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Solubilization of Lipid-Soluble Vitamins in Water by Forming Complexes with Poly(N-vinylpyrrolidone)

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Lipid-soluble vitamins A_1, E, D_2, and K_1 were solubilized in water by forming complexes with poly(N-vinylpyrrolidone)(PVP). The effects of ultraviolet (UV) irradiation and hydrogen peroxide on the vitamin-PVP complexes in water were examined by measuring absorption spectra, and compared with those on the vitamins in ethanol.

We previously devised the methods to solubilize chlorophylls in water by forming complexes with water-soluble macromolecules.[1] According to one of the methods, we have recently succeeded in solubilizing lipid-soluble vitamins in water. The aim of this paper is to report the procedure for solubilizing lipid-soluble vitamins and their spectroscopic properties in water.

Vitamin A_1 (all-trans-retinol), D_2, and K_1 were purchased from Kanto Chemical Co., Inc., and vitamin E purchased from Kishida Chemical Co., Ltd. They were used without further purification. PVP: molecular weight, 40000, manufactured by Kishida Chemical Co., Ltd. was purified by reprecipitation in water-acetone.

Lipid-soluble vitamins were solubilized in water as follows. Ethanol (5 ml) containing 0.5 mg of vitamins A_1, D_2, and K_1 or 4 mg of vitamin E was added to 5 ml of ethanol containing 1.0 g of PVP. The solution was evaporated to a dry vitamin-PVP film under a reduced pressure at room temperature. A small amount of water was added onto the film, and stirred gently at room temperature until a homogeneous paste was formed. The paste was diluted with water to a given concentration of the aqueous vitamin-PVP complex solution. The solution thus obtained were perfectly transparent.

Absorption spectra at room temperature were measured with a double beam spectrophotometer, UVIDEC-510 (Japan Spectroscopic Co., Ltd.). UV irradiation was performed with a fluorescence lamp (Mitsubishi GL-15) placed 10 cm from a quartz cuvette containing the vitamin solution.

Figure 1 shows the absorption spectra of the lipid-soluble vitamin/PVP complexes in water and the vitamins in ethanol. The absorption peaks of the vitamins in ethanol were observed at 325 nm for vitamin A_1, at 292 nm for vitamin E, at 217 and 265 nm for vitamin D_2 and at 223, 244, 249, 265, and 272 nm for vitamin K_1. These spectral features are well consistent with those published in literature.[2] On the other hand, the absorption peaks of the vitamin-PVP complexes in water were observed at 318 nm for vitamin A_1, at 295 nm for vitamin E, at 270 nm for vitamin D_2 and at 244, 250, 265, and 272 nm for vitamin K_1. Thus, for all the

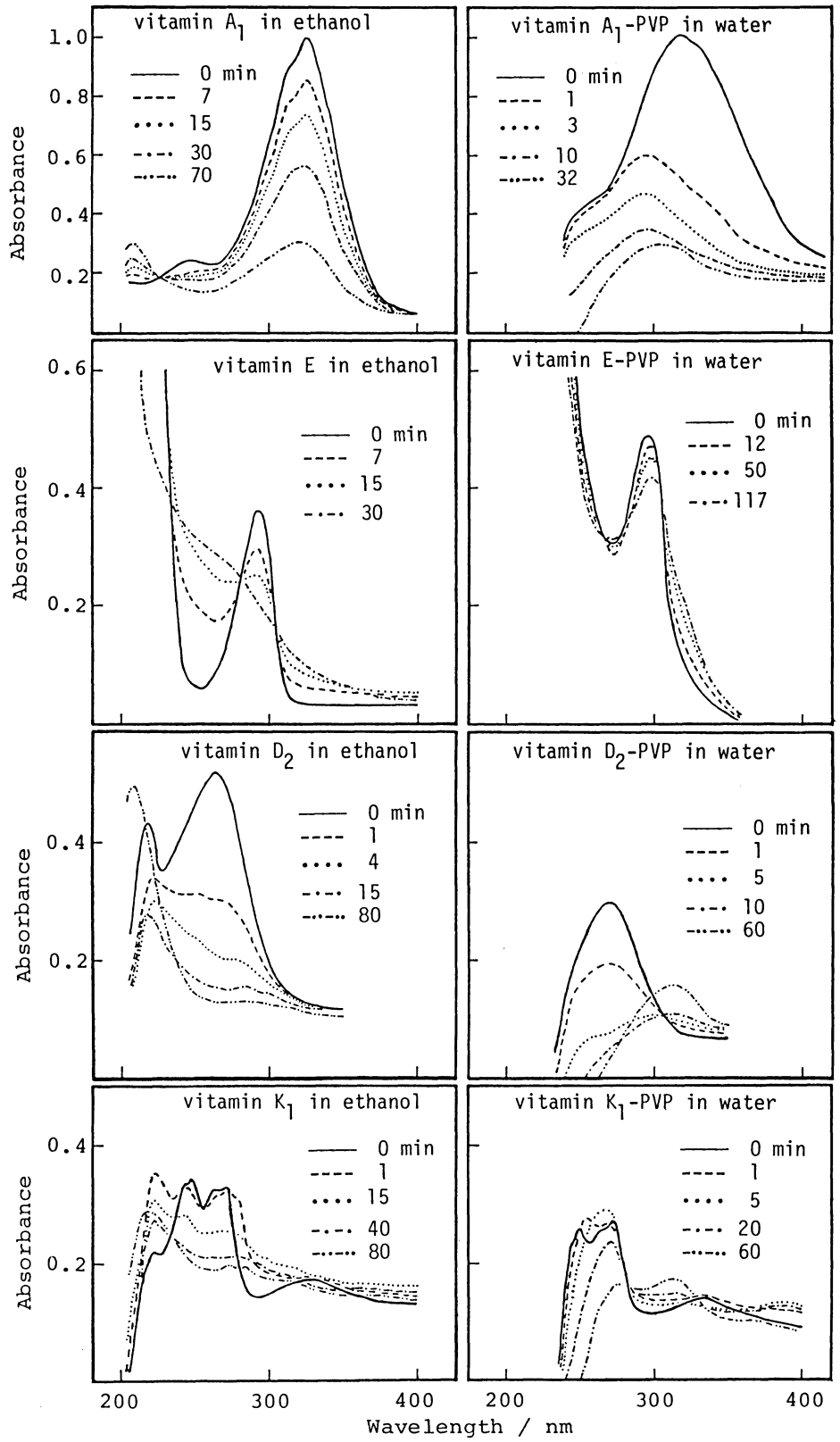

Fig. 1. Absorption spectra of lipid-soluble vitamin/PVP complexes in water and vitamins in ethanol, and their time-dependent changes caused by irradiation of UV light. Concentrations of vitamin are 5 μg ml^{-1} (A_1, D_2, and K_1) or 40 μg ml^{-1} (E).

vitamins, the absorption spectrum of the vitamin-PVP complex in water was, generally speaking, similar in shape and position to that of the corresponding vitamin in ethanol.

Figure 1 also shows the time-dependent spectral changes caused by UV irradiation. The absorption peaks of all the vitamins both in water and in ethanol were decreased in intensity by UV irradiation (see also Fig. 2). However, it should be also noted in Fig. 1 that, for all the vitamins, the absorption spectrum of the vitamin-PVP complex in water were changed by UV irradiation in a different way from that of the corresponding vitamin in ethanol. The peak at 318 nm of the vitamin A_1-PVP complex was shifted to shorter wavelength by UV irradiation, while that at 325 nm of vitamin A_1 in ethanol was not. The absorption minimum at 253 nm of vitamin E in ethanol was progressively increased in intensity with irradiation time, but that at 272 nm of the vitamin E-PVP complex was not. In the absorption spectra of the vitamin D_2 and K_1-PVP complexes, a new peak appeared near 313 nm on UV irradiation.

Figure 2 illustrates the photodegradation of the vitamins in different states by UV irradiation. The vitamin E-PVP complex in water was degraded more slowly than vitamin E in ethanol. On the other hand, the vitamin A_1, D_2, and K_1-PVP complexes were destroyed more rapidly than the corresponding vitamins in ethanol. These results imply that PVP stabilized vitamin E more effectively against UV irradiation than the other vitamins. It is also noted in Fig. 2, however, that the rates of photodegradation of all the vitamins in aqueous ethanol (80%) solutions were different from those of the corresponding vitamins in ethanol. This suggests that the medium of water or ethanol was an important factor in the effects of UV irradiation on the spectroscopic properties of vitamins, in addition to the presence of PVP. Recently, Shibata et al.[3] reported that the vitamin E, D_2, and K_1-egg albumin complexes in water were more stable against UV irradiation in the presence of hydrogen peroxide than the corresponding vitamins in ethanol.

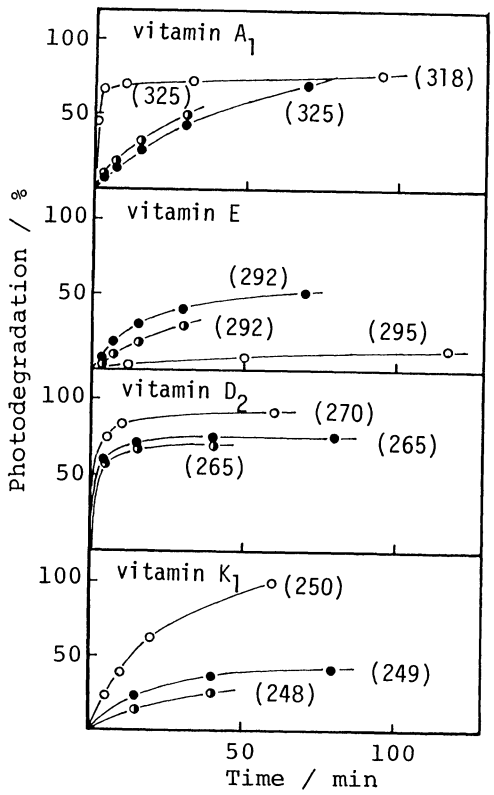

Fig. 2. Photodegradation of lipid-soluble vitamins in different states by irradiation of UV light; vitamin-PVP complex in water (o), vitamin in ethanol (•) and vitamin in aqueous ethanol (80%) solution (⊙). The wavelengths monitoring the photodegradation are shown in parentheses.

Figure 3 shows the effects of hydrogen peroxide on the spectroscopic properties of the vitamin-PVP complexes in water and the vitamins in ethanol. The absorption

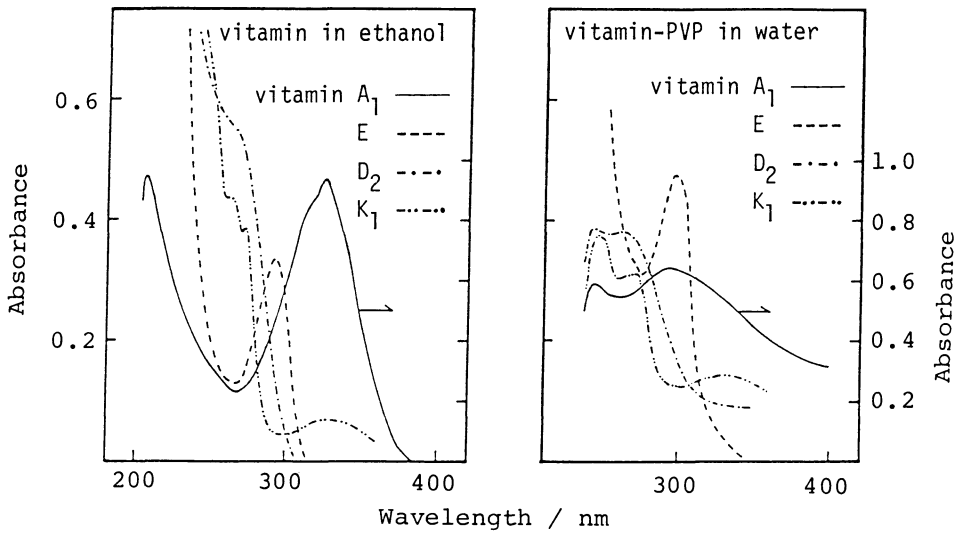

Fig. 3. Absorption spectra of vitamins in ethanol and vitamin-PVP complexes in water, in the presence of hydrogen peroxide (5×10^{-3} mol dm^{-3}). Concentration of vitamins are the same as in Fig. 1.

spectra of the vitamin E-PVP complex in water and vitamin E in ethanol were not changed by addition of hydrogen peroxide. The absorption peak at 318 nm of the vitamin A_1-PVP complex in water was decreased in intensity and shifted to 293 nm by hydrogen peroxide, though the peak at 325 nm of vitamin A_1 in ethanol was not affected by it. The intensities of absorption in the shorter wavelength range for vitamins D_2 and K_1 in ethanol were greatly increased by hydrogen peroxide, while those for their PVP complexes in water slightly increased by it, suggesting that PVP stabilized these vitamins against the oxidative stress of hydrogen peroxide.

From the above results, it is concluded that PVP solubilized vitamins A_1, E, D_2, and K_1 in water, and that it stabilized vitamin E against UV irradiation and did vitamins D_2 and K_1 against the oxidative stress of hydrogen peroxide. It is very interesting to determin the size and shape of the lipid-soluble vitamin/PVP complexes and to elucidate the interactions between PVP and vitamins. These investigations are now in progress.

References

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