



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

FT-IR spectroscopy combined with DFT calculation to explore solvent effects of vinyl acetate



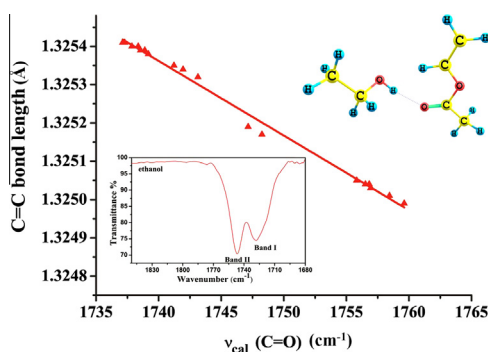
Yi Chen, Hui Zhang, Qing Liu*

Department of Chemistry, Zhejiang University, Zheda Road No. 38, Hangzhou 310027, PR China

HIGHLIGHTS

- $\nu(\text{C}=\text{O})$ of VAc is employed to reflect chemical reactivity of C=C group in VAc.
- Correlations between the $\nu_{\text{cal}}(\text{C}=\text{O})$ and solvent parameter equations suggest limitation of using the PCM model.
- Long-range electrostatic solvation free energies of VAc are calculated by the SMD model.
- Ab initio calculation allow assignments of the $\nu_{\text{exp}}(\text{C}=\text{O})$ in alcohol solvents.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 December 2013
 Received in revised form 16 January 2014
 Accepted 27 January 2014
 Available online 6 February 2014

Keywords:

Solvent effects
 Vinyl acetate
 FT-IR
 DFT
 PCM
 Ab initio

ABSTRACT

The infrared vibration frequencies of vinyl acetate (VAc) in 18 different solvents were theoretically computed at Density Function Theory (DFT) B3LYP/6-311G* level based on Polarizable Continuum Model (PCM) and experimentally recorded by FT-IR spectroscopy. The solvent-induced long-range bulk electrostatic solvation free energies of VAc (ΔG_{elec}) were calculated by the SMD model. The C=O stretching vibration frequencies of VAc were utilized as a measure of the chemical reactivities of the C=C group in VAc. The calculated and experimental C=O stretching vibration frequencies of VAc ($\nu_{\text{cal}}(\text{C}=\text{O})$ and $\nu_{\text{exp}}(\text{C}=\text{O})$) were correlated with empirical solvent parameters including the KBM equation, the Swain equation and the linear solvation energy relationships (LSER). Through ab initio calculation, assignments of the two C=O absorption bands of VAc in alcohol solvents were achieved. The PCM, SMD and ab initio calculation offered supporting evidence to explain the FT-IR experimental observations from differing aspects.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Vinyl acetate (VAc) is primarily utilized as a monomer to manufacture polymers including polyvinyl alcohol resin, synthetic fiber and multipurpose adhesive [1]. A variety of reports manifest that the polymerization process is affected by the properties of the monomer and the reaction conditions of temperature and pressure,

but also by the solvent used in reaction owing to solute–solvent interactions [2–5].

Infrared spectroscopy offers an effective tool to explore solute–solvent interactions. Vibration spectra of molecules depend not only on the strength of bond within molecules, but also on the chemical environments surrounding them. Thus, solvent-induced shifts of vibration frequency of solute provide an insight into solute–solvent interactions. There are a number of investigations covering this field carried out by FT-IR [6–9], but they lack theoretical supports for feasible mechanisms of solute–solvent interactions.

* Corresponding author. Tel.: +86 571 87951289.
 E-mail address: liuqing@zju.edu.cn (Q. Liu).

A number of attempts were made by chemists to explore solvent effects through establishing empirical solvent parameter equations. The KBM equation was the first theoretical equation involving solvent-induced solute stretching vibration frequency shifts, which was developed in 1937 by Kirkwood, Bauer and Magat to describe the solvent effects [10]. The model equation is shown in Eq. (1):

$$\frac{\nu_{\text{gas}} - \nu_{\text{sol}}}{\nu_{\text{gas}}} = A \frac{\epsilon - 1}{2\epsilon - 1} = A(\epsilon) \quad (1)$$

Here ν_{gas} is the vibration frequency of a solute in the gas phase, ν_{sol} is the frequency of a solute in the solvent, ϵ is the dielectric constant of the solvent, and A is a constant, which is dependent on the dimensions and electrical properties of the solute vibration dipole.

The Swain equation is utilized as a multi-parameter equation to describe the solvent effects, which includes the solvent parameters of A_j and B_j [11]. The model equation of Swain applied in infrared spectroscopy is shown in Eq. (2).

$$\nu = \nu_0 + aA_j + bB_j \quad (2)$$

ν is the vibration frequency of a solute in presence of a solvent. ν_0 is the ν of the solute unaffected by the solvent acidity or the solvent basicity. A_j is a measure of the solvent hydrogen-bond donor (HBD) acidity and B_j is a measure of the solvent hydrogen-bond acceptor (HBA) basicity. The coefficients measure the relative susceptibility of the solvent-dependent solute vibration frequency ν to the indicated solvent parameters.

The linear solvation energy relationships (LSER) is another multi-parameter equation used to describe the solvent effects, which includes the Kamlet–Taft's solvent parameters π^* , δ , α and β [12]. The model equation of LSER applied in infrared spectroscopy is shown in Eq. (3)

$$\nu = \nu_0 + (s\pi^* + d\delta) + a\alpha + b\beta \quad (3)$$

Here ν is the vibration frequency of solute in a solvent. ν_0 is the regression value of ν in cyclohexane. π^* is a measure of solvent dipolarity/polarizability. δ is a polarizability correction term for poly-chlorinated aliphatic hydrocarbon and aromatic solvents. α is a measure of the solvent hydrogen-bond donor (HBD) acidity. β is a measure of the solvent hydrogen-bond acceptor (HBA) basicity. The regression coefficients s , d , a and b in Eq. (3) measure the relative susceptibilities of the solvent-dependent solute vibration frequency ν to the indicated solvent parameters. The KBM, LSER and Swain solvent parameters of 18 different solvents are presented in Table 1.

Quantum chemical methodology has been extensively employed to investigate solvent effects. The Polarizable Continuum Model (PCM), pioneered by Tomasi and co-workers, provides a theoretical tool for studying solvent effects by introducing dielectric medium which self-consistently polarizes the solute charge distribution [14]. Continuum models are based on the assumptions that electrostatic solute–solvent interactions do not depend on the molecular structure of the solvent and that the dielectric response of the medium is uniform and linear at all positions outside the space that defines the solute. The assumptions are poor when strong, specific interactions between a solute and one or more first-shell solvent molecules are present [15].

The model of SMD, a new implementation of Gaussian 09, is characterized by its capacity to calculate the solvation free energies (ΔG) which consist of two components: the long-range electrostatic contribution (ΔG_{elec}) and the short-range, nonelectrostatic contribution ($\Delta G_{\text{non-elec}}$). The ΔG_{elec} arises from a self-consistent reaction field treatment that involves solving the nonhomogeneous Poisson equation for electrostatics based on the integral-equation-formalism polarizable continuum model

Table 1
KBM, LSER and Swain solvent parameters of 18 different solvents.

Solvent	$f(\epsilon)^a$	π^{*b}	δ^b	α^b	β^b	A_j^c	B_j^c
n-Hexane	0.186	−0.04	0	0	0	0.01	−0.01
Cyclohexane	0.203	0.00	0	0	0	0.02	0.06
Diethyl ether	0.345	0.27	0	0	0.47	0.12	0.34
Toluene	0.245	0.54	1	0	0.11	0.13	0.54
Tetrahydrofuran	0.405	0.58	0	0	0.55	0.17	0.67
Benzene	0.231	0.59	1	0	0.10	0.15	0.59
Tetrachloromethane	0.226	0.28	0.5	0	0.10	0.09	0.34
1,4-Dioxane	0.223	0.55	0	0	0.37	0.19	0.67
1,2-Dichloroethane	0.431	0.81	0.5	0	0.10	0.30	0.82
Acetonitrile	0.479	0.75	0	0.19	0.40	0.37	0.86
Dichloromethane	0.422	0.82	0.5	0.13	0.10	0.33	0.80
Chloroform	0.359	0.58	0.5	0.20	0.10	0.42	0.73
1-Butanol	0.459	0.47	0	0.84	0.84	0.61	0.43
2-Butanol	0.454	0.40	0	0.69	0.80		
1-Propanol	0.465	0.52	0	0.84	0.90	0.63	0.44
2-Propanol	0.460	0.48	0	0.76	0.84	0.59	0.44
Ethanol	0.471	0.54	0	0.86	0.75	0.66	0.45
Methanol	0.478	0.60	0	0.98	0.66	0.75	0.50

^a $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$; $f(\epsilon)$ is the parameter of KBM solvent equation [10].

^b Parameters of LSER solvent equation [13].

^c Parameters of Swain solvent equation [13].

(IEF-PCM) and the $\Delta G_{\text{non-elec}}$ originates from short-range interactions between the solute and solvent molecules in the first solvation shell [16]. The $\Delta G_{\text{non-elec}}$ assumed by the SMD model is labeled as the cavity-dispersion-solvent-structure term because the $\Delta G_{\text{non-elec}}$ is exactly a manifestation of cavitation, dispersion and solvent structure effects, being proportional to the solvent-accessible surface areas of the individual atoms of the solute [17,18]. Therefore, only ΔG_{elec} has been comprehensively analyzed in present work.

Although many investigations based on theoretical computation have been carried out in terms of polymerization process (chain initiation, propagation, transfer and termination) [19–22], there are rarely reports utilizing Density Functional Theory (DFT) computation to discuss solvent effects on VAc. In present work, FT-IR Spectroscopy was implemented to probe experimental characterization. Calculations were carried out using DFT protocols based on PCM or SMD model in combination with empirical solvent parameters, in order to figure out the extent to which the calculated results agree with the experimental observations.

Experimental details

Infrared spectra were recorded with experimental temperature of 294 K on a Nicolet Nexus 670 FTIR spectrometer which is equipped with a Ge/KBr beam-splitter and a DTGS detector. For all spectra, 10 scans recorded at 2 cm^{-1} resolution were averaged. The gaseous state spectrum of vinyl acetate (VAc) was recorded using a 100 mm path-length gas cell with KRS-5 windows. The solution spectra were measured using 0.2 mm path-length KBr cells with the concentration ranging from 4.0×10^{-3} mol L^{-1} to 5.0×10^{-3} mol L^{-1} . The corresponding solvent spectra were recorded under the same condition as the background spectra. All solvents were of analytical purity and were distilled prior to use. The Nicolet Omnic software, Version 7.3, was used for all data manipulation. The data files were transferred to a computer for analysis using a digital curve-fitting program (Origin 8.0).

Computational methods

A series of quantum chemical calculations of optimization and frequencies were performed at DFT (B3LYP and B3PW91) with 9 different basis sets using Gaussian 09 suite of programs. Gaussian View and Chemcraft programs were applied to obtain the assign-

Download English Version:

<https://daneshyari.com/en/article/1229937>

Download Persian Version:

<https://daneshyari.com/article/1229937>

[Daneshyari.com](https://daneshyari.com)