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Effect of Solvents on the Charge Transfer Absorption Bands of the Complexes between Various Electron Donors and Menadione

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The previous papers[2,3] reported the charge transfer absorption bands of the complexes formed between menadione and various electron donors such as N,N-diethylaniline, salicylic acid, caffeine, *etc.*, in either chloroform or phosphate buffer of pH 7.0.

The present paper describes the measurement of charge transfer absorption bands of the complexes in ethanol, dioxan, and heptane, and the effect of solvents on the position of charge transfer absorption bands.

Experimental

Materials——Menadione, chloroform, and various electron donors used in the present work were the same as described in previous papers.[2,3] Ethanol (anhydrous) and dioxan used were of G.R. grade chemicals,

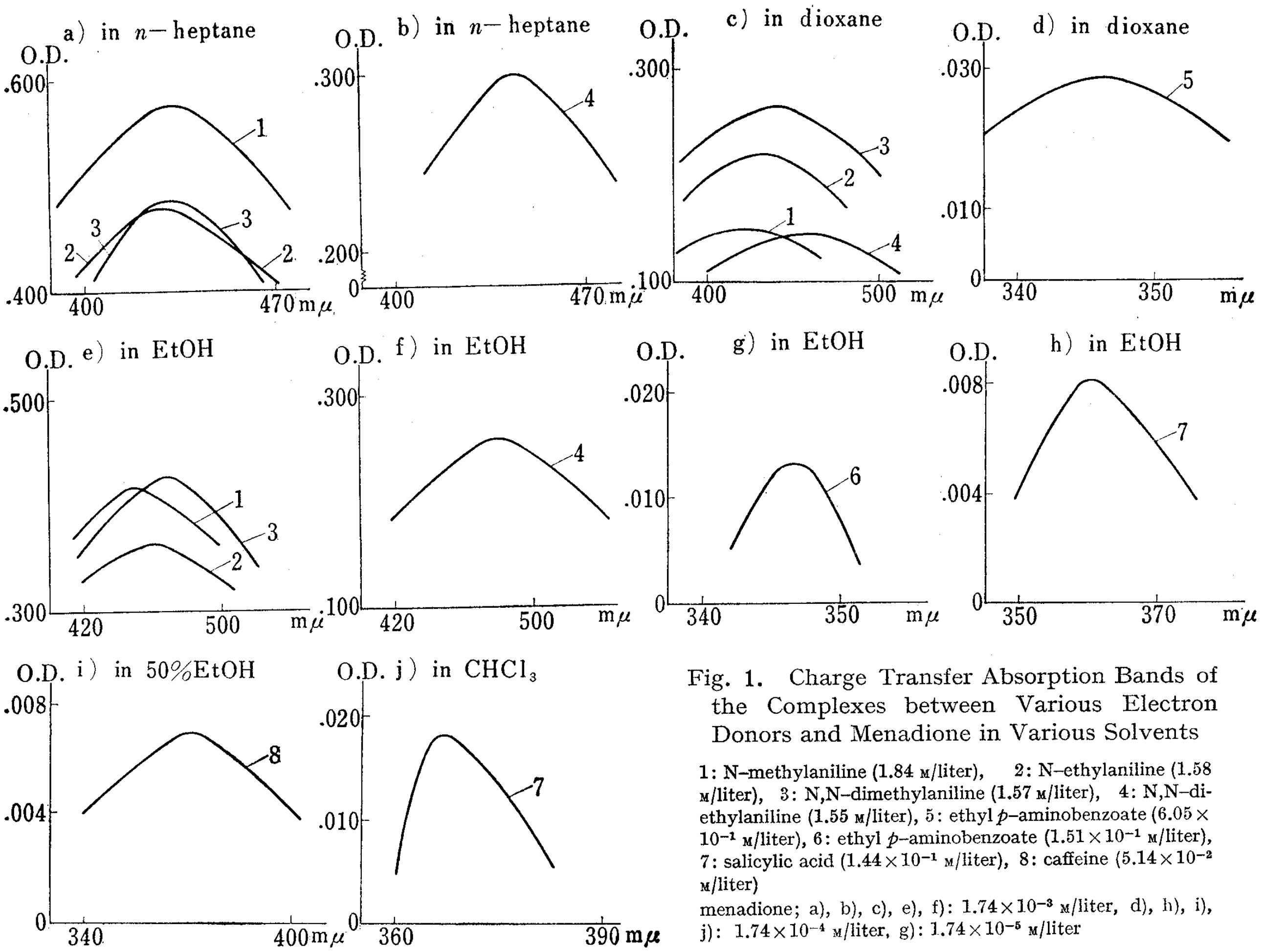

Fig. 1. Charge Transfer Absorption Bands of the Complexes between Various Electron Donors and Menadione in Various Solvents

1: N-methylaniline (1.84 M/liter), 2: N-ethylaniline (1.58 M/liter), 3: N,N-dimethylaniline (1.57 M/liter), 4: N,N-diethylaniline (1.55 M/liter), 5: ethyl *p*-aminobenzoate (6.05×10^{-1} M/liter), 6: ethyl *p*-aminobenzoate (1.51×10^{-1} M/liter), 7: salicylic acid (1.44×10^{-1} M/liter), 8: caffeine (5.14×10^{-2} M/liter)
menadione; a), b), c), e), f): 1.74×10^{-3} M/liter, d), h), i), j): 1.74×10^{-4} M/liter, g): 1.74×10^{-5} M/liter

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[1] Location: *Takada, Toshima-ku, Tokyo.*
[2] S. Hata, *Chem. Pharm. Bull.* (Tokyo), **16, 1 (1968).**
[3] S. Hata and S. Tomioka, *Chem. Pharm. Bull.* (Tokyo), 16, 1397 (1968).

purchased from the Wako Pure Chemicals Co., Ltd., and heptane was of Spectro Grade chemical purchased from the Tokyo Kasei Co., Ltd.

Measurement of Absorption Spectra——The absorption spectra were measured with a Hitachi photoelectric spectrophotometer EPU–2A, equipped with thermospacers to maintain the cell compartments at 24°+0.1°, and the optical path of the cell was 10 mm. Results of the measurements are shown in Fig. 1 as differential spectra.

Results and Discussion

The charge transfer absorption bands of the complexes between menadione and various electron donors such as N,N–diethylaniline, ethyl *p*–aminobenzoate, caffeine, *etc.*, in ethanol, dioxan, and heptane are shown in Fig. 1, and the absorption maxima of those charge transfer complexes determined are tabulated in Table I. These results suggest that the energies for the charge transfer complex formation may be decreased by the increased polarity of the solvents.

However, ethanol itself is a fairly good localized electron donor and it can be expected to compete with various electron donors for menadione, with which it predominantly forms a charge transfer complex. Hence, energies for the charge transfer complex formation between menadione and relatively weak electron donors such as salicylic acid and caffeine tend to increase in the case of ethanol.

Moreover, it is known that the dissociation of the complexes into free radicals is observed in aqueous solution when a strong charge transfer complex is formed, such as that between chloranil and N,N,N′,N′–tetramethyl–*p*–phenylenediamine.[4] However, the charge transfer complexes between menadione and either caffeine or salicylic acid are relatively weak, and the above phenomenon has not been observed in an aqueous solution.

Consequently, it can be concluded that, because of its poor electron–donating capacity and highly polar character, aqueous medium is the most appropriate for the charge transfer complex formation between menadione and relatively weak electron donors such as salicylic acid and caffeine.

TABLE I. Effect of Solvents on the Position (in mμ) of the Charge Transfer Absorption Bands of the Complexes between Various Electron Donors and Menadione

Solvent / Donor	Phosphate buffer[a]	EtOH	$CHCl_3$	Dioxane	*n*–Heptane
Salicylic acid	380[3]	360	366	—	—
Caffeine	390[3]	370[b]	386[2]	—	—
Ethyl *p*–aminobenzoate	—	347	373[2]	346	—
N–Methylaniline	—	452	440[2]	420	431
N–Ethylaniline	—	460	442[2]	432	425
N,N–Dimethylaniline	—	470	471[2]	440	430
N,N–Diethylaniline	—	480	480[2]	455	444

a) pH 7.0 *b*) 50% EtOH

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4) R. Foster and T.J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).