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The Effect of Solvent on the α -Effect(3): Nucleophilic Substitution Reactions of Aryl Acetates in MeCN-H₂O Mixtures of Varying Compositions

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Second-order rate constants have been measured spectrophotometrically for the reactions of substituted phenyl acetates with butane-2,3-dione monoximate and *p*-chlorophenoxide anions in MeCN-H₂O mixtures of varying compositions. The reaction rate, unexpectedly, decreased remarkably upon initial additions of MeCN to H₂O up to 30-40 mole % MeCN, and followed by a gradual increase upon further additions of MeCN. The change in solvent composition also influenced the magnitude of the α -effect, i.e., the α -effect increased as the mole % MeCN increased. The solvent dependent α -effect for the present system appears to indicate that the differential solvation between the α -effect nucleophile and the corresponding normal nucleophile is not solely responsible but the difference in the transition-state stabilization is also responsible for the α -effect in organic solvent-rich region.

Introduction

Edwards and Pearson classified a group of nucleophiles which showed abnormally enhanced reactivity toward a variety of substrates relative to their basicity toward hydrogen.¹ A common feature of such nucleophiles is the possession of one or more unshared pairs of electrons adjacent to the nucleophilic center (the α -position). Thus, this enhanced reactivity has been termed α -effect¹ and nucleophiles exhibiting the α -effect include both uncharged nucleophiles such as hydrazines, hydroxylamine and methoxylamine and anionic ones such as peroxy anions, hypochlorite, oximates,

hydroxamates anions, etc.

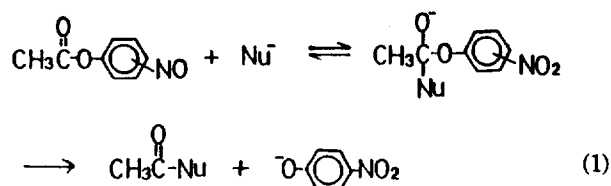
Numerous studies have been performed to investigate the origin of the α -effect,² including (a) destabilization of the ground-state due to repulsion between nonbonding electron pairs;³ (b) stabilization of the transition-state by overlap of the orbitals of the lone pair of electrons in the α -position;^{1,4} (c) product stability;⁵ (d) intramolecular general acid and base catalysis;⁶ (e) polarizability;^{1,7} (f) solvation effects.^{8,9} However, any one of these effects alone does not fully account for the cause of the α -effect. Especially factor (f) has been the subject of controversy. It has been claimed that solvent effect is insignificant as the origin of the α -effect⁸ but other studies,

including theoretical molecular orbital calculations, indicate that solvation should be an important factor.⁹

In our recent communications,¹⁰ it has been demonstrated that the α -effect is significantly solvent dependent for the reaction of *p*-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (Ox^-) as the α -effect nucleophile, in comparison with *p*-chlorophenoxide (ArO^-) as the corresponding normal nucleophile in aqueous dimethyl sulphoxide (DMSO) and in aqueous acetonitrile (MeCN). We have now expanded our study to the reactions of *m*-nitrophenyl acetate (MNPA) with the same nucleophile set of (Ox^-) and (ArO^-) in MeCN- H_2O mixtures of varying compositions to investigate the effect of solvent on the α -effect systematically.

Experimental

Materials. The aryl acetates in the present study were prepared by the known procedures in literature and their purities were confirmed by means of melting points and IR and NMR spectra. *p*-Chlorophenol and butane-2,3-dione monoxime were purchased from Aldrich and were recrystallized before use. Doubly glass distilled water was boiled and cooled under a nitrogen atmosphere just before use. All solutions were prepared and stored under a nitrogen atmosphere and transferred by means of gas-tight syringes. MeCN- H_2O solutions of various mole % MeCN were prepared by weight. Only freshly prepared solutions were used in the kinetic studies.



Kinetics. The rates of reactions were followed spectrophotometrically with a Hitachi U-2000 spectrophotometer equipped with a thermostated cell holder. The temperature inside the cell was kept constant at $25.0 \pm 0.1^\circ\text{C}$ with a LESLAB RTE-110 Model constant temperature circulator. Reactions were followed at a fixed wavelength (λ_{max} of ArO^-). Typically, reaction was initiated by adding $5 \mu\text{l}$ of a 0.02 M solution of the aryl acetate in MeCN by syringe to a 10 mm cuvette containing the reaction mixture made up of MeCN- H_2O , *p*-Cl- $\text{C}_6\text{H}_4\text{OH}$ (or $\text{CH}_3\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{NOH}$) and 0.5 equiv of NaOH solution or Me_4NOH solution for MeCN-rich media. Generally, the ester concentration was 4×10^{-5} M while the phenoxide (ArO^-) and oximate (Ox^-) concentrations were varied over the range $(1-60) \times 10^{-3}$ M and $(0.9-7) \times 10^{-3}$ M, respectively. Usually five different concentrations of ArO^- or Ox^- were employed to obtain the second-order rate constants from linear plots of k_{obsd} versus concentrations of nucleophiles.

Results

The reactions of aryl acetates with the nucleophiles of (ArO^-) and (Ox^-) were monitored spectrophotometrically by following the appearance of the generated aryloxide ion. The reaction studied here obeyed pseudo-first-order kinetics up

Table 1. Summary of the Second Order Rate Constant (k_{Ox^-} , $\text{M}^{-1}\text{s}^{-1}$) for the Reaction of Substituted Phenyl Acetates ($\text{CH}_3\text{C}(\text{O})\text{OC}_6\text{H}_4\text{X}$) with Ox^- in Various MeCN- H_2O Mixtures at 25.0°C

| mole% MeCN | k_{Ox^-} , $\text{M}^{-1}\text{s}^{-1}$ | |
|------------|--|------|
| | PNPA ^a | MNPA |
| 0 | 65.8(65.8) ^b | 52.3 |
| 10 | 37.2(—) | 29.3 |
| 20 | 29.5(139) | 20.5 |
| 30 | 29.2(—) | 17.5 |
| 40 | 35.6(740) | 19.0 |
| 50 | 45.6(1,680) | 21.6 |
| 60 | 67.5(3,850) | 29.5 |
| 70 | 122 (8,200) | 49.9 |
| 80 | 263 (17,200) | 100 |
| 90 | 943 (40,500) | 339 |

^a data from ref. 10b; ^b data in parentheses are from ref. 10a for the reactions in DMSO- H_2O mixtures.

Table 2. Summary of The Second Order Rate Constants (k_{ArO^-} , $\text{M}^{-1}\text{s}^{-1}$) for The Reaction of Substituted Phenyl Acetates ($\text{CH}_3\text{C}(\text{O})\text{OC}_6\text{H}_4\text{X}$) with ArO^- in Various MeCN- H_2O Mixtures at 25.0°C

| mole% MeCN | k_{ArO^-} , $\text{M}^{-1}\text{s}^{-1}$ | |
|------------|---|-------|
| | PNPA ^a | MNPA |
| 0 | .685(.685) ^b | .320 |
| 10 | .385(—) | .121 |
| 20 | .255(.760) | .0661 |
| 30 | .197(—) | .0495 |
| 40 | .198(.280) | .0481 |
| 50 | .217(.590) | .0489 |
| 60 | — .266(1.36) | .0563 |
| 70 | .391(3.47) | .0700 |
| 80 | .712(9.48) | .102 |
| 90 | 2.12 (33.4) | .204 |

^a data from ref. 10b; ^b data in parentheses are from ref. 10a for the reactions in DMSO- H_2O mixtures.

to at least 90% of the total reaction. An equivalent amount of the free phenol or the oxime was added in order to suppress formation of hydroxide ion by solvolysis as described previously.²⁴ Pseudo-first-order rate constants (k_{obsd}) were obtained from the Guggenheim equation. Second-order rate constants were obtained from the slopes of the linear plots of k_{obsd} vs. the concentration of the nucleophiles. The intercept values of these plots were very small indicating the contribution of hydroxide ion and/or water to the rate was negligible.

In Table 1 are presented the second-order rate constants for the reactions of substituted phenyl acetates with Ox^- at 25°C in various compositions of MeCN- H_2O mixtures. The corresponding data for reactions of substituted phenyl acetates with ArO^- are given in Table 2. The data are demonstrated graphically in Figures 1 and 2. The dependence of

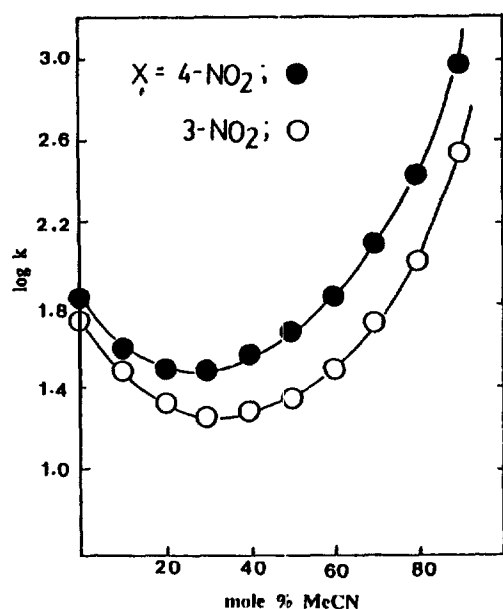


Figure 1. Plots showing dependence of $\log k$ on solvent composition for the reaction of butane-2,3-dione monoximate ion (Ox^-) with substituted phenyl acetates, $\text{CH}_3\text{C}(\text{O})\text{OC}_6\text{H}_4\text{-X}$.

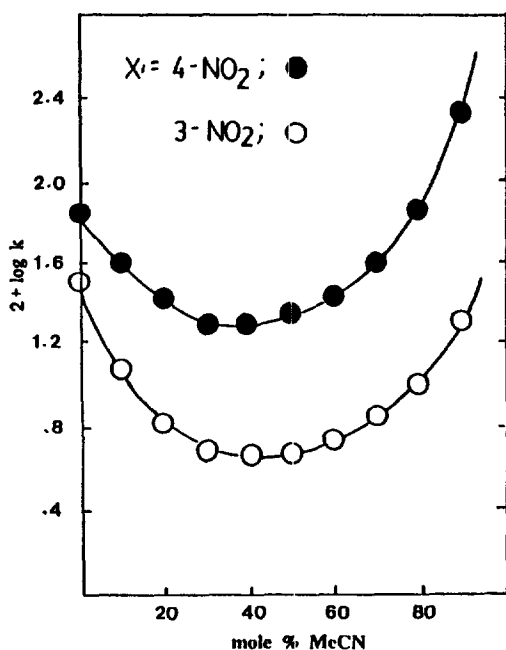


Figure 2. Plots showing dependence of $\log k$ on solvent composition for the reaction of *p*-chlorophenoxide ion (ArO^-) with substituted phenyl acetates, $\text{CH}_3\text{C}(\text{O})\text{OC}_6\text{H}_4\text{-X}$.

the magnitudes of the α -effect ($k_{\text{Ox}^-}/k_{\text{ArO}^-}$) on solvent compositions for the present reaction system is summarized in Table 3 and plotted in Figure 3.

Discussions

Solvent Effect on Rate. Remarkable rate enhancements have often been observed for anionic nucleophilic substitution reactions as solvent changes from H_2O to dipolar aprotic solvents.¹¹ Such rate enhancements have frequently

Table 3. Summary of the Magnitude of the Alpha-Effect ($k_{\text{Ox}^-}/k_{\text{ArO}^-}$) for the Reaction of $\text{CH}_3\text{C}(\text{O})\text{OC}_6\text{H}_4\text{-X}$ with Ox^- and ArO^- in Various MeCN- H_2O Mixtures at 25.0°C

| mole% MeCN | $k_{\text{Ox}^-}/k_{\text{ArO}^-}$ | |
|------------|------------------------------------|------|
| | PNPA ^a | MNPA |
| 0 | 96(96) ^b | 163 |
| 10 | 97(-) | 243 |
| 20 | 116(183) | 309 |
| 30 | 148(-) | 353 |
| 40 | 180(264) | 395 |
| 50 | 210(285) | 442 |
| 60 | 254(283) | 524 |
| 70 | 312(236) | 713 |
| 80 | 369(181) | 982 |
| 90 | 445(121) | 1660 |

^adata from ref. 10b; ^bdata in parentheses are from ref. 10a for the reactions in DMSO- H_2O mixtures.

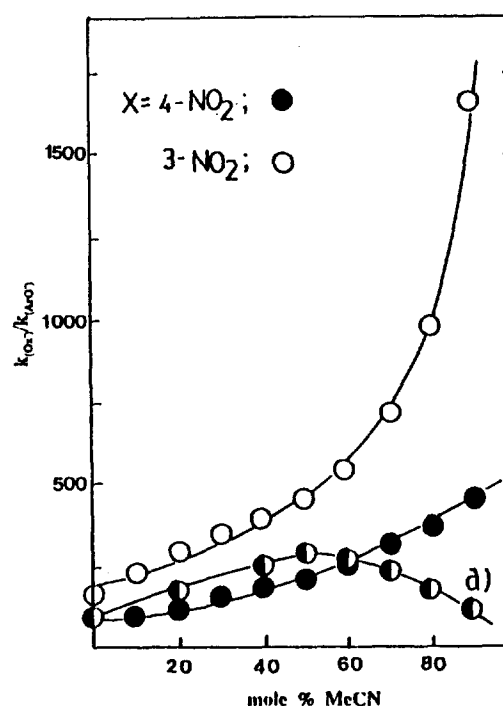


Figure 3. Plots showing dependence of the α -effect ($k_{\text{Ox}^-}/k_{\text{ArO}^-}$) on solvent composition for the reactions of substituted phenyl acetates, $\text{CH}_3\text{C}(\text{O})\text{OC}_6\text{H}_4\text{-X}$ with Ox^- and ArO^- at 25.0°C. a) The data are taken from ref. 10a for the reaction of PNPA with Ox^- and ArO^- in DMSO- H_2O mixtures.

been attributed to desolvation of anionic nucleophiles upon the solvent transfer. Since it has been known that the negative charge end of MeCN is exposed whereas the positive one is not, the anionic nucleophiles in the present system would be strongly desolvated in MeCN.¹¹ Therefore, significant rate enhancements would have been expected for the present reaction system upon the addition of MeCN to H_2O .

However, the present rate data are quite opposite to the expectation. As shown in Table 1 and Figure 1 there is an

initial decrease in rate upon the initial addition of MeCN to H₂O and followed by a gradual increase in rate upon further addition of the aprotic solvent. For example, the second-order rate constant for the reaction of PNPA with Ox⁻ decreases from 65.8 M⁻¹s⁻¹ in H₂O to 29.2 M⁻¹s⁻¹ in 30 mole% MeCN and then increases to 943 M⁻¹s⁻¹ in 90 mole% MeCN. Similar results have been obtained for the reactions of ArO⁻ with aryl acetates as is seen in Table 2 and Figure 2. However, such a decrease in the rate constant is more pronounced for the less reactive reaction system, i.e. the rate constant for the reaction of MNPA with ArO⁻ decreases from 0.320 M⁻¹s⁻¹ in H₂O to 0.0481 M⁻¹s⁻¹ in 40 mole% MeCN.

The Brønsted coefficients, β_{nuc} , have been reported to be 0.79 and 1.04 for the reactions of aryloxides with PNPA and MNPA, respectively.¹² Since the magnitude of β_{nuc} value has been considered as a measure of charge development at the transition-state,¹²⁻¹⁴ the reaction of MNPA would experience more negative charge development on the transition-state than that of PNPA. Thus the former would exhibit more significant rate decrease than the latter, if MeCN is more repulsive to the more negatively charged transition-state. In fact, the rate retardation is more pronounced for the MNPA system than the corresponding PNPA system. Therefore, the unusual rate decrease appears to support our previous proposal that the anionic transition state becomes more desolvated than the anionic nucleophile upon the initial addition of MeCN to H₂O.^{10c}

Solvent Behavior. Interestingly, it is seen from Figures 1 and 2 that rate constant reaches at a minimum near 33 mole% MeCN for all the reaction system. However, such an observation of rate minima near 33 mole% MeCN is not specific to the present reaction but is, rather, one of many characteristic features of the mixtures of this composition. Studies of some physicochemical properties of the mixtures have also showed extrema at this composition, such as excess volume¹⁵ and excess entropy¹⁶ of mixing, energy-volume coefficient, isothermal compressibility¹⁷ and enthalpies of transfer for various anions.¹⁸ The extrema observed at this solvent composition most likely stems from the strong tendency of MeCN to form complexes with H₂O molecules, since at 33.3 mole% MeCN is the stoichiometric ratio of 1 : 2 for MeCN : H₂O. In fact, spectroscopic evidence for 1 : 2 MeCN-H₂O complex has also been reported.¹⁹

From the studies on the volumetric, viscosity and dielectric properties²⁰ and vapor pressure measurements,²¹ the cavities inside the aqueous frame work of the water lattice are suggested to be progressively filled with MeCN up to 33 mole% MeCN, and broken to smaller ones after filling the cavities in MeCN-rich region. Thus, the larger the anion is the more the energy of cavity formation would be required in this solvent region. This would be a possible explanation for the present rate retardation, since the large transition state would require more energy for the cavity formation than the small ground state up to near 33 mole% MeCN.¹⁰

On the other hand, the large aggregates formed in H₂O-rich region have been suggested to be progressively broken to smaller ones upon further addition of MeCN. Thus, the energy of cavity formation beyond 33 mole% MeCN would be considered to be reduced by structure breaking action of MeCN in this region.¹⁸ Consequently, the size of anionic

species would be a less important factor than the charge density to influence desolvation of anionic species in this region. In fact the rate becomes faster in the MeCN-rich region as generally expected.

Solvent Effect on the α -Effect. The effect of solvent on the α -effect has been suggested to be important based on theoretical and experimental studies. HO⁻ has been known to be more strongly solvated in H₂O than HOO⁻ by 12 kcal/mole.²² Thus, the high nucleophilic reactivity of HOO⁻ compared to HO⁻ has often been attributed to the differential solvation energy.^{9a} In fact, DePuy *et al.* found no α -effect in the gas phase reaction of methyl formate with HOO⁻ and HO⁻.^{9c} Similarly, *ab initio* calculations showed that HOO⁻ could not exhibit the α -effect in gas phase.^{9b} Thus, the α -effect observed in solution phase has been ascribed to solvation phenomena.⁹

On the contrary, it has been claimed that solvent effects on the α -effect are insignificant since no appreciable differences in the α -effect have been found in H₂O and in organic solvents, such as for the reaction of *p*-dimethylaminotropylium cation with substituted hydrazines in H₂O and in methanol,^{8b} and for the reactions of carbonyl and phosphinate esters with peroxides anions in H₂O and in toluene.^{8a} Also a significant α -effect observed for the reaction of PNPA with various types of amines in MeCN led to the suggestion that solvation effects are not responsible for the observed α -effect.^{8c} Recently, Jencks *et al.* also raised a question on the role of solvent in the gas phase reaction and attributed the α -effect to the enhanced thermodynamic affinity of α -effect nucleophiles to substrates.^{8e}

The contradiction concerning the solvent effect is considered to originate mainly from lack of systematic studies. For example, reaction media such as toluene,^{8a} methanol,^{8b} acetonitrile,^{8c} 50% aqueous acetone,^{8d} or even the gas phase^{8b,c} have been used. The use of such solvents or solvent mixture make the results of limited value. The finding of an α -effect in any particular solvent other than H₂O is too isolated a result to eliminate the role of solvation on the α -effect. Alternatively, the discovery of no α -effect in the gas phase is not considered necessarily to indicate that solvent effects are solely responsible for the α -effect.

In Table 3 is nicely demonstrated that a two point analysis of the α -effect could be misleading. The α -effect in H₂O would not be much different from the one in DMSO, while it varies significantly in the mixed solvent as the solvent composition changes (e.g., a maximum α -effect ca. 50 mole% DMSO). Therefore, if the experiments has been performed only in the two pure solvents (H₂O and DMSO), the effect of solvent on the α -effect would have been observed to be insignificant. Similarly, the importance of solvent effect on the α -effect is well demonstrated in Figure 3, i.e., the α -effect is increasing with increasing the mole% of MeCN for both PNPA and MNPA systems.

The Origin of the α -Effect. It has been suggested that the pK_a value of the two nucleophiles ArO⁻ and Ox⁻ varies in a similar manner upon changing of solvent compositions.^{10a} Furthermore, the reaction mechanism would not be considered to be affected upon the medium change.²⁴ Thus, the present solvent dependent α -effect is not considered to originate either from any difference in the basicities of two nucleophiles or any change in the reaction mechanism as the sol-

vent composition changes.

Although many evidences for a concerted S_N2 -like mechanism have been suggested for various types of acyl-transfer reactions,¹² the present reaction has generally been believed to proceed *via* a step-wise mechanism.²³⁻²⁵ Furthermore, either the reaction proceeds *via* one or two-step mechanism, the attack of the anionic nucleophiles on the substrate is considered to be involved in the rate-determining transition-state for the present reaction system.²³⁻²⁶ Accordingly, any difference in solvation of the nucleophile (Ox^-) has been reported to be less solvated than the corresponding normal nucleophile (ArO^-) in H_2O .²⁷ Thus, the difference in solvation of the two nucleophiles would be considered to be responsible for the α -effect in the H_2O -rich media.

However, if the solvation difference between the two nucleophiles is mainly responsible for the α -effect, the magnitudes of the α -effect for the reaction of the two substrates would be expected to be similar to each other in all the solvent compositions. In fact, the α -effects for the two substrates differ slightly from each other in the H_2O -rich region, while the ones in the MeCN-rich region are significantly different as shown in Figure 3. Accordingly, differences in solvation energy for the two nucleophiles is not considered to be fully responsible for the α -effect particularly in the latter region.

As shown in Figure 3, the magnitude of the α -effect for the MNPA system is larger than the one for the PNPA system in all the solvent region, which is in the same order of β_{nuc} value for the two reaction system. This is consistent with the general trend that the α -effect is proportional to the β_{nuc} values.^{5b} Since the magnitude of β_{nuc} value has also been considered as a measure of the degree of bond formation at the transition-state,¹²⁻¹⁴ the larger the β_{nuc} value is the more the influence would be transmitted to the transition-state. Thus, factors influencing the stability of the transition-state in various ways² would be more pronounced for the reaction having larger β_{nuc} and consequently the α -effect would become larger as β_{nuc} value increases. On this basis, the significant difference in the α -effect between the PNPA and MNPA systems particularly in the MeCN-rich media would be considered to originate from a difference in stabilization of the transition-state.

Conclusions

Changes in the medium composition influence both reaction rates and the α -effect significantly for the present reaction system. The unusual rate decrease upon the addition of MeCN to H_2O suggests that the large transition-states is more desolvated than the small anionic nucleophiles since the former would require more cavity formation energy than the latter. The present solvent dependent α -effect suggests that the differential solvation energy between Ox^- and ArO^- is not solely responsible but the difference in stabilization of the transition-state is also responsible for the α -effect in organic solvent-rich media.

Acknowledgement. Financial support of this research by the Korea Science and Engineering Foundation is grateful

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Solubilization of Alcohols in Aqueous Solution of Cetylpyridinium Chloride

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The critical micelle concentration (CMC) values of cetylpyridinium chloride (CPC) in some alcohol-aqueous solutions were determined by UV-Vis spectroscopy at 25°C. The CMC of CPC was increased with the addition of methanol and ethanol, while with the addition of propanol it was decreased because of the solubilization of propanol into the micelle of CPC. The ratio (β) of the number of counterions to that of surfactant ions associated into micelles in alcohol (methanol, ethanol and propanol) aqueous solutions was measured by using the Shinoda equation¹⁷. The ratio of counterion binding to the CPC micelles in methanol- and ethanol-water mixtures was larger than in pure water, while the ratio in propanol-water mixture might be much decreased.

Introduction

A large number of studies have been reported on the effect of various electrolytes and alcohols on the micellization of nonionic and anionic surfactants¹⁻⁷.

The association of ionic surfactant in aqueous solution is governed by two opposing forces⁸: The hydrophobic force between the hydrophobic tails attracts the surfactant molecules or surfactant ions to the micelle core from the aqueous bulk solution. The ionic head groups, on the other hand, favor the aqueous bulk phase, because the electrostatic repulsive force between the head groups prevents the surfactant molecules from associating. In this connection, the effects of inorganic salts and alcohols on the aggregation (micellization) of ionic surfactant may be discussed. The effect of inorganic electrolytes is explained in terms of the shielding of the electrostatic repulsion by the counterions^{9,10}, while the effect of alcohols which have a long hydrophobic part is explained from the reduction of the free energy of mixing and the reduction of the surface charge density by the alcohols entering in the palisade layer of the micelle^{11,12}. Therefore, the effect of short chain alcohols on the micellization of a cationic surfactant may be interesting.

From these points of view, we have studied the effect of short chain alcohols (methanol, ethanol, and propanol) on the micelle formation of cationic surfactant, cetylpyridinium chloride (CPC) in aqueous KCl-solutions. The CMC values

of CPC in alcohol-salt (KCl)-water mixtures were determined by the UV-Vis. spectroscopy method previously reported¹⁰. The ratio (β) of the number of counterion to that of surfactant ion in micelles was measured in order to understand the solubilization of propanol more clearly.

Experimental

Materials. Cetylpyridinium chloride (CPC) and KCl were used as received from Merk A. G. without further purification. The organic additives (methanol, ethanol, and propanol) were received from Merk A. G. and distilled before use. The water used in all experiments was Millipore "reagent grade" water. The specific conductivity of this water was $1.8 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Method. The critical micelle concentration (CMC) values of CPC in alcohol-salt-water mixtures were determined by the UV spectroscopy method. Optical densities of about 12 sample concentrations of CPC were read from the digital display at 271 nm with a double-beam Shimadzu Model 265 spectrophotometer. The solutions in the cell compartment were thermostated at 25°C for about 15 minutes before the measurements were started.

Results and Discussion

The Effect on CMC. The CMC values of CPC in seve-