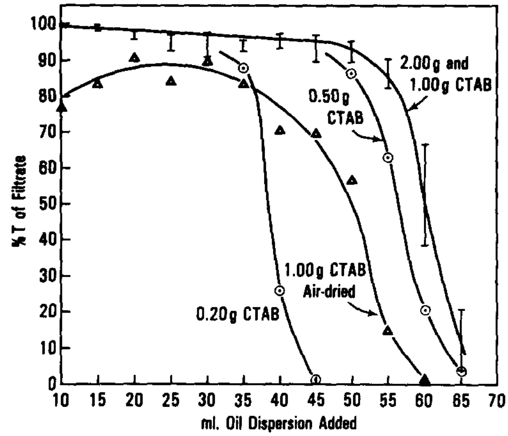

Fig. 5. Effect of (1) the amount of CTAB used in ion exchange reactions and (2) air-drying the straw–CTAB adduct on oil absorbency properties.

Apparently, hydrogen bonds formed on drying are not totally disrupted when the sample is placed back into an aqueous system, thus limiting penetration of dispersed oil into the product.

The amount of ionically bound quaternary ammonium cation present in a typical straw–CTAB adduct was estimated by two separate techniques. In the first method, we allowed NaOH(0·24 N)-treated straw to react with benzyltriethylammonium chloride according to the method given for CTAB in the Experimental section to give an adduct where the quaternary ammonium substituent could be easily determined by its UV absorbance. Benzyltriethylammonium cation was displaced from the resulting adduct by contacting an accurately weighed sample of adduct with a known volume of 0·1 N HCl. From the UV absorbance of the resulting HCl solution and the experimentally determined extinction coefficient of benzyltriethylammonium chloride, a benzyltriethylammonium cation concentration of 2·3% by weight, or 12 meq per 100 g of adduct, was calculated. Interestingly, this benzyltriethylammonium adduct did not function as an oil absorbent when tested by our procedure.

In the second method, the C_{16} quaternary ammonium cation content of a product prepared from NaOH(0·24 N)-treated straw and 2·00 g of CTAB was directly determined by infrared spectroscopy. Comparison of absorption in the C-H region with absorptions of a series of straw–CTAB mixtures of known composition (see Experimental section) indicated a C_{16} quaternary ammonium cation content of 3·9% by weight (13·7 meq per 100 g of adduct).

CONCLUSIONS

A derivative of straw, useful for removing emulsified oil from water, is easily prepared by treating straw with sodium hydroxide solution and contacting the resulting product with CTAB to exchange hexadecyltrimethylammonium cations for sodium. Although final products are hydrophilic enough to allow easy penetration of aqueous emulsions, the C_{16} quaternary ammonium cation (present as about 4% of the total adduct weight) confers sufficient hydrophobicity on straw–CTAB adducts to permit absorption of oil.

Conditions for the alkaline pretreatment must be chosen carefully, since ion exchange properties of straw are largely due to uronic acid groups in the alkali-soluble hemicellulose. Alkali concentration and temperature must be high enough to convert straw into high surface-area fibers and particles; however, conditions must not be so vigorous as to dissolve excessive amounts of hemicellulose.

Oil absorbencies of straw–CTAB adducts are roughly comparable to absorbencies found earlier for CTAB-treated cellulose-*g*-poly(acrylic acid) (Fanta *et al.*, 1985). The simplicity of our straw–CTAB preparation should make this process commercially more attractive.

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