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The Effect of Pressures on Cation-Cellulose Interactions in  
Cellulose/Ionic Liquid Mixtures

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**ABSTRACT**

Cation-cellulose interactions in binary mixtures of [EMIM][OAc] and cellulose have been investigated using high-pressure infrared spectroscopy. At low concentrations of cellulose, almost no changes were observed in the imidazolium C<sup>2</sup>-H frequency; on the other hand, at high concentrations of cellulose, increases in the C<sup>2</sup>-H vibration frequency were observed under ambient pressure. As the pressure was elevated, the imidazolium C<sup>2</sup>-H absorption of the [EMIM][OAc]/cellulose mixtures underwent band-narrowing and blue-shifts in the frequency. These observations suggest that high pressures may strengthen the hydrogen bonds formed between C<sup>2</sup>-H and cellulose, possibly forcing the cellulose to dissociate clusters of ionic liquid through enhanced cation-cellulose interactions. In contrast to the cation-cellulose interaction results, the COO<sup>-</sup> absorption of the anion does not show dramatic changes under high pressures. Our results indicate the possibility of enhanced cation-cellulose interactions through pressure elevation, demonstrating that high pressures may have the potential to tune the relative contributions of cation-cellulose and anion-cellulose interactions in cellulose/ionic liquid mixtures.

## I. INTRODUCTION

Because conventional fuels, i.e., petroleum and natural gas, are continuously adding to atmospheric pollution, the development of environmentally benign energy sources has become more and more attractive in recent years. As an abundant natural biopolymer, cellulose could serve as a renewable biofuel in the future.<sup>1,2</sup> Cellulose is a crystalline fibrous material with long chains of linked glucose sugar monomers, and the strong hydrogen-bond network ensures that cellulose has stable physical and chemical properties. Because natural cellulose is insoluble in water and the usual organic solvents, converting cellulose into biofuels is difficult, which is primarily caused by the highly ordered structures of cellulose. Various approaches<sup>1-3</sup> have been explored for understanding the exact nature of the ordered structures and hydrogen bonding in cellulose. The results of these studies<sup>1-3</sup> indicate that polymer chains are attached by hydrogen bonds between the O-H groups of neighboring chains with some disordered regions located at defects in the fibers and at the surfaces.

Room temperature ionic liquids are a class of fluid systems that could potentially be used as a replacement for traditional organic solvents, and ionic liquid cations often involves positively charged nitrogen or phosphorus groups, such as imidazolium and phosphonium, to prevent ions from packing easily.<sup>4,5</sup> Negligible volatilities and the broad range of liquid states make ionic liquids attractive

alternatives to volatile organic solvents, leading to discussions of ionic liquids as green solvents.<sup>4,5</sup> The most extensively studied ionic liquids are 1-alkyl-3-methylimidazolium salts which feature asymmetric cation. Based on the results of previous studies, ionic liquids may possess hydrogen bonds, but the role of hydrogen bonding in ionic liquids is not well understood.<sup>4-9</sup> Various studies have been performed to elucidate the role of weak hydrogen bonding (C-H---O or C-H---X) in the structure of ionic liquids.<sup>4-10</sup> With three hydrogen atoms bound to the imidazolium ring of 1-alkyl-3-methylimidazolium salts, the most acidic proton, i.e., the C<sup>2</sup> proton, may prefer to form hydrogen bonds with anions. The structures of 1-alkyl-3-methylimidazolium salts should be considered as networks of anions and cations, linked by hydrogen bonds. One of the attractive features of ionic liquids is the higher-order aggregate structure that results from polar / nonpolar phase separation. Self-assembly and the spatial microheterogeneity of ionic liquids have been suggested,<sup>4,5,7-10</sup> and the alkyl side chain length seems to influence supramolecular aggregation behaviors which may lead to an ordered local environment. For example, Triolo et al. proposed that the nano-structural organization may exist in asymmetric imidazolium ions presenting alkyl chains even as short as butyl chain.<sup>10</sup>

Several ionic liquids have been identified by previous studies to be effective in

enhancing cellulose dissolution.<sup>11-22</sup> For example, ionic liquids based on the alkyimidazolium cation and acetate anion (or halide anion) were found to dissolve high amount of cellulose.<sup>11-13</sup> The acetate anions or halide anions in imidazolium-based ionic liquids have been shown to act as electron donor centers via the interaction between the anions and O-H groups of cellulose. The cellulose miscibility of ionic liquids is obviously influenced by the choice of anion species, and the ability of ionic liquids to dissolve cellulose is strongly related to the hydrogen bond basicity of the anions. The hydrogen bonding interactions for cellulose/ionic liquid mixtures with varying anions are complex due to pronounced anion-cellulose interactions. Various studies have been performed to elucidate the predominant role of ionic liquid anions in the dissolution of cellulose, but the interactions of cellulose with cations have received minimal attention.<sup>12-20</sup> However, some research groups infer that cation-cellulose interactions, such as imidazolium C-H...O hydrogen bonds, have a non-negligible role in cellulose/ionic liquid mixtures.<sup>12,13</sup> The importance of designing cationic part of amino acid-based ionic liquids for the dissolution of cellulose was reported by Ohira and co-workers.<sup>22</sup> The amino group of amino acid-based ionic liquids was also found to interrupt the hydrogen bonding in the cellulose.<sup>22</sup> In this study, to obtain detailed insight into the cation-cellulose interactions, we apply high pressures to probe the local structures of the C-H groups

of cations in the presence of cellulose.

In studies of chemical systems, interest in pressure as an experimental variable has increased, and high pressures allow the controlled change of intermolecular interactions.<sup>23-27</sup> The application of high pressure is the ideal tool to continuously tune the bonding properties of ionic liquid mixtures.<sup>23-27</sup> At high pressures, the various degrees of solvation may arise from the reorganization of the hydrogen bond network and geometry. Previous studies of ionic liquid/triblock copolymer mixtures indicated that high pressures stabilize the hydrogen bonds formed between imidazolium C-H and the triblock copolymer, possibly forcing the triblock copolymer molecules to dissociate the clusters of ionic liquids.<sup>23,27</sup> In this study, we apply high pressure to investigate the structural organization in cellulose/ionic liquid mixtures.

## II. EXPERIMENTAL SECTION

Samples were prepared using 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc], > 95%, UniRegion Bio-Tech) and cellulose powder (50  $\mu\text{m}$  particle size, Fluka). The solutions with low cellulose concentration were prepared by mixing before sonication for an additional hour at room temperature. For mixtures with high cellulose concentrations, a higher temperature (water bath at ca. 70°C) and a longer mixing time was required to dissolve the cellulose. All spectra were measured at room temperature (about 25°C). A diamond anvil cell (DAC) of Merrill–Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures up to ca. 2 GPa. Two type-IIa diamonds were used for mid-infrared measurements. The sample was contained in a 0.3-mm-diameter hole in a 0.25-mm-thick inconel gasket mounted on the diamond anvil cell. To reduce the absorbance of the samples,  $\text{CaF}_2$  crystals (prepared from a  $\text{CaF}_2$  optical window) were placed into the holes and compressed to be transparent prior to inserting the samples. A droplet of the sample filled the empty space in the gasket hole in the DAC, which was subsequently sealed when the opposing anvils were pushed toward one another. Infrared (IR) spectra of the samples were measured on a Perkin-Elmer Fourier transform spectrophotometer (model Spectrum RXI) equipped with a lithium tantalite (LITA) mid-infrared detector. The infrared beam was condensed through a 5X beam



condenser onto the sample in the diamond anvil cell. We typically chose a resolution of  $4\text{ cm}^{-1}$  (data point resolution of  $2\text{ cm}^{-1}$ ) and compiled 1000 scans for each spectrum. To remove the absorption of the diamond anvils, the absorption spectra of DAC were measured first and then subtracted from those of the samples. Pressure calibration follows Wong's method.<sup>28,29</sup> The spectra of samples measured at ambient pressure were taken by filling samples in a cell having two  $\text{CaF}_2$  windows without spacers.

### III. RESULTS AND DISCUSSION

Figure 1 displays the infrared spectra of pure [EMIM][OAc] (Fig. 1a) and [EMIM][OAc]/cellulose mixtures having cellulose equal to 4 wt% (Fig. 1b) and 13 wt% (Fig. 1c), recorded under ambient pressure. The spectrum of pure [EMIM][OAc] (Fig. 1a) shows three alkyl C-H bands, i.e., 2873, 2922, and 2978  $\text{cm}^{-1}$  in the 2800–3000  $\text{cm}^{-1}$  region.<sup>25-27</sup> We also found that coupled imidazolium C-H stretching peaks may be located at 3050 and 3140  $\text{cm}^{-1}$  as showed in Fig.1a.<sup>25-27</sup> Comparing the spectral features in Figs. 1b and 1c with those in Fig.1a, no appreciable changes of the alkyl C-H stretching frequencies were observed in the presence of cellulose under ambient pressure. Note that the imidazolium C-H bands at 3050 and 3140  $\text{cm}^{-1}$  display blue shifts in frequency as more cellulose was added (Fig. 1c). As a result of hydrogen bonding between imidazolium C-H and cellulose, the spectrum (Fig.1c) shows that the major imidazolium C-H absorptions were shifted to 3063 and 3142  $\text{cm}^{-1}$ . This result is remarkably different from that for the alkyl C-H groups in Fig.1.

Figure 2 shows the frequencies of the two imidazolium C-H bands with respect to the weight percentages of cellulose. As revealed in Fig.2, the 3050  $\text{cm}^{-1}$  band ( $\text{C}^2\text{-H}$ ) is more concentration -sensitive than the band at ca. 3140  $\text{cm}^{-1}$  ( $\text{C}^{4,5}\text{-H}$ ). This fact could be related to the well-known acidity of  $\text{C}^2\text{-H}$ .<sup>4-7</sup> In light of this

finding, we were able to attribute the frequency shift of the imidazolium C-H modes to the reorganization of the hydrogen-bond network by the presence of cellulose molecules. Cellulose molecules appear to be capable of breaking cation-anion interactions via the formation of stable imidazolium C-H --- cellulose interactions. Based on the results in Fig.1 and 2, cation-cellulose interactions appear to play a non-negligible role in cellulose/ionic liquid mixtures. Considering Fig. 2A in more detail, we observe almost no change in the imidazolium C<sup>2</sup>-H frequency at low cellulose concentrations, i.e., < 4 wt%. In contrast, Fig. 2 reveals increases in the frequencies of the signal for the imidazolium C<sup>2</sup>-H vibration at high cellulose concentrations (> 4 wt%). This discontinuity in frequency may indicate a clustering of [EMIM][OAc] and a slight perturbation of neighboring ions within the clusters by the presence of cellulose at low concentrations (< 4 wt%). Cellulose molecules may disturb the weaker inter-cluster interactions instead of the intra-cluster associations at low cellulose concentrations. Previous investigations have suggested that ionic liquids tend to form associated structures by the charge ordering of anions and the imidazolium ring.<sup>6-8</sup> The associated structure means larger ion clusters (or ion pairs), and the dissociated species may be smaller ion clusters (or free ions). Although the local organization between the ionic species is preliminary governed by electrostatic interactions, the C<sup>2</sup>-H---O interactions between the positive H atoms in the

imidazolium C<sup>2</sup>-H groups and the negative O atoms in cellulose molecules may be a compensatory mechanism providing additional stability and enhancing the dissociation of cation-anion clusters at high concentrations of cellulose (> 4 wt%). Our results in Fig.1 and 2 indicate the formation of a certain cellulose structure around the imidazolium C<sup>2</sup>-H group of [EMIM][OAc] at high concentrations of cellulose (> 4 wt%), but the details remain unclear.

Figure 3 displays the IR spectra of pure [EMIM][OAc] recorded at ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g). As the pressure was elevated, the C-H spectral features show bandwidth broadening. After comparison with the absorption obtained at ambient pressure (Fig.3a), no significant changes in the band frequencies of C-H vibrations occurred as the sample was compressed (Fig. 3b-g). Thus, pure [EMIM][OAc] in Fig. 3b-g may behave like a liquid or glass (pressure-induced frozen liquid) due to the pressure-induced transition via a linked hydrogen-bonding network between the cation and anion.

Figure 4 presents the infrared spectra of the [EMIM][OAc]/cellulose mixture featuring 7 wt% of cellulose, recorded under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g). As the pressure was elevated to 0.3 GPa (Fig. 4b), the imidazolium C<sup>2</sup>-H

stretching absorption underwent an appreciable change in frequency and bandwidth.

The hydrogen-bonding networks are likely perturbed by high pressures, and the sharper absorption of the C<sup>2</sup>-H band observed in Fig.4b-g may arise from changes in the local structures of C<sup>2</sup>-H. The bandwidth narrowing suggests that high-order and anisotropic interactions may have occurred with cellulose molecules and anions tending to form ordered morphologies around the imidazolium C<sup>2</sup>-H moiety. We note that the bandwidth narrowing revealed in Fig.4 is not observed in the pressure-dependent absorption spectra of pure [EMIM][OAc] in Fig.3. That is, cellulose can change the structural organization of [EMIM][OAc] by introducing cation-cellulose interactions.

As showed in Fig.4b, the imidazolium C<sup>2</sup>-H stretching bands were blue-shifted to 3091 cm<sup>-1</sup>, and the pressure-induced frequency shift may originate from the modification of imidazolium C<sup>2</sup>-H-cellulose contacts upon compression. In a number of cases, the C-H---O interactions lead to shortening of the C-H bond, i.e., blue-shifting hydrogen-bonding, rather than the lengthening that is generally considered a typical feature of a hydrogen bond.<sup>30-33</sup> Consistent models have been previously proposed for the theoretical understanding of C-H---O interactions,<sup>30-33</sup> and hydrogen-bonded networks can be modified by varying the pressure. Thus, we may be able to attribute the blue shift observed in Fig.4b to strengthening of the C<sup>2</sup>-H---O

contacts upon compression or the partial replacement of  $C^2-H\cdots$ anion interactions with  $C^2-H\cdots$ cellulose interactions. The enhanced  $C^2-H\cdots O$  interactions can be attributed to both the cooperative and geometric effects of hydrogen bonds. High pressures stabilize the hydrogen bonds formed between  $C^2-H$  and cellulose, possibly forcing the cellulose to dissociate the clusters of ionic liquid through enhanced  $C^2-H\cdots O$  interactions. As the pressure was further elevated in Fig.4c-g, we observe no drastic change in the pressure-dependence of the imidazolium C-H spectral features. This behavior revealed in Fig.4b-g indicates that the cation-cellulose association is the stable (or favorable) configurations up to the pressure of 2.5 GPa.

Figure 5 shows the pressure -dependence of the frequencies of the imidazolium C-H bands of pure [EMIM][OAc] and [EMIM][OAc]/cellulose mixtures. The imidazolium  $C^2-H$  peaks (at ca.  $3050\text{ cm}^{-1}$ ) of [EMIM][OAc]/cellulose mixtures initially underwent blue-shifts in the frequency as the pressure increased to 0.3 GPa and, then underwent mild shifts in frequency upon the pressure increase from 0.3 to 2.5 GPa. As revealed in Fig.5B, the discontinuous jump occurring around 0.3 GPa becomes less obvious for the imidazolium  $C^{4,5}-H$  peaks (at ca.  $3140\text{ cm}^{-1}$ ). This observation demonstrates that the high pressure method can be a useful tool for probing the strength of weak C-H hydrogen bonds, i.e.,  $C^2-H\cdots O > C^{4,5}-H\cdots O > \text{alkyl C-H}\cdots O$ , under high pressures. The cellulose molecules appear to be capable of

breaking or weakening the cation-anion interactions as a result of the formation of stable C<sup>2</sup>-H---O interactions under high pressures.

To illustrate the anion-cellulose interactions under high pressures, we present IR spectra of the [EMIM][OAc]/cellulose mixture (7 wt% of cellulose) in the spectral range between 1450 and 1700 cm<sup>-1</sup> in Figure 6. As revealed in Fig. 6a, the absorption band at ca. 1575 cm<sup>-1</sup> is assigned to the antisymmetric stretching vibration of the COO<sup>-</sup> group of the anion.<sup>34</sup> As the mixture was compressed to 0.3 GPa, the carbonyl vibration was slightly red-shifted to 1573 cm<sup>-1</sup> (Fig.6b). We notice that almost no changes in frequency occur as the pressure is further increased (Fig.6c-g). As revealed in Fig. 6, the elevation of pressure does not have a drastic effect on the band frequency of the COO<sup>-</sup> group of the anions for the [EMIM][OAc]/cellulose mixture. These results are significantly different from the blue -shifts of the imidazolium C-H groups of cations observed for the [EMIM][OAc]/cellulose mixtures in Fig.4 and 5. Our results in Fig.6 indicate that high pressure does not dramatically perturb the anion-cellulose interactions. Thus, the role of cellulose in ionic liquids is complex and depends on the supramolecular structures of ionic liquids. The cellulose addition partially disrupts hydrogen- bonding networks between cations and anions at high concentrations of cellulose under ambient pressure. High pressures may induce the enhancement of weaker cation-cellulose interactions via

C<sup>2</sup>-H---O weak hydrogen bonds. Nevertheless, the anion-cellulose interactions are not significantly disturbed by the pressure elevation. This study demonstrates that the cation-cellulose interactions can be distinguished from anion-cellulose or cation-anion interactions using high-pressure vibrational spectroscopy. Anions have been known to play a large role in cellulose dissolution, and the ability of anions to form hydrogen bonds with cellulose has also been previously reported<sup>17-20</sup>. In the past, most of studies on ionic liquid/ cellulose mixtures focused on the contributions from anion-cellulose interactions under ambient pressure. In contrast to anions, the role of cations remains less clear. Our results show that cations can actively participate in the dissolution process, and the contribution of cation---cellulose interactions may increase upon compression. Unfortunately we have the difficulty to measure the solubility of cellulose under high pressures due to the limitation of our high pressure apparatus (DAC).

The present results suggest a possible mechanism of cellulose dissolution under various pressures. Under ambient pressure, the anions of ionic liquids tend to form hydrogen bonds with the cellulose surface and cause dissolution of cellulose. Some cation-anion hydrogen bonding may be switched to cation-cellulose hydrogen bonding under the condition of high pressure. A possible explanation for this effect is the pressure-enhanced C-H---O interaction between imidazolium C-H and cellulose



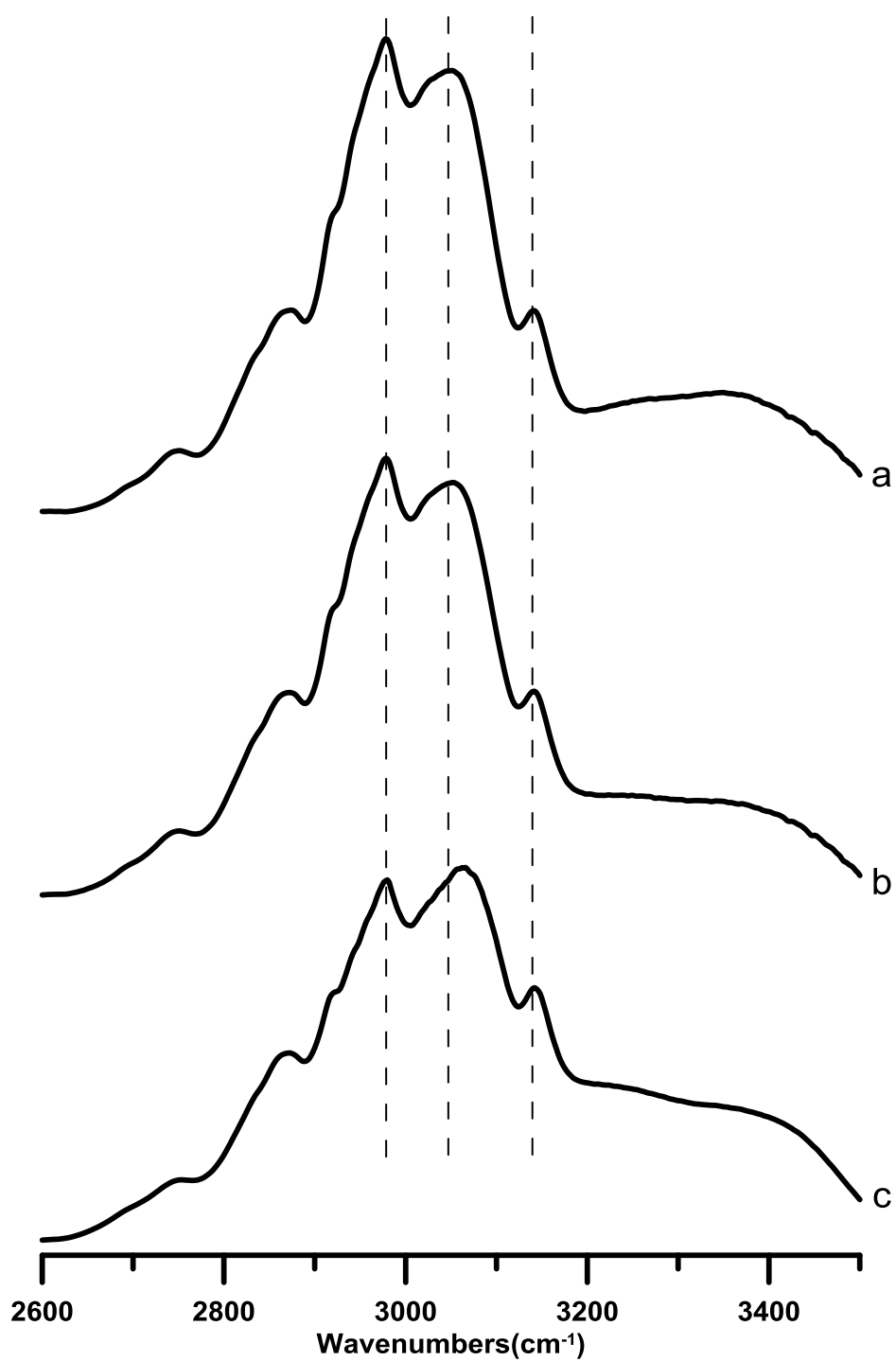
molecules. The specific properties of compressed ionic liquid/ cellulose mixtures may offer the possibilities of their applications in industrial fields. Our results suggest the potential for modifying cellulose structures via high pressures, while the cellulose regenerated from pressure cycling may be easily biodegraded due to reduced crystallinity. The use of precipitated cellulose may decrease the reaction time to transform cellulose to various chemicals. Recently some researchers<sup>35</sup> showed that high pressures may be applied for reversible cellulose separations from ionic liquid mixtures, and the precipitation of cellulose occurs by introducing compressed carbon dioxide as a physical (non-reactive) anti-solvent.

#### IV. CONCLUSION

Pressure-dependent spectra of pure [EMIM][OAc] and [EMIM][OAc]/cellulose mixtures were obtained. The concentration -dependence of the IR spectral features indicates that the C<sup>2</sup>-H band is more concentration -sensitive than the C<sup>4,5</sup>-H band under ambient pressure. The infrared spectral features indicate that high pressures stabilize the hydrogen bonds formed between C<sup>2</sup>-H and cellulose. Cellulose molecules may perturb the cation-anion clusters as a result of the formation of stable cation-cellulose interactions under high pressures. In this study, we also investigated the relative strength of C-H---O interactions, i.e., C<sup>2</sup>-H---O > C<sup>4,5</sup>-H---O > alkyl C-H---O, under high pressures. The elevation of pressure does not significantly change the spectral features of the COO<sup>-</sup> groups of the anions. The cationic effect on the dissolution of cellulose in ionic liquids may be enhanced upon compression.

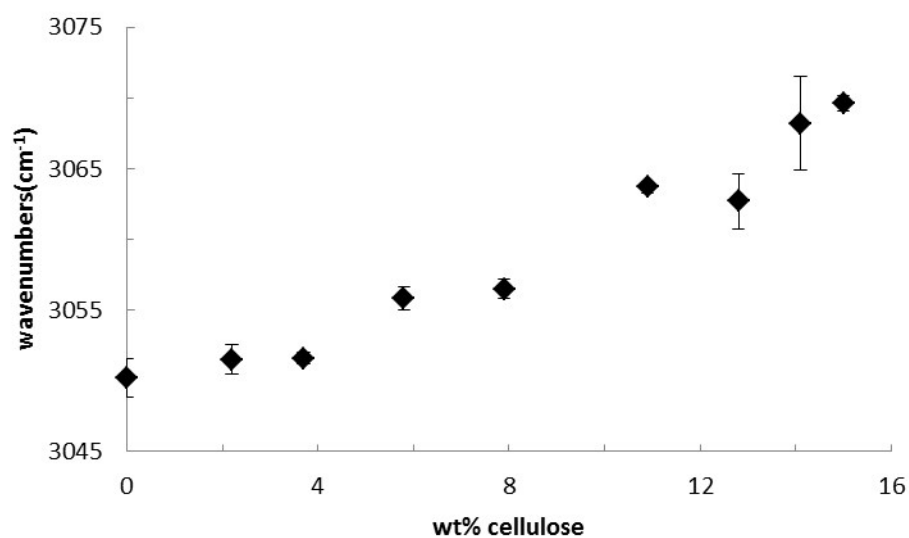
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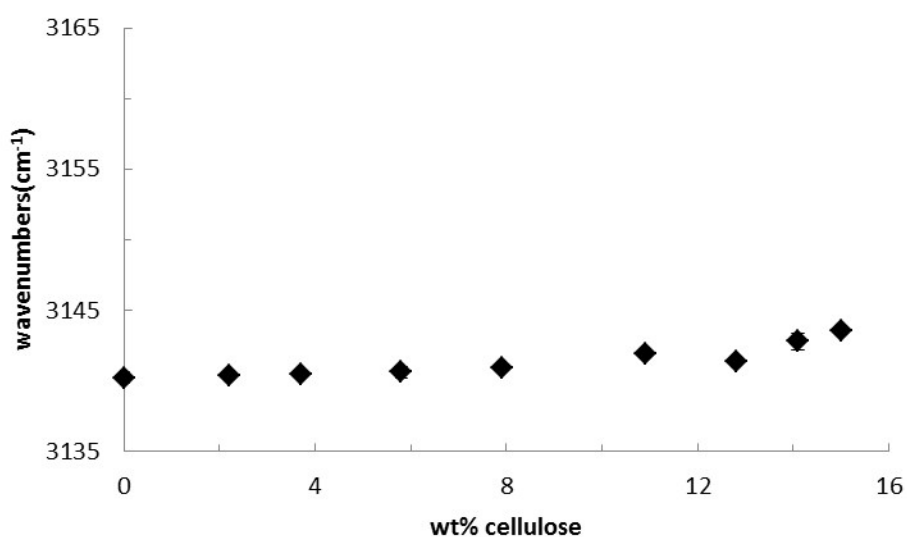


**Figure 1.** Infrared spectra of pure [EMIM][OAc] (curve a) and mixtures of cellulose/[EMIM][OAc] featuring 4 (curve b) and 13 (curve c) wt % of cellulose, recorded under ambient pressure.

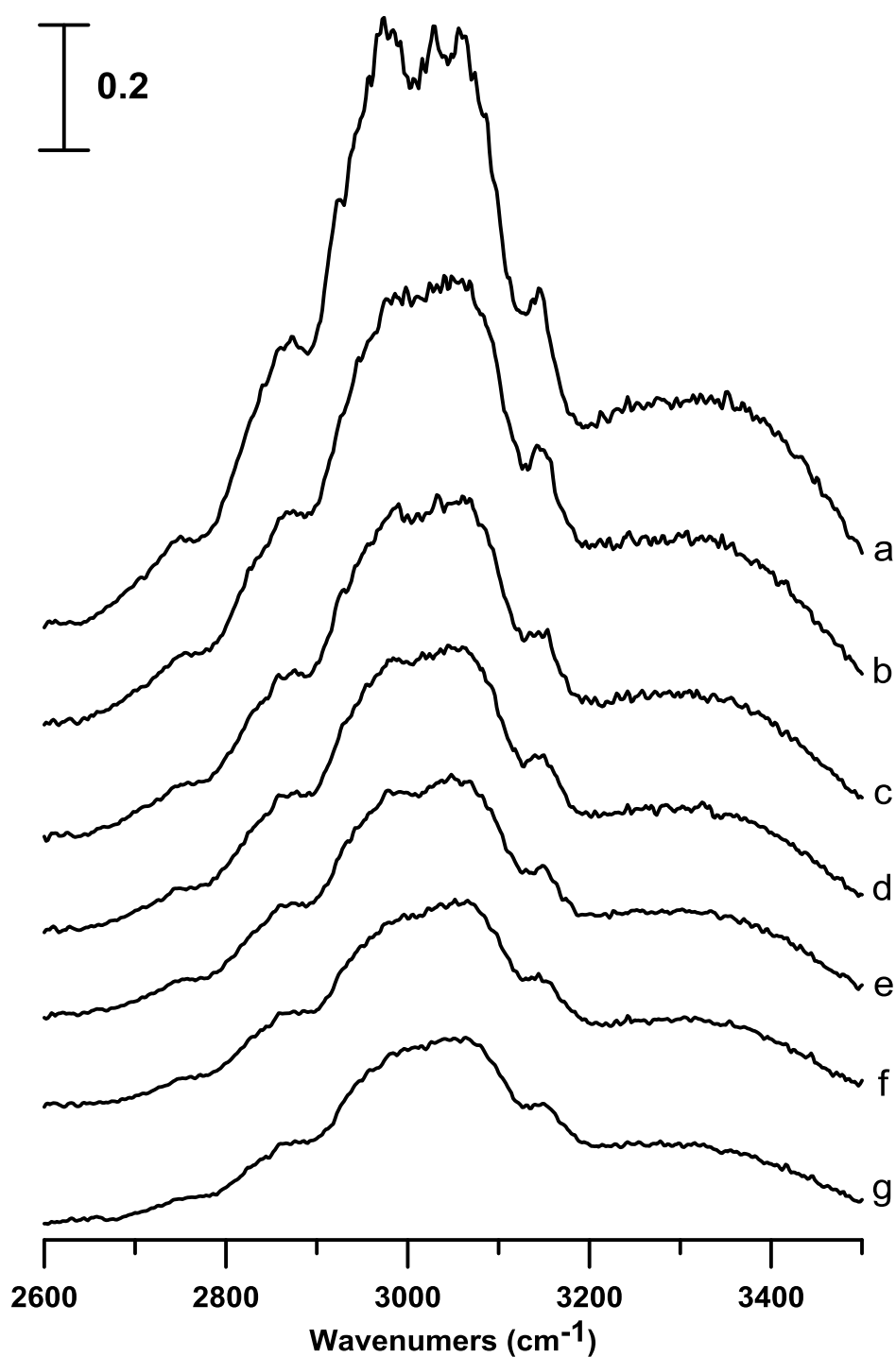
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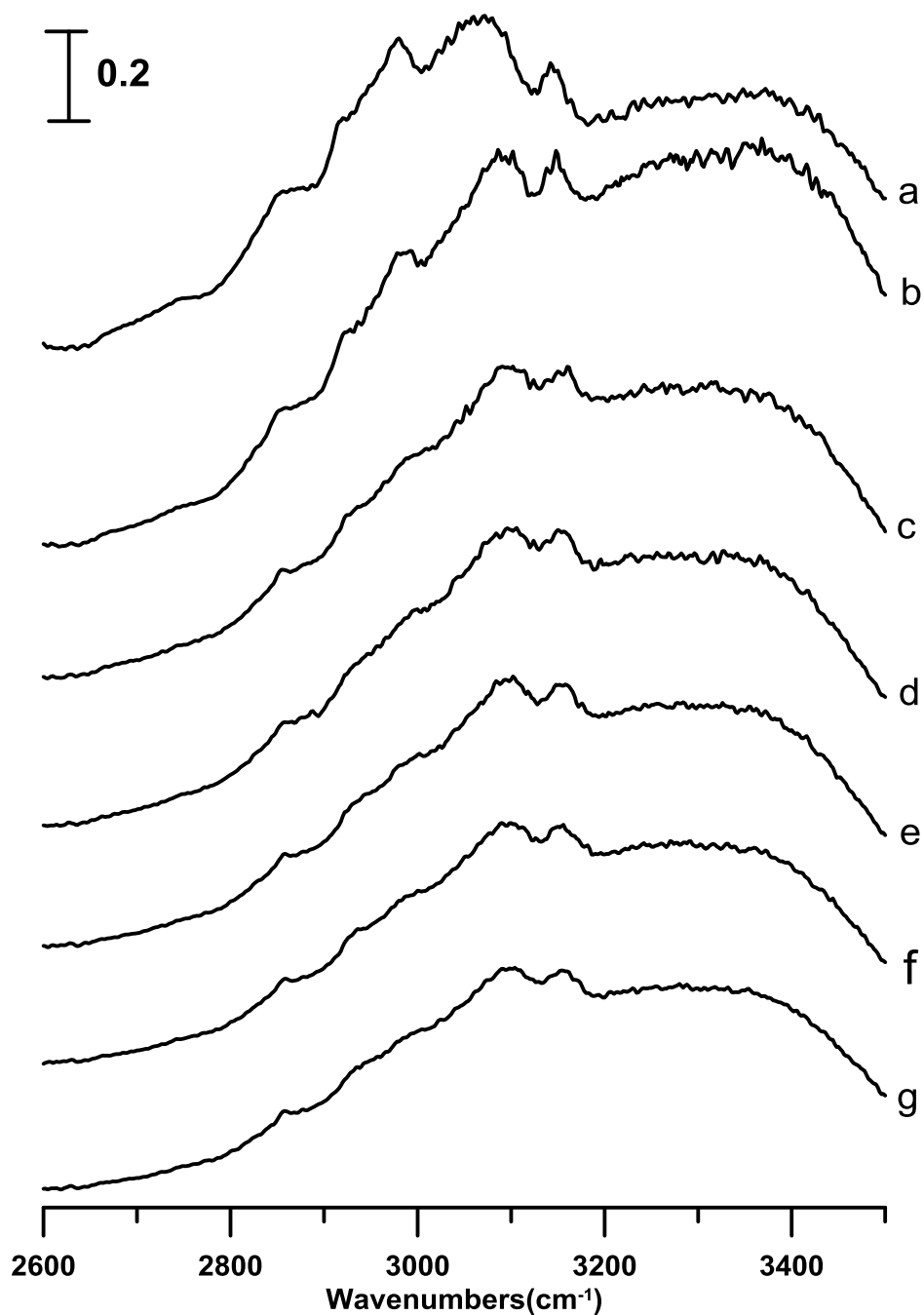
B



**Figure 2.** Concentration-dependence of the stretching frequencies of the imidazolium C-H bands [the bands at (A) 3050 and (B) 3140  $\text{cm}^{-1}$ ].

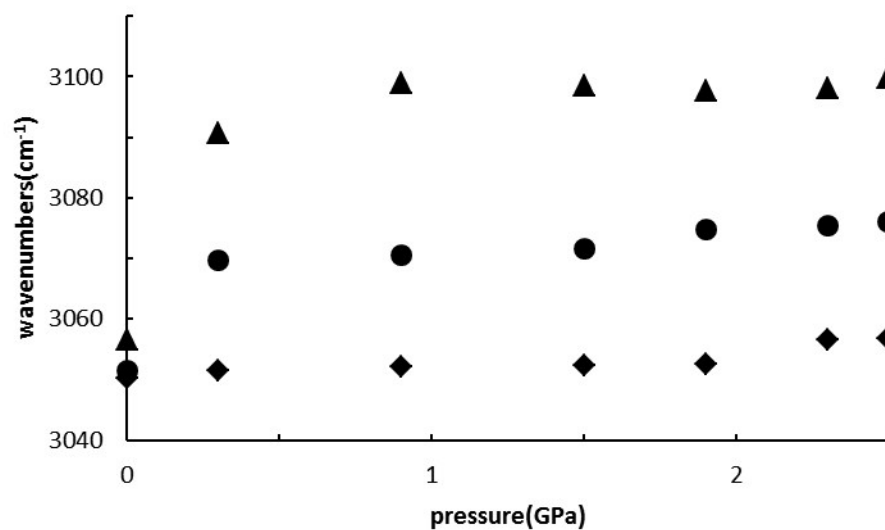


**Figure 3.** IR spectra of pure [EMIM][OAc] obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g).

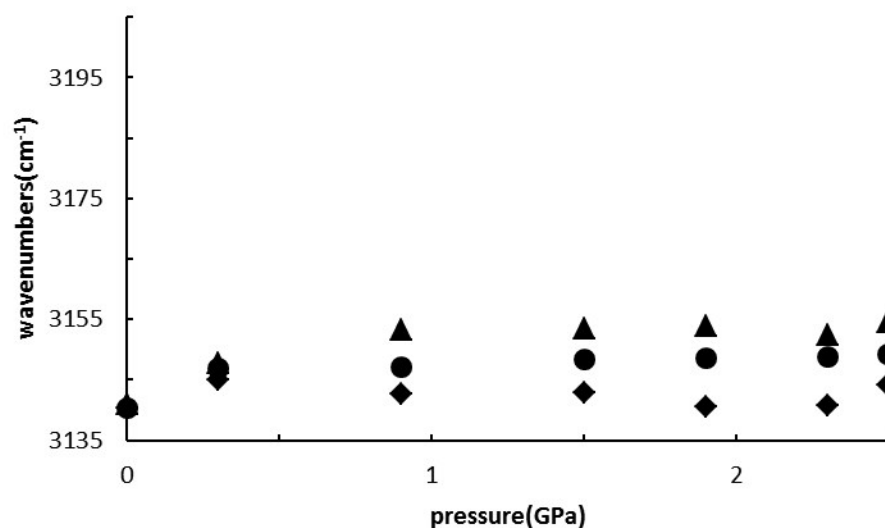


**Figure 4.** IR spectra of the cellulose/[EMIM][OAc] mixture featuring 7 wt % of cellulose, recording under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g).

A

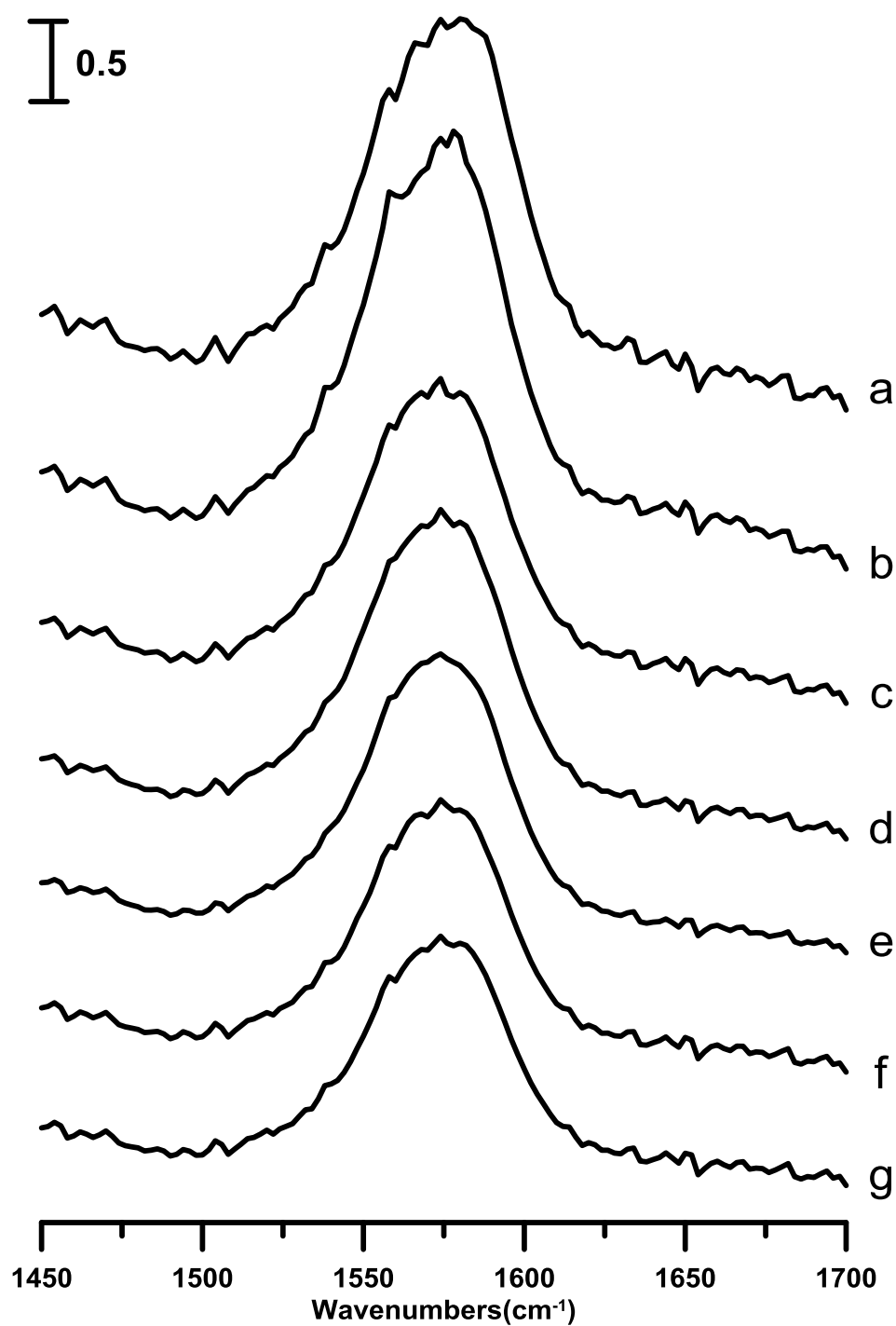


B



**Figure 5.** Pressure-dependence of the imidazolium C-H stretching frequencies [the bands at (A) 3050 and (B) 3140 cm<sup>-1</sup>] of pure [EMIM][OAc] (diamonds) and cellulose/[EMIM][OAc] mixtures featuring cellulose content of 2 (circles) and 7 (triangles) wt %.





**Figure 6.** IR spectra of the cellulose/[EMIM][OAc] mixture featuring 7 wt % of cellulose, recording under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g).

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