# Host–Guest Interactions Between Macrocycles and Methylsubstituted Anilinium Ions

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The binding characteristics and analytical applications of anilinium ion complexes with 18–crown–6 were studied by polarography and NMR. First, the electrochemical reduction of the 10 species of mono and dimethylsubstituted anilinium ion complexes with 18–crown–6 as host in methanol are examined. The addition of 18–crown–6 to anilinium guest solution the polarographic waves remain well defined but shifted toward more negative potentials, indicating the complex formation. The values of formation constants, log $K$ for 10 species of methylsubstituted anilinium ion complexes with 18–crown–6 varies from 2.7 to 4.8 in methanol at 25 °C. The stability order of complexes for 18–crown–6 is anilinilum>4–methyl>3,4–dimethyl>3–methyl>3,5–dimethyl>2,4–dimethyl>2,5–dimethyl>2,3–dimethyl>2–methyl>2,6–dimethylanilinium ion. The steric hindrance shows significant effect. Second, Proton NMR was used to elucidate their interaction characteristics. From the results of so called NMR titration techniques, the behaviors of binding sites on complexation, and the stoichiometry and stability order of complex were obtained. And the later results show the satisfactory agreement with the quantitative values obtained by polarography. Finally, the individual determinations of anilinium ion mixtures were also accomplished by addition of 18–crown–6. In some mixtures of methyl or dimethylanilinium ions the reduction peaks of differential pulse method appeared into one unresolved wave attributed to the small difference of half-wave potential, $\Delta E_{1/2}$. In the presence of 18–crown–6, the polarographic waves were resolved into individual maxima because of the shift toward more negative direction by the difference of selectivity of anilinium ions with 18–crown–6. It may be concluded that quantitative analysis of methylanilinium ion mixture make possible because the half-wave potential shift by the selectivity difference due to the steric hindrance between methyl group and 18–crown–6 on complexation.

## Introduction

Cram and his co–workers[1,2] called the synthesis and study of highly structured organic complexes the field of host–guest chemistry. In the chemical sense the host is usually an organic molecule containing specific receptor whose binding sites converge while the guest is normally a metal or organic cation, whose binding sites diverge. Host–guest interactions have recognized importance in many biological processes, including enzyme catalysis and inhibition, membrane transport and antibody–antigen interactions.[1]

The X-ray structures of many host–guest complexes of crown ethers with ammonium and substituted ammonium ions have been reported.[3] The -$NH_3^+$ group lies in the perching position out of oxygens of crown ring, rather than in the nesting position.[4] In contrast, in the crystalline complex[5] of potassium thiocyanate with 18–crown–6, the potassium ion lies at the center of the crown ring, in the ideal nesting position. Extensive NMR[6,7] and other thermodynamic studies led recently to the characterization of arenediazonium[8] and organic ammonium[9,10] cation complexes formed by crown ethers as host in solution state.

The electrochemical behavior of some methylsubstituted anilinium ions as guests will be especially examined in relation to the structure and the conformation of macrocyclic host–guest complexes. As a part of the systematic investigation of the characteristics of interaction of organic cation guest with crown ether, we have determined stoichiometry, log K and binding properties of guests for complex formation of 18–crown–6 with 10 species of anilinium ions by polarography and $^1$H-NMR.

In general, the reactions of organic compounds at a microelectrode are more complex than those for inorganic species. Despite these handicaps, organic polarography has proved fruitful for the determination of structure, and quantitative analysis of mixtures, and occasionally, for the qualitative identification of compounds.

We reported here the stabilities of 18–crown–6 complex with some mono and dimethylsubstituted anilinium cations. It was found that the stabilities were very sensitive to steric interference from methyl substituent group of benzene in each positions as was demonstrated qualitatively by Gokel and Cram[11]. In addition, we also reported the effect of the presence of macrocyclic host on the individual determinations of anilinium ion mixtures by differential pulse polarography.

## Experimental

**Reagents.** The following chemicals were obtained from the indicated supplier: 18–crown–6 (Aldrich); aniline (Merck); 2–methylaniline, 3–methylaniline, 4–methylaniline, 2,6–dimethylaniline, 3,5–dimethylaniline, 2,3–dimethylaniline, 3,4–dimethylaniline, 2,5–dimethylaniline (Tokyo Kasei); tetrabutylammonium chloride (Merck).

The anilinium chlorides were prepared as following.[9] Approximately 3-5 g of each methylsubstituted aniline was mixed with 100 m*l* of anhydrous diethyl ether. Anhydrous hydrogen chloride gas was slowly bubbled through the ether solution, causing salt formation and subsequent precipitation.

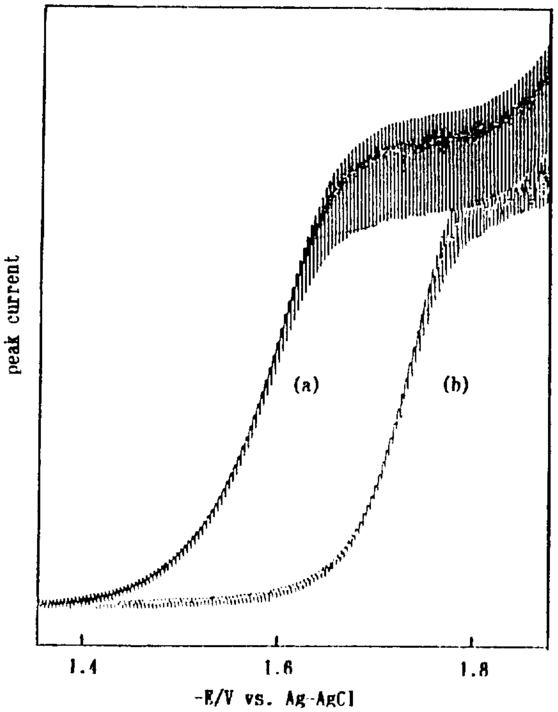


**Figure 1.** Polarograms of $1.0 \times 10^{-3}$ M 3,5-dimethylanilinium ion in (a) absence and (b) presence of $1.0 \times 10^{-2}$ M 18-crown-6 in methanol at 25.0 °C.

The salt was filtered from ether solution, washed with more diethyl ether, and then recrystallized from absolute ethanol/ether, 18-crown-6 was recrystallized from acetonitrile and dried at 60 °C in vacuum oven. Methanol (Merck GR) was used without further purification.

**Instrument and Working Procedures.** All of polarograms were obtained with a Princeton Applied Research Model 274 polarographic analyzer and recorded on a Houston Instrument Model 200 $x-y$ recorder. All of the measurements were carried out with the dropping mercury electrode with mechanically regulated drop time in a three electrode system in methanol at 25 ± 0.1 °C. The auxiliary counter electrode was a Pt-wire and a Ag-AgCl reference electrode was place in a 0.1 M tetrabutylammonium chloride solutions in methanol and connected to the electrolyzed solution by means of a capillary junction containing an asbestos fibre. The supporting electrolyte was 0.05 M tetrabutylammonium perchlorate. The solutions were deaereated with purified nitrogen gas for 5 minutes before each measurements. The polarography was operated in the normal DC or differential pulse mode with the drop time set to 1.0 sec. The scan rate was 2.5 or 5 mV $s^{-1}$.

Proton NMR spectra were measured on a Bruker AW80 spectrometer (80 MHz) at 34 °C. Chemical shifts of each protons among both macrocycle and guest ion were determined by a frequency counter within an error of ± 0.2 Hz, relative to TMS or DMSO zero lockings. The concentrations of guest salts were held constant at about 0.05 M, and the maxima concentrations of host were kept in the range of 0.08 to 0.12 M by stepwise additions of host stock solution, same as guest solution except host, with the aid of gas tight microsyringes. And the reverse procedures were also accomplished at constant concentrations of guests at about 0.05 M.

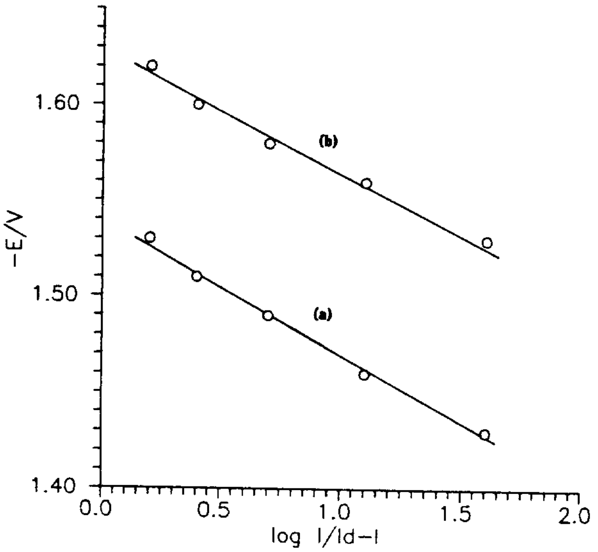


**Figure 2.** Plots of $-E$ *vs.* $\log[I/I_d - I]$ for (a) 3,5-dimethylanilinium ion and (b) its complex with 18-crown-6 in methanol at 25.0°C.

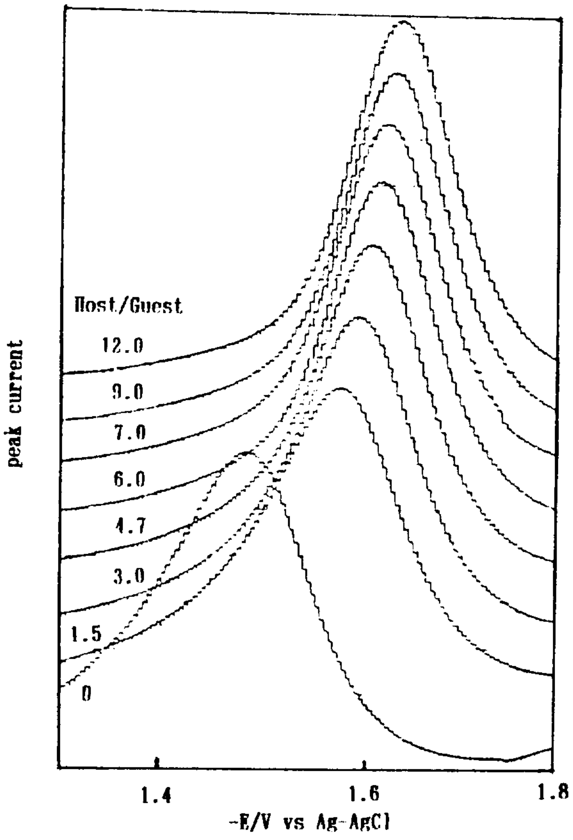


**Figure 3.** Differential pulse polarograms of $1.0 \times 10^{-3}$ M anilinium ion at various host/guest mole ratio in methanol at 25.0 °C.

## Results and Discussions

**Polarographic Determinations of Stability Constant.** In polarographic study the significant quantity for the stability of the complex is the half wave potentials, $E_{1/2}$ of the complex and of the free guest ion. In Figure 1, the half wave potential of the complex is shifted to more negative potential when the concentration of 18-crown-6 is increased.

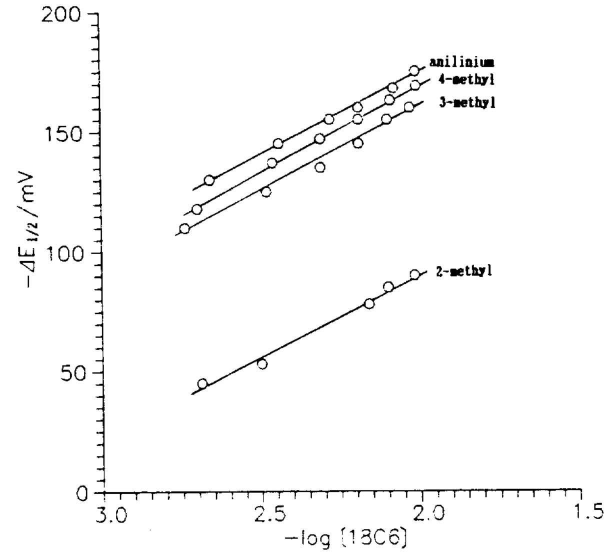


**Figure 4.** Dependence of half-wave potentials for the monomethyl substituted anilinium ions on the concentration of free 18-crown-6 in methnol at 25.0 °C.

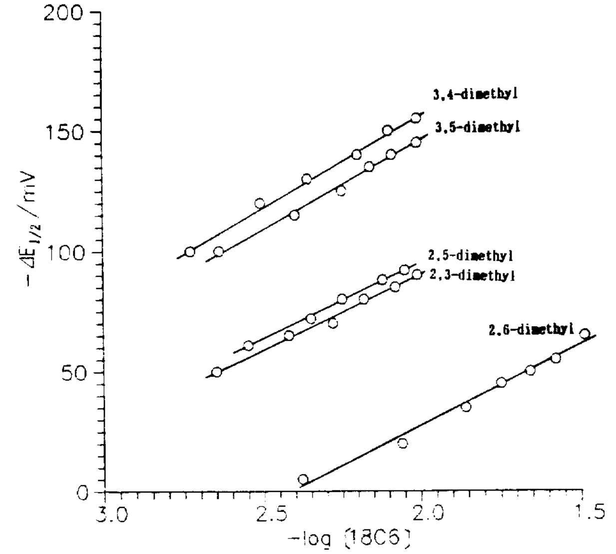


**Figure 5.** Dependende of half-wave potentials for the dimethyl substituted anilinium ions on the concentration of free 18-crown-6 in methanol at 25.0 °C.

From the types of the plots of Figure 2, the reduction of all anilinium ions under investigation and their complexes with 18-crown -6 are characterized by the reversible and one-electron wave with the slope $dE/d[\log I/(I_d-I)]$ = 61 to 70 mV. After addition of 18-crown-6 to the guest solutions the slopes are nearly not changed whereas the whole waves are shifted to more negative potentials. This behavior is significant for the fast charge transfer across the electrode interface resulting in the establishment of an equilibrium between the free and complexed guest ions in solution and guest molecules dissolved in the amalgam.[12]

The differential pulse waves for the anilinium ion complexes in presence of excess host shifted toward more negative potentials as shown in Figure 3. Figure 4 and 5 show the dependences of the half-wave potential of the mono and dimethylsubstituted anililium complexes on the host concentrations, respectively. On the basis of plots of these type the stability constants, log $K$ and the stoichiometry of complex, $p$ were determined by equation (1);

$$E_{1/2}=(E_{1/2})_c-(E_{1/2})_f$$

$$=0.0591/\mathrm{n}\log K-0.0591/\mathrm{n}\log K-0.0591\,p/n\,\log[I/I]_f \quad (1)$$

**Table 1.** The Half-wave Potentials of FreE Guests, and the Stoichiometry and Stability Constants of 18-crown-6 Complexes with Guests in Mthanol at 25.0 °C.

| Guest ions | $-E_{1/2}$ vs Ag/AgCl | $p$ | log $K$ |
|---|---|---|---|
| anilinium | 1.47 | 1.00 | 4.84 |
| 2-methylanilinium | 1.56 | 0.95 | 3.47 |
| 3-methylanilinium | 1.58 | 0.99 | 4.57 |
| 4-methylanilinium | 1.62 | 1.07 | 4.65 |
| 2,3-dimethylanilinium | 1.60 | 1.00 | 3.52 |
| 2,4-dimethylanilinium | 1.61 | 1.05 | 3.70 |
| 2,5-dimethylanilinium | 1.58 | 1.02 | 3.52 |
| 2,6-dimethylanilinium | 1.51 | 1.07 | 2.72 |
| 3,5-dimethylanilinium | 1.65 | 0.97 | 4.41 |
| 3,4-dimethylanilinium | 1.54 | 0.99 | 4.64 |

In Table 1 are listed the values of log $K$ and $p$ for the interaction of anilinium ion and nine of its mono and dimethylsubstituted analogues with 18-crown-6. The most notable features of the data are the strength of the complexes formed and the sensitivity of binding strength to the steric properties of the guest cations. Substitution of one methyl group onto aromatic group results in a decrease of complex stability. Moreover substitution of one methyl group onto the different positions result in sensitive changes in complex stability as shown in the sequence;

anilinium>*para* - methyl>*meta* - methyl>*ortho* - methyl

The substitution of a methyl group onto *ortho* position causes the stability constant to drop in value by above an order of magnitude. While the substitution at the *para* position results in a little decrease of stability. These results are consistent with those predict from steric considerations. Substitution onto the *ortho* positions has the largest destabilizing effect on the stability.

Substitutions of an additional methyl group give the dimethylsubstituted anilinium cations and results in further loss of stability as shown in the sequence;

3,4-methyl>3,5-dimethyl>2,4-dimethyl
2,5-dimethyl>2,3-dimethyl>2,6-dimethyl

In the dimethylanilium series, substitutions in the 2 and 6 (two *ortho*) positions result in the largest loss of stability. The analogues substituted in the 3 and 5 (two *meta*) positions has less and in 4 (one *para*) position has least effect. The fact binding constants of dimethylanilinium complexes are smaller than those of unsubstituted or monosubstituted analogues suggests that the methyl substituents in phenyl group des-

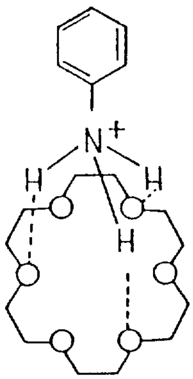
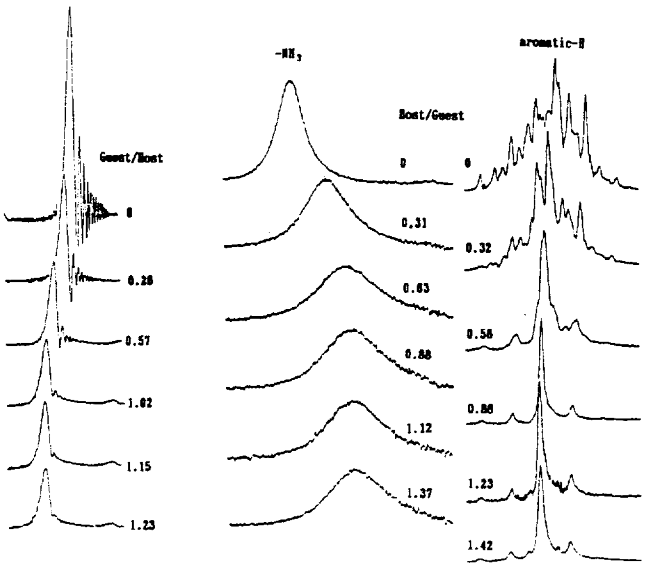


**Figure 6.** Diagrammatic representations of binding of anilinium ion to 18-crown-6.[8] Dashed lines indicate hydrogen bonds.



DMSO locking (2.2 ppm)
(a)

TMS locking
(b)

**Figure 7.** NMR spectra of (a) 0.05 M 18-crown-6 at various guest/host mole ratio and (b) 0.05 M anilinium ion at various host/guest mole ratio in $CDCl_3$/DMSO (10:1 v/v).

tabilized the complex cooperatively except the case of the *para* substitutions of 2,4- and 3,4-dimethylanilinium ions.

X-ray crystallography has shown that the mode of binding of anilinium cation to 18-crown-6 correspond to the simplified structure in Figure 6.[13] The ammonium protons are much closer to the cyclic polyether ligand to take the hydrogen bond. Noteworthy feature of this structure is that the three NH-0 hydrogen bonds are arranged in a tripod and the -$NH_3^+$ group lies in the perching position[4] out of host oxygens, not in the nesting position. For this reason, substitution of bulky group on the *ortho* position of anilinium cation is expected to interfere more than those of *meta* or *para* position substituent.

**Characteristics of Host-Guest Interactions by $^1$H-NMR.** The NMR-shift methods have been widely used to determine the association constants for diamagnetic complexes, although there still remain problems of interpretation[14] and accuracy[15] in range of log $K$>4. The NMR studies of macrocyclic complexation reactions with diamagnetic guest ions not only result in important information on the selectivity and stoichiometry of complexation formations but also lead to a better understanding of donor-acceptor properties of atoms in binding sites of host-guest system. This area of research, however has received less attention than the ubiquitous thermodynamic studies.

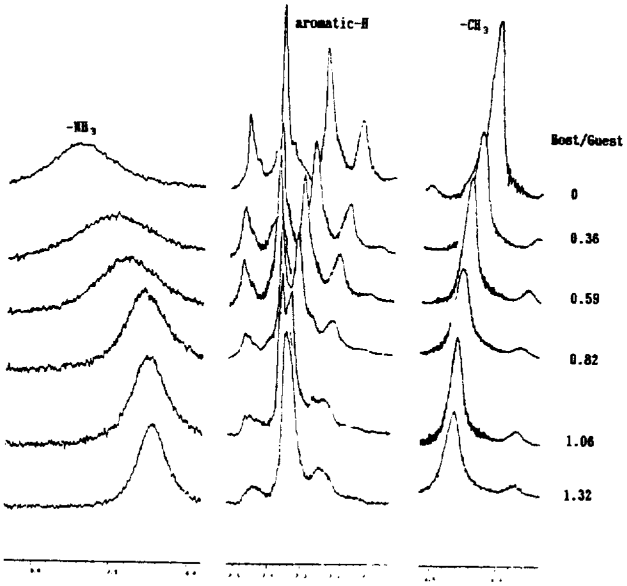


**Figure 8.** NMR spectra of 0.05 M 4-methylanilinium ion at various host/guest mole ratio in $CDCl_3$/DMSO (10:1 v/v).

The $^1$H-NMR titration technique is well suited for a complexation study of 18-crown-6 with several anilinium ions.[15,16] The stepwise addition of the guest cation into the host solution of fixed concentration and its reverse procedures were accomplished respectively. Some of the results of spectral series are shown in Figure 7 and 8.

Without exception one population-average resonance was observed indicating the exchange of the guest ion between free and complexes host is faster than the NMR time scale. The effects of incremental additions of each guest ions into 18-crown-6 were all qualitatively similar. Figure 7(a) is a typical example. In Figure 8, the spectra of 4-methylanilinium chloride alone consist of one multiplet due to the aromatic protons at about 7.3 ppm, and two singlets of methyl and ammonium protons at about 2.3 and 8.2 ppm relative to TMS reapectively. The multiplets for the aromatic protons are characteristics of a four-spin AA'BB' coupled system for typical 1,4,-disubstituted benzene.

The addition of 18-crown-6 to the solution produces a gradual diamagnetic shift of guest protons except ammonium protons. In Figure 7 and 8, among the guest protons the greater shifts were observed for ammonium protons. Since the induced chemical shift depends mainly on the nearest neighboring interaction, this observation means that ammonium protons of guest cation is attached to three point of host oxygen atoms suggested in Figure 6.

The stoichiometry of these complex formation could be obtained by plotting the shifts of guest or host proton resonance positions as function of host/guest or guest/host mole ratio. According to Figure 9 and 10 induced shift varies linearly with the mole ratio until the ratio of 1:1 reached. It

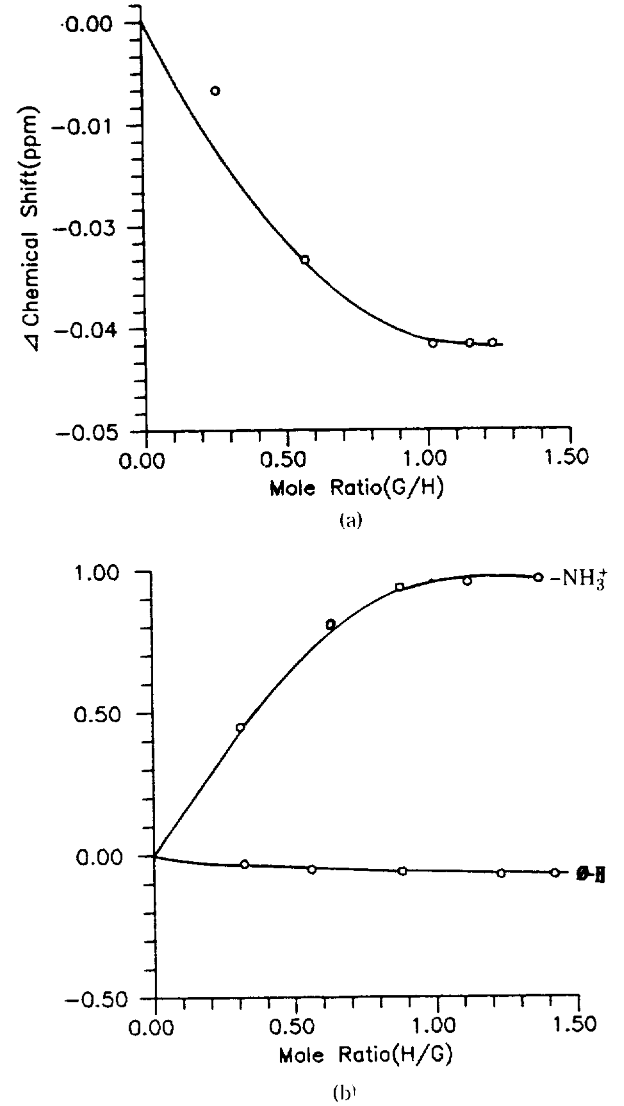


**Figure 9.** Proton chemical shift of (a) 0.05 M 18-crown-6 at various guest/host mole ratio and (b) 0.05 anilinium ion at various host/guest mole ratio in $CDCl_3$/DMSO (10:1 v/v).

could be deduced that these host-guest systems form 1:1 complex and these results show the satisfactory agreement with the $p$ values obtained by polarography in Table 1.

From the plots of Figure 11, the behavior of the chemical shifts of ammonium protons for several methylsubstituted anilinium ions are a function of the mole ratio can be approximately divided into 2 groups:

1. The chemical shift varies lineally with the mole ratio until the mole ratio of 1:1 is reached. It indicate the formation of a stable 1:1 complex.
2. The stepwise addition of ligand in guest solutions were lead to gradually upfield shifts the guest resonances and the chemical shifts does not seem to reach a limiting value even at fairly high value of mole ratio. A typical example is the behaviors of the 2-methyl and 2,6-dimethylanilinium systems and it is indicative of the formation of a weak complex.

No attempt was made to calculated the formation constants from the variation of the chemical shift as a function of mole ratio as described here. However, it is to be expected

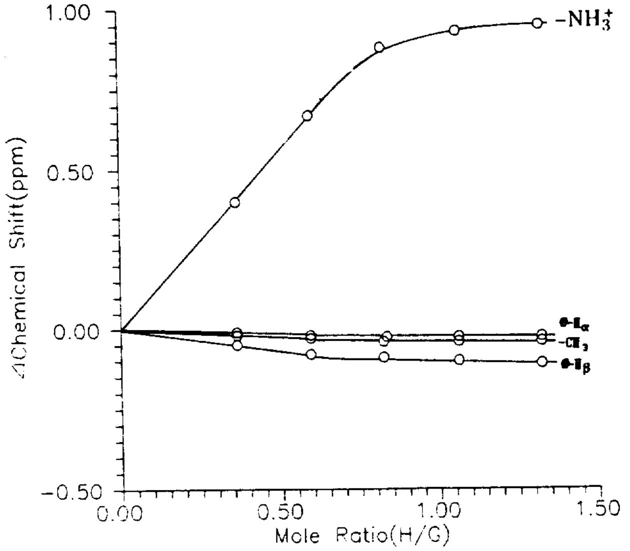


**Figure 10.** Proton chemical shift of 0.05 M 4-methylanilinium ion at various host/guest mole ratio in $CDCl_3$/DMSO (10:1 v/v).

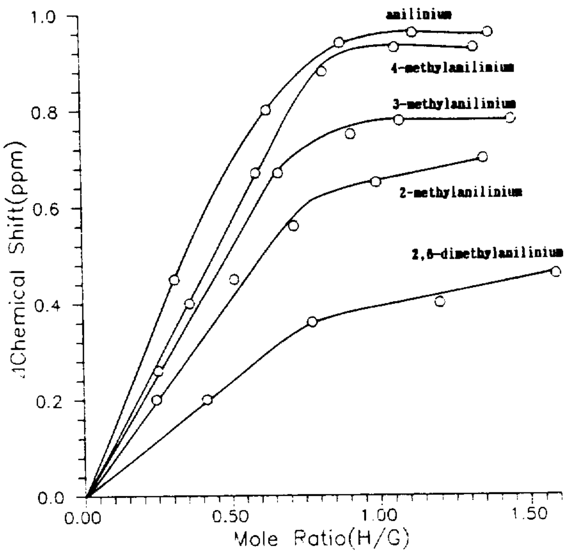


**Figure 11.** Proton chemical shift of ammonium of guest ion at various host/guest mole ratio in $CDCl_3$/DMSO (10:1 v/v).

that the magnitude of variation is a sensitive probe of the interaction as shown in the sequence;

anilinium>4-methylanilinium>3-methylanilinium

2-methylanilinium>2,6-methylanilinium

Comparison of this sequence with the quantitative values obtained by polarography in Table 1 shows a satisfactory agreement.

**Polarographic Determination of Mixtures of Anilinium Ions by Addition of Host.** Frequently organic polarography has proved fruitful for the determination of structure, quantitative analysis of mixtures[17], and occasionally, for the qualitative identification of compounds. The reductions of methylanilinium ions ($1.0 \times 10^{-3}$ M) were measured in methanol and 0.05 M tetrabutylammonium perchlorate was used as supporting electrolyte. In these conditions the

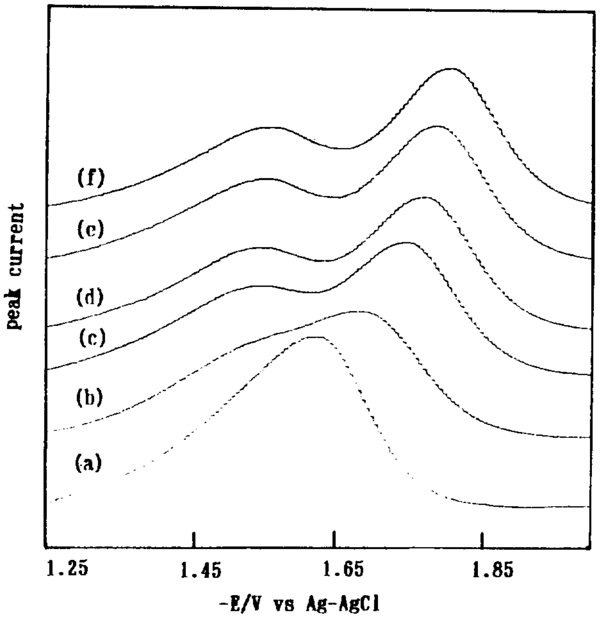


**Figure 12.** Differential pulse polarograms for a mixture of 4-methyl and 2,6-dimethylanilinium ions (both 0.001 M) by incremental additions of 18-crown-6 in 0.05 M tetrabutylammonium perchlorate methanolic solution. The mole ratio of 4-:2,6-:18-crown-6 are (a) 1:1:0, (b) 1:1:1, (c) 1:1:3, (d) 1:1:5, (e) 1:1:7 and (f) 1:1:10.

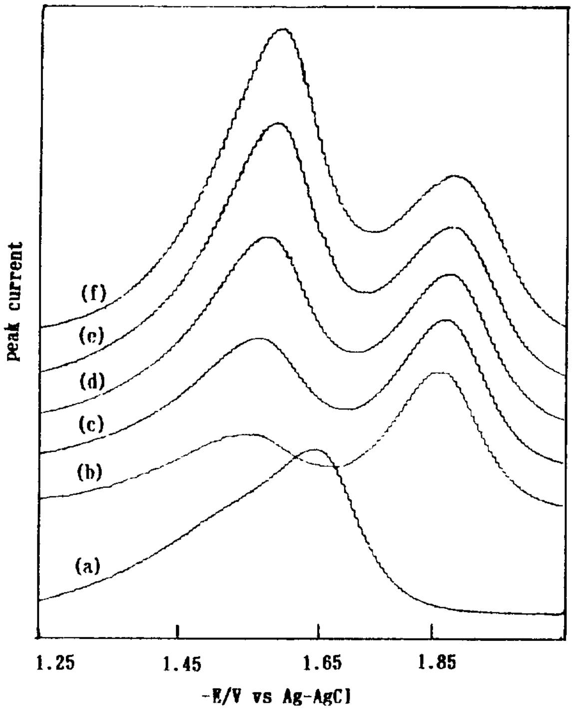


**Figure 13.** Differential pulse polarograms for a mixture of 2,6-dimethyl and 3,4-dimethylanilinium ions by additions of excess 18-crown-6, and incremental additions of 2,6-dimethylanilinium chloride as standard substance in 0.05 M tetrabutylammonium perchlorate methanolic solution. The mole ratio of 2,6-:3,4-:18-crown-6 are (a) 1:1:0, (b) 1:1:10, (c) 1.5:1:10, (d) 2:1:10, (e) 2.5:1:10 and (f) 3:1:10.

half-wave potentials of most guest ions were found at about -1.6 V/Ag-AgCl and the results are also listed in Table 1.

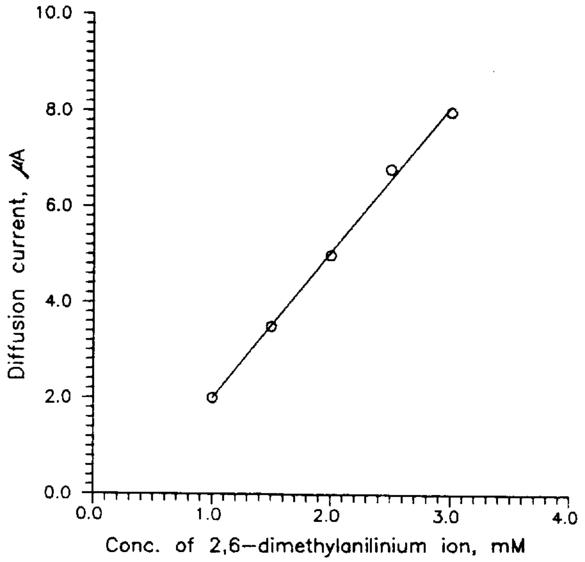


**Figure 14.** Plot of the peak current *vs* concentrations of 2,6-dimethylanilinum chloride in the solution of Figure 13.

The half-wave potential shifts slightly to the negative directions with all types of methylsubstitutions. More important one is, however individual peak maxima cannot be observed for each substances with half-wave potentials differing by as little as 0.01 to 0.05 V. This limitation results from the lower value than the required half-wave potential difference, 0.05 V or above, for resolution of waves by differential pulse methods.[18]

In Figure 12-(a), the 1:1 mixture of 2,6-dimethyl and 4-methylanilinium ions give the one asymmetric unresolved wave as expected. The serial attempts were made to resolve the individual maxima of each species by addition of different amount of 18-crown-6 into this mixture. It was interesting to note that when the ratio of host to guest reaches above 5 the resolved two maxima were observed. As expected, it could be found that the left one is for 2,6-dimethyl and right one is for 4-methyl analogue by the standard additions of each species.

In Figure 13-(a) and (b), also, the peak for the 1:1 mixture of 2,6-dimethyl and 3,4-dimehylanilinium were resolved by additions of excess (10 times) of 18-crown-6, and after incremental additions of 2,6-dimethylanilinium chloride into this solution the height of left one increased gradually due to the presence of 2,6-dimethylanilinium ion complex with 18-crown-6 in solution. In Figure 14, the relation between added amount of 2,6-dimethylanilinium ion and diffusion current gave a straight line in these conditions. The detail procedures and results will be discussed in our preceding paper.[19] Consequently, the mixture of substituted anilinium ions with similar reduction properties could be determined qualitatively and quantitatively by addition of 18-crown-6 due to the selectivity difference.

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# Parametric Study of DF–$CO_2$ Transfer Chemical Laser by the Numerical Model Simulation

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The effects of the concentration and the pressure of reactants on laser output were reported in the previous study. The present study is made of the following main parameters on laser characteristics; the initial temperature of the reaction mixture, inert gas (He) added in the reaction mixture, and the level of initiation as a function of time. As the initial temperature of reaction mixture decreases, both the output energy and the duration time increase. Especially, the output energy is linearly proportional to the inverse of the initial temperature. In order to obtain a proper lasing for a given condition, a sufficient amount of He must be added: The optimum ratio of [He] to $[D_2 + F_2 + CO_2]$ is found to be greater than 2. In addition, the time dependence of level of initiation (TDLI) shows no significant difference in total output energy from that of the premixed model, but only the power profile.

## Introduction

A DF–$CO_2$ transfer chemical laser (TCL) is a type of $CO_2$ laser which releases a high power of $10.6\mu m$ beam. While in the conventional $CO_2$ laser the $N_2$ gas added plays a central role to improve the lasing efficiency[1], in TCL the function of $N_2$ is replaced with the excited DF molecules[2]. Namely, it achieves a population inversion of $CO_2$ by the vibrational energy transfer of excited DF molecules formed by $(D_2 + F_2)$ chain chemical reactions. Since the population inversion of $CO_2$ is achieved from the chemical reactions, the phenomena occurring in this laser system are very complicated[2]. In order to get a better understanding of the mechanism of how the laser operates, model simulations of this system have the developed extensively[3-11]. We reported the results of the calculation of power in which show[12] good agreement between the previous experimental and theoretical studies reported in the literature. Additionally, we discussed the optimum lasing conditions for the initial concentration ratios of reaction mixture ($D_2$:$F_2$:$CO_2$:He) by comparing the result of the experiment with the calculation. However, there are various important other aspects in the operation of the DF–$CO_2$ TCL, which have been reported little in the literature. These include the role of the initial temperature of reaction mixture to lasing efficiency and energy; the role of added inert He gas in the reaction mixture; the change of laser characteristics such as intensity and duration profile, governed by the duration of the reaction–initiating pulse.

In general, oscillation takes place between two vibrational levels of (00°1) and (10°0) in $CO_2$ laser[13]. To obtain a strong laser action, the (00°1) level must be over–populated. Note that an increased temperature of reaction mixture suppresses the power releasing followed by a rising population of (10°0) level. However, only a few reports are available on detailed results of systematic theoretical calculations for this laser (TCL). First, we describe the effects of initial temperature of the reaction mixture at several conditions.

The reaction mixture of DF–$CO_2$ TCL often contains the