Model Study on the Complex Formation between Phenols and Polymers Carrying a Cyclic Amide Moiety: Interaction of Phenols with 1,*n*-Bis[1-(2-oxopyrrolidin)yl]alkanes

Ichiro Atobe, Toshikazu Takata, and Takeshi Endo*

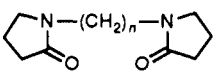
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Received November 9, 1990; Revised Manuscript Received April 22, 1991

ABSTRACT: Complex formation behavior between phenols and alkanes containing two pyrrolidone moieties at both termini [1,*n*-bis[1-(2-oxopyrrolidin)yl]alkanes (1,*n*-DPAs)], as model compounds of polymers carrying an amide group in the side chain, was investigated by means of ^{1}H NMR, IR, and UV. In the IR study, a frequency decrease of the carbonyl absorption of 1,*n*-DPAs upon addition of phenol was observed, which was suggested to result from hydrogen bonding. The frequency change occurred independent of the methylene chain length and the presence of solvent but its magnitude depended on the concentration. ^{1}H NMR chemical shifts of 1,*n*-DPAs were clearly changed by addition of phenols. Most signals of 1,*n*-DPAs shifted to higher field, while only signals of methylene protons adjacent to the carbonyl group shifted to lower field. Detailed ^{1}H NMR study using 1,3-DPA, phenols, and related compounds indicated that the interaction between 1,*n*-DPAs and phenols could be attributed to the favorable formation of charge-transfer stacking (C-T stacking) as well as hydrogen bonding. Furthermore, the strength of the interaction between 1,*n*-DPAs and phenols was affected by the para substituents of the phenols and the polarity of the solvents. UV study demonstrated that 1,*n*-DPAs formed 1:2 complexes with phenol (pyrrolidone group:phenol = 1:1). The driving force of the complex formation is believed to be due not only to hydrogen bonding but also to C-T stacking.

Introduction

Polymers having cyclic amide or urethane structures are known to form stable complexes with active hydrogen compounds such as phenols and carboxylic acids.[1-10] We have already reported complex formation of polymers carrying an oxazolidone moiety with these compounds.[11-17] This phenomenon is regarded as an interesting adsorption–desorption behavior that is applicable to deodorization of strong smelling materials and controlled release of drugs and perfumes. Nevertheless, few fundamental studies on the interaction between polymers and active hydrogen compounds have been carried out in detail and therefore such applications have not been frequently carried out. In recent years, scattered studies have been reported on interactions with low molecular weight compounds,[18] but it is still difficult to understand the adsorption behavior based on complex formation. To clarify the basis of the interaction is of great importance, which should be useful in order to further develop our studies on complex formation between polymers carrying an oxazolidone or a pyrrolidone moiety and phenols and to apply them to actual materials. In this paper, we describe detailed complex formation behavior between 1,*n*-bis[1-(2-oxopyrrolidine)yl]alkanes (1,*n*-DPAs) as model compounds of the polymers and phenols, which are studied by means of ^{1}H NMR, UV, and IR.



1, *n*-DPA (*n* = 3, 5, 9)

Experimental Section

Materials. 1,*n*-DPAs were synthesized according to the method of our previous paper.[19] Solvents and reagents (phenol, para-substituted phenols, anisole, and nitrobenzene) were purified by common methods.

Measurement. FT-IR spectra were recorded on a JASCO FT-IR/3 spectrophotometer. ^{1}H NMR spectra were measured with a JNM PMX-60si NMR spectrometer (60 MHz) using tetramethylsilane as an internal standard. UV spectra were obtained with a Hitachi 200-10 spectrophotometer.

Measurement of IR Spectra. Each 1,*n*-DPA was mixed with phenol in molar ratios ranging from 0 to 10 (DPA/phenol) in dichloromethane ([C] = 0.0125–0.05 mol dm^{-3}) or without solvent. In the absence of solvent, the mixture was fused by heating in an oil bath at 50 °C for 5 min and then a portion of the mixture was subjected to the IR measurement (neat). When the solvent was used, after stirring the mixture at 25 °C for 2 h, IR spectra were recorded by using a liquid cell. The carbonyl absorption bands of pyrrolidone groups were measured to within 2 cm^{-1}.

Measurement of ^{1}H NMR Spectra. 1,*n*-DPA was mixed with one of the phenols in molar ratios ranging from 0 to 8 (phenol/DPA) without solvent. The mixture was melted by heating at 50 °C in an oil bath for 5 min. ^{1}H NMR spectra of the resulting oily mixtures were measured at a concentration of [C] = 0.5 mol dm^{-3} in $CDCl_3$. The change of chemical shift was measured with an error of ±0.02 ppm.

Measurement of UV Spectra. 1,3-DPA and phenol were mixed in molar ratios ranging from 1.0:0 to 0:1.0 (phenol/1,3-DPA) in carbon tetrachloride. The total mole concentration was kept at a constant value, 3.92 × 10^{-3} mol dm^{-3}. Each of the mixtures was subjected to UV spectrum measurement and absorbance at 284 nm was plotted. The difference spectrum between the solution of the mixture and a solution of phenol with the same concentration ([C] = 3.92 × 10^{-3} mol dm^{-3}) was measured.

Results and Discussion

Interaction between 1,*n*-DPA and Phenols. 1,*n*-DPAs and phenols were mixed in several molar ratios in organic solvents or without solvent, and IR, ^{1}H NMR, and UV spectra of the mixtures were recorded. From the results obtained the interaction is discussed.

(1) IR Study. Three kinds of 1,3-DPA solutions in dichloromethane (concentration 0.05, 0.025, and 0.0125 mol dm^{-3}) were prepared. Phenol was then added to these solutions in molar ratios of phenol/DPA ranging from 0 to 10, and the frequency of the carbonyl adsorption in IR was measured. Results are summarized in Figure 1; they clearly indicate that the carbonyl adsorption of the pyrrolidone group is shifted to 20 cm^{-1} lower frequencies by addition of phenol (from 1682 to 1662 cm^{-1}).

0024-9297/91/2224-5046$02.50/0

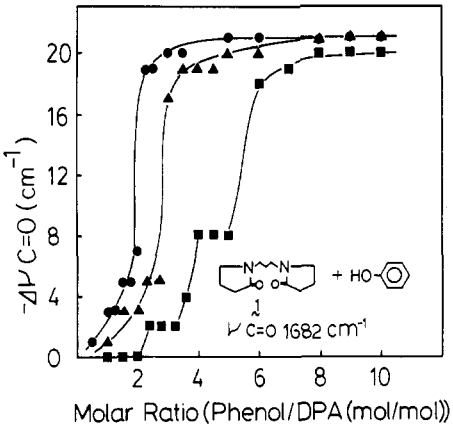


Figure 1. Shift of the carbonyl absorption of 1,3-DPA by addition of phenol in CH_2Cl_2 in IR. Initial concentration of 1,3-DPA: 0.05 mol dm^{-3} (●), 0.025 mol dm^{-3} (▲), 0.0125 mol dm^{-3} (■).

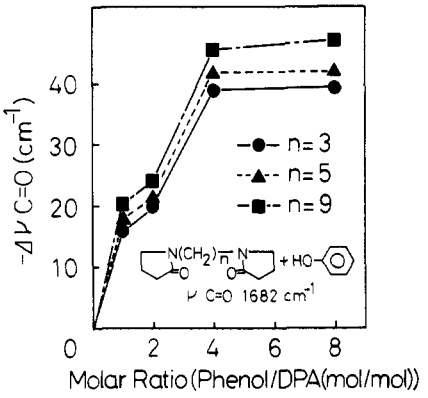


Figure 2. Effect of the methylene chain length on the shift of carbonyl adsorption of DPAs by addition of phenol without solvent in IR.

This shift is in good accord with reported results.[20] As shown in Figure 1, the maximum shift achieved was independent of the concentration of 1,3-DPA, although the magnitude of the shift strongly depended on the initial concentration of 1,3-DPA. These results suggest that the interaction is at equilibrium, i.e., the degree of the shift directly corresponds to the concentration of the complex formed. As generally accepted, the shift of the carbonyl absorption to lower frequencies is attributable to hydrogen bonding of 1,3-DPA with a phenolic hydroxyl group. 1,5- and 1,9-DPAs, which have longer methylene chains than 1,3-DPA, showed the same IR behavior as 1,3-DPA in the cases without solvent (Figure 2).

The shift value of the carbonyl absorption to lower frequencies by addition of phenol increased according to the increase of the molar ratio of the added phenol, and the maximum shift reached about 40 cm^{-1}, which was two times greater than that in solution (in dichloromethane). No effect of the methylene chain length on the shift of the carbonyl adsorption upon addition of phenol was observed in either with or without solvent. From these results, it is concluded that the carbonyl adsorption shift of 1,3-DPA takes place upon addition of phenol, presumably due to hydrogen bonding, which is independent of both the methylene chain length and the presence of solvent but depends on their concentration.

(2) ^{1}H NMR Study. ^{1}H NMR spectra of the DPAs and mixtures of the DPAs and phenols were measured in $CDCl_3$ at 27 °C. The ^{1}H NMR spectra were clearly changed by addition of phenols to $CDCl_3$ solutions of DPAs in all cases. The change of chemical shift of each signal of 1,3-DPA versus the mole ratio of added phenol (phenol/1,3-DPA)

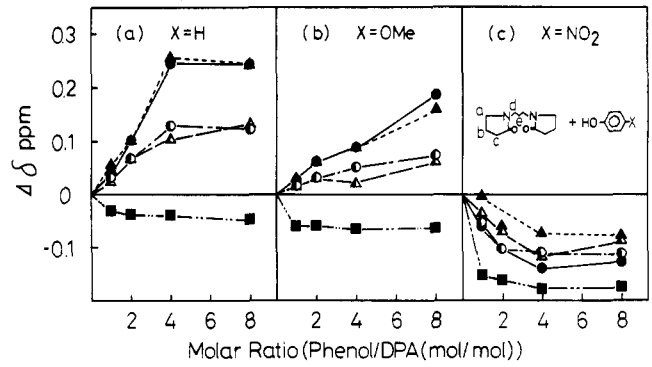
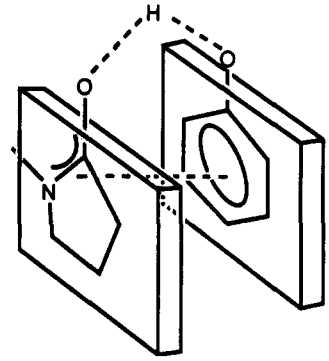


Figure 3. Effect of the para substituents of phenols on the change of the ^{1}H NMR chemical shift of 1,3-DPA by addition of phenols in $CDCl_3$ (total concentration = 0.5 mol dm^{-3}): a (●); b (▲); c (■); d (◐); e (▲).

is plotted in Figure 3a. ^{1}H NMR signals, a, b, d, and e were shifted to higher field whereas only signal c was shifted to lower field. This result seems to suggest that the observed shifts are based on charge-transfer stacking (C-T interaction) between the pyrrolidone group and phenol in addition to hydrogen bonding. The chemical shift change can be explained by assuming the stacking structure shown below, formed by C-T interaction between the phenolic



benzene ring and the amide group of the DPA, which would be strengthened by hydrogen bonding between the phenolic hydroxyl group and the amide carbonyl group. Hydrogen bonding decreases the electron density of the amide group whereas the C-T stacking causes electron donation from the phenolic benzene ring to the amide group. In this case the signals of the protons, a, b, d, and e, shift to higher field due to the ring current effect of the benzene ring of phenol, while that of proton c shifts to lower field owing to lowered electron density by hydrogen bonding, although the shift would be determined by the difference between the two effects. Therefore, the occurrence of the interaction between the DPA and phenol can be attributed to the favorable formation of C-T stacking and hydrogen bonding.

a. Substituent Effects. Results of the ^{1}H NMR study of the interaction between 1,3-DPA with phenols having *p*-methoxy and *p*-nitro groups are shown in Figure 3b,c. The change with *p*-methoxyphenol was entirely similar to that with phenol. However, all proton signals shifted to lower field upon addition of *p*-nitrophenol. Slightly smaller changes of the chemical shifts with *p*-methoxyphenol than those with phenol appear to indicate a negative effect of the *p*-methoxy group which suppresses the C-T stacking by its steric hindrance and/or weakens acidity of the phenolic hydroxyl group, although the electron density of the benzene ring of *p*-methoxyphenol is higher than that of phenol. Dissociation constants of a few phenols are given in Table I, which supports the

Table I
Dissociation Constants of Phenols[a]

phenol derivatives	pK_a	phenol derivatives	pK_a
phenol	9.98	*p*-nitrophenol	7.15
p-methoxyphenol	10.21	*p*-*tert*-butylphenol	10.25

[a] Reference 21.

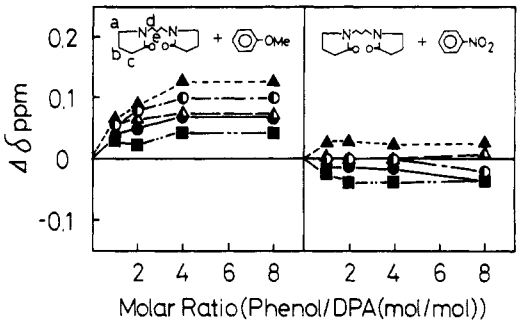


Figure 4. Comparison of the change of ^{1}H NMR chemical shifts of 1,3-DPA by addition of anisole and nitrobenzene in $CDCl_3$ (total concentration = 0.5 mol dm^{-3}): a (●); b (▲); c (■); d (◐); e (tul).

above assumption.

On the other hand, the fact that there is no proton signal shift to higher field by addition of *p*-nitrophenol can be accounted for by the absence of C-T stacking and formation of strong hydrogen bonding. These can be reasonably attributed to the presence of the bulky *p*-nitro group and to the high acidity of the phenol (pK_a = 7.15, Table I). The electron withdrawing due to hydrogen bonding causes the lower field shifts of all the protons of 1,3-DPA.

b. Effect of C-T Stacking. In the above discussion, the importance of C-T stacking is emphasized for complex formation. To evaluate the C-T stacking, the interaction between 1,3-DPA and anisole or nitrobenzene, which do not form hydrogen bonds, was examined by the same ^{1}H NMR method. As shown in Figure 4, all the signals are slightly shifted to higher field by addition of anisole, while little shift change was observed in the case of nitrobenzene.

The shift change in the case of anisole unambiguously demonstrates the presence of C-T stacking between 1,3-DPA and anisole, i.e., between the amide group and the benzene ring. Furthermore, the small higher field shift of signal c on addition of anisole seems to indicate electron transfer from the benzene ring to the pyrrolidone ring, and it is therefore concluded that the lower field shift of signal c by addition of phenol results mainly from hydrogen bonding. Thus, the electron density of the methylene group adjacent to the amide carbonyl of DPA is increased by the C-T stacking but is decreased by hydrogen bonding, i.e., signal c shifts to higher field by C-T stacking but to lower field by hydrogen bonding. The observed shift, therefore, results from the sum of the two effects.

c. Effect of Steric Hindrance. The magnitude of the interaction between 1,3-DPA and *p*-methoxyphenol is smaller than that between 1,3-DPA and phenol (Figure 3a,b). This difference was attributed to the steric hindrance of the methoxy group. To confirm this, the interaction between 1,3-DPA and *p*-*tert*-butylphenol was studied (Figure 5).

The benzene ring of *p*-*tert*-butylphenol is probably more electron rich than that of phenol due to electron donation from the *tert*-butyl group, and accordingly *p*-*tert*-butylphenol is less acidic than phenol (Table I). However, the degree of chemical shift change by *p*-*tert*-butylphenol was smaller than those by phenol and *p*-methoxyphenol,

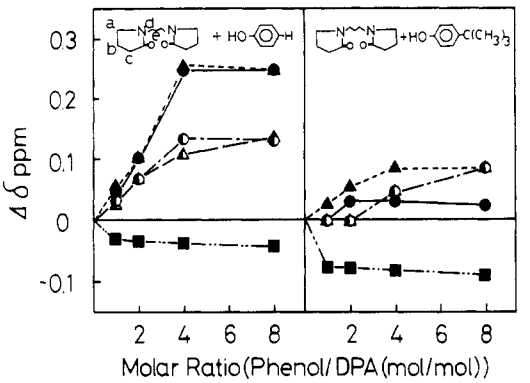


Figure 5. Comparison of change of the ^{1}H NMR chemical shifts of 1,3-DPA by addition of phenol and *tert*-butylphenol in $CDCl_3$ (total concentration = 0.5 mol dm^{-3}): a (●); b (▲); c (■); d (◐); e (▲).

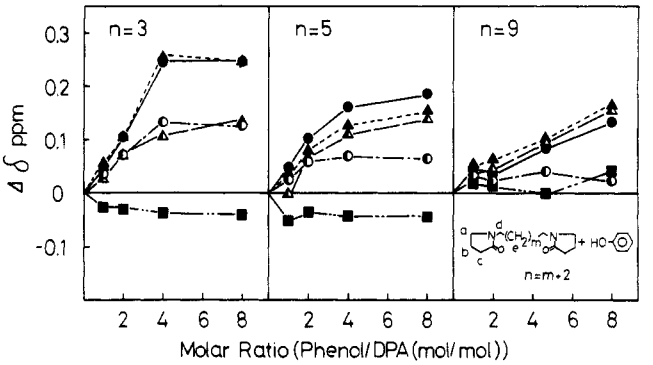


Figure 6. Effect of the methylene chain length on the change of the ^{1}H NMR chemical shifts of DPAs by addition of phenol in $CDCl_3$ (total concentration = 0.5 mol dm^{-3}): a (●); b (▲); c (■); d (◐); e (▲).

as shown in Figure 5. Therefore, C-T stacking of the *p*-*tert*-butylphenol with 1,3-DPA should be small owing to the steric hindrance of the *tert*-butyl group. Proton signal c shifted largely to the lower field. This means that hydrogen bonding is effectively operative. The larger lower field shift of singal c in the case of *tert*-butylphenol than that in phenol is explained by the above argument that the carbonyl-linked methylene (methylene c) is affected not only by hydrogen bonding but also by C-T stacking, which cause opposite effects. In comparison of phenol, *p*-methoxyphenol, and *p*-*tert*-butylphenol, the effect of *p*-methoxyphenol (Figure 3b) is reasonably accepted, because *p*-methoxyphenol is as acidic as *p*-*tert*-butylphenol but capable of forming the C-T stacking more easily. Thus, it is confirmed that C-T stacking is actually suppressed by steric hindrance.

d. Effect of Methylene Chain Length. The effect of the methylene chain length of 1,*n*-DPA (*n* = 3, 5, and 9) on complex formation with phenol was examined. The degree of chemical shift change decreased with increase of the methylene chain length, as shown in Figure 6. The fact that the shifts of the proton signals of 1,5-DPA are smaller than those of 1,3-DPA is probably attributable to both weaker C-T stacking and hydrogen bonding between, 1,5-DPA and phenol. In the case of 1,9-DPA the chemical shift of proton c was hardly changed and changes of other proton signals were smaller than those of 1,3-DPA. These results indicate formation of very weak hydrogen bonding and C-T stacking. However, the IR results (Figure 2) clearly demonstrate the occurrence of hydrogen bonding independent of the methylene chain length, which is inconsistent with the NMR results. Whereas the NMR study deals with the interaction *in solution*, the IR study

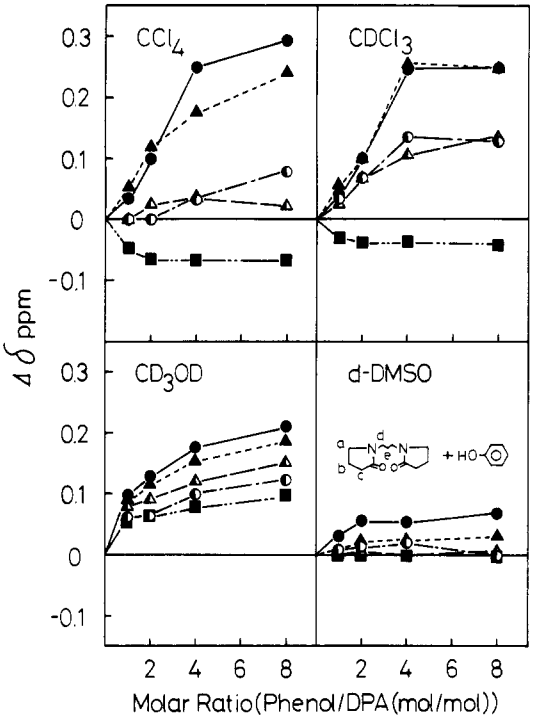
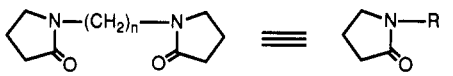


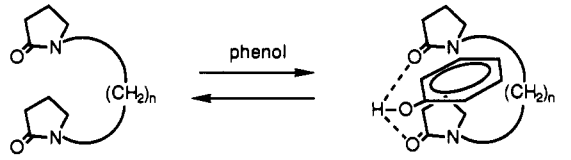
Figure 7. Effect of solvent on the change of the ^{1}H NMR chemical shift of 1,3-DPA by addition of phenol in $CDCl_3$ (total concentration = 0.5 mol dm^{-3}): a (●); b (▲); c (■); d (◐); e (▲).

describes interactions in the absence of solvent. Therefore, the different result between the IR and NMR studies would be explained by assuming that the longer methylene chain effectively suppresses the interaction *in solution*.

This effect of the methylene chain length cannot be explained clearly at present but some explanations can be offered. First, steric hindrance is an important factor in the effect. As shown below, the steric hindrance of group R might increase with increase of the methylene chain-length when group R can be regarded as a substituent on the nitrogen atom. The steric hindrance suppresses the intermolecular interaction with phenol. This is consistent with the pronounced steric effect of the substituents of phenols on C-T stacking, as mentioned above.



Second is the intramolecular association effect of pyrrolidone groups at both termini. When the sandwich-type complex formation is considered as illutrated, an increase of methylene chain length would weaken the complexation because of an increase of freedom of the flexible methylene chain. However, weak hydrogen bonding in the case of n = 9 does not seem to be well explained by this idea.



A third explanation arises from a possible hydrophobic effect of the methylene chain. The hydrophobic methylene chain may prevent the access of phenol for complexation. A unique surfactant activity of 1,9-DPA may also contributed to its special behavior.[19] At any rate, the effect of the methylene chain length is complicated, although the steric effect is most likely to be operative.

Table II
Physical Constants of Solvents

solvent	dielectric constant[a]	dipole moment[a]	Gutmann DN[b]	Gutmann AN[b]
CCl_4	2.238	0		
$CHCl_3$	4.806	1.15		
MeOH	32.63	2.87	19.0	41.3
DMSO	46.68	3.9		19.3

[a] Reference 22. [b] Reference 23.

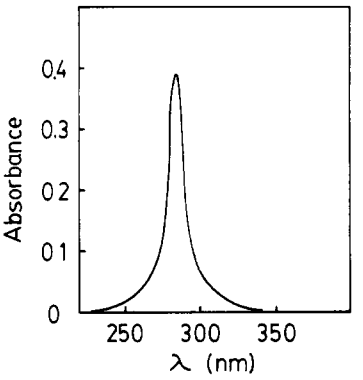


Figure 8. Differential UV spectrum between phenol and phenol + 1,3-DPA in CCl_4 (phenol concentration = 3.92×10^{-3} mol dm^{-3}).

e. Solvent Effect. The interaction is presumably affected strongly by solvent, i.e., solvent and polarity proton content must control complex formation. Figure 7 shows the effect of the solvent on the ^{1}H NMR chemical shift change for each proton of 1,3-DPA in complex formation with phenol. The physical constants of the solvents used are listed in Table II. The magnitude of the change (Figure 7) clearly depends on the solvent polarity and follows the order CCl_4 > $CHCl_3$ > MeOH > DMSO, as expected. That is, the interaction of solvent with 1,3-DPA or phenol is negligibly small in the absence of solvent or in less polar solvents such as CCl_4, whereas it is substantial in polar solvents such as DMSO. In MeOH, only C-T stacking appears to be operative, since MeOH unambiguously interfere with hydrogen bonding between 1,3-DPA and phenol. As a result, all signals are shifted to higher field. Meanwhile, DMSO strongly interacts with phenol on the basis of hydrogen bonding presumably to inhibit the interaction of phenol with 1,3-DPA. Therefore, the shift change was small. Thus, the solvent effect is consistent with the above-mentioned results in the IR and NMR studies.

(3) UV Study. The differential UV spectrum of a mixture of 1,3-DPA and phenol is shown in Figure 8. When 1,3-DPA was added to a CCl_4 solution of phenol (λ_{max} = 270 nm), a new peak appeared at 284 nm. This peak results from complex formation. Compositions of the complex formed between 1,3-DPA and phenol were estimated by the continuous variation method by plotting the absorbance of the mixture at 284 nm. The continuous variation curve as indicated in Figure 9 suggests the formation of a 1:2 complex of 1,3-DPA and phenol, although the curve is not very smooth.

Conclusion

Complex formation between phenols and 1,n-DPAs as model compounds for polymers carrying pyrrolidone moieties was examined by IR, ^{1}H NMR, and UV. In the IR study, the carbonyl adsorption of the pyrrolidone group was shifted to 20 cm^{-1} lower frequencies by addition of phenol in dichloromethane, while in the case without

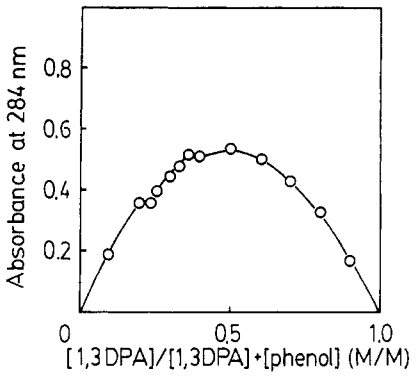


Figure 9. Continuous variation curve of a mixture of phenol and 1,3-DPA in CCl_4 (mixture concentration = 3.92×10^{-3} mol dm^{-3}).

solvent it was shifted to 40 cm^{-1} lower frequencies. The shift of the carbonyl absorption could result from hydrogen bonding, and the range of the shift was attributed to the extent of complexation. ^1H NMR studies indicated that the interaction between 1,*n*-DPAs and phenols was caused by both C-T stacking and hydrogen bonding. Furthermore, the strength of the interaction was affected by the methylene chain length of 1,*n*-DPA, para-substituents of phenols, and the polarity of the solvent. The UV spectrum of the mixture of 1,3-DPA and phenol showed a new peak at 284 nm, which corresponded to that of the complex. It was also found that 1,*n*-DPA could form a 1:1 complex with phenol (pyrrolidone group/phenol).

Thus, in this work the two factors for the complexation, C-T interaction and hydrogen bonding, and the effect of them on the complexation are discussed and clarified. The results obtained are expected to contribute to designing novel polymers capable of complexing with active hydrogen compounds such as phenols.

References and Notes

(1) Horn, D. Ditter, W. *Proc. Int. Symp. Povidone* **1983**, 800.
(2) Horn, D.; Ditter, W. *J. Pharm. Sci.* **1982**, *71*, 1021.
(3) Copes, J. P.; Randall, D. I. U.S. Pat. 3,988,351, 1976.
(4) Molyneux, P.; Vekavakayanondha, S. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2912.
(5) Molyneux, P.; Vekavakayanondha, S. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 635.
(6) Olsson, L.; Samuelson, O. *J. Chromatgr.* **1974**, *93*, 189.
(7) Mccarthy, T. J. *Pharm. Weekbl.* **1973**, *108*, 449.
(8) Bandyopadhay, P.; Rodriguez, F. *Polymer* **1972**, *13*, 119.
(9) Tousignant, W. F.; Sovish, R. C. U.S. Pat. 3,226,372, 1965.
(10) Walls, W. E.; Tousignant, W. F. U.S. Pat. 2,872,321, 1959.
(11) Endo, T.; Okawara, M. *Makromol. Chem.* **1968**, *112*, 49.
(12) Endo, T.; Numazawa, R.; Okawara, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1101.
(13) Endo, T.; Numazawa, R.; Okawara, M. *Makromol. Chem.* **1969**, *123*, 46.
(14) Endo, T.; Okawara, M. *Makromol. Chem.* **1971**, *146*, 237.
(15) Endo, T.; Numazawa, R.; Okawara, M. *Makromol. Chem.* **1971**, *146*, 247.
(16) Endo, T.; Okawara, M. *Kobunshi Kagaku* **1971**, *28*, 260.
(17) Endo, T.; Numazawa, R.; Okawara, M. *Kobunshi Kagaku* **1972**, *29*, 177.
(18) Randall, D. I.; Smolin, E. M.; Copes, J. P. *Nature* **1973**, *244*, 369.
(19) Takata, T.; Atobe, I.; Kitamura, N.; Endo, T. *J. Am. Oil Chem. Soc.* **1990**, *67*, 739.
(20) Badger, R. M.; Bauer, S. H. *J. Chem. Phys.* **1937**, *5*, 839.
(21) Kostenbauer, H. B.; Higuch, T. *J. Am. Pharm. Assoc. Sci. Ed.* **1956**, *45*, 518.
(22) Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Wiley-Interscience: New York, 1970.
(23) Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific & Technical: England, 1987; p 197.

Registry No. 1, 3-DPA, 48149-56-0; 1, 5-DPA, 129301-49-1; 1, 9-DPA, 129301-52-6; PhOH, 108-95-2; $MeOC_6H_4$-*p*-OH, 150-76-5; $NO_2C_6H_4$-*p*-OH, 100-02-7; *t*-BuC_6H_4-*p*-OH, 98-54-4.