Transfer of Individual Ions from H_2O to D_2O. Gibbs Energy of Transfer of Dimethylmaleate Ion

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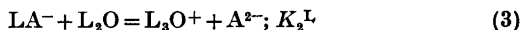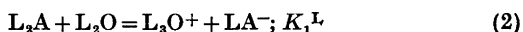Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50, Finland

The Gibbs energy of transfer of dimethylmaleate ion from light to heavy water was determined using appropriate assumptions. This determination comprised the measurements of the first and second acidity constants of dimethylmaleic acid and the dehydration constant of the acid both in H_2O and D_2O. The evaluation of the transfer free energy of dimethylmaleate ion from H_2O to D_2O was based on the separation of transfer and exchange effects in the equilibria of dimethylmaleic acid dissociation in light and heavy water. The contributions of cations Ag^+ and Ba^{2+} to the Gibbs energy of transfer were estimated on the basis of the solubilities of silver and barium dimethylmaleates in H_2O and D_2O.

The thermodynamics of transfer of solutes from one solvent to another gives valuable information about the structure of the solutions. Considering electrolytes as solutes, the assignment of the Gibbs energy of transfer to contributions of individual ions can be made using appropriate extrathermodynamic assumptions.[1] Most common methods of evaluation, in this context, are the tetraphenylarsonium – tetraphenylboride, the large anion – large molecule, the large cation – large molecule assumptions and the modifications of the Born equation. Furthermore, depending on the solutes in question some special ways to estimate these ionic contributions are available.
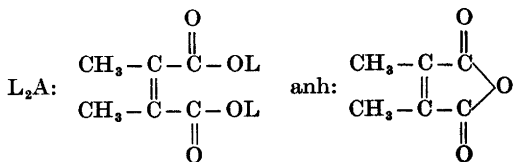
Taking the $H_2O - D_2O$ system as an example, the most reliable results, perhaps, have been obtained by using certain specific procedures. One among the first methods of estimation was to pay no attention to the contribution of cations in the Gibbs energy of transfer.[2] One useful assumption is to neglect the Gibbs energy of transfer of the L_3O^+ ion (L = H or D) from

light to heavy water.[3] This assumption seems reasonable considering the structural features of the system. The other method is to apply suitable acid – base equilibria in H_2O and D_2O.[4] These equilibria must be abnormal in the sense that the isotopic exchange effects can be eliminated from the equations derived for the total isotope effect. This method has been succesfully applied to carbonic and sulfurous acids to evaluate the Gibbs energy of transfer of carbonate and sulfite ions.[4] To determine the Gibbs energy of transfer of dimethylmaleate ion we shall apply a similar method.

Three equilibria (1) – (3) exist for dimethylmaleic acid

$$L_2A = anh + L_2O; \quad K_d{}^L \tag{1}$$

$$L_2A + L_2O = L_3O^+ + LA^-; \quad K_1{}^L \tag{2}$$

$$LA^- + L_2O = L_3O^+ + A^{2-}; \quad K_2{}^L \tag{3}$$

in water. In these three equations the abbreviations presented below are used. It must also be noticed that L denotes either H or D. From

$$L_2A: \quad \begin{matrix} O \\ \parallel \\ CH_3 - C - C - OL \\ \parallel \\ CH_3 - C - C - OL \\ \parallel \\ O \end{matrix} \qquad anh: \quad \begin{matrix} O \\ \parallel \\ CH_3 - C - C \\ \parallel \qquad \qquad \rangle O \\ CH_3 - C - C \\ \parallel \\ O \end{matrix}$$

the derived equations for the isotope effects of the equilibrium constants, the isotopic fractionating factors, ϕ_1 for L_2A and ϕ_2 for LA^-, can be eliminated. Assuming the Gibbs energy of transfer to be zero for the L_3O^+ ion, the transfer effect for the dianion, A^{2-}, can be evaluated. The generally accepted value of 0.69

(with three significant figures 0.686) [4] for l, the isotopic fractionating factor of the L_3O^+ ion, is needed in the calculations.[5a] To get the cationic contributions to the Gibbs energy of transfer, the solubilities of silver and barium dimethylmaleates in light and heavy water were measured.

EXPERIMENTAL

Reagents. Heavy water with a deuterium mol fraction of 0.998 was purchased from Norsk Hydro. Light water was distilled water. Both waters were boiled under reduced pressure to eliminate dissolved gases. The dimethylmaleic anhydride was a *purissimum* product delivered by Fluka AG. Its purity was found to be (99.8 ± 0.4) % when titrated against a standard solution of NaOH. The preparation of the silver and barium salts of dimethylmaleic acid was carried out by first synthesizing potassium dimethylmaleate. From it and $AgNO_3$ and $BaCl_2$ the wanted salts could be precipitated in water solution.[6–8] The purities were 100.0 % for the silver salt determined by ignition and weighing, and 99.6 % for the barium salt determined by titration of the anion.

The other reagents were of analytical grade and were used as received.

Methods. The dehydration constant of dimethylmaleic acid was determined kinetically by the method described by Eberson.[9] The kinetics were followed by a Unicam UV Spectrophotometer SP 1700 using a wavelength of 256 nm where the anhydride has its maximum absorption.

If the rate constant for the forward reaction (1) is denoted by k_1 and that for the reverse reaction, k_{-1}, the observed rate constant can be presented by eqn. (4). Here c_L denotes the lyonium ion concentration. The dehydration

$$k_{exp} = k_{-1} + \frac{k_1}{1 + K_1^L(1/c_L) + K_1^L K_2^L(1/c_L)^2} \quad (4)$$

constant, K_d^L, can be expressed by the aid of the rate constants as k_1/k_{-1}. It can be concluded on the basis of eqn. (4) that $k_{exp} = k_{-1}$ when c_L is sufficiently low. For calculations eqn. (4) can be modified to a more suitable form (5). The approximative value for $1/K_d^L$ can be evaluated

$$\frac{1}{(k_{exp}/k_{-1}) - 1} = \frac{1}{K_d^L} + \frac{K_1^L}{K_d^L}(1/c_L) + \frac{K_1^L K_2^L}{K_d^L}(1/c_L)^2 \quad (5)$$

by determining k_{exp} when the lyonium concentration is relatively high. The best value for k_{-1} is then calculated from eqn. (5) using an iterative procedure. The ionic strength of the buffer solutions which regulated c_L was 0.0100

mol dm^{-3}. Adjusting the ionic strength did not affect the results more than did experimental errors.

The first acidity constant of dimethylmaleic acid was determined by the method of potentiostatic titration. A more detailed description of the method has been presented earlier.[10,11] The measurable (apparent) first acidity constant has, owing to the dehydration equilibrium, the form expressed by eqn. (6). It was our aim to determine both the first and the

$$K_1^L(\text{app}) = K_1^L/(1 + K_d^L) \quad (6)$$

second acidity constants by potentiostatic titration. However, the accuracy of the method was not sufficiently high in the region of the second constant. Therefore, the first constant was determined considering the acid as monobasic with the degree of deprotonation having values between 0.15 and 0.38. The highest value of the ionic strength in the measurements was about 0.012 mol dm^{-3} at the end of the titration. The titration mixture contained 0.0100 mol dm^{-3} of KCl.

The second acidity constant was determined by measuring the pL values of buffer solutions prepared of NaOH solution and the acid. The procedure was similar to that applied earlier.[12] The ionic strength of the buffers with different acid/anion ratios was regulated to 0.0100 mol dm^{-3} both in H_2O and D_2O. The value given by the fifty-fifty buffer was chosen to be used in further calculations. The deuterium oxide correction for the glass electrode was that presented earlier.[13] The measurements were carried out on a digital pH-meter constructed in our laboratory using a combined glass silver − silver chloride electrode by Metrohm.

The solubilities were determined in sealed conical flasks kept in a thermostated water bath. The flasks were covered to prevent the possible decomposition of solutes by light. A Lauda thermostat was employed to control the temperature within 298.15 ± 0.10 K in all measurements (including those of the equilibrium constants). The contents of the flasks could be stirred with a magnetic stirrer. The time for equilibration was 10 days. The samples were taken through a glass wool layer by a pipette, transferred to weighing glasses, weighed and analyzed. The methods of analysis of the amounts of solutes were as follows. The total amount of acid and anhydride was titrated by potentiometric titration with a standard solution of NaOH. A sample of barium dimethylmaleate solution was evaporated and the residue weighed. The weighed samples of silver dimethylmaleate solutions were titrated potentiometrically using a standard NaI solution and silver and mercurous sulfate electrodes.

The activity corrections for the constants, *i.e.* for the acidity constants and the solubility products, were made by the Debye-Hückel extrapolation (7). In this equation the symbols

$$-\log y_\pm = \frac{z_+ z_- A I^{1/2}}{1 + (Ba)I^{1/2}} \qquad (7)$$

have their usual definitions. Constant A has values of 0.5107 and 0.5140 in H$_2$O and D$_2$O, respectively. Ionic size parameter (Ba) has a value of 1.65 for the barium salt and 1.24 for the silver salt in both waters.[13] The effect of the activity corrections was greatest on the solubility product of barium dimethylmaleate. In the other cases it could have been omitted. Where solely nonelectrolytes were handled, as in the calculations of dehydration constants, activity corrections were unnecessary.

RESULTS AND DISCUSSION

In the determination of the dehydration constants, $K_d{}^L$, the obtained first-order rate constants k_{exp} in H$_2$O and D$_2$O, respectively, are presented in Table 1. Applying the mean values in Table 1 the data were set to follow eqn. (5) by the aid of a program of least squares on a Wang 2200 computer. The obtained constants for eqn. (5) are reported in Table 2.

The apparent first acidity constants of dimethylmaleic acid in light and heavy water are collected in Table 3. The method of calculations was similar to that described earlier.[10] The second acidity constants of the acid are presented in Table 4 and the measured solubility data in Table 5.

The constants determined in this work are in good agreement with those reported earlier. Koskikallio reports for $K_d{}^H$ a value of 3.2 at 293 K and for p$K_1{}^H$ that of 3.2 at 313 K.[14] Eberson gives the values 5.3 for $K_d{}^H$ and 3.0 for p$K_1{}^H$ at 293 K.[9]

When equilibria (1) − (3) take place in light and heavy water the following equations, considering the isotopic exchange and medium, i.e. the transfer effects, are obtained:[15]

$$\frac{K_d{}^H}{K_d{}^D} = \phi_1{}^2 F_d \qquad (8)$$

$$\frac{K_1{}^H}{K_1{}^D} = \frac{K_1{}^H(\text{app})}{K_1{}^D(\text{app})} \frac{(1+K_d{}^H)}{(1+K_d{}^D)} = l^{-3} \phi_2{}^{-1} \phi_1{}^2 F_1 \qquad (9)$$

$$\frac{K_2{}^H}{K_2{}^D} = l^{-3} \phi_2 F_2 \qquad (10)$$

In the equations l is the isotopic fractionating factor for the L$_3$O$^+$ ion, ϕ_1 and ϕ_2 are the fractionating factors for L$_2$A and LA$^-$, respec-

Table 1. The observed first-order rate constants k_{exp} in H$_2$O and D$_2$O measured in various buffer solutions and at 298.15 K.

pL	H$_2$O $k_{exp}/(\text{ks})^{-1}$	D$_2$O $k_{exp}/(\text{ks})^{-1}$
	Buffer: LCl	
2.00	26.49(12) [a]	13.86(3) [a]
2.00	27.15(10)	13.93(4)
2.00	26.82(15)	13.65(4)
	26.82 [b]	13.81 [b]
	Buffer: Formic acid − formate	
3.00	17.54(4)	
3.00	17.49(6)	
3.00	17.34(6)	
	17.46 [b]	
3.30	12.68(6)	10.40(4)
3.30	12.75(4)	10.27(3)
3.30		10.37(4)
	12.71 [b]	10.35 [b]
3.50	10.53(4)	8.96(3)
3.50	10.26(4)	8.87(2)
3.50	10.45(3)	8.96(3)
	10.41 [b]	8.93 [b]
3.70	8.83(3)	7.60(1)
3.70	8.76(4)	7.64(3)
3.70	8.83(2)	
	8.81 [b]	7.62 [b]
3.90	7.29(5)	6.21(2)
3.90	7.57(4)	6.28(2)
3.90	7.78(3)	6.30(2)
	7.55 [b]	6.26 [b]
4.00	6.93(6)	5.58(2)
4.00	7.24(3)	5.58(2)
4.00	7.13(3)	5.59(2)
	7.10 [b]	5.58 [b]
4.10	6.69(2)	5.02(2)
4.10	6.74(5)	5.03(2)
4.10	6.64(2)	4.89(2)
	6.69 [b]	4.98 [b]
4.20	6.49(3)	4.52(2)
4.20	6.23(3)	4.57(2)
4.20	6.46(2)	4.44(2)
	6.37 [b]	4.53 [b]
	Buffer: Acetic acid − acetate	
5.20	5.17(3)	
5.20	5.14(1)	
5.20	5.23(1)	
	5.18 [b]	
5.80		2.13(1)
5.80		2.08(1)
5.80		2.14(1)
		2.12 [b]

[a] Standard errors in parentheses. [b] Mean values.

tively. The transfer terms include the transfer effects according to the following scheme:

F_d contains the transfer of
(1) L$_2$A from H$_2$O to D$_2$O

Table 2. The parameters calculated from eqn. (5) in H_2O and D_2O at 298.15 K.

Parameter	H_2O	D_2O
k_{-1}, ks^{-1}	5.043	2.098
$1/K_d^L$	0.2017(38)	0.1735(18)
K_1^L/K_d^L, mmol m^{-3}	[227.5(13)]	[40.81(58)]
$K_1^L K_2^L/K_d^L$, mmol^2 m^{-6}	[−22.53(8367)]	[197.7(353)]
corr. coeff.	0.99994	0.9998
K_d^L	4.958	5.764

Table 3. The apparent first acidity constants of dimethylmaleic acid in H_2O and D_2O determined by potentiostatic titration at 298.15 K.

H_2O Z^a	l^b/mol m^{-3}	pK_1^H(app)	D_2O Z^a	l^b/mol m^{-3}	pK_1^D(app)
0.2518	10.94	4.071	0.1678	10.59	4.565
0.2821	10.99	4.051	0.1909	10.62	4.566
0.3157	11.03	4.057	0.2269	10.68	4.572
0.3171	11.03	4.053			
0.3651	11.10	4.075			
		[4.061(7)]^c			[4.568(3)]^c

^{a} Degree of deprotonation. ^{b} Average ionic strength. ^{c} Mean values with their standard errors.

Table 4. The second acidity constants of dimethylmaleic acid in H_2O and D_2O determined by buffer method at 298.15 K.

Buffer ratio $(c_{LA^-}/c_{A^{2-}})$	pK_2^H	pK_2^D
0.250	6.036	6.636
0.500	6.010 ^{a}	6.606 ^{a}
0.750	6.010	6.617

^{a} Used in further calculations.

(2) anh from D_2O to H_2O
F_1 contains the transfer of
(1) L_2A from H_2O to D_2O
(2) LA^- from D_2O to H_2O
(3) L_3O^+ from D_2O to H_2O
F_2 contains the transfer of
(1) LA^- from H_2O to D_2O
(2) A^{2-} from D_2O to H_2O
(3) L_3O^+ from D_2O to H_2O

Assuming ideal conditions (this is justified, since the ionic strength lies in the magnitude of 0.01 mol dm^{-3} and since we are studying

differences) the F terms can be presented by eqns. (11) − (13) where c_H and c_D stand for concentrations in H_2O and D_2O, respectively. It must be noticed that the concentration ratios

$$F_d = (c_D/c_H)_{L_2A} \, (c_H/c_D)_{anh} \tag{11}$$

$$F_1 = (c_D/c_H)_{L_2A} \, (c_H/c_D)_{LA^-} \, (c_H/c_D)_{L_3O^+} \tag{12}$$

$$F_2 = (c_D/c_H)_{LA^-} \, (c_H/c_D)_{A^{2-}} \, (c_H/c_D)_{L_3O^+} \tag{13}$$

in equations (11) − (13) ought to be replaced by the corresponding (inverse) ratios of activity coefficients.[15] Here the above presentation is, however, practical because of the ideality assumption. Another assumption made in this work is that the transfer effects have similar magnitudes despite the isomeric isotopic form of the molecule transferred. This assumption seems to be valid, since the transferred molecules are relatively large. The explanations for the validity of this assumption for the L_3O^+ ion have been analyzed by Salomaa.[3]

The fractionating factors ϕ_1 and ϕ_2 can be eliminated from eqns. (8), (9), and (10) by simple operations to give eqn. (14). The product of the F terms, which gives the total transfer effect, can be presented with the aid of eqns.

Table 5. Solubilities of dimethylmaleic acid + anhydride, silver dimethylmaleate and barium dimethylmaleate in H_2O and D_2O at 298.15 K.

H_2O $s/10^{-3}$ mol dm^{-3}	pK_s^H	D_2O $s/10^{-3}$ mol dm^{-3}	pK_s^D
Acid + anhydride			
36.87		32.91	
36.93		32.86	
36.90 [a]		32.88 [a]	
Ag$_2$A			
1.758		1.492	
1.757		1.499	
1.758 [a]	7.6621	1.496 [a]	7.8731
	7.6717 [b]		7.8819 [b]
BaA			
36.26		24.00	
36.00		23.84	
36.19		24.00	
36.19 [a]	2.8828	23.95 [a]	3.2414
	3.8389 [b]		4.0856 [b]

[a] Mean values. [b] Extrapolated to zero ionic strength.

$$\frac{K_1^H(\text{app})}{K_1^D(\text{app})} \times \frac{(1+K_d^H)}{(1+K_d^D)} \times \frac{K_2^H}{K_2^D} \times \frac{K_d^D}{K_d^H} =$$
$$= l^{-6}F_d^{-1}F_1F_2 \qquad (14)$$

(11) − (13). By performing cancellations and assuming that $(c_H/c_D)_{L_3O^+} = 1$, eqn. (15) is obtained. The main source for the transfer

$$F_d^{-1}F_1F_2 = (c_D/c_H)_{\text{anh}}(c_H/c_D)_{A^{2-}} \qquad (15)$$

effect would thus be the transfer of the anhydride from H_2O to D_2O and that of the dimethylmaleate ion from D_2O to H_2O.

Finally, the transfer effect (16) for the dianion, A^{2-}, is obtained with the aid of eqns. (14) and (15).

$$(c_D/c_H)_{A^{2-}} = (c_D/c_H)_{\text{anh}}l^{-6} \times$$
$$\left[\frac{K_1^H(\text{app})}{K_1^D(\text{app})} \frac{(1+K_d^H)}{(1+K_d^D)} \frac{K_2^H}{K_2^D} \frac{K_d^D}{K_d^H}\right]^{-1} \qquad (16)$$

The Gibbs energies of transfers which were calculated with the aid of Tables 2, 3, 4, and 5 and eqn. (16) are reported in Table 6. It must be noticed that the value for $(c_D/c_H)_{\text{anh}}$ was calculated by the aid of the total acid − anhydride solubility, the respective dehydration, and the first acidity constants.

Qualitatively the standard Gibbs energies reported in Table 6 for individual ions confirm the earlier observations, *viz.* that univalent cations have transfer energies from light to heavy water which are slightly positive while

the energies for divalent cations are somewhat higher.[5b] Anions have Gibbs energies which are generally higher than those for cations.[5b] This agrees well with the fact that anions necessarily interact with isotopically different hydrogen atoms in H_2O and D_2O, while cations interact with similar oxygen atoms in both solvents. That the Gibbs energies of transfer of divalent cations are higher than those for monovalent cations may depend on their greater densities of charge, which force the water molecules to reorient in a higher degree than happens in the solutions of monovalent cations. The Gibbs energies of transfer for nonelectrolytes are either negative or positive depending on the polarity of their molecules or on the number of polar sites in their molecules.[16,17] The magnitude of

Table 6. The standard Gibbs energies of transfer of some dimethylmaleic acid derivatives from H_2O to D_2O at 298.15 K.

Compound	ΔG_t^θ/J mol^{-1}
Anhydride	292
Dimethylmaleate ion (= A^{2-})	975
Ag$_2$A	1200
BaA	1408
Ag$^+$	112
Ba^{2+}	433

the transfer free energy for the anhydride is reasonable considering the polar oxygen atoms in the anhydride molecule. The ΔG_t^0 values obtained here for Ag^+ and Ba^{2+} ions are lower than the values estimated earlier for these ions by applying inorganic salts and different assumptions. These earlier values range from 200 J mol^{-1} to 500 J mol^{-1} for the Ag^+ ion.[16-20] For the Ba^{2+} ion the value of 470 J mol^{-1} has been reported.[21]

The influence of the assumptions on the results is difficult to estimate. However, if the L_3O^+ ion would have a fixed transfer energy, it might be slightly positive. That would cause a certain increase in the value of the transfer energy of the A^{2-} ion. This brings about a decrease in the values of Gibbs energies of transfer for cations. This may be possible but hardly reliable. When thinking of the ideality assumption, we can only conclude that its influences are negligible compared to the experimental errors. This is because we are studying differences and both solvents greatly resemble each other.

There may be a systematic error in the obtained results that makes both cationic contributions a little lower than the earlier values. The standard errors which are evaluated on statistical basis range from 10 J mol^{-1} (Ag_2A) to 90 J mol^{-1} (Ba^{2+} ion). Of course, these experimental errors in this somewhat complicated procedure can be one reason for differences. The system itself is also different from that by which the earlier results have been determined. It can be thought that the differences rise from some specific details of this complicated inorganic−organic solute−solvent system. For instance, the calculation of the Gibbs energy of transfer for the anhydride is carried out on a generalized basis. In reality, the whole equilibrium (1) with the isotopic exchange reaction is transferred from light to heavy water. This may cause a certain unreliability in the estimated value of $(c_D/c_H)_{anh}$. It can hardly be assumed that the transfer effects of the acid and the anhydride would be of equal magnitude, because their structures differ distinctly. The exchange effect contributes a portion to this which is difficult to estimate. The relatively large activity corrections for the solubility product of BaA may be the cause to some extent of the unreliability of the obtained values. However,

making these corrections certainly increases the accuracy. Finally, it must be concluded that the procedure gives fairly good estimates of the ionic contributions of the Gibbs energy of transfer from light to heavy water.

It would be interesting to determine the Gibbs energies of transfer for alkali metal salts of dimethylmaleic acid, because the thermodynamics of transfer of alkali metal cations nowadays lies on a relatively firm basis. Great difficulties are encountered when choosing the method of determination, because the solubilities of the salts in question are too high for the saturated solutions to be assumed ideal.

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