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Evolutional mechanism of 1-ethyl-3-methyl-imdazolium acetate uptaking water from air detected with a new coupled method: Two-dimensional correlation difference spectroscopy

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ABSTRACT

A new concept by coupling two-dimensional correlation spectroscopy (2D-COS) (particularly synchronous perturbation-correlation moving-window 2D-COS (s-PCMW2D-COS)) and difference spectroscopy (DS), i.e., 2D-CODS (particularly s-PCMW2D-CODS), is proposed in this study. Four steps (i.e., original spectra, DS, s-PCMW2D-COS, and sliced spectra in sequence) are proposed to produce s-PCMW2D-CODS with the original data. Computational simulated spectra in the same/opposite direction with linear/nonlinear comparison are used to illustrate the s-PCMW2D-CODS. It is shown that the relationship for comparing intensity along the perturbation variable is clearer, more accurate and more direct by s-PCMW2D-CODS than by original spectra, DS, or s-PCMW2D-COS. Finally, a practical example of utilizing s-PCMW2D-CODS to investigate the dynamically atmospheric water sorption process in acetate-based ionic liquid (IL) 1-ethyl-3-methlyl-imidazolium acetate ([EMIM][Ac]) via in-situ infrared spectroscopy (IR) is given. It is found that OH of the atmospheric water is affected first due to their weaker hydrogen-bonding network than that of [EMIM][Ac]; then, the cation ring $C_{4,5}H$ is freed followed by C_2H because of the weaker hydrogen-bonding interaction between $C_{4,5}H$ and anion than that between C_2H and anion; finally, the alkyl H (i.e., C_bH, $C_{6,7}H$, C_8H) is interrupted owning to their lower hydrogen-bonding donating ability than the cation ring H (i.e., C_2H, $C_{4,5}H$) with O of water and their higher hydrophobicity.

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1. Introduction

Generalized two-dimensional correlation spectroscopy (G-2D-COS, all the abbreviations are listed in Table 1) was pioneered by Noda in 1989 [1–4]. The form of G-2D-COS is expressed on a plane between two spectral variable (e.g., wavelength, wavenumber) axes. G-2D-COS includes a pair of spectra, i.e., synchronous (s-G-2D-COS) and asynchronous two-dimensional correlation spectroscopy (as-G-2D-COS). The interpretation of G-2D-COS is empirically according to Noda's Rule [2]. The function of G-2D-COS is to qualitatively (rather than quantitatively) compare changes of the spectral (e.g., IR, UV, NMR, and XRD) intensity induced by the perturbation variables (e.g., temperature, pressure, concentration, and time). The averaging effect for the comparison of intensity change rate is hard to eliminate during the application process [5].

Auto-MW2D-COS was first proposed by applying auto-correlation moving-window technique to G-2D-COS in 2000 [6]. Compared to traditional G-2D-COS, auto-MW2D-COS provides detail information of intensity variable along the perturbation direction. Auto-MW2D-COS can be expressed on a plane consisting of a spectral axis and a perturbation variable axis. The main advantage of auto-MW2D-COS is that it can quantitatively (not only qualitatively) visualize the intensity changes perturbed by an external factor. Approximately, auto-MW2D-COS is always positive, because its proportion to a squared derivative of the spectral intensity along the perturbation variable. Thus, it is suitable to deal with the comparison of same positive (rather than negative) direction changes in intensity along the perturbation variable [5].

Then, Morita et al. proposed a new concept of perturbation-correlation moving-window techniques based on G-2D-COS (i.e., PCMW2D-COS) in 2006 [7]. The PCMW2D-COS can be interpreted with Morita's Rule [7]. It is composed of a pair of synchronous (s-PCMW2D-COS) and asynchronous (as-PCMW2D-COS) modes, corresponding to the first-order and the negative second-order differentials, respectively. In each mode, the expression is described on a plot with a perturbation variable and a spectral variable. Not only same positive direction but also other comparison in direction could be discriminated via PCMW2D-COS, compared to auto-MW2D-COS [7]. The critical points could also be qualified and quantified as auto-MW2D-COS does, which could also be used to the comparison of change directions [7]. Other spectroscopic techniques include sample–sample correlation [8], wavenumber–wavenumber correlation [9], hybrid modes [10], and global phase angle description [11,12].

For the advantage of PCMW2D-COS over G-2D-COS and auto-MW2D-COS, PCMW2D-COS has attracted particularly more attention

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Table 1
Abbreviations and symbols used in this paper.

Abbreviation or symbols	Full name
ILs	Ionic liquids
AcILs	Acetate-based ionic liquids
H_2O	Water
[EMIM][Ac]	1-ethyl-3-methyl-imidazolium acetate
RS	Reference spectrum
OS	Original spectroscopy
DS	Difference spectroscopy
2D-COS	All the kinds of two-dimensional correlation spectroscopy
2D-CODS	Two-dimensional correlation difference spectroscopy
G-2D-COS	Generalized two-dimensional correlation spectroscopy
MW2D-COS	Moving-window two-dimensional correlation spectroscopy
auto-MW2D-COS	Auto-correlation moving-window two-dimensional correlation spectroscopy
PCMW2D-COS	Perturbation-correlation moving-window two-dimensional correlation spectroscopy
s	Synchronous
as	Asynchronous
s-G-2D-COS	Synchronous generalized two-dimensional correlation spectroscopy
as-G-2D-COS	Asynchronous generalized two-dimensional correlation spectroscopy
s-PCMW2D-COS	Synchronous perturbation-correlation moving-window two-dimensional correlation spectroscopy
s-PCMW2D-CODS	Synchronous perturbation-correlation moving-window two-dimensional correlation difference spectroscopy
as-PCMW2D-COS	Asynchronous perturbation-correlation moving-window two-dimensional correlation spectroscopy
p	Perturbation variable
s	Spectra variable
i	Intensity variable
s_o	Spectral peak position
Γ	Representing spectral peak full-width at half height even though Γ is not exactly equal to spectral peak full-width at half height.

in either academic study or industrial application than G-2D-COS and auto-MW2D-COS [13–18]. Moreover, the above three spectroscopic techniques were less susceptible to the noise than the corresponding derivative analysis [5].

On the other hand, difference spectrum (DS) is a common spectroscopic analyzing technique by subtracting the reference spectrum from the measured spectrum. Through DS, more subtitle information (e.g., change in peak position and peak intensity) could be obtained.

In this study, two-dimensional correlation difference spectroscopy (2D-CODS) is proposed by coupling two-dimensional correlation spectroscopy and difference spectroscopy, which is shown in Scheme 1a. Owing to the advantage of PCMW2D-COS, we mainly focus on 2D-CODS based on PCMW2D-COS, i.e., PCMW2D-CODS. Specifically, s-PCMW2D-COS could reveal more information than as-PCMW2D-COS. Thus, our attention is drawn on the combination between s-PCMW2D-COS and DS (s-PCMW2D-CODS).

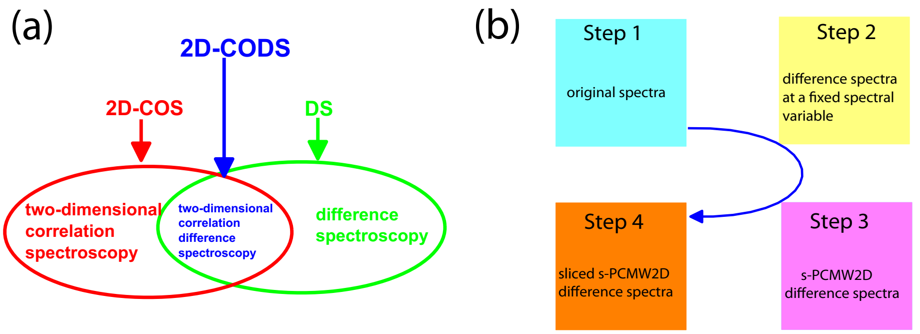
Ionic liquids (ILs) which are composed of organic cation and organic or inorganic anion, usually show a liquid state around room temperature. They have been attracting much attention because of their green properties (e.g., negligible vapor pressure, high thermal stability) and high tunability (e.g., by altering cation, anion, or/and both) [19,20]. They are enormously studied and applied in many fields, such as humidity regulation, moisture absorbent, sour gas capture, biomass dissolution, and chemical reaction [21–34]. In terms of the processing of biomass, AcILs have a better ability than other kinds of ILs, particularly for [EMIM][Ac] [24,35–40]. Furthermore, the contamination or mixture with water (Scheme 2) would alter the structure, properties and application of AcILs (particularly for the regeneration of biomass) [40–42]. Choosing the dynamic interaction between air moisture and [EMIM][Ac] is due to the high hygroscopicity of AcILs [43–45]. Utilizing IR technique is mainly because of its powerful ability to detect interaction mechanism for intra- or/and inter-molecules. IR is widely used in many reports related to the interaction mechanism among ILs or between ILs and other substances [13,46–53]. Thus, the proposed coupled s-PCMW2D-CODS was used to investigate the dynamic interaction mechanism of atmospheric water absorbed in acetate-based ionic liquid (AcIL) 1-ethyl-3-methyl-imidazolium acetate ([EMIM][Ac], Scheme 2) via attenuated total reflectance infrared (ATR-IR) spectroscopy.

The paper is organized as follows. First, we introduced the theory and definition of s-PCMW2D-CODS. Then, the rules of s-PCMW2D-CODS were given and discussed, and computational simulations in different situations (same direction, opposite direction, linear comparison, and nonlinear comparison) were conducted to illustrate the as-proposed idea of s-PCMW2D-CODS. In this section, we select a curve with a constant change rate as the reference spectrum (e.g., Bands A1, B1, C1 and D1) for all the simulated conditions. The constant change rate of reference spectra is good for an easier determination of the relationship between the compared spectra and data analysis. To corroborate the proposed s-PCMW2D-CODS is clearer, more accurate and more direct than s-PCMW2D-COS, and selection of an easier reference spectra is presented in spite of only slight difference (shift down by a constant distance) between s-PCMW2D-CODS and s-PCMW2D-COS. Finally, s-PCMW2D-CODS was used to investigate the dynamic interaction mechanism of atmospheric water absorbed in [EMIM][Ac] ATR-IR spectroscopy.

2. Experimental section

2.1. Materials and ATR-IR experiments

[EMIM][Ac] was supplied by Lanzhou Greenchem ILs, LICP, CAS, Lanzhou, China. The purity of [EMIM][Ac] was over 98.5%. [EMIM][Ac] was put in the vacuum oven for drying at 60 °C for about 70 h before use. The impurities of [EMIM][Ac] were also measured. The parameters of attenuated total reflection (ATR-IR, Prestige-21) spectra were listed as follows: 584 mm^2 surface areas, 4600 cm^{-1} to 400 cm^{-1} ranges,



Scheme 1. Proposed photographic presentation of couple two-dimensional correlation difference spectroscopy 2D-COS and difference spectra DS to produce perturbation-correlation moving-window two-dimensional correlation difference spectroscopy s-PCMW2D-CODS (a), and four steps to obtain s-PCMW2D-CODS (b).

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