

# Hydrogen Isotope Disproportionation and Fractionation Equilibria in the H<sub>2</sub>O–D<sub>2</sub>O Solvent System. IV.\* Fractionation of Deuterium between 3,3-Dimethyl-2-butanone and Water

Pirketta Scharlin

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku, Finland

Scharlin, Pirketta. 1986. Hydrogen Isotope Disproportionation and Fractionation Equilibria in the H<sub>2</sub>O–D<sub>2</sub>O Solvent System. IV.\* Fractionation of Deuterium between 3,3-Dimethyl-2-butanone and Water. – Acta Chem. Scand. A40: 221–226.

Fractionation of deuterium between 3,3-dimethyl-2-butanone and water has been studied at 298.15 K in different H<sub>2</sub>O–D<sub>2</sub>O liquid mixtures. A value of 0.840(6) was obtained for the fractionation factor of 3,3-dimethyl-2-butanone and a value of 2.85(6) for the equilibrium constant of the disproportionation reactions of the substrate, assuming the equilibrium constants of the two disproportionation reactions to be equal to each other. The effect of a breakdown of the rule of the geometric mean in the isotope disproportionation reactions of the substrate and the solvent water on the isotope fractionation equilibria of substrates with three exchangeable hydrogens is discussed.

In previous papers,<sup>1–3</sup> the deuterium isotope fractionation equilibria of substrates with one and two exchangeable hydrogens were studied in the H<sub>2</sub>O–D<sub>2</sub>O solvent system. When fractionation factors for substrates containing three exchangeable hydrogens are measured, there are two isotope disproportionation equilibria of the substrate in addition to the isotope disproportionation reaction of solvent water to be taken into account in discussing the fractionation equilibria. To simplify the calculations, the rule of the geometric mean<sup>4</sup> (RGM) is usually assumed to be valid for the isotope disproportionation equilibria. There is, however, no experimental verification of the applicability of the RGM to the substrates with three exchangeable hydrogens. On the other hand, it has been shown that the RGM does not hold for the isotope disproportionation equilibrium of solvent water<sup>1,5–9</sup> and that the neglect of the deviations from the RGM in the isotope disproportionation reaction of solvent water may introduce an error of about 6% in the fractionation factors.<sup>1,8</sup> The aim of this work was to obtain more experimental informa-

tion on the hydrogen isotope disproportionation equilibria in the liquid phase and on the combined effect of the isotope disproportionation in substrate and solvent water on the fractionation equilibria.

## Experimental

*Materials.* 3,3-dimethyl-2-butanone (Fluka AG, purum) was distilled once before used.

For the equilibration experiments, the sodium hydroxide–sodium deuterioxide solutions, in which the deuterium isotope mole fraction of water varied between 0.1 and 0.9, were prepared as described in Ref. 3.

The deuterium oxide used was a product of Norsk Hydro-elektrisk Kvaestofaktieselskab. The deuterium isotope mole fraction of D<sub>2</sub>O was reported to be 0.998.

*Equilibration experiments.* The performance of equilibrations was similar to that described in Ref. 3. The concentration of the catalyst was 0.07 mol dm<sup>-3</sup>, the volume of the catalyst–water solution was 40 cm<sup>3</sup>, the amount of substrate was 0.0046 mol and the time of equilibration was 3 h.

\*Parts I, II and III. See Refs. 1–3.

Table 1. Mole ratios of deuterium and protium in 3,3-dimethyl-2-butanone equilibrated in different H<sub>2</sub>O–D<sub>2</sub>O mixtures and the experimental fractionation factors  $\varphi'(\text{SH}_3)$  at 298.15 K.

$x(\text{D};\text{L}_2\text{O})^a$	$\frac{n(\text{D};\text{SL}_3)^b}{n(\text{H};\text{SL}_3)}$	$\varphi'(\text{SH}_3)^{b,c}$
0.116	0.1105(14)	0.842(11)
0.213	0.222(2)	0.821(8)
0.325	0.400(6)	0.832(13)
0.434	0.639(9)	0.833(11)
0.509	0.873(8)	0.842(8)
0.600	1.266(6)	0.844(4)
0.721	2.181(8)	0.844(3)

<sup>a</sup> $x(\text{D};\text{L}_2\text{O})$  is the deuterium isotope mole fraction of water.

<sup>b</sup>Mean values of 4–5 determinations with standard errors of mean.

<sup>c</sup>The experimental fractionation factor is defined by  $\varphi'(\text{SH}_3) = \{n(\text{D};\text{SL}_3)/n(\text{H};\text{SL}_3)\} : \{x(\text{D};\text{L}_2\text{O})/[1 - x(\text{D};\text{L}_2\text{O})]\}$ .

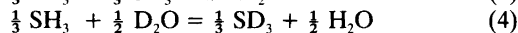
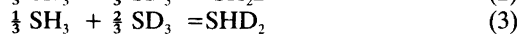
**NMR measurements.** The measurements were made with a Jeol JNM-PMX 60 NMR spectrometer immediately after the substrate was extracted from the equilibrium mixture. In 3,3-dimethyl-2-butanone, only the  $\alpha$ -hydrogens are exchangeable under the conditions used in the experiments. Thus the peak due to the protons of the *tert*-butyl group remains unchanged during deuteration and acts as an internal standard in the measurements. The positions of the NMR peaks used in the measurements were  $\delta [\text{C}(\text{CH}_3)_3] = 1.09$  ppm and  $\delta (\text{CH}_3) = 2.05$  ppm. 5 to 10 successive integral recordings were carried out from each extract. Before the integrals of the equilibrated substrates, the integrals of undeuterated 3,3-dimethyl-2-butanone were recorded. The results from the equilibrations are listed in Table 1. In the following text notation SH<sub>3</sub> is used for 3,3-dimethyl-2-butanone (CH<sub>3</sub>)<sub>3</sub>CCOCH<sub>3</sub>.

## Discussion

### Calculation of $K(\text{SH}_2\text{D})$ and $K(\text{SHD}_2)$

When the substrate SH<sub>3</sub> containing 3 isotopically exchangeable hydrogens is dissolved in water of arbitrary deuterium content, the following inde-

pendent equilibria, written for one exchangeable hydrogen, are set up: disproportionation equilibrium (1) between isotopically different waters, isotope disproportionation equilibria (2) and (3) of the substrate SL<sub>3</sub> (L = H,D) and isotope fractionation equilibrium (4) between the substrate and the solvent water. Other isotope exchange equilibria involved can be presented by combinations of the equilibria (1)–(4).



In the following approach, it is assumed that in the expressions of equilibrium constants, the activities can be replaced by mole fractions. The equilibrium constants of the equilibria (1), (2), (3) and (4) are expressed by eqns. (5), (6), (7) and (8), respectively.

$$K(\text{HDO}) = \frac{x(\text{HDO})}{x(\text{H}_2\text{O})^\dagger x(\text{D}_2\text{O})^\dagger} \quad (5)$$

$$K(\text{SH}_2\text{D}) = \frac{x(\text{SH}_2\text{D})}{x(\text{SH}_3)^\dagger x(\text{SD}_3)^\dagger} \quad (6)$$

$$K(\text{SHD}_2) = \frac{x(\text{SHD}_2)}{x(\text{SH}_3)^\dagger x(\text{SD}_3)^\dagger} \quad (7)$$

$$\varphi(\text{SH}_3) = \left[ \frac{x(\text{SD}_3)}{x(\text{SH}_3)} \right]^\dagger \left[ \frac{x(\text{H}_2\text{O})}{x(\text{D}_2\text{O})} \right]^\dagger \quad (8)$$

In the equilibrated substrate SL<sub>3</sub>, the mole ratio of deuterium and protium expressed in terms of the mole fractions of the different SL<sub>3</sub> species is given by eqn (9).

$$\frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} = \frac{3x(\text{SD}_3) + 2x(\text{SHD}_2) + x(\text{SH}_2\text{D})}{3x(\text{SH}_3) + 2x(\text{SH}_2\text{D}) + x(\text{SHD}_2)} \quad (9)$$

Replacing  $x(\text{SH}_2\text{D})$  and  $x(\text{SHD}_2)$  in eqn. (9) by the expressions from eqn. (6) and (7) and then using eqn. (8), eqn. (10) can be derived for the computation of the equilibrium constants  $\varphi(\text{SH}_3)$ ,  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  from the experimental data given for 3,3-dimethyl-2-butanone in Table 1.

$$\begin{aligned}
 & 3 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{3}{2}} \varphi(\text{SH}_3)^3 + \left[ 2 - \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} \right] K(\text{SHD}_2) \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \varphi(\text{SH}_3)^2 \\
 & + \left[ 1 - 2 \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} \right] K(\text{SH}_2\text{D}) \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) - 3 \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} = 0
 \end{aligned} \quad (10)$$

$$\begin{aligned}
 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} &= \frac{[2x(\text{D};\text{L}_2\text{O}) - 1] K(\text{HDO})}{4[1 - x(\text{D};\text{L}_2\text{O})]} \\
 &+ \frac{\sqrt{[2x(\text{D};\text{L}_2\text{O}) - 1]^2 K(\text{HDO})^2 + 16x(\text{D};\text{L}_2\text{O}) [1 - x(\text{D};\text{L}_2\text{O})]}}{4 [1 - x(\text{D};\text{L}_2\text{O})]}
 \end{aligned} \quad (11)$$

The ratio  $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^{\frac{1}{2}}$  is a function of the deuterium isotope mole fraction of water,  $x(\text{D};\text{L}_2\text{O})$ , and can be calculated from eqn. (11) with different values for  $x(\text{D};\text{L}_2\text{O})$  in Table 1. Eqn. (11) has been derived in the previous paper.<sup>1</sup>

The calculations were performed with a DEC system-10 computer. A value of 3.76<sup>1</sup> was used for  $K(\text{HDO})^2$ . The computed optimum values are  $\varphi(\text{SH}_3) = 0.833(4)$ ,  $K(\text{SH}_2\text{D}) = 2.77(4)$  and  $K(\text{SHD}_2) = 2.94(2)$ .

According to the RGM, the equilibrium constants  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  are equal to one another. It seems quite improbable that  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  would differ as much as the values obtained by the method above indicate. Obviously the accuracy of the experimental data is not satisfactory for a determination of  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  separately. Therefore, the values of  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  were also determined assuming that  $K(\text{SH}_2\text{D}) = K(\text{SHD}_2)$ . This assumption is justified, *e.g.*, on the basis of the theoretical calculations made for the disproportionation reactions of ammonia,  $2 \text{NH}_3 + \text{ND}_3 = 3 \text{NH}_2\text{D}$  and  $\text{NH}_3 + 2 \text{ND}_3 = 3 \text{NHD}_2$ ; the values  $K(\text{NH}_2\text{D})^3 = 24.61$  and  $K(\text{NHD}_2)^3 = 24.53$  can be calculated from the partition function ratios.<sup>10</sup> These values correspond to a value of 2.91 for both  $K(\text{NH}_2\text{D})$  and  $K(\text{NHD}_2)$ . Likewise, the values of 25.87 and 25.89 have been calculated<sup>8</sup> for the equilibrium constants of the disproportionation reactions of lyonium ions,  $2 \text{H}_3\text{O}^+ +$

$\text{D}_3\text{O}^+ = 3 \text{H}_2\text{DO}^+$  and  $\text{H}_3\text{O}^+ + 2 \text{D}_3\text{O}^+ = 3 \text{HD}_2\text{O}^+$ , respectively. These values correspond to a value of 2.96 for both  $K(\text{H}_2\text{DO}^+)$  and  $K(\text{KD}_2\text{O}^+)$ .

The fractionation factor  $\varphi'(\text{SH}_3)$ , which can be determined experimentally, is defined by eqn. (12).

$$\begin{aligned}
 \varphi'(\text{SH}_3) &= \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} \cdot \frac{n(\text{D};\text{L}_2\text{O})}{n(\text{H};\text{L}_2\text{O})} \\
 &= \frac{3x(\text{SD}_3) + 2x(\text{SHD}_2) + x(\text{SH}_2\text{D})}{3x(\text{SH}_3) + 2x(\text{SH}_2\text{D}) + x(\text{SHD}_2)} \\
 &\cdot \frac{2x(\text{H}_2\text{O}) + x(\text{HDO})}{2x(\text{D}_2\text{O}) + x(\text{HDO})}
 \end{aligned} \quad (12)$$

Using eqns. (5), (6), (7) and (8), an expression (13) can be derived for  $\varphi'(\text{SH}_3)$ . Assuming then that  $K(\text{SH}_2\text{D}) = K(\text{SHD}_2) = K(\text{SL}_3)$  and solving eqn. (13) for  $K(\text{SL}_3)$ , eqn. (14) is obtained for the computation of the equilibrium constants  $\varphi(\text{SH}_3)$  and  $K(\text{SL}_3)$ .

With different values of  $\varphi'(\text{SH}_3)$  and  $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^{\frac{1}{2}}$  (Table 1 and eqn. (11)), the values  $K(\text{SL}_3) = K(\text{SH}_2\text{D}) = K(\text{SHD}_2) = 2.85(6)$  and  $\varphi(\text{SH}_3) = 0.840(6)$  can be computed for the equilibrium constants of reactions (2), (3) and (4), respectively.

$$\varphi'(\text{SH}_3) = \frac{3 \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \varphi(\text{SH}_3)^2 + 2K(\text{SHD}_2) \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) + K(\text{SH}_2\text{D})}{3 + 2K(\text{SH}_2\text{D}) \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) + K(\text{SHD}_2) \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \varphi(\text{SH}_3)^2} \cdot \varphi(\text{SH}_3)$$

$$\frac{2 + \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} K(\text{HDO})}{2 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + K(\text{HDO})}, \quad (13) \quad K(\text{SL}_3) = \frac{3}{\varphi(\text{SH}_3)} \cdot \frac{\text{A} \left\{ \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}}, \varphi'(\text{SH}_3) \right\}}{\text{B} \left\{ \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}}, \varphi'(\text{SH}_3) \right\}}. \quad (14)$$

In eqn. (14), the expression for the numerator is

$$\text{A} \left\{ \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}}, \varphi'(\text{SH}_3) \right\} = \left\{ 2 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + K(\text{HDO}) \right\} \varphi'(\text{SH}_3) - \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \left\{ 2 + \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} K(\text{HDO}) \right\} \varphi(\text{SH}_3)^3,$$

and the expression for the denominator is

$$\text{B} \left\{ \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}}, \varphi'(\text{SH}_3) \right\} = \left\{ 2 + \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} K(\text{HDO}) \right\} \left\{ 2 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) + 1 \right\} - \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi'(\text{SH}_3) \left\{ 2 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + K(\text{HDO}) \right\} \left\{ \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) + 2 \right\}.$$

*Effect of Values of  $K(\text{SH}_2\text{D})$ ,  $K(\text{SHD}_2)$  and  $K(\text{HDO})$  on  $\varphi(\text{SH}_3)$*

The dependence of the measured fractionation factor  $\varphi'(\text{SH}_3)$  on the equilibrium constants  $K(\text{SH}_2\text{D})$ ,  $K(\text{SHD}_2)$  and  $K(\text{HDO})$  can be discussed in terms of a relative fractionation factor  $\varphi_r(\text{SH}_3)^6$ , for which an expression is here derived.

The limit value for the fractionation factor  $\varphi'(\text{SH}_3)$  (v. eqn. 13), when the deuterium content of water approaches zero, is given by eqn. (15). In the previous paper<sup>3</sup>, an expression (16) was given for the relative fractionation factor  $\varphi_r(\text{SH})$  of a substrate with one exchangeable hydrogen. When comparing eqns. (16) and (13), it can be seen that the last factor of eqn. (13) can be replaced by  $2K(\text{HDO})^{-1} \varphi_r(\text{SH})$ .

$$\lim_{x(\text{D}_2\text{O}) \rightarrow 0} \varphi'(\text{SH}_3) = \varphi_0(\text{SH}_3) = \frac{2}{3} K(\text{HDO})^{-1} K(\text{SH}_2\text{D}) \cdot \varphi(\text{SH}_3), \quad (15)$$

$$\varphi_r(\text{SH}) = \frac{1}{2} K(\text{HDO}) \frac{K(\text{HDO}) \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + 2}{2 \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + K(\text{HDO})} \quad (16)$$

Dividing eqn. (13) by eqn. (15), an expression (17) is obtained for the relative fractionation factor  $\varphi_r(\text{SH}_3)$ .

$$\frac{\varphi'(\text{SH}_3)}{\varphi_0(\text{SH}_3)} = \varphi_r(\text{SH}_3) = 3K(\text{SH}_2\text{D})^{-1} \varphi_r(\text{SH})$$

$$\frac{3 \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \varphi(\text{SH}_3)^2 + 2K(\text{SHD}_2) \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) + K(\text{SH}_2\text{D})}{3 + 2K(\text{SH}_2\text{D}) \left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) + K(\text{SHD}_2) \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \varphi(\text{SH}_3)^2} \quad (17)$$

As in the case of the deuterium fractionation between  $\text{SH}_2$  and water,<sup>3</sup> an accurate determination of the deuterium – protium ratio in the equilibrated  $\text{SL}_3$  by the NMR method is quite difficult at higher solvent deuterium content. With the increasing deuterium content of the substrate, the NMR integral ratio for  $\text{SL}_3$  is even more unfavourable than it is for  $\text{SL}_2$ . In addition, only one model for  $\text{SH}_3$  was examined in this work. Therefore, in the following, the dependence of the fractionation factor  $\varphi'(\text{SH}_3)$  on the deuterium content of solvent water is illustrated by giving some different values for  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$ . A value of  $3.76^{\dagger}$  is used for  $K(\text{HDO})$ .

If the RGM were valid for the isotope disproportionation equilibria (1), (2) and (3),  $\varphi'(\text{SH}_3)$  would be a constant and the relative fractionation factor  $\varphi_r(\text{SH}_3)$  would be unity over the whole range of  $x(\text{D};\text{L}_2\text{O})$ . Using the value of 0.833 computed for  $\varphi(\text{SH}_3)$  from eqn. (10), the relative fractionation factor  $\varphi_r(\text{SH}_3)$  was calculated from eqn. (17) with different values for  $K(\text{SH}_2\text{D})$  and

$K(\text{SHD}_2)$ . The values used in the calculations are:  $K(\text{SH}_2\text{D}) = 2.77$  and  $K(\text{SHD}_2) = 2.94$ , which are the values obtained in this work for  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  separately from eqn. (10),  $K(\text{SH}_2\text{D}) = 2.73$  and  $K(\text{SHD}_2) = 2.96$ , which are the lower and higher error limits of  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  respectively,  $K(\text{SH}_2\text{D}) = 2.81$  and  $K(\text{SHD}_2) = 2.92$  which are the higher and lower error limits of  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  respectively, obtained in this work. The relative fractionation factor  $\varphi_r(\text{SH}_3)$  was also calculated assuming that  $K(\text{SH}_2\text{D}) = K(\text{SHD}_2) = K(\text{SL}_3) = 2.85(6)$  and  $\varphi(\text{SH}_3) = 0.840$  which are the values computed from eqn. (14). The calculated values of  $\varphi_r(\text{SH}_3)$  are listed in Table 2.

The maximum value of  $|1 - \varphi_r(\text{SH}_3)|$  presents the greatest error introduced into the values of  $\varphi(\text{SH}_3)$  by neglecting the deviations from the RGM in the isotope disproportionation equilibria (2) and (3). The error seems to increase the more the values of  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  differ from each other. From Table 2, it can also be seen that

Table 2. Relative fractionation factor  $\varphi_r(\text{SH}_3)$  calculated with different values for equilibrium constants  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)^a$

$x(\text{D};\text{L}_2\text{O})^b$	$\varphi_r(\text{SH}_3)$					
	$K(\text{SH}_2\text{D}) = 2.77$ $K(\text{SHD}_2) = 2.94$	2.73 2.96	2.81 2.92	2.79 2.79	2.85 2.85	2.91 2.91
0.1	1.015	1.022	1.011	1.006	1.002	0.999
0.2	1.031	1.042	1.020	1.013	1.005	0.998
0.3	1.043	1.059	1.029	1.020	1.008	0.997
0.4	1.053	1.072	1.035	1.027	1.012	0.997
0.5	1.060	1.081	1.041	1.036	1.016	0.997
0.6	1.064	1.086	1.044	1.045	1.020	0.997
0.7	1.065	1.085	1.045	1.054	1.025	0.997
0.8	1.061	1.079	1.043	1.065	1.030	0.998
0.9	1.053	1.067	1.039	1.076	1.036	0.998

<sup>a</sup> $K(\text{HDO}) = 3.76^{\dagger}$ . The values of  $\varphi_r(\text{SH})$  needed in the calculation of  $\varphi_r(\text{SH}_3)$  are given in the earlier paper.<sup>1</sup>

<sup>b</sup> $x(\text{D};\text{L}_2\text{O})$  is the deuterium isotope mole fraction of water.

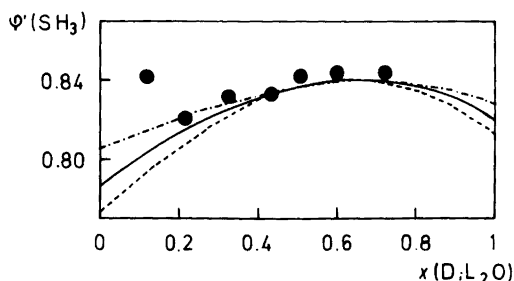


Fig. 1. Dependence of fractionation factor  $\varphi'(\text{SH}_3)$  upon the deuterium isotope mole fraction of water,  $x(\text{D};\text{L}_2\text{O})$ , with different values for equilibrium constants  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$ . At solvent composition of  $x(\text{D};\text{L}_2\text{O}) = 0.5$ , the value of  $\varphi'(\text{SH}_3)$  was in each case fixed at 0.837, the mean value of the experimental fractionation factors measured for 3,3-dimethyl-2-butanone (Table 1). The other values of  $\varphi'(\text{SH}_3)$  for drawing the curves in the above figure were calculated using the  $\varphi_i(\text{SH}_3)$  values given in Table 2. The circles represent the experimental  $\varphi'(\text{SH}_3)$  values from Table 1.

----- =  $K(\text{SH}_2\text{D}) = 2.81$ ,  $K(\text{SHD}_2) = 2.92$   
 ————— =  $K(\text{SH}_2\text{D}) = 2.77$ ,  $K(\text{SHD}_2) = 2.94$   
 ..... =  $K(\text{SH}_2\text{D}) = 2.73$ ,  $K(\text{SHD}_2) = 2.96$ .

the deviations from the RGM in the hydrogen isotope disproportionation in  $\text{L}_2\text{O}$  and  $\text{SL}_3$  cancel each other almost completely when  $K(\text{SH}_2\text{D}) = K(\text{SHD}_2) = 2.91$ , which is a value involving about the same degree of deviation from the

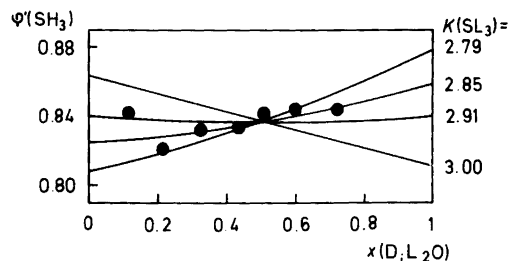


Fig. 2. Dependence of fractionation factor  $\varphi'(\text{SH}_3)$  upon the deuterium isotope mole fraction of water,  $x(\text{D};\text{L}_2\text{O})$ , with different values for  $K(\text{SL}_3)$ , assuming  $K(\text{SH}_2\text{D}) = K(\text{SHD}_2)$ . At solvent composition of  $x(\text{D};\text{L}_2\text{O}) = 0.5$ , the value of  $\varphi'(\text{SH}_3)$  was in each case fixed at 0.837, the mean value of the experimental fractionation factors measured for 3,3-dimethyl-2-butanone. Other values of  $\varphi'(\text{SH}_3)$  for drawing the lines in the above figure were calculated using the  $\varphi_i(\text{SH}_3)$  values given in Table 2. The circles represent the experimental  $\varphi'(\text{SH}_3)$  values measured for 3,3-dimethyl-2-butanone (Table 1).

RGM value 3 as the value 3.76<sup>1</sup> for  $K(\text{HDO})$  from the RGM value 2. In such cases, the errors introduced into the values of  $\varphi(\text{SH}_3)$  are negligible.

Fig. 1 illustrates the dependence of the fractionation factor  $\varphi'(\text{SH}_3)$  upon the deuterium isotope mole fraction of water,  $x(\text{D};\text{L}_2\text{O})$ , with different values for equilibrium constants  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$ . The dependence of  $\varphi'(\text{SH}_3)$  upon  $x(\text{D};\text{L}_2\text{O})$ , calculated on the assumption that  $K(\text{SH}_2\text{D}) = K(\text{SHD}_2)$  is illustrated in Fig. 2. If  $K(\text{SH}_2\text{D})$  and  $K(\text{SHD}_2)$  are given the RGM value 3, the deviations from the RGM would be confined to the solvent water, and the relative fractionation factor  $\varphi_i(\text{SH}_3)$  would be the same as  $\varphi_i(\text{SH})$ . The dependence of  $\varphi'(\text{SH}_3)$  upon  $x(\text{D};\text{L}_2\text{O})$  would also be the same as for the fractionation of a single hydrogen site, the greatest error being about 6%. The correction of  $\varphi'(\text{SH}_3)$  to obtain  $\varphi(\text{SH}_3)$  would be the same as that of  $\varphi'(\text{SH})$  given in the previous paper.<sup>1</sup> From Figs. 1 and 2, it can be seen that the dependence of  $\varphi'(\text{SH}_3)$  upon  $x(\text{D};\text{L}_2\text{O})$  does not support any great deviations from the RGM. However, since small deviations exist and since the cancellation of the deviations between the isotope disproportionation equilibria of substrate and solvent water may not be complete, it is preferable to carry out the fractionation factor measurements at a solvent composition close to  $x(\text{D};\text{L}_2\text{O}) = 0.5$  rather than at either end of the  $x(\text{D};\text{L}_2\text{O})$  range to obtain the value of the equilibrium constant  $\varphi(\text{SH}_3)$  of the fractionation reaction (4).

**Acknowledgements.** Financial aid from the Emil Aaltonen Foundation, and from the Finnish Cultural Foundation is gratefully acknowledged.

## References

1. Scharlin, P. *Acta Chem. Scand. A* 36 (1982) 117.
2. Scharlin, P. *Acta Chem. Scand. A* 38 (1984) 275.
3. Scharlin, P. *Acta Chem. Scand. A* 38 (1984) 529.
4. Bigeleisen, J. *J. Chem. Phys.* 23 (1955) 2264.
5. Kresge, A. J. and Chiang, Y. *J. Chem. Phys.* 49 (1968) 1439.
6. Gold, V. *Trans. Faraday Soc.* 64 (1968) 2770.
7. Salomaa, P. *Acta Chem. Scand.* 23 (1969) 2095.
8. More O'Ferrall, R. A., Koepl, G. W. and Kresge, A. J. *J. Am. Chem. Soc.* 93 (1971) 9.
9. Van Hook, W. A., *Chem. Commun.* (1972) 479.
10. Bron, J., Chang, C. F. and Wolfsberg, M. Z. *Naturforsch. Teil A* 28 (1973) 129.

Received January 6, 1986.