Adsorption of Uric Acid Derivatives in Water by Poly(vinyldiaminotriazine) through Hydrogen Bonding

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In aqueous solutions, poly(2-vinyl-4,6-diamino-1,3,5-triazine) efficiently adsorbs uric acid, xanthine, and theobromine by using three complementary hydrogen bonds. The adsorption is selective and reversible, indicating a strong potentiality for the practical application.

Removal of uremic toxins such as uric acid and urea from aqueous phase is crucially important for clinical use and other purposes.[1,2] However, selective binding of these toxins in water is difficult, mainly because hydrogen bonds, required for the precise recognition of these toxins, are easily destroyed by the competition with the water molecules (note that most of the hydrogen-bonding artificial receptors previously studied are effective only in aprotic solvents such as chloroform).[3-6]

In the present communication, we report that poly(2-vinyl-4,6-diamino-1,3,5-triazine) (PVDT) selectively recognizes uric acid derivatives in water through hydrogen bond formation. The uremic toxins are efficiently removed from water, with non-hydrogen bonding guests left in aqueous phase.

When an aqueous solution of uric acid was incubated at 25 °C with PVDT (which is insoluble in water), almost all the uric acid (more than 97%) was rapidly adsorbed by PVDT and disappeared from the liquid phase (see Figure 1).[7] The equilibrium was attained within 15 min. Significant adsorption was also observed with xanthine and theobromine: more than half (80% and 51% for xanthine and theobromine, respectively) was adsorbed by PVDT under the same conditions as employed above. The virtually same adsorption efficiency was obtained when the guest concentration was smaller (when [theobromine] = 0.06 μmol cm^{-3}, 52% of the guest was adsorbed). In contrast, caffeine, in which the imide residue in theobromine is N-methylated, was hardly adsorbed under the identical conditions.[8] Apparently, the present adsorption is ascribed to the formation of three complementary hydrogen bonds between the imide residue of the guest and the 4,6-diaminotriazine residue in PVDT (see the hydrogen bonding patterns in Figure 2). The argument is further supported by the fact that 4-hydroxypyridine, a guest having only one hydrogen bonding site, was not adsorbed at all by PVDT.

The adsorption is totally reversible. Thus, more than 60% of the xanthine and the theobromine, adsorbed by PVDT at 25 °C, was released to the aqueous phase when the temperature was raised to 70 °C. The desorption of uric acid is less efficient, reflecting its stronger binding to PVDT (about 20% of

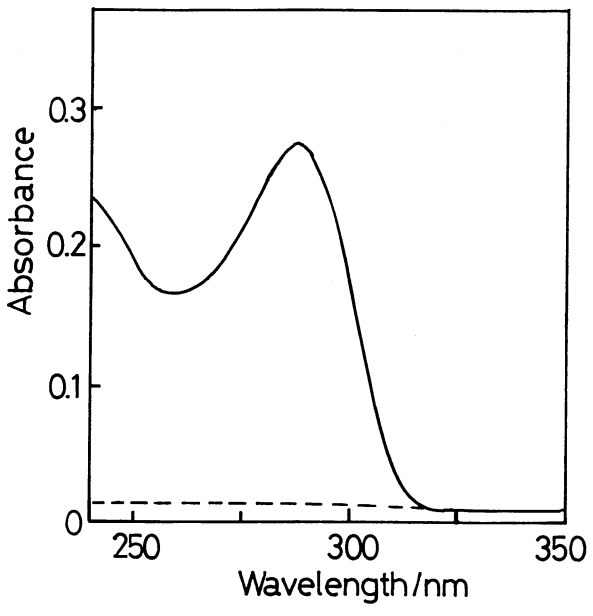

Figure 1. Electronic absorption spectra of the aqueous solution of uric acid before (solid line) and after (broken line) the contact with PVDT. One milliliter of the solution of uric acid (0.12 μmol cm^{-3}) was treated with 10 mg of PVDT at 25 °C for 1 h (see Ref. 7 for the experimental detail).

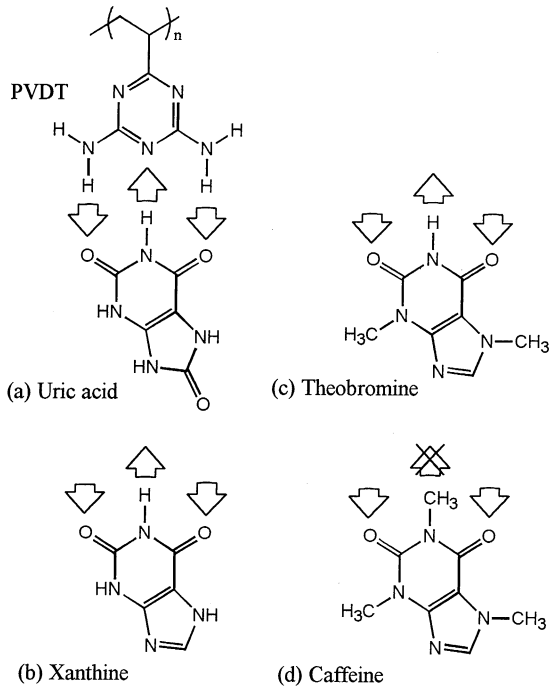

Figure 2. Structures of the guests and their hydrogen bondings with PVDT. The open arrows show the complementary hydrogen bonds.

the adsorbed guest was released at 70 °C).

The present results are highly in contrast with the previous results that hydrogen bonds are formed only in aprotic solvents.[3-5] Assumedly, aprotic microspheres are provided by PVDT and the hydrogen bonds are efficiently formed therein. It is noteworthy that a solid of 2-vinyl-4,6-diamino-1,3,5-triazine, which is almost insoluble in water, did not adsorb theobromine to a measurable extent. Use of the polymer is absolutely required here.

In conclusion, PVDT reversibly adsorbs uric acid derivatives through hydrogen bond formation in bulk water. The present finding should open the way to molecular design of the artificial receptors which selectively bind various compounds in water and thus are applicable to selective removal of them from water.

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7 PVDT was prepared by polymerizing 2-vinyl-4,6-diamino-1,3,5-triazine (0.29 mol dm^{-3}) in DMSO at 70 °C with AIBN (3.9 mmol dm^{-3}) as radical initiator. In the adsorption experiments, 10 mg of PVDT (involving 73 μmol of diaminotriazine residue) in a form of fine powder was incubated in 1 ml of aqueous solution of guest (0.12 μmol cm^{-3}) with an intermittent shaking. Although no buffer agents were used to avoid undesirable effects, the pH was maintained at 6.0 $\pm$ 0.5. Then the mixture was centrifuged, and the liquid phase was analyzed by a UV-VIS spectrophotometer.

8 Only 10% of the initially charged caffeine was adsorbed by PVDT.