TABLE 1 Parameters for Water near the Surface of a C-phycocyanin Protein (Hydrated-Lyophilized Sample, $h = 0.40$)

T (°C)	a (Å)	Confined water (D_{local}, 10^{-5} cm^2/sec)	Confined water (D_t, 10^{-5} cm^2/sec)	Bulk water (D_t, 10^{-5} cm^2/sec)	Confined water (τ_0, ps)	Bulk water (τ_0, ps)
40	4.5	1.28	1.52	3.20	5.9	0.90
25	4.3	0.97	1.20	2.30	6.6	1.10
0	4.0	0.84	0.76	1.10	8.2	3.00

TABLE 2 Parameters for Water Confined in a 25% Hydrated Vycor Sample

T (°C)	a (Å)	Confined water (D_{local}, 10^{-5} cm^2/sec)	Confined water (D_t, 10^{-5} cm^2/sec)	Bulk water (D_t, 10^{-5} cm^2/sec)	Confined water (τ_0, ps)	Bulk water (τ_0, ps)	Confined water (τ_1, ps)	Bulk water (τ_1, ps)
25	4	0.92	2.45	2.30	15	1.10	1.5	1.10
−5	3	0.38	1.36	0.907	20	4.66	1.8	1.57
−15	3	0.26	1.20	0.574	25	8.90	2.0	1.92
−35	2						3.1	

allows the protein to initiate its function (24). Tables 1 and 2 give, respectively, for hydrated protein ($h = 0.4$) and for 25% hydrated Vycor the values of the diffusion coefficients D_{local} and D_t for confined water as compared with the diffusion coefficient D_t of bulk water. The residence time τ_0 (59,79) and the hydrogen bond lifetime τ_1 (59,79) are also given as a function of temperature.

For hydrated protein (Table 1), the values obtained for D_{local} are lower than those of bulk water. They are close to those obtained at the same temperature for 25% H_2O-hydrated Vycor (Table 2) what demonstrates the influence of the hydrophilic groups on the water molecules when one reaches monolayer coverage. This shows that the diffusive motion of water molecules is strongly retarded by interactions with a protein surface.

However, in contrast with the case of water in hydrated Vycor, the values of D_t for hydration water in the protein are smaller than that of bulk water. This is due to some influence of hydrophobic residues of protein, at the vicinity of the protein surface, which, in fact, is not as hydrophilic as that of Vycor. We are, thus, able to detect the effect of the substrate (59).

Figure 9A gives, respectively, the Arrhenius plots of τ_0 for water of hydration at the surface of a protein (59) as compared with those of water in Vycor at different levels of hydration (79) and bulk water (72).

The residence time τ_0 of confined water from 25% hydrated Vycor and hydrated protein are always longer than the residence time of bulk water, at the same temperature. They increase rapidly as either the temperature or the level of hydration decreases. For example, for the 25% hydrated Vycor sample $\tau_0 = 25$ ps at −15°C.

The hydrogen bond lifetimes τ_1 for confined water are close to that of bulk water (79). They have an Arrhenius temperature dependence (Fig. 9B) while the residence time τ_0 does not exhibit such a behavior (Fig. 9A).

Figure 10 gives the evolution of the vibrational density of states for H_2O-hydrated protein C-phycocyanin as a function of temperature for two levels of hydration $h = 0.5$ and 0.25.