Sucrose Inversion in H2O – D2O

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Sucrose Inversion in $H_2O - D_2O$

Kinetic studies in $H_2O - D_2O$ on the mutarotation of glucose,[1] the decomposition of nitramide[2] and the hydrogen ion catalyzed inversion of sucrose,[3, 4] for which the ratios k_{D_2O}/k_{H_2O} are about 1 : 3.8, 1 : 6, 2.1 : 1, respectively, show that the velocity constant $k_{H_2O-D_2O}$ does not vary linearly with the fraction of heavy water, $F_{D_2O} = \Delta s/0.1079$. The negative departure from linearity, which all exhibit, increases in the above order. Since $k_{H_2O-D_2O}$ probably depends only indirectly upon the medium it is important to consider other substances which may be present in isotopic modifications and kinetically significant.
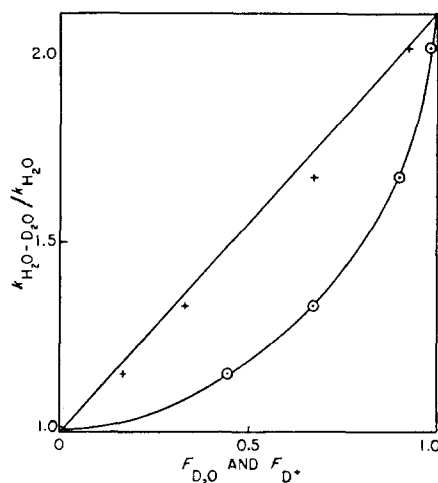

Fig. 1.

Since the inversion of sucrose in H_2O is catalyzed specifically by H^+ it seems likely that a simple relationship will exist between $k_{H_2O-D_2O}$ and the fraction of heavy hydrogen ion $F_{D^+} = (D^+)/(D^+)+(H^+)$. In Table I the first two columns give the data[3, 4] reported for this reaction and values of F_{D^+} in the third column are obtained from the equilibrium constant $K_1 = 15.7$[5] for the exchange reaction

$$H_2O + 2D^+ = D_2O + 2H^+. \qquad (1)$$
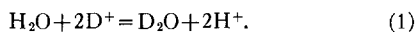
It will be seen from the graph that a plot of $k_{H_2O-D_2O}/k_{H_2O}$ vs. F_{D^+} gives a nearly straight line (crosses), for an extrapolated value of 2.1 for k_{D_2O}/k_{H_2O}.

This is a specific application of a more general method which has already been applied to explain kinetic measurements on the mutarotation of glucose.[1] It may be applied to sucrose inversion without the necessity of identifying any substance, on the simple assumption that $k_{H_2O-D_2O}/k_{H_2O}$ varies linearly with the fraction $F_X = DX/HX+DX$ of some reactant or intermediate involved in the process of inversion. For each measured $k_{H_2O-D_2O}/k_{H_2O}$ there is an experimental F_{D_2O} and a corresponding F_X, which is obtained on the basis of the assumed linear dependence

$$F_X = [(k_{H_2O-D_2O})/k_{H_2O} - 1]/1.1. \qquad (2)$$

For any F_{D_2O} the corresponding $R_w = (HDO)/(H_2O)$ is simply calculated, and $R_X = (HX)/(DX) = 1 - F_X/F_X$. Since $R_x R_w = K_x = K_3$ for the reaction

$$DX + H_2O = HX + HDO. \qquad (3)$$

Constancy of K_x values over the range $H_2O - D_2O$ is a satisfactory test for the assumption made, as the last column of the table shows. Although it has been possible to identify K_x in the present instance with K_4 for the equilibrium (4)

$$D^+ + H_2O = H^+ + HDO, \quad K_4 = 7.2 \; [6] \qquad (4)$$
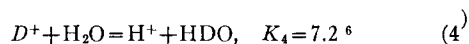
and in the previous example with the isotopic equilibrium constant for tetramethyl glucose, it can obviously be applied independently of any assumptions concerning the identity of HX and without foreknowledge of K_x. The method is not restricted to kinetic measurements.

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[1] Hamill and La Mer, J. Chem. Phys. **4**, 144 (1936).
[2] La Mer and Greenspan, unpublished measurements.
[3] Moelwyn-Hughes and Bonhoeffer, Naturwissenschaften **22**, 174 (1934).
[4] Gross, Suess and Steiner, ibid. **22**, 662 (1934).
[5] La Mer and Korman, preliminary measurements by E.M.F., unpublished.
[6] From (1) and $(HDO)^2/(D_2O)(H_2O) = 3.27$.

A New Comparison of the Viscosity of D_2O with that of H_2O

In an attempt to find a basis for comparison of the viscosity of D_2O with that of H_2O that might aid in explaining the observed difference,[1] it was noticed that at 15, 20, 25, 30 and 35°C, respectively, the viscosity of D_2O is almost the same as that of H_2O at a temperature 8.5° lower; or if $\eta_{H_2O} = f(T)$, then $\eta_{D_2O} = f(T - B)$ where f is the same function in both cases, and B is approximately 8.5°. This would explain the observed decrease in the ratio η_{D_2O}/η_{H_2O} with increasing temperature.[2] Several other physical properties of the two waters show somewhat analogous variations, e.g., the melting point of D_2O is 3.8°C,[3] and the temperature of maximum density for D_2O is 11.6°C,[4] 7.6° higher than that of H_2O.

The data are summarized in Table I. Column 1 gives the temperature, column 2 the viscosity of H_2O in millipoises,[5] column 3 the ratio η_{D_2O}/η_{H_2O},[2] and column 4 the viscosity

Table I.

$\dfrac{\Delta s}{0.1079}$	$\dfrac{k_{H_2O}-D_2O}{k_{H_2O}}$	F_{D^+}	(H_2O)	(HDO)	$\dfrac{(HDO)}{(H_2O)}$	F_x	R_x	K_x
0.000	1.00	0.000						
0.444	1.15	0.169	17.84	25.92	1.45	0.14	6.2	8.9
0.671	1.33	0.332	6.57	23.32	3.54	0.30	2.3	8.3
0.90	1.67	0.677	0.65	9.78	15.0	0.61	0.64	9.6
0.981	2.01	0.921	0.025	2.10	84	0.92	0.087	7.3
1.000	(2.10)	1.000						

TABLE I. *The viscosity of D_2O compared with that of H_2O.*

T (°C)	η_1 Viscosity[1] of H_2O (milli-poises)	η_2^2/η_1[2]	η_2 Viscosity of D_2O (mp)	η_1 compare with previous column	$(1/\eta_1)^{0.5}$ exp.	$(1/\eta_1)^{0.5}$[3] calc.	$(1/\eta_2)^{0.5}$ exp.	$(1/\eta_2)^{0.5}$[4] calc.
−4	20.5				7.0	7.0		
0	17.93_8				7.47	7.52		
5	15.18_8	1.309	19.88		8.11	8.13	7.09	7.09
−3.5				20.1				
10	13.09_7	1.286	16.85		8.74	8.74	7.71	7.70
1.5				17.02_5				
15	11.44_7	1.267	14.50		9.35	9.35	8.30	8.31
6.5				14.50_4				
20	10.08_7	1.249	12.60		9.96	9.96	8.91	8.92
11.5				12.56_0				
25	8.94_9	1.232	11.03		10.57	10.57	9.52	9.53
16.5				11.01_4				
30	8.00_4	1.215	9.73		11.18	11.18	10.14	10.14
21.5				9.72_4				
35	7.20_8	1.198	8.64		11.78	11.79	10.76	10.75
26.5				8.64_8				

[1] *International Critical Tables.*
[2] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933).
[3] $(1/\eta_1)^{0.5}_{calc.} = 0.122T + 7.52$.
[4] $(1/\eta_2)^{0.5}_{calc.} = 0.122T + 6.48$.

of D_2O. In columns 4 and 5 the viscosity of D_2O at several temperatures is compared with that of H_2O at a tempera-ture 8.5° lower. The agreement of the viscosity of D_2O at temperatures between 15° and 35° with the corresponding H_2O viscosity is very satisfactory. At the two lowest temperatures, 5° and 10°, respectively, D_2O has the same viscosity as H_2O at a temperature 8.2° lower.

To facilitate comparisons, $(1/\eta)^{0.5}$, which varies almost linearly with temperature, was plotted as a function of temperature. The values of $(1/\eta)^{0.5}$ for H_2O and D_2O, calculated from the experimental data are shown in columns 6 and 8, respectively. The values calculated from the equations $(1/\eta_1)^{0.5}_{calc.} = 0.122T + 7.52$, and $(1/\eta_2)^{0.5}_{calc.} = 0.122(T-8.5) + 7.52 = 0.122T + 6.48$ are given in columns 7 and 9. These equations are purely empirical and do not hold at temperatures much above 35°C, but do show the relations $\eta_1 = f(T)$ and $\eta_2 = f(T-8.5)$ for the range 5° to 35°C.

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[1] Most recent determination, $\eta_{D_2O}/\eta_{H_2O} = 1.22996$ at 25°C, Jones and Fornwalt, J. Chem Phys. **4**, 30 (1936).
[2] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933).
[3] La Mer and Baker, J. Am. Chem. Soc. **56**, 2641 (1934).
[4] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 3057 (1933).
[5] *International Critical Tables.*