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Origins of Heat Evolution in Mixing Water and Dimethyl Sulfoxide

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Abstract—Dimethyl sulfoxide (DMSO) is one of small amphiphiles composed of both hydrophobic and polar groups. DMSO and water mix uniformly accompanied by intense heat evolution but molecular reasons of the negative molar excess enthalpy and entropy remain ambiguous since the 1940s. We present an interpretation on the origins, based on our results of IR and NMR measurements and simulations. Our interpretation can shed new light on the roles of water molecules in biological systems.

I. INTRODUCTION

Heat evolutions observed on mixing water and a small amphiphile like alcohols have been related to self-association among water molecules through hydrogen(H)-bondings among water molecules around hydrophobic groups, which were considered to be stronger enough than those formed in bulk water [1]. Such the “Hydrophobic hydration” has been the most widely used model of the water until thermodynamic, nuclear magnetic resonance (NMR) and simulation studies of aqueous solutions of clathrate-formers suggest that clathrate hydration is a more realistic model for hydrophobic hydration [2].

We have been skeptical about the interpretation of ‘hydrophobic hydration’, because roles of electronegative atoms like O and N of polar groups in amphiphiles solved in water in inter- and intramolecular polarization were not taken into consideration. We have been carrying out measurements of infrared (IR) and NMR spectra of aqueous binary mixtures of alcohols, ketones, and furans with varying compositions [3]. In this work, we measured the ¹H-chemical shift of water protons via NMR; and $\nu(\text{O-D})$ stretching vibration spectra of HOD and $\nu(\text{H-O-H})$ bending vibration spectra of water in IR, and $\nu(\text{C-H})$ stretching vibration spectra of the methyl groups, with varying the compositions via FTIR.

II. RESULTS.

We summarize in Fig. 1, the changes of chemical shifts for the water protons, the protons, and the carbons in DMSO caused by increasing water content. From the curves on Left column (A), mixing water with DMSO causes weakening of the H-bond donating strength of the O-H groups in water, which is contrary to the picture described by hydrophobic hydration.

The origin of the blue shift of $\nu(\text{C-H})$ induced by a weak H-bond, $\text{C-H}\cdots\text{OH}_2$, was interpreted in terms of (1) polarization of the C-H bond, and (2) re-hybridization of the three C-H sp_3 orbitals followed by their contraction, where blue-shift of $\nu(\text{C-H})$ vibration band occurs due to increase of the electron density in the C-H bond [3].

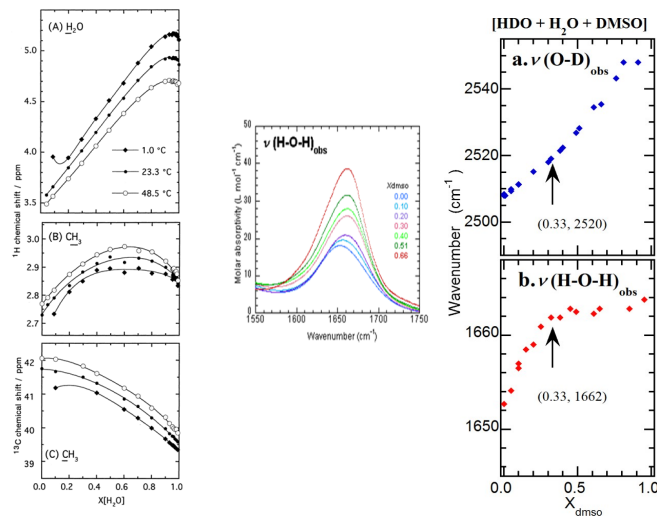


Fig. 1. Left column: Chemical shifts for the (A) ¹H protons of the water, (B) ¹H protons of the methyl groups in DMSO, and (C) ¹³C carbons of the methyl groups in DMSO, in binary aqueous mixtures of DMSO with respect to concentration and temperature. Center column: Molar absorption spectra for the bending vibration band of the water in differing concentrations of binary mixtures of DMSO. Right column: Changes of O-D stretching vibration frequency, $\nu(\text{O-D})$, in (HDO + H₂O + DMSO) mixtures, and the bending vibration frequency $\nu(\text{H-O-H})$ for the water in the binary mixtures with DMSO.

We have found that the heat evolution comes from the difference in the ease of localization of the oxygen electrons between $\text{C-H}\cdots\text{OH}_2$ (a weak H-bond [3]) and in $\text{O-H}\cdots\text{OH}_2$ (the conventional H-bond). In the former, oxygen electrons cannot delocalize easily due to weak H-bonding; the accumulation of other electrons and friction among them results in heat evolution. Whereas in the latter, the formation of $\text{O-H}\cdots\text{OH}_2$ (the conventional H-bond), delocalization of the oxygen electrons can occur more easily.

Roles of water molecules in the interaction between or among the two types of H-bonds are not well understood, even though many kinds of amphiphiles exist in both animals and plants as biological reactors. Our results emphasize that weak hydrogen bonds play important roles in biological systems.

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