Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 162 (2016) 109–114

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

A QSPR study on the solvent-induced frequency shifts of acetone and dimethyl sulfoxide in organic solvents

Yu Heng Ou, Chia Ming Chang *, Ying Shao Chen

Environmental Molecular and Electromagnetic Physics (EMEP) Laboratory, Department of Soil and Environmental Sciences, National Chung Hsing University, Taichung 40227, Taiwan

ARTICLE INFO

Article history:
Received 16 October 2015
Received in revised form 5 March 2016
Accepted 7 March 2016
Available online 10 March 2016

Keywords:
Quantitative structure–property relationship
Solvent-induced frequency shift
Acetone
Dimethyl sulfoxide
Quantum-chemical descriptor
Four-element theory

ABSTRACT

In this study, solvent-induced frequency shifts (SIFS) in the infrared spectrum of acetone and dimethyl sulfoxide in organic solvents were investigated by using four types of quantum-chemical reactivity descriptors. The results showed that the SIFS of acetone is mainly affected by the electron-acceptance chemical potential and the maximum nucleophilic condensed local softness of organic solvents, which represent the electron flow and the polarization between acetone and solvent molecules. On the other hand, the SIFS of dimethyl sulfoxide changes with the maximum positive charge of hydrogen atom and the inverse of apolar surface area of solvent molecules, showing that the electrostatic and hydrophilic interactions are main mechanisms between dimethyl sulfoxide and solvent molecules. The introduction of the four-element theory model-based quantitative structure–property relationship approach improved the assessing quality and provided a basis for interpreting the solute–solvent interactions.

1. Introduction

Solvents affect several important functions of solutes when a chemical reaction occurs; therefore, the solute–solvent interaction plays an important role in a variety of physical and chemical processes in solution. In order to explore the solute–solvent interactions, there have been a lot of studies applying infrared spectral measurements for detecting the solvent-induced frequency shifts (SIFS) of solutes [1–11]. In these studies, a number of quantitative models including physicochemical properties of solvents have also been presented to explain the solvent-induced frequency shifts. Fawcett et al. have studied the solvent-induced frequency shifts of the $C\equiv N$ stretching vibration of acetonitrile in various organic solvents [1]. They concluded that the solvent's basicity as estimated by the Gutmann donor number [12] or the solvent acidity as estimated by the Gutmann acceptor number [13] is correlated to the SIFS of acetonitrile. Cha et al. have studied the solvent induced frequency shifts in the infrared spectrum of acetone in organic solvents [3]. Four solvent parameters including solvent basicity (Gutmann donor number), solvent acidity (Gutmann acceptor number), solvent polarity, and solvent polarizability were considered to examine the solvent dependence of the SIFS. They concluded that the CO stretching frequency has strong correlation with the acceptor number of the solvent, which serves as Lewis acids.

A type of linear free energy relationship (LFER), or the linear solvation energy relationship (LSER) was proposed by Kamlet, Taft, and their colleagues to describe the solvent effects in solution [14]. The LSER model relates a bulk property to molecular parameters used to account for cavity formation, dipole moment/polarizability, and hydrogen-bonding effects. The cavity term is a measure of the energy needed to overcome cohesive solvent–solvent molecule interactions to form a cavity for the solute molecule. The dipolarity/polarizability terms are measures of the energy of solute–solvent dipole and induced dipole interactions which contribute to solution formation. Hydrogen bonding terms measure the energy of interaction when a solute–solvent complex is formed. Liu et al. use LSER to investigate the infrared spectroscopy of 2-acetylthiophene (ACTH) in different polar and non-polar organic solvents [4]. They found that the LSER shows a better correlation than the solvent acceptor number (AN).

Famini, Wilson and co-workers have developed a set of quantum-chemical derived parameters to alternative the terms in the conventional LSER model [15,16]. According to the conceptual density functional theory [17], Chang has proposed a DFT-based liner solvation energy relationships for the solvent-induced shifts of the carbonyl ($C = O$) stretching frequency of acetone in polar and nonpolar organic solvents [18]. Four descriptors, namely, (1) the solvation free energy of solute in continuous dielectric medium, (2) the global interaction energy of the solute–solvent system, (3) the maximum electrostatic potential on the hydrogen atom of the solvent molecule, and (4) the maximum condensed nucleophilic Fukui function (or nucleophilic condensed local softness) of the solvent molecule, those which explained both

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* Corresponding author.
E-mail address: abinitio@dragon.nchu.edu.tw (C.M. Chang).
URL: http://chiaming.wikispaces.com/ (C.M. Chang).

http://dx.doi.org/10.1016/j.saa.2016.03.009
1386-1425/

Table 1
HF/6-31G(d,p) calculated results of reactivity descriptors[a] of solvent compounds.

No.	Solvents	μ (au)	η (au)	TSA (nm^2)	$-\mu^+$ (au)	μ^- (au)	s^+_{max} (au)	s^-_{max} (au)	$\rho^+_{max(H)}$ (au)	$-\rho^-_{max}$ (au)	APSA (nm^2)
1	Acetic acid	−0.100	0.252	1.997	−0.026	−0.225	0.601	0.987	0.361	0.590	0.966
2	Trifluoroacetic acid	−0.148	0.251	2.244	0.022	−0.273	0.649	0.962	0.378	0.578	0.070
3	Acetonitrile	−0.111	0.298	1.829	−0.038	−0.260	0.646	0.770	0.180	0.454	1.241
4	Benzonitrile	−0.130	0.197	2.842	0.031	−0.228	0.351	0.349	0.186	0.452	2.266
5	Acetone	−0.095	0.219	2.189	−0.015	−0.204	0.557	1.051	0.159	0.516	1.734
6	Dimethyl sulfoxide	−0.053	0.230	2.269	−0.062	−0.169	1.103	1.133	0.172	0.786	1.556
7	Methanol	−0.073	0.287	1.633	−0.070	−0.217	1.480	1.021	0.335	0.634	0.973
8	Ethanol	−0.070	0.283	1.985	−0.071	−0.212	1.486	1.028	0.335	0.639	1.401
9	Propan-1-ol	−0.069	0.281	2.310	−0.071	−0.210	1.519	1.031	0.335	0.647	1.733
10	Propan-2-ol	−0.070	0.277	2.244	−0.068	−0.208	1.224	1.036	0.332	0.645	1.740
11	*t*-Butanol	−0.070	0.270	2.492	−0.065	−0.206	0.850	1.051	0.329	0.650	2.060
12	Nitromethane	−0.184	0.248	1.933	0.060	−0.308	0.606	0.762	0.187	0.454	0.884
13	Nitrobenzene	−0.152	0.182	2.757	0.060	−0.243	0.596	0.331	0.218	0.471	1.863
14	Dimethylacetamide	−0.067	0.231	2.635	−0.049	−0.182	0.611	0.693	0.141	0.687	2.250
15	Dimethylformamide	−0.073	0.237	2.389	−0.045	−0.192	0.709	0.651	0.180	0.639	1.926
16	*N*-Methylformamide	−0.082	0.250	2.104	−0.043	−0.207	0.687	0.715	0.315	0.676	1.283
17	Formamide	−0.079	0.249	1.762	−0.046	−0.203	0.663	1.021	0.322	0.730	0.482
18	Benzene	−0.088	0.213	2.488	−0.019	−0.194	0.301	0.273	0.148	0.148	2.488
19	Hexane	−0.103	0.326	3.098	−0.060	−0.267	0.261	0.303	0.111	0.332	3.098
20	1,2-Dichloroethane	−0.140	0.286	2.313	−0.003	−0.283	0.551	0.759	0.191	0.291	2.313
21	Dichloromethane	−0.152	0.276	1.994	0.014	−0.290	0.769	0.788	0.213	0.359	1.994
22	Chloroform	−0.173	0.263	2.221	0.042	−0.304	0.679	0.648	0.254	0.355	2.221
23	Diethylether	−0.046	0.274	2.671	−0.091	−0.183	0.452	0.918	0.126	0.634	2.581
24	Propylene carbonate	−0.128	0.309	2.552	−0.026	−0.283	0.682	0.384	0.152	0.619	1.618

[a] μ: chemical potential; η:chemical hardness; TSA: total surface area; $-\mu^+$: the negative of charge-acceptance chemical potential; μ^-: charge-donation chemical potential; s^+_{max}: the maximum nucleophilic condensed local softness; s^-_{max}: the maximum electrophilic condensed local softness; $\rho^+_{max(H)}$: the maximum positive charge of hydrogen atom in organic compounds; $-\rho^-_{max}$: the negative of the maximum negative charge in organic compounds; APSA: apolar surface area.

the nonspecific and specific effects of solute–solvent interactions, were the governed parameters.

In our previous study, we presented a successful quantitative structure–property relationship (QSPR) model, considering four types of interactions (electron flow, electrostatic, polarization and hydrophilic interactions), to elucidate the reaction properties of metal ions and organic compounds in various systems [19]. A difference in electronic chemical potential between the two molecular systems leads to a charge transfer and a deformation of the electron cloud. When two non-deformable ions with opposite charges are interacted in a non-contact state, the electrostatic interaction is formed. In a polarization interaction, two molecular systems are attracted to each other through the fluctuation of the deformable electron cloud. The atoms are attracted to each other by the polarization interaction until the distance between them equals the sum of their van der Waals radii. Hydrophilic groups attract water molecules without the deformable electron density

Table 2
MP2/6-31G(d,p) calculated results of reactivity descriptors[a] of solvent compounds.

No.	Solvents	μ (au)	η (au)	TSA (nm^2)	$-\mu^+$ (au)	μ^- (au)	s^+_{max} (au)	s^-_{max} (au)	$\rho^+_{max(H)}$ (au)	$-\rho^-_{max}$ (au)	APSA (nm^2)
1	Acetic acid	−0.133	0.267	2.027	−0.001	−0.266	0.554	0.931	0.368	0.607	0.974
2	Trifluoroacetic acid	−0.178	0.264	2.238	0.046	−0.310	0.586	0.912	0.388	0.590	0.072
3	Acetonitrile	−0.145	0.313	1.814	−0.012	−0.301	0.615	0.720	0.182	0.466	1.233
4	Benzonitrile	−0.151	0.195	2.840	0.054	−0.249	0.400	0.398	0.189	0.472	2.265
5	Acetone	−0.128	0.234	2.201	0.011	−0.245	0.530	0.993	0.162	0.540	1.738
6	Dimethyl sulfoxide	−0.088	0.242	2.277	−0.033	−0.209	1.018	1.084	0.171	0.789	1.555
7	Methanol	−0.104	0.297	1.641	−0.044	−0.253	1.409	0.974	0.338	0.640	0.970
8	Ethanol	−0.102	0.293	1.982	−0.044	−0.248	1.426	0.984	0.338	0.647	1.398
9	Propan-1-ol	−0.102	0.291	2.308	−0.044	−0.247	1.452	0.986	0.338	0.655	1.726
10	Propan-2-ol	−0.104	0.284	2.244	−0.038	−0.246	1.207	1.002	0.335	0.653	1.740
11	*t*-Butanol	−0.107	0.274	2.489	−0.030	−0.244	0.878	1.029	0.331	0.658	2.052
12	Nitromethane	−0.163	0.226	1.933	0.050	−0.276	0.678	0.831	0.191	0.445	0.884
13	Nitrobenzene	−0.169	0.190	2.885	0.074	−0.264	0.622	0.316	0.223	0.460	1.954
14	Dimethylacetamide	−0.089	0.234	2.620	−0.028	−0.206	0.586	0.679	0.169	0.685	2.227
15	Dimethylformamide	−0.094	0.241	2.389	−0.027	−0.214	0.674	0.637	0.183	0.640	1.926
16	*N*-Methylformamide	−0.101	0.255	2.112	−0.027	−0.228	0.652	0.695	0.320	0.680	1.284
17	Formamide	−0.109	0.266	1.759	−0.024	−0.242	0.600	0.955	0.327	0.735	0.480
18	Benzene	−0.114	0.216	2.501	0.006	−0.223	0.296	0.269	0.148	0.148	2.501
19	Hexane	−0.116	0.305	3.092	−0.036	−0.269	0.278	0.325	0.111	0.331	3.092
20	1,2-Dichloroethane	−0.145	0.260	2.311	0.015	−0.276	0.605	0.834	0.189	0.293	2.311
21	Dichloromethane	−0.152	0.257	1.997	0.023	−0.280	0.824	0.842	0.212	0.361	1.997
22	Chloroform	−0.170	0.238	2.225	0.051	−0.289	0.748	0.714	0.253	0.355	2.225
23	Diethylether	−0.083	0.279	2.675	−0.057	−0.222	0.441	0.897	0.127	0.644	2.583
24	Propylene carbonate	−0.121	0.275	2.567	−0.017	−0.258	0.738	0.437	0.155	0.636	1.612

[a] μ: chemical potential; η:chemical hardness; TSA: total surface area; $-\mu^+$: the negative of charge-acceptance chemical potential; μ^-: charge-donation chemical potential; s^+_{max}: the maximum nucleophilic condensed local softness; s^-_{max}: the maximum electrophilic condensed local softness; $\rho^+_{max(H)}$: the maximum positive charge of hydrogen atom in organic compounds; $-\rho^-_{max}$: the negative of the maximum negative charge in organic compounds; APSA: apolar surface area.