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Spectral characteristics of ethylene sorbed by silver-containing ionic liquids studied by *in situ* ATR-FTIR spectroscopy

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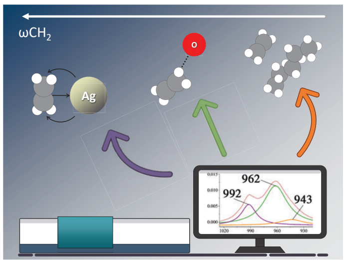
The spectral characteristics of ethylene absorbed by ionic liquids (ILs) containing silver ions were studied by *in situ* ATR-FTIR spectroscopy at high pressure. Three different states of ethylene were observed based on the band shift of out-of-plane bending vibrations (ωCH$_2$) due to van der Waals interactions, hydrogen bonds, and π-complex formation with silver ions. Thus, ethylene can be used as an IR-sensitive probe molecule for characterizing interactions with ILs and other substances.



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The separation of ethylene and ethane mixtures is a key stage in the extremely expensive and energy-intensive process of olefin purification. Thus, the development of alternative ways for separating light hydrocarbon mixtures is of considerable current importance.[1]

Ionic liquids (ILs) are promising functional solvents[2] for the selective separation of the mixtures of a paraffin and a corresponding olefin.[3,4]

Reversible chemical complexation with Cu^{I} and Ag^{I} salts is of interest for increasing the selectivity of separation[5,6] due to the formination of a π-complex, which can be described by the Dewar–Chata–Duncanson model.[7]

IR spectroscopy can be used for studying the π-complex formation[8,9] based on the position of a C=C band of olefin stretching vibrations in the region of 1650–1450 cm^{-1}. For ethylene, the C=C band is IR active only if the symmetry is lowered as a result of interaction (adsorption) with an active site.[10] The strength of the complex is characterized by a shift of the stretching vibration band of the C=C bond ($\Delta\nu_{C=C}$ to 200 cm^{-1}) relative to that of the free olefin. The position of this band is affected by the electron-withdrawing and electron-donating properties of the coordinating metal.[11] Note that, due to a wide spectral range of the $\nu_{C=C}$ bands of olefins forming the π-complex, it is correct to compare spectroscopic data only for the same metals or ligand environments because this significantly influences the position of the band. The π-complex formation also affects the band position of out-of-plane bending vibrations (ωCH$_2$) at 1000–900 cm^{-1}, leading to a blueshift.[12] Thus, a large shift of the ωCH$_2$ band was observed[13–16] upon the interaction of ethylene with a metal–organic framework (MOF) containing Ni^{2+}, Cu^{2+}, and Ag^{+} ions, due to the formation of the π-complex. The ωCH$_2$ band has a very high intensity, but it is located in the region where it is often overlapped with the bands of the material itself.[17]

Previously,[18] we discussed in detail the influence of the alkyl chain length of IL cations on the sorption of ethylene. The ωCH$_2$ band was suitable for studying interactions between sorbed ethylene and the IL, while it was almost impossible to detect other bands. The ethylene absorption resulted from van der Waals interactions and hydrogen bonding with the IL anion, thus affecting the ωCH$_2$ band position.

Here, we used *in situ* ATR-FTIR spectroscopy to study the spectral characteristics of ethylene sorbed by silver salt solutions in ILs. The experimental procedure was described in detail previously.[19] A specially designed high-pressure cell was placed around the diamond ATR crystal, onto which the ionic liquid was dropped, and sealed with a Teflon O-ring (see Online Supplementary Materials, Figure S1). C_2H_4 was introduced with a hand pump (HiP 87-6-5).

First of all, the spectra of absorbed ethylene were obtained in non-polar and polar solvents (dodecane, water, and ethylene glycol).

During the sorption of ethylene by dodecane, an intense band characteristic of ωCH$_2$ appeared in the spectrum at 947 cm^{-1}. A slight shift of this band relative to that of pure ethylene (943 cm^{-1})[18] reflects weak van der Waals interactions (Figure S2). Upon the sorption of ethylene by water (Figure 1), a very weak broad band at 962 cm^{-1} was observed in the spectrum. However, during the sorption of ethylene by a 1 M aqueous solution of AgNO$_3$, a significant blueshift of the ωCH$_2$ to 988 cm^{-1} was found. We attribute this shift to the π-complex based on published data.[13–16] Moreover, the integral intensity of the ethylene band increased essentially, indicating an increment in the amount of dissolved olefin. Silver ions in aqueous solutions are predominantly represented as the aqua complexes $[Ag(H_2O)_2]^+$.[20] If ethylene glycol was used, the band was observed at 956 cm^{-1} (Figure S3), and the main difference in ethylene sorption was caused by non-polar interactions leading to a redshift because the acidity of water and ethylene glycol is approximately the same (pK_a = 15.7 and 15.1, respectively). In ethylene sorption by a 1 M AgNO$_3$ solution in ethylene glycol, the ωCH$_2$ bans was also shifted to 983 cm^{-1} (Figure S3) because of the formation of the π-complex.

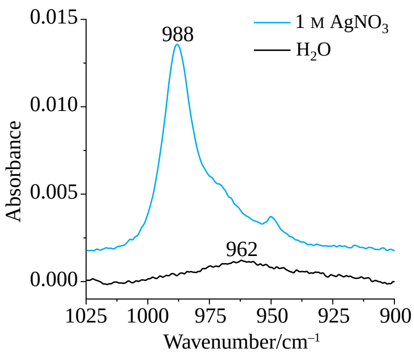

Figure 1 ATR-FTIR spectra obtained after subtracting the initial spectra of water and an aqueous solution of $AgNO_3$ (1 M) at atmospheric pressure and an ethylene pressure of 20 atm. The C_2H_4 out-of-plane bending mode is observed.

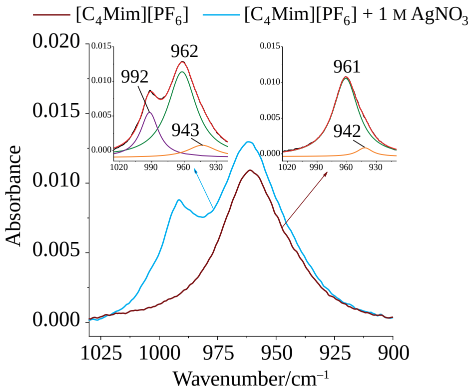

Figure 2 ATR-FTIR spectra of ethylene absorbed by $[C_4Mim][PF_6]$ IL and IL + $AgNO_3$ at an ethylene pressure of 20 atm. Subtraction was used.

Next, the spectral characteristics of ethylene sorbed by $AgNO_3$–IL solutions were studied. Table 1 shows the experimental ωCH_2 band positions of ethylene absorbed by various ILs, $AgNO_3$–IL solutions, and other solvents (the concentration of silver salts was 1 M). The shift to about 980 cm^{-1} is likely due to silver ion binding. For some $AgNO_3$–IL solutions, it was impossible to detect the shift of ωCH_2. We also failed to find the π-complex upon the sorption of ethylene by an aqueous solution of ammonia.

It could be assumed that the Ag^I salt dissolves to form a complex $[AgL_i]^{1-i}$, where L is a ligand (for example, an IL anion). The formation constant of these systems is much larger than that of $[Ag(C_2H_4)L_i]^{1-i}$, which, given the low concentration of dissolved ethylene, is essential for the replacement of the solvent/anion ligand by ethylene (Table S2). Thus, the absence of π-complexes in the presence of ammonia and halide anions seems to be associated with larger stability constants than those for ethylene. A similar influence of the IL anion on the catalytic activity of $Ni(PPh_3)_2Cl_2/2PPh_3$ in aryl reduction was also observed.[21]

As an example, Figure 2 shows the ATR-FTIR spectra of absorbed ethylene, in which it was possible to detect the complex. When $AgNO_3$ was added, an additional band at 992 cm^{-1} was found in the spectrum, which was associated with the π-complex, with the two previous bands remaining almost unchanged. Thus, three spectrally different states of ethylene were simultaneously present in the solution.

In this work, we obtained for the first time the IR spectra of ethylene in π-complexes with silver ions in IL solutions. The ωCH_2 band characterized the type of ethylene interaction, and ranges of 942–947, 950–965, and 970–995 cm^{-1} can be attributed to weak van der Waals interactions, hydrogen bonded ethylene, and π-complexes, respectively. The complex formation was significantly affected by the IL anion, which can block silver binding sites in some cases. Thus, ethylene can be used as an IR-sensitive probe molecule for characterizing the interaction and thermodynamic parameters of ethylene sorption by ionic liquids.

Table 1 The band positions of out-of-plane bending vibrations of ethylene during sorption by various solvents, where AgX is a silver compound in which X is the IL anion or Cl$^-$ in aqueous solutions.

Solvent	Silver compound		
	–	$AgNO_3$	AgX
H_2O	962 (v. weak)	988	-
$NH_{3\,aq}$	962 (v. weak)	964	962
$C_2H_4(OH)_2$	956	983	-
$C_{12}H_{26}$ (dodecane)	947	-	-
$[C_4Mim][PF_6]$	962	992/962	-
$[C_4Mim][BF_4]$	959	982/965	-
$[C_4Mim][OAc]$	956	956	957
$[C_4Mim][HSO_4]$	963	961	-
$[C_4Mim][C_8H_{17}OSO_3]$	947 (wide)	972/954	-
$[C_6Mim][Cl]$	957	-	957
$[C_6Mim][Br]$	956	956	956

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.040.

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