Finally, by replacing a^2 by $1 - b^2$, one obtains

$$\Delta E_{mn}' = 2b^2\left\{IP_n - EA_m + (c_s^n)^2[q_r + 2(c_r^m)^2]\frac{\Gamma}{\epsilon} - (c_r^m)^2 q_s\frac{\Gamma}{\epsilon} - (c_r^m)^2(c_s^n)^2\Gamma\left(\frac{2}{\epsilon} - 1\right)\right\} + 4ab(c_r^m c_s^n \beta) - b^4\left[IP_n - EA_n + IP_m - EA_m - 2(c_r^m)^2(c_s^n)^2\Gamma\left(\frac{2}{\epsilon} - 1\right)\right] \quad (A1)$$

The interaction between all other combinations of orbitals can be found easily by a similar treatment.

Appendix II

Minimization of the electron transfer energy with respect to the variational parameters a and b is included here.

$$\Delta E_{mn} = \Delta E_{mn}' + \Delta solv_{mn}$$

where $\Delta E_{mn}'$ has the value derived in Appendix I and $\Delta solv_{mn}$ that of eq 5. The variational treatment applied to this expression leads to the following equation for the perturbational energy

$$\Delta E_{mn} = M(m,m) + M(n,n) + \sqrt{[M(m,m) - M(n,n)]^2 + 4M(m,n)^2}$$

where the matrix elements M are

$$M(m,m) = 0$$

$$M(n,m) = c_r^m c_s^n \beta$$

$$M(n,n) = IP_n - EA_m + (c_s^n)^2(q_r + 2(c_r^m)^2)\frac{\Gamma}{\epsilon} - (c_r^m)^2 q_s\frac{\Gamma}{\epsilon} - (c_r^m)^2(c_s^n)^2\Gamma\left(\frac{2}{\epsilon} - 1\right) - b^2\left[IP_n - EA_n + IP_m - EA_m - 2(c_r^m)^2(c_s^n)^2\Gamma\left(\frac{2}{\epsilon} - 1\right)\right] - \sum_s \frac{x_s(c_s^n)^2}{R_s}\left(1 - \frac{1}{\epsilon}\right)[q_s - 2b^2x_s(c_s^n)^2] + \sum_r \frac{x_r(c_r^m)^2}{R_r}\left(1 - \frac{1}{\epsilon}\right)[q_r + 2b^2x_r(c_r^m)^2]$$

and with the following transformations

$$E_m^* = IP_m + q_s(c_r^m)^2\frac{\Gamma}{\epsilon} - a^2\left[IP_m - EA_m - (c_r^m)^2(c_s^n)^2\Gamma\left(\frac{2}{\epsilon} - 1\right)\right] - \sum_r \frac{x_r(c_r^m)^2}{R_r}\left(1 - \frac{1}{\epsilon}\right)[q_r + 2b^2x_r(c_r^m)^2]$$

$$E_n^* = IP_n + [q_r + 2(c_r^m)^2](c_s^n)^2\frac{\Gamma}{\epsilon} - b^2\left[IP_n - EA_n - (c_r^m)^2(c_s^n)^2\Gamma\left(\frac{2}{\epsilon} - 1\right)\right] - \sum_s \frac{x_s(c_s^n)^2}{R_s}\left(1 - \frac{1}{\epsilon}\right)[q_s - 2b^2x_s(c_s^n)^2] \quad (A2)$$

The final perturbation energy becomes (after correction for double account of electron–electron interaction)

$$\Delta E_{mn} = E_n^* - E_m^* + b^2[(E_m^* - E_n^*)_{b^2} - (E_m^* - E_n^*)_{b^2=0}] + \sqrt{(E_m^* - E_n^*)^2 + 4(c_r^m)^2(c_s^n)^2\beta^2} \quad (A3)$$

When the perturbation is small, *i.e.*, $4\beta^2 << (E_m - E_n)^2$ and therefore $b^2 \rightarrow 0$, then this expression can be further reduced and approximated by

$$\Delta E_{mn} = \frac{2(c_r^m)^2(c_s^n)^2\beta^2}{E_m^* - E_n^*} \quad (A4)$$

Proton Magnetic Resonance Studies of Water as Hydrogen Donor to Tributyl Phosphate[1]

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Abstract: Proton magnetic resonance studies are reported of hydrogen bonding between water protons and tributyl phosphate (TBP) in carbon tetrachloride medium in the range 10–45°. When the mole fraction of water is below 2.0×10^{-3}, self-association of water is negligible, and the data are treated in a manner which permits the determination of the equilibrium constants K_1 and K_2 of the reactions $OH_2 + TPB = OH_2 \cdot TBP$ and $OH_2 \cdot TBP + TBP = OH_2 \cdot (TBP)_2$, respectively. The ratio of K_1 to K_2 increases with decrease in temperature, the ratios being 7 and 10 at 45 and 10°, respectively. The enthalpy changes on the hydrogen-bond formation are: $\Delta H_1 = -4.1 \pm 0.2$ kcal/mole and $\Delta H_2 = -2.0 \pm 0.3$ kcal/mole. The H_2O proton magnetic resonance of the $OH_2 \cdot (TBP)_2$ species appears to move to lower field with decrease in temperature.

Because of the predominance of water as a medium in living systems, the hydrogen-bonding properties of water have been of particular interest to chemists and biologists. As part of an extensive program in this laboratory on the use of the proton magnetic resonance

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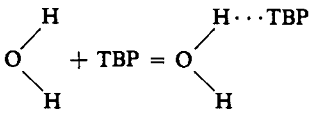
(pmr) method for study of water as a hydrogen donor,[2,3] this paper presents the results of water bonding to tributyl phosphate (TBP) in the temperature range 10 to 45°. TBP serves as a model for hydrogen bonding of OH_2 to the phosphoryl oxygen.

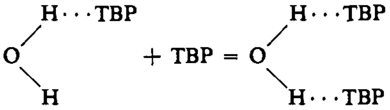
Another reason for the choice of TBP as hydrogen acceptor is that this compound has won very widespread use in extraction of metal ions from aqueous phase into an organic medium. In fact, Marcus[4] mentioned that the literature on TBP exploded to such an extent that a bibliography became obsolete while in preparation. The organic phase, however, contains water, and it becomes of importance to obtain thermodynamic parameters of the water–TBP interaction. Although many investigators have reported studies on the water–TBP system,[5–9] only Whitney and Diamond[6] obtained an equilibrium constant for the reaction

$$H_2O + TBP_{(o)} = H_2O\cdot TBP_{(o)} \qquad (1)$$

where (o) indicates the organic phase. The "H_2O" in eq 1 is erroneous, since water in aqueous phase is not monomeric. In our experiments, we use a three-component system consisting of carbon tetrachloride, TBP, and water, the water being at such low concentrations that its self-association becomes negligible. The results presented here represent the first time that thermodynamic equilibrium constants for the reactions



(2)



(3)

and the associated enthalpy changes on the hydrogen-bond formation have been determined.

Calculation of Equilibrium Constants. In our experiments water is the hydrogen donor at low concentrations (mole fraction in the range of $X_w = 0.0005$ to 0.02) in TBP–carbon tetrachloride mixtures. As the concentration of water increases, water polymerizes to a greater extent, resulting in a downfield shift of the water proton signal. In the limit of zero water concentration, $X_w = 0$, three species will be assumed: monomeric water; the 1:1 complex, $OH_2\cdot TBP$; and the 1:2 complex, $OH_2\cdot(TBP)_2$. The three species are considered to be in equilibrium according to eq 2 and 3. The characteristic pmr frequencies of the 1:1 and 1:2 complexes are designated ν_{11} and ν_{12}, respectively. The characteristic pmr frequency of monomeric water, ν_M, is taken to be the frequency of the water signal in "pure" carbon tetrachloride (in the range $X_w < 0.001$) and has been reported by Muller and Simon.[10]

Since hydrogen-bonding equilibria usually involve very rapid reactions, the frequency of the water protons at zero water concentration, ν_0, may be taken to be the weighted average of ν_M, ν_{11}, and ν_{12}, so that

$$\nu_0 = (X_M/X_w)_0\nu_M + (X_{11}/X_w)_0\nu_{11} + (X_{12}/X_w)_0\nu_{12} \qquad (4)$$

where $(X_M/X_w)_0$, $(X_{11}/X_w)_0$, and $(X_{12}/X_w)_0$ are the fractions of water present as monomeric water and the 1:1 and 1:2 complexes in the limit of zero water concentration, respectively, and $(X_M/X_w)_0 + (X_{11}/X_w)_0 + (X_{12}/X_w)_0 = 1$.

The equilibrium constants of eq 2 and 3 are given by the relations $K_1 = X_{11}/(X_M X_{TBP})$ and $K_2 = X_{12}/(X_{11}X_{TBP})$, so that

$$\begin{aligned}(X_{11}/X_w)_0 &= K_1X_{TBP}(X_M/X_w)_0 \\ (X_{12}/X_w)_0 &= K_2X_{TBP}(X_{11}/X_w)_0\end{aligned} \qquad (5)$$

If we further assume that ν_{11} is related to ν_{12} and ν_M by the relation

$$\nu_{11} = p\nu_{12} + (1 - p)\nu_M \qquad (6)$$

where p is a weighting factor and is an adjustable parameter, then combination of eq 4–6 yields

$$\nu_0 - \nu_M = \frac{(\nu_{12} - \nu_M)(pK_1X_{TBP} + K_1K_2X_{TBP}^2)}{1 + K_1X_{TBP} + K_1K_2X_{TBP}^2} \qquad (7)$$

This equation is similar to eq 7 of ref 10 for $p = 0.5$. The dependence of ν_0 on X_{TBP} at each temperature is then governed by the four parameters, ν_{12}, p, K_1, and K_2. Trial values of the four parameters were each adjusted until the difference between the observed frequencies and values calculated by eq 7 was minimized. Best values of ν_{12}, p, K_1, and K_2 were obtained in this manner using a CDC G-20 computer.

Experimental Section

Materials. TBP was washed with 4% aqueous sodium hydroxide solution, then with 0.1 *M* nitric acid solution, and finally with distilled water until the organic layer was clear and the washings were neutral. The washed product was distilled under reduced pressure. Carbon tetrachloride was Fisher Spectroanalyzed liquid. Both compounds were kept over molecular sieves.

Pmr Measurements. All the pmr spectra were obtained with a Varian Associates Model A-60 nmr spectrometer. Samples were prepared and transferred to 5-mm precision nmr tubes in an atmosphere of nitrogen, and the tubes were then immersed in liquid nitrogen, evacuated, and sealed. During the running of the spectra the temperature remained constant to within ±1°, as indicated by the separation in cycles per second between two peaks in ethylene glycol or methanol. TBP was used as an internal reference, because the addition of nonpolar tetramethylsilane (TMS) to hydrated or partially hydrated TBP precipitates water.[9] The frequency of the water protons was measured relative to the strongest line of the butyl CH_3 group to within ±0.2 cps, using the usual sideband calibration technique. To allow conversion of the data to a scale based on TMS, we examined a mixture of TBP and TMS dissolved in carbon tetrachloride and found the TBP peak at −55.5 cps relative to TMS. The frequency of this peak is essentially independent of the TBP:carbon tetrachloride ratio.

Results

The chemical shifts of the water proton signal at four temperatures are reported in Table I for several sets of samples, each with varying water concentrations at a fixed solvent composition, S, defined as

$$S = (\text{moles of TBP})/(\text{moles of TBP + moles of } CCl_4) \qquad (8)$$

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[2] F. Takahashi and N. C. Li, *J. Am. Chem. Soc.*, **88**, 1117 (1966).

[3] S. F. Ting, S. M. Wang, and N. C. Li, *Can. J. Chem.*, **45**, 425 (1967).

[4] Y. Marcus, *Chem. Rev.*, **63**, 139 (1963).

[5] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).

[6] D. C. Whitney and R. M. Diamond, *J. Phys. Chem.*, **67**, 209 (1963).

[7] J. W. Roddy and J. Mrochek, *J. Inorg. Nucl. Chem.*, **28**, 3019 (1966).

[8] C. J. Hardy, D. Fairhurst, H. A. C. MacKay, and A. M. Willson, *Trans. Faraday Soc.*, **60**, 1626 (1964).

[9] E. Bullock and D. G. Tuck, *ibid.*, **59**, 1293 (1963).

[10] N. Muller and P. Simon, *J. Phys. Chem.*, **71**, 568 (1967).

The data in Table I show no systematic variation of the chemical shift with varying water concentration below 2.0 × 10^{-3} mole fraction. This suggests that self-association of water is negligible in this concentration range, and therefore the average of the frequencies in this concentration range at any particular value of S may be taken to be ν_0, the limiting frequency at zero water concentration. The water proton signal moves downfield with increasing water concentration beyond 2.0 × 10^{-3} mole fraction, due to increasing self-association. Our result obtained at 8.3 × 10^{-2} mole fraction of water concentration, $S = 1$, and 21°, 181.6 cps, is in good agreement with the result of Bullock and Tuck,[9] 182.3 cps, at 9.1 × 10^{-2} mole fraction, $S = 1$, and 22°.

Table I. Chemical Shift of Water Protons as a Function of Composition and Temperature for Dilute Solutions of Water in TBP–Carbon Tetrachloride Mixtures

Solvent compn, S	Water concn, mf × 10^4	ν, cps downfield from TMS 10°	21°	35°	45°
0.044	5.90	139.0	131.7	122.6	115.5
	11.8	138.8	131.6	122.6	115.5
	17.3	138.7	132.1	122.5	115.6
0.062	6.98	146.5	139.6	131.2	124.6
	10.4	146.8	139.5	131.2	124.9
	16.2	146.8	139.6	131.1	124.9
	23.1		140.2	131.7	
	35.7		141.0	132.5	
	48.7		141.9	133.3	
0.081	4.97	152.1	145.8	137.3	130.6
	9.16	152.0	145.4	137.3	131.3
	18.5	152.1	145.6	137.3	130.8
0.115	8.11	158.3	152.4	143.9	138.2
	11.9	158.7	152.3	143.9	138.5
	15.1	158.6	152.4	144.2	138.5
	30.5		153.2	144.7	
	62.3		154.4	145.8	
	82.7		155.7	147.0	
	101		157.2	148.4	
0.165	4.52	164.1	158.3	149.5	145.2
	8.13	164.0	158.0	149.5	145.0
	18.8	164.0	158.3	149.6	145.3
	42.7		158.9	150.0	
	72.9		160.3	151.3	
	97.0		161.3	152.2	
	121		162.9	153.7	
0.30	7.35	172.8	166.7	160.5	155.3
	14.2	172.7	166.7	160.7	155.2
	19.2	172.8	166.9	160.3	155.1
	88.5		167.4	161.1	
	156		169.3	162.8	
	207		170.7	164.0	
	258		171.3	164.5	
0.46	5.26	177.1	172.2	165.5	160.3
	9.04	177.1	172.5	165.6	160.5
	18.1	177.4	172.4	165.6	160.4
	77.3		173.1	165.9	
	261	174.4	174.4	167.4	
	344		175.4	168.3	
	427		176.3	169.0	
0.74	6.33	180.2	175.8	169.3	164.5
	10.2	180.3	175.6	169.5	164.3
	16.7	180.1	175.7	169.4	164.7
	124		176.3	169.8	
	412		176.9	170.3	
	543		178.0	171.4	
	670		179.3	172.5	
1.00	7.05	182.1	177.9	172.0	167.3
	10.6	182.0	178.2	172.1	167.4
	17.4	182.0	178.0	171.9	167.3
	67.3		178.5	172.4	
	178		179.2	172.7	
	516		180.0	173.5	
	833		181.6	175.0	

Table II, column 2, gives the values of ν_M, obtained by linear interpolation of the measured water proton frequencies in carbon tetrachloride at different temperatures.[10] Although the signal moves linearly to higher fields as the temperature is raised, Muller and Simon ascribed this to a temperature dependence of the solvent effect of carbon tetrachloride on the water and not to water self-association effects.

Table II. Parameters Obtained for Water–TBP Bonding

Temp, °C	ν_M, cps	ν_{12}, cps	K_1	K_2	Std dev in ν_0, cps
45	63.5	173.5 ± 0.5	41 ± 1	6.0 ± 0.2	0.48
35	64.4	177.5 ± 0.5	50 ± 1	6.8 ± 0.2	0.71
21	65.4	183.0 ± 0.5	69 ± 2	7.8 ± 0.2	0.38
10	66.0	186.5 ± 0.5	93 ± 2	9.0 ± 0.3	0.30

Table II also lists the best values of ν_{12}, K_1, and K_2 at four temperatures. The best value of p at each temperature is 0.60 ± 0.02. The standard deviation between the observed ν_0 and the values calculated by eq 7 is listed in Table II, column 6. Figure 1 illustrates the agreement between calculated and observed shifts at four temperatures.

From plots of log K *vs.* $1/T$, the following enthalpy changes of reactions 2 and 3 are obtained: $\Delta H_1 = -4.1 \pm 0.2$ kcal/mole; $\Delta H_2 = -2.0 \pm 0.3$ kcal/mole. The values of ΔS are calculated from the known relationship between equilibrium constant, enthalpy, and entropy changes: $\Delta S_1 = -5.5$ eu; $\Delta S_2 = -2.7$ eu.

Discussion

Table II shows that ν_{12} decreases with increasing temperature, in agreement with the trend observed for carboxylic acids,[11] 2-propanol,[12] and 2-methyl-6-*t*-butylphenol.[13] Muller and Reiter[11] suggest that the nmr frequency of the complexed species, ν_c, depends quite strongly on the degree of excitation of the hydrogen-bond-stretching vibrational mode. They reason that, because this is an unusually low-frequency motion, several excited states are significantly populated even at temperatures as low as 200°K, and their calculations do show a temperature dependence of ν_c. It must be mentioned here that Muller and Simon[10] conclude that the possible variation of the hydrogen-bond shift in the dioxane–water–carbon tetrachloride system with temperature could not be accurately determined, and that Takahashi and Li[2] assume that $(\nu_{12} - \nu_{11})$ is approximately independent of temperature in their study of water bonding to tetrahydrofuran, acetone, and N,N-dimethylacetamide.

The ratio of K_1 to K_2 varies from 7 at 45° to 10 at 10°, mainly as a result of a difference of 2 kcal/mole between ΔH_1 and ΔH_2. It is interesting to note that Takahashi and Li[2] postulate that K_2 would be about an order

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(11) N. Muller and R. C. Reiter, *J. Chem. Phys.*, **42**, 3265 (1965).
(12) F. Takahashi and N. C. Li, *J. Phys. Chem.*, **68**, 2136 (1964).
(13) F. Takahashi and N. C. Li, *ibid.*, **69**, 1622 (1965).

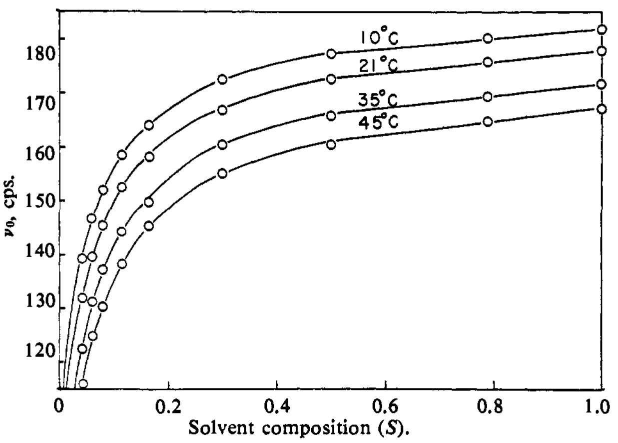

Figure 1. Plots of ν_0 vs. solvent composition S (eq 8) at four temperatures. The solid curves represent calculated values using parameters from Table II, $p = 0.60$, and letting $X_{TBP} = S$ in eq 7.

smaller than K_1, and that Muller and Simon[10] find that the ratio of K_1 to K_2 in the water–dioxane–carbon tetrachloride system is about 15:1 at room temperature and increases slightly with decreasing temperature. The larger K_1 over K_2 may be accounted for by considering that when one of the water hydrogens is bonded to TBP, the water oxygen becomes more basic and the other hydrogen (nonbonded) loses its acidity and hence its hydrogen-donor strength.

The values of K_1 and K_2 listed in Table II were used to calculate the fraction of the total water present in each of the three forms: monomeric water, W, $TBP \cdot H_2O$, and $2TBP \cdot H_2O$, as a function of solvent composition. The results, presented graphically in Figure 2, show that the presence of uncomplexed water may be neglected for S larger than 0.6, and this is the assumption used by Takahashi and Li[2] in their study of water bonding to tetrahydrofuran, acetone, and N,N-dimethylacetamide. At smaller values of S, uncomplexed water begins to appear. It is appropriate to mention here that Mohr, *et al.*,[14] from the infrared spectra of water–base systems in carbon tetrachloride, found that at low base concentrations free water and a 1:1 water–base complex are present, whereas at higher base concentrations a 1:2 complex is formed.

From infrared evidence, Hardy, *et al.*,[8] conclude that TBP is a stronger hydrogen acceptor than dioxane. Comparison of our equilibrium constants listed in Table II for water bonding to TBP with the corresponding values reported by Muller and Simon[10] leads to the same conclusion, except that we now have a thermodynamic measure of comparison.

Whitney and Diamond[6] carried out experiments on the extraction of water into dilute TBP in carbon tetrachloride solutions and reported that the equilibrium constant of eq 1 is 0.15 l./mole at 23°, assuming that water in the aqueous phase is "H_2O." Actually, as has been pointed out by Luz and Yagil,[15] a water molecule in an aqueous solution is not a uniquely defined species, and in pure water molecules may form from one up to four hydrogen bonds with neighboring water molecules or may not be bonded at all. In order to go from eq 1 to eq 2, therefore, eq 9 needs to be considered

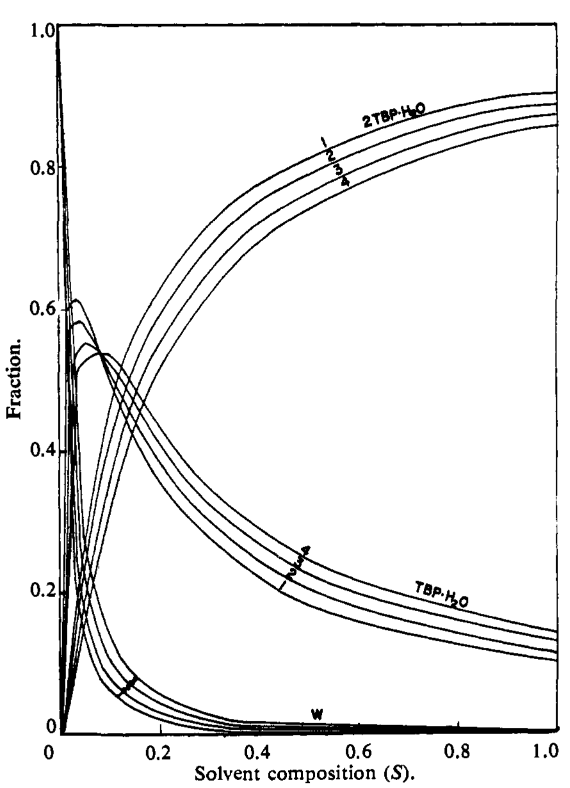

Figure 2. Fraction of water present as free monomer water (W), 1:1 complex ($TBP \cdot H_2O$), and 2:1 complex ($2TBP \cdot H_2O$) in dilute solutions of water in TBP–carbon tetrachloride mixtures, as a function of solvent composition at (1) 10°, (2) 21°, (3) 35°, (4) 45°.

$$(H_2O)_{\text{polymer}} = (H_2O)_{\text{monomer}} \quad K_{H_2O} \tag{9}$$

The equilibrium constant of eq 2, K_1, then is given by the relation

$$K_1 = 0.15/K_{H_2O} \text{ l./mole} \tag{10}$$

at 23°. K_{H_2O} at 23° can be calculated from the estimated values of $\Delta H°$ and $\Delta S°$ for the reaction polymer = monomer in liquid water given in Table V of ref 16 and takes on the values 0.05, 0.001, and 0.002, depending on the method used. From eq 10, K_1 therefore can have the values 3, 75, and 150 l./mole, all at 23°.

According to Table II, the K_1 value in the mole fraction scale is 69 at 21°. The molar equilibrium constant is calculated to be 6.6 l./mole and refers to eq 2. The value therefore is much higher than 0.15 l./mole obtained by Whitney and Diamond[6] which refers to eq 1, and not to eq 2. The "H_2O" in eq 1, however, actually consists of clusters of molecules of different sizes, and it is no wonder that so much uncertainty exists in the determination of the equilibrium constant for the reaction polymer = monomer in liquid water.

Our values of K_1 and K_2 are calculated from data at zero water concentration. The water in eq 2 and 3 therefore refers to the monomeric species only, and the 1:1 as well as the 1:2 complexes in eq 2 and 3 represent also uniquely defined species.

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[14] S. C. Mohr, W. D. Wilk, and G. M. Barrow, *J. Am. Chem. Soc.*, 87, 3048 (1965).

[15] Z. Luz and G. Yagil, *J. Phys. Chem.*, 70, 554 (1966).

[16] D. P. Stevenson, *ibid.*, 69, 2145 (1965).