

## A general view on hydrophobicity

Kenichiro Koga, Mario Ishizaki

*Department of Chemistry, Okayama University, Japan*

Solubility of hydrophobes in water is very low. There are, however, many other combinations of solutes and solvents that give low solubility. For example, argon dissolves very little in hydrazine. What grants a special interest to hydrophobes in water is the following observation: transfer of a hydrophobic solute in water is in fact energetically favorable, that is, the transfer is entropically so unfavorable that the net solvation free energy is large and positive [1]. This is thermodynamically equivalent to that the solubility of hydrophobes in water becomes even lower as the temperature is raised. This temperature dependence of solubility is well known for noble gases and many hydrocarbons in water.

Above arguments implicitly assume the process of solvation or the process of temperature change is carried out at fixed pressures. The constant-pressure condition is a natural choice for most experiments; the constant-volume condition is another possible choice, often employed in theoretical calculations. If the original phase from which a solute is transferred is an ideal gas and the final phase is some condensed phase  $\beta$ , difference between solvation entropy  $\Delta S_p^*$  for a constant-pressure condition and  $\Delta S_V^*$  for a constant-volume condition, or equivalently difference between solvation enthalpy  $\Delta H_p$  for a constant-pressure process and solvation energy  $\Delta U_V$  for a constant-volume process, is given by

$$\frac{\Delta S_p^*}{k} - \frac{\Delta S_V^*}{k} = \frac{\Delta H_p}{kT} - \frac{\Delta U_V}{kT} = \frac{\epsilon^\beta \overline{V}_A^\beta}{k\chi_\beta} - 1$$

where  $\epsilon^\beta$  is the coefficient of thermal expansion,  $\chi_\beta$  the isothermal compressibility, and  $\overline{V}_A^\beta$  the molar volume of solute, all defined in the  $\beta$  phase. For infinitely dilute Lennard-Jones (LJ) solutions [2], these solvation thermodynamic quantities are calculated as functions of  $\epsilon$  and  $\sigma$ , the solute-solvent LJ energy and size parameters. It was found that the solvation analogous to the hydrophobic hydration is realized for a wide range of the LJ parameters if the constant-volume process is assumed. If the constant-pressure is assumed the range of the parameters in which the “hydrophobic hydration” is realized still exists but is very small. We will compare what we found for the LJ solution with those in a realistic model solvent of water.

[1] B. Widom, P. Bhimalapuram, and K. Koga, *Phys. Chem. Chem. Phys.*, **5**, 3085-3093 (2003).

[2] M. Ishizaki, H. Tanaka, K. Koga, *Phys. Chem. Chem. Phys.* **13**, 2328-2334 (2011).