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Solvent Isotope Effect of H_2O and D_2O on the Partition Coefficient of 1,3-Di-*n*-alkyl-1,3-propanedione

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Synopsis. The apparent partition coefficients of seven 1,3-di-*n*-alkyl-1,3-propanediones have been determined in dodecane/H_2O and dodecane/D_2O systems. From the results, the transfer free energies of β-diketones from H_2O to D_2O, $\Delta G_{H_2O \to D_2O}$, have been calculated and are discussed in terms of the cavity formation energy.

In solvent extraction, the partition process of a metal chelate formed in an aqueous phase is one of the most important processes governing the distribution ratio of a metal ion. The partition coefficient of a metal chelate is primarily determined by the hydrophobic character which is a substantial part of the chelate formed by the reaction of a metal ion with a hydrophobic extractant. A quantitative discussion of the hydrophobicity of the extractant, however, is not thoroughly recognized. In this study the interaction between water and 1,3-di-*n*-alkyl-1,3-pentanediones has been examined, the latter compounds being well-known as extractants, by partition experiments in the dodecane/H_2O and dodecane/D_2O systems. The reason for employing β-diketones is that the size of the hydrophobic part of the reagent can be varied stepwise by changing the chain length of the *n*-alkyl group. D_2O is considered to be more structured than H_2O,1) so that partition experiments in the two systems will provide useful information on the hydrophobic interaction between water and the reagents.

Experimental

Materials. Reagent grade acetylacetone (2,4-pentanedione) was purified by fractional distillation. Other normal chain β-diketones were synthesized by the Claisen acylation.2) The crude products were purified by the copper salt method3) and subsequently distilled under reduced pressure. Dodecane (Tokyo Kasei G. R.) was agitated twice with a mixture of fuming sulfuric acid and sulfuric acid (1 : 4) overnight, washed with water and distilled under reduced pressure. Redistilled water was used throughout the experiments and heavy water (Merk 99.7%) used as purchased.

Partition Experiments. A certain volume (5 ml or 4 ml) of the dodecane solution of the β-diketone (below 10^{-2} M) and an equal volume of H_2O (5 ml) or D_2O (4 ml) were stirred by a magnetic stirrer for 6 h in a thermostated glass vessel at 25±0.05 °C. After being allowed to stand for 1 h, an aliquot of the aqueous phase was pipetted into a quartz cell and the transmittance at the absorption maximum recorded for each β-diketone on a Hitachi 356 spectrophotometer. Partition coefficients were obtained from the initial concentration and the concentration in the aqueous phase determined photometrically. Partition experiments were repeated a minimum of three times.

Results and Discussion

The observed partition coefficients (P_{H_2O} and P_{D_2O}) are listed in Table 1 and as can be seen the partition coefficients appear to increase with the carbon numbers of the *n*-alkyl group. P_{D_2O} values appear to be slightly less than the P_{H_2O} values for the smaller diketones, but slightly greater for the larger diketones. The ratios of P_{D_2O}/P_{H_2O}, which are shown in Table 1, differ from unity revealing the solvent isotope effect on the partition coefficient.

From the partition coefficient data, the transfer free energy of the β-diketone from H_2O to D_2O ($\Delta G_{H_2O \to D_2O}$) has been estimated using,

$$\Delta G_{H_2O \to D_2O} = RT \ln\left(\frac{P_{D_2O}}{P_{H_2O}} \cdot \frac{V_{H_2O}}{V_{D_2O}}\right), \tag{1}$$

where V is the molar volume of the solvent. The results are also listed in the last column of Table 1. Since the diketones are in the keto and enol forms in solution and possess reactive protons, *viz.* an enol proton and a methyne proton for the enol form and methylene protons for the keto form, a change in the keto-enol equilibrium will be the result of H–D exchange and/or by the solvent effect of H_2O and D_2O. The PMR spectra of acetylacetone in D_2O provides that all the reactive protons are replaced by deuteron in D_2O. However, since the ratio of the molar ex-

Table 1. The partition coefficients a) and the free energies of transfer from H_2O to D_2O at 25 °C

β-Diketone	P_{H_2O}	P_{D_2O}	P_{D_2O}/P_{H_2O}	$\Delta G_{H_2O \to D_2O}$ (cal mol^{-1})
2,4-Pentanedione	0.69±0.04	0.64±0.03	0.93	−47±30
2,4-Hexanedione	2.41±0.14	2.27±0.25	0.94	−40±7
2,4-Heptanedione	11.7±0.2	10.9±0.4	0.93	−44±10
2,4-Octanedione	43.5±0.3	48.7±6.6	1.12	63±6
3,5-Octanedione	37.5±0.4 b)	43.8±1.6 b)	1.17	89±28
2,4-Nonanedione	194±29	253±5	1.30	157±6
4,6-Nonanedione	144±2 b)	198±2 b)	1.38	187±12

a) Partition coefficients are shown with the standard deviation at 95% confidence level.
b) An average value of two experiments. The precision refers to the range of the two values.

tinction coefficients in H_2O and D_2O, which is thought to reflect the difference in the keto-enol equilibrium constant in the two solvent,[4] is constant (*ca.* 1.03) for most diketones, it is to be expected that the transfer free energies of the enol and keto forms will show a similar trend to the observed transfer free energy including those of the keto and enol forms. Hence, in this study the apparent transfer free energy of β-diketones will be discussed.

From Table 1, it may be seen that $\Delta G_{H_2O \to D_2O}$ is approximately zero for smaller compounds but positive for larger β-diketones. A large compound, however, does not always show a positive value of transfer free energy, *e.g.*, Jolicoeur *et al.*[5] have reported a negative value for 3-decanone (-270 ± 36 cal mol^{-1}).

The free energy of transfer can conveniently be divided into three contributions;[6]

$$\Delta G_{H_2O \to D_2O} = \Delta G(\mathrm{CAV}) + \Delta G(\mathrm{SOL}) + \Delta G(\mathrm{STR}), \quad (2)$$

where the terms on the righthand side of Eq. 2 represent the solvent isotope effect on the free energy due to CAV, the process of cavity formation in the solvent; SOL, the solvation of the polar group of the molecule; STR, the structural rearrangement of the solvent around the cavity enclosing the solute. $\Delta G(\mathrm{SOL})$ is expected to reflect the interactions between the solvent and both the carbonyl group of the keto form and the hydroxyl group of the enol form. Dahlberg[7] reported that the transfer free energy for acetone is close to zero and consequently there will be no serious difference between the free energies of the H-bond and D-bond to the carbonyl oxygen. Dahlberg furthermore reported the transfer free energy of benzene (0 ± 15 cal mol^{-1}) and benzyl alcohol (-9 ± 20 cal mol^{-1}) and from these data, it is expected that ΔG(SOL) for β-diketones is slightly negative and is not the dominant factor in the present situation.

The hydrogen bonding energy in D_2O is thought to be larger than that in H_2O in consideration of the greater cohesive energy density of D_2O than H_2O, and consequently the structural change around the solute molecule will be more extensive in D_2O. Hence, $\Delta G(\mathrm{STR})$ will show a negative value with increasing carbon number in the *n*-alkyl chain due to hydrophobic hydration around the group. This factor may be important in the case of decanone, but is not dominant here. Dahlberg reported that $\Delta G_{H_2O \to D_2O}$ for 3-methylacetylacetone showed a fairly large value (+200 cal mol^{-1}) and interpreted this result from the general tendency that a solute which possesses both ring and branches shows a positive value.[7] The present results appear to support this hypothesis.

Since the amount of void is greater in D_2O than in H_2O, the small solute molecules which can occupy void without excessive disruption of the hydrogen bonds in the solvent will be better accommodated in D_2O (negative $\Delta G(\mathrm{CAV})$). The bulky molecules which disrupt a significant number of hydrogen bonds will show a positive $\Delta G(\mathrm{CAV})$. This hypothesis appears to be supported by the recent solution theory, *viz.* the scaled particle theory amended by Stillinger.[8] Lucas and Bury[9] have computed $\Delta G_{H_2O \to D_2O}$ for a nonpolar solute using this theory and plotted the result as a function of solute hard sphere diameter, a_2. The plot of the transfer free energy is slightly negative for $a_2 < \approx 3.0$ Å and positive for $a_2 > 3.0$ Å. This is consistent with the trend observed in this study.

From the above discussion, it has been concluded that the positive transfer free energy observed for the larger β-diketones is attributable to the contribution from the cavity formation work. Since the most important process in solvent extraction is the partition of the metal chelate coordinated by a hydrophobic ligand, more attention needs to be focused on the cotribution of cavity formation in the extraction process.

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