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Determination of Derivatives of Phenol with a Modified Electrode Containing β -Cyclodextrin

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Voltammetric determination of phenol derivatives, such as phenol, *o*-, *m*-, and *p*-cresols was studied with a β -Cyclodextrin (β -CD) modified-carbon paste electrode composing of the graphite powder and Nujol oil. Phenol derivatives were chemically deposited via the complex formation with β -CD by immersing the CME into a sample solution. The resulting surfaces were characterized with cyclic and differential pulse voltammetry. Treating the CME with 1 M nitric acid for five sec after a measurement could regenerate the electrode surface. Linear sweep and differential pulse voltammograms were recorded for the above system to optimize the experimental parameters for analysing the phenol derivatives. In this case, the detection limit for phenols was 5.0×10^{-7} M for 25 min of the deposition time with differential pulse voltammetry. The relative standard deviation was $\pm 5.2\%$ of 3.0×10^{-6} M (four repetitions). The interference effect of the following organic compounds was also investigated; Bezoic acid, hippuric acid, *o*-, *m*-, and *p*-methylhippuric acid. Adding the organic compounds into the sample solution reduces the peak current of the phenols to about 25%.

Introduction

A cyclodextrin (CD) is cyclic carbohydrates consisting of glucose units that associate with other organic compounds. The unique property of CD is that it forms the inclusion complex with the guest compounds in the cavity.^{1,2} Guest compounds incorporated in the CD cavity include various organic species of appropriate size, especially aromatic compounds. The mole ratio of the guest to host (CD) is usually 1 : 1 and 2 : 1. Exceptions include sometimes carboxylic acid and molecules which have long chains such as methyl orange.^{3,4} Another distinctive characteristic of CD is that it can form crystalline insoluble complexes with many hydrocarbons.⁵ While there are several studies for the chromatographic separation of organic species with CD via the inclusion complex formation,^{1,2,6} few studies of the electrochemical behavior of organic species in the presence of CD has been done so far.⁷⁻¹¹ Moreover, the direct analysis of organic spe-

cies using CD in electrochemical methods have been done less than that of the electrochemical behaviors of the CD derivatives.

Osa *et al.* reported that the effects of added α - and β -CDs on the half-wave potentials and the diffusion coefficients of *o*-, *m*-, and *p*-nitrophenols and determining the dissociation constants of CD-phenol complexes.⁹ Based on this, Matsue *et al.* investigated about a regioselective electrode system aimed at determining *o*-nitrophenol with a poly(perfluoro sulfonic acid)-coated electrode which was based on the regiorecognition ability of α -CD in the presence of *p*-nitrophenol.¹² They suggested that *p*-nitrophenol binded with α -CD in the Nafion layer. Nagase *et al.* developed the voltammetric anion responsive sensors based on ordered membrane assemblies containing cyclodextrin polyamine deposited on glassy carbon electrodes by the Langmuir-Blodgett method.¹³

We used the properties of β -cyclodextrin(β -CD), which is a cyclic carbohydrate consisting of seven glucose units¹ which can associate and capture the phenol derivatives. This was used to analyze these compounds in an aqueous solution

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with a modified-electrode. The chemically modified electrodes (CMEs) can selectively sense a species in a solution phase. Generally, to preconcentrate the test species is done by using the electrode modified with organic ligands that reacts with the test species through the complexation or the adsorption. This forms insoluble compounds in an aqueous solution. Using CME gives little interference when exchanging the sample solution with a clean electrolyte prior to performing the analysis step. One might bypass the host electroactive species interfering at the analysis step. Of these CMEs, the carbon paste electrodes (CPEs) were used in many cases to analyze metal ions due to its unique advantages that it can be readily prepared and easily regenerated to a new electrode surface. While many papers for determining the metal ions using CMEs¹⁴⁻¹⁷ have been published, there are a few reports for determining organic species with CMEs.¹⁸⁻²⁰

In this study, we have developed the method for the determination of simple phenol derivatives such as, phenol, *o*-, *m*-, and *p*-cresol with a β -CD modified carbon paste electrode. This work characterizes the performance of the analysis with the β -CD modified CPE and optimizes experimental parameters affecting the response of the electrode in the followings: Electrode composition, pH dependency, deposition time, interference effect, etc. In addition, we determined the detection limits by using cyclic voltammetry and differential pulse voltammetry at the optimum condition examined in this experiment.

Experimental

Reagents. β -CD obtained from Katayama Chemical Co. (Japan) was purified by recrystallization in distilled water twice. A special grade of phenol from Ishizu Pharmaceutical Co. (Japan) and special grade of *o*-, *m*-, and *p*-cresol from Junsei Chemical Co. (Japan) were used. The graphite powder was from Aldrich (USA) and doubly purified in ethanol. Buffer components were of the analytical grade and used without further purification. All other reagents were used in the experiment without further purification. Pure distilled water was obtained from a Milli-Q system (18 M ohm/cm).

Electrodes. 10 g of the graphite powder was put into a nitrogen purged absolute ethanol solution and it was washed by stirring. The graphite powder was treated by this method several times then dried at 90 °C for 24 hours in a vacuum oven. We made the mixture of the graphite powder and β -CD in the various weight ratios: 0, 20, 30, 40, 50, and 60 (w/w%). The CPEs were constructed by packing the graphite paste, which was mixed of 3 mL Nujol oil and 5 g of the powder mixture into a 1ml polyethylene syringe. The electrode body was made by cutting the edge of the polyethylene syringe with a razor; the piston of the syringe was used to support the paste. The copper wire through the flank of the piston was used to connect the carbon paste to the equipment. Before using the CPE in each measurement, the electrode surface was rubbed with a clean paper until its surface became smooth and shiny. To regenerate the electrode surface, we immersed it in 1 M nitric acid solution for five sec before each experiment. The electrode was used repeatedly after rinsing the electrode several times with distilled water. The pretreatment process for the CPE

allowed us to use the electrode 10 times. Before the measurements, the electrode was activated in the sample solution at high concentration (1.0×10^{-2} M), repeating the deposition and oxidation step several times.

Apparatus. Cyclic and differential pulse voltammograms were recorded with a Princeton Applied Research Model 273 potentiostat/galvanostat and a Kipp and Zonen Model 90B X-Y recorder. All measurements were done with a three electrode system. The reference electrode was Ag/AgCl connected with a 0.1 M KNO_3 bridge to prevent the interference of chloride ions. The working electrode was the CPE with a diameter of 0.5 cm; the auxiliary electrode was a platinum wire. The test sample solution was thermostated at 20 ± 0.1 °C. The voltage scan range was from -0.3 V to 1.2 V. The voltage scan rate in CV and DPV was 100 mV/sec and 5 mV/sec, respectively.

Process of Analysis. The standard solution of 1.0×10^{-2} M *o*-, *m*-, *p*-cresol and phenol were diluted to an adequate concentration and used immediately before each measurement. The preconcentration of the test species on the electrode surface was accomplished by immersing the CPE modified with β -CD into a stirred sample solution for a certain time. After that, the electrode was immediately taken out of the preconcentration solution and rinsed thoroughly with deionized water. Then it was inserted into a separate measuring solution containing a supporting electrolyte only. Before measurement, the dissolved oxygen was removed by passing nitrogen gas through the solution for 10 min.

Results and Discussion

Voltammetric Behavior of Phenol Derivatives on CME. Figure 1 shows the cyclic voltammograms recorded for the *m*-cresol deposited-CPEs modified with β -CD, and the unmodified electrode in a blank solution. The content of β -CD in the CPEs was 60% with respect to graphite in weight percent. Figure 1(a) and (b) show CVs recorded for the unmodified electrodes in a KNO_3 solution after transferring it from the preconcentration solution of cresol and thoroughly washing the CPEs with the distilled water. They were exposed to a 1.0×10^{-2} M *m*-cresol solution containing an acetate buffer then transfer the electrode in the KNO_3 solution. While the CV in Figure 1(a) has no peak over the potential range from -0.3 V to 1.2 V, the CV of (b) has a broad small anodic peak at around 0.6 V due to the physical adsorption of *m*-cresol onto the CPE surface at the high concentration of the sample solution. Although the unmodified CPE was used, the peak appeared little to owe to the adsorption of the sample on the electrode surface at high concentration of an analyte. However, it did not appear on the CVs recorded at the lower concentration of a sample solution (1×10^{-3} M). Figure 1(c) is the CV recorded for the modified CPEs containing 60% β -CD in a KNO_3 solution followed by transferring the CPEs from a blank acetate buffer solution. Figure 1(d) is the CV recorded for the modified electrode in the KNO_3 solution followed by the preconcentration in an acetate buffer solution containing 1.0×10^{-4} M *m*-cresol. Although the CV of β -CD itself showed a small redox peak near 0.5 V (Figure 1(c)), this peak does not disturb the analysis of the sample in a given concentration range, because all the sample peaks appear around $+0.7$ V.

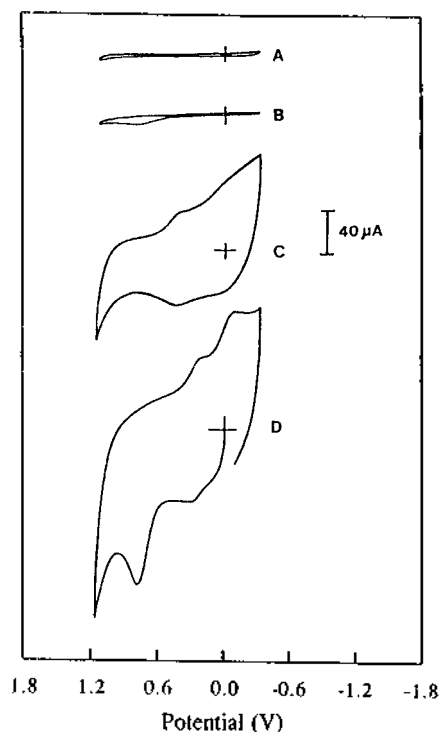


Figure 1. Cyclic Voltammograms recorded for the unmodified carbon paste electrode (A and B) and for the β -CD modified carbon paste electrode (C and D) in a KNO_3 solution, after the preconcentration in a blank buffer solution (A and C) and in a 1.0×10^{-2} M cresol containing the buffer solution (B) and in a 1.0×10^{-4} M cresol containing buffer solution (D), respectively.

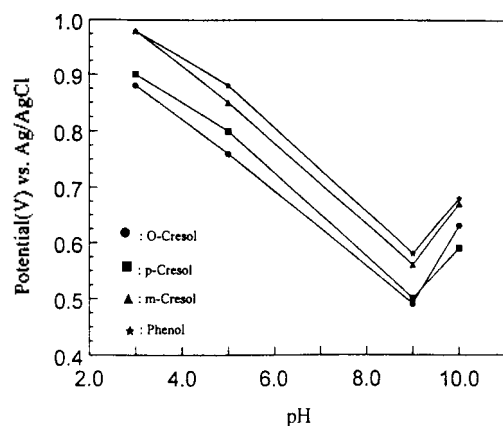


Figure 2. The plot of the oxidation potentials of phenol and cresols preconcentrated on the CME according to the pH of the measuring solution. (●: o-Cresol, ■: p-Cresol, ▲: m-Cresol, ★: Phenol).

The redox peak appeared around 0.5 V shifted to the more negative potential of about 0.3 V on the phenol capturing electrode (Figure 1(d)). This shift strongly indicates that the preconcentration was possibly due to the formation of the complex between β -CD and phenols. Because, β -CD in the paste electrode might easily present in a liquid phase in the Nujol oil although β -CD was on the electrode surface. Thus, as like that in a bulk solution, the phenol was captured

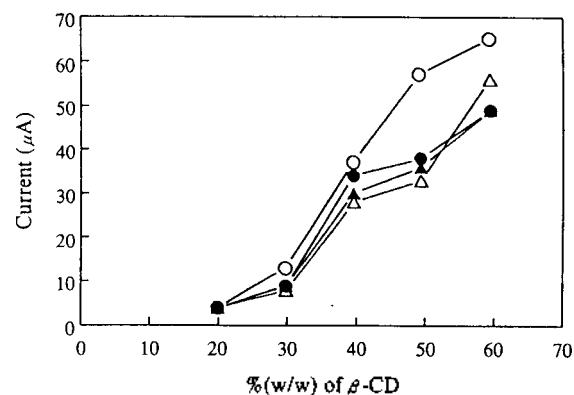


Figure 3. Plot for the peak current vs. weight ratios of the β -CD and graphite in the CME; pH 3 and preconcentration time is 10 min. (○: p-cresol, ●: m-cresol, △: phenol, ▲: o-cresol; the concentration is 1.0×10^{-4} M, respectively).

by β -CD on the electrode via complex formation. As well as this result, Matsue *et al.* also have suggested that p-nitrophenol binded with α -CD in the Nafion layer.¹²

Figure 2 is the plot for the shift of the oxidation potentials of the phenol and cresols, which were captured on the electrode through the complexation with β -CD, with respect to the pH change of a measuring blank solution. The oxidation potential of the test species adsorbed on the CPE was more positive in the order of phenol > m-cresol > p-cresol > o-cresol at the same pH. One exception is that o-cresol was more positive than p-cresol around pH 10. The difference of the anodic peak potential of the inclusion complexes of the β -CD in relation to the phenol and cresols themselves should be proportional to the strength of complexation. The capability of the β -CD modified CPE to capture the test species relates to how well β -CD forms a complex with the ones in the sample solution. Thus, the strength of complexation increases in the order of o-cresol < p-cresol < m-cresol < phenol. The pH dependency of the anodic potential of the test species preconcentrated on the CPE shows the linearity in the range from pH 3 to 9. The slope was 54 mV/pH suggesting that the number of electrons that participated in the oxidation of the inclusion complex is approximately the same as the number of protons. (This does not appear in the text.) This differs from the oxidation mechanism of phenols themselves in a CH_2Cl_2 - HFSO_3 solution by a two electron and one proton reaction.²¹ The different reaction routes may be due to the difference in solvent and/or a different structure of the inclusion complex form.

Optimization of analysis conditions. To determine the optimum composition ratio of β -CD to graphite in CPE, the electrode was made in the composition ratio of 0, 20, 30, 40, 50, and 60% (w/w). Figure 3 shows the plot obtained for the peak current variation according to the composition of the β -CD with respect to graphite in CPE. The CPE containing β -CD was immersed in the 1.0×10^{-4} M o-, m-, p-, and phenol solution, respectively, for 10 min deposition on the modified CPEs. After thorough washing with distilled water, the electrodes were transferred to a supporting electrolyte solution (pH 3, acetate buffer solution). The anodic oxidation current of analytes captured on the modified CPE increased

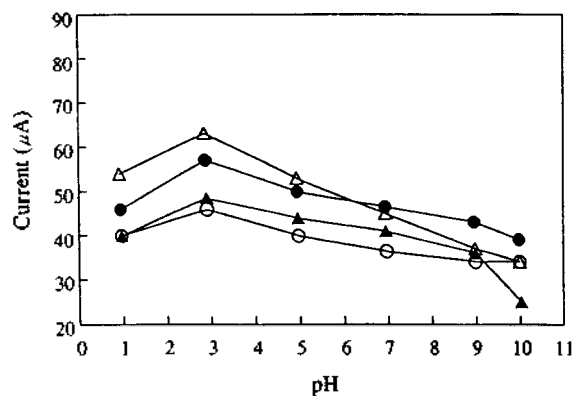


Figure 4. pH dependency of the anodic current of the test species in buffer systems. (○ : phenol, ● : o-cresol, △ : p-cresol, ▲ : m-cresol; the concentration is 1.0×10^{-4} M, respectively.).

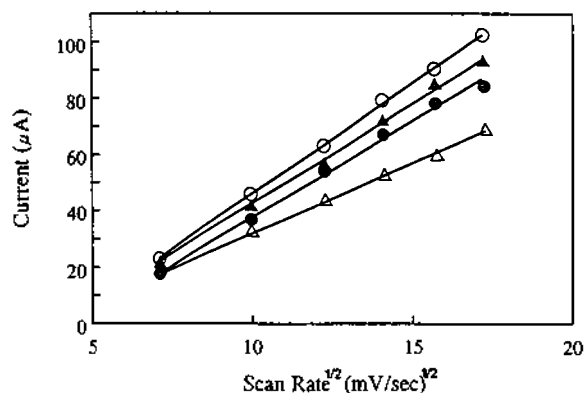


Figure 5. The plot of the anodic peak height of the test species on the CME vs. the scan rate. The predeposition time is 10 min. The content of β -CD was 60%(W/W). (○ : p-cresol, ● : m-cresol, △ : o-cresol; the concentration is 1.0×10^{-4} M, respectively.).

as the content of β -CD in CPE increased to 60%. However, the modified electrode was not useful due to the low sensitivity by the high resistance of the modified CPE when the content was over 60%. Thus, we determined the optimum composition of β -CD in the CPE to 60%(w/w).

Figure 4 shows the pH dependency of the peak currents to the test species in the following buffer systems: hydroperchloric acid, citric acid/ sodium citrate, acetic acid/sodium acetate, and sodium hydrogen phosphate/ sodium hydroxide. All four test species have the largest peak current at pH 3. The peak height of the anodic current falls as the pH rises, except when the peak current drops below pH 3. This is due to the instability of β -CD in a strong acidic medium. β -CD is usually stable in basic medium, but its reactivity increases in acidic medium.²² Although the reactivity of β -CD should be higher in an alkaline medium than acidic medium, the complexation is more difficult than in the weak acid medium owing to the deprotonation of the β -CD molecules. Thus, we took pH 3 as an optimum pH for analysing the test species.

Figure 5 shows a plot of the variation of the anodic peak height of phenols on CME containing β -CD according to the

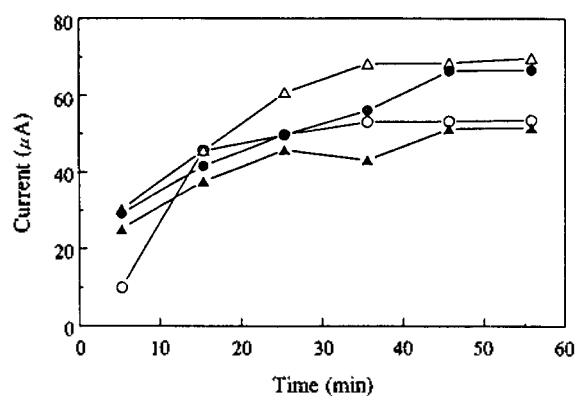


Figure 6. The plot of the anodic peak current of the test species vs. the predeposition time. pH of the predeposition solution is 3 and scan rate is 100 mV/sec. (○ : o-cresol, ● : m-cresol, △ : p-cresol, ▲ : phenol; the concentration is 1×10^{-4} M, respectively.).

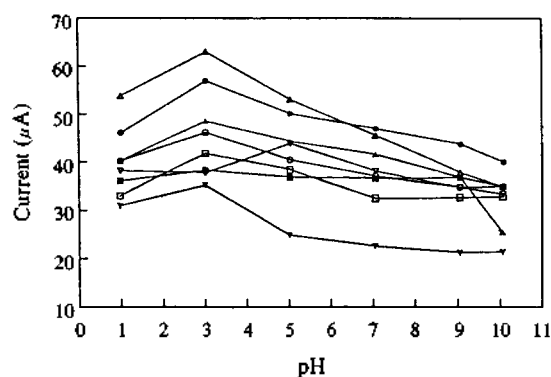


Figure 7. Interference effect of the other organic compounds according to the pH change of the measuring solution. (○ : phenol, = : phenol+other compounds, ● : o-Cresol, □ : o-Cresol+other compounds, △ : p-Cresol, ▽ : p-Cresol+other compounds, ▲ : m-Cresol, ■ : m-Cresol+other compounds; the concentration is 1×10^{-4} M, respectively.).

change of the scan rate. Although, the plot did not through the zero point due to the background current and /or including the experimental error, the peak current was approximately proportional to the square root of the scan rate. This says that the anodic oxidation reaction of the complexes was controlled by the diffusion of counter ions or the stripping of phenol captured on the modified CPE.

The effect of the predeposition time on the anodic peak current of the 1.0×10^{-4} M o-, m-, p- cresol, and phenol solution at pH 3 was shown in the Figure 6. The anodic current was plotted accordingly by varying the deposition time at 5, 15, 25, 35, 45, and 55 min in the sample solution. In this case, the scan rate of the linear sweep voltammetry was 100 mV/sec. Increasing the deposition time led to the large anodic peak current at the given concentration until the time reached 30 min. The elevation of the peak height according to the deposition time gradually reduced after around 25 min because the active sites of the electrode surface were fully saturated by the analytes. Although β -CD is slightly soluble in water (1.85 g/100 mL), Nujol oil make the solubility of β -CD lower than when it expose to aqueous

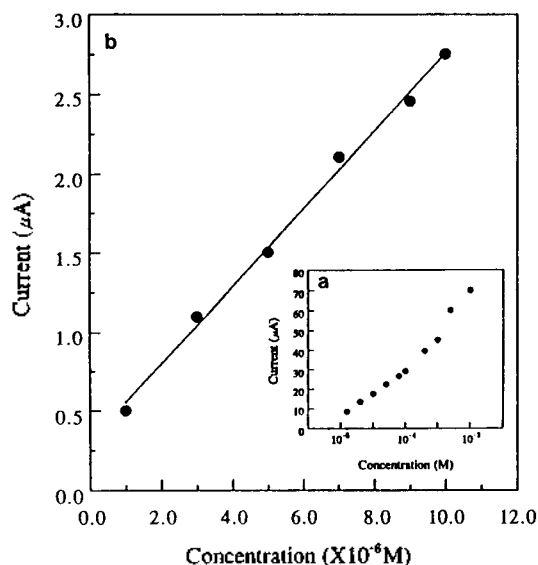


Figure 8. Calibration curve of phenol by using linear sweep voltammetry (a) and p-cresol in differential pulse voltammetry (b).

media solely. Thus, there is no risk of the instability of the electrode surface during measurements within the analysis time window.

Some compounds that form sparingly soluble inclusion complexes with β -CD should disturb the analysis of phenol and its derivatives. Thus, we investigated the interference effect of an organic species that was expected to disturb the complexation for the analysis of phenols at various pH of the measuring solution as shown in Figure 7. Some organic compounds such as benzoic acid, hippuric acid, o-, m-, and p-methyl hippuric acid which were metabolites produced from solvents such as, benzene, xylene, toluene along with cresols that might interact with β -CD was examined. To test the interference effect of these species, we mixed those organic compounds with each test species to have a final concentration of 1×10^{-4} M. The CMEs were then deposited for 10 min. In the cases of m-, o-cresol, and phenol the peak currents of CVs were decreased to 25-30% compared to the one without the addition of organic compounds to the test solution. While adding all the above organics to a solution containing p-cresol led to decreasing the peak current to 50% at maximum, this indicated that the organics might be complexed with β -CD, so the reduction of the peak current of the analytes could take place. Other organic species except the above compounds were expected to form inclusion complexes with β -CD and may reduce the response of the CME. From these results, the optimum condition for the analysis of o-, m-, p-cresol, and phenol using the CPE containing β -CD was as follows: The contents of β -CD with respect to the graphite in the CPE was 60% in weight/weight percent; the acetic acid/acetate buffer solution (pH 3) was used for the deposition of the analyte (the deposition time was 30 min); and the anodic peak for the analytes deposited on the modified CPE was obtained at the voltage sweep range of -0.3 V to 1.2 V in a 0.1 M KNO_3 solution (scan rate for the analysis was 100 mV/sec).

The calibration plots for phenol and p-cresol were sepa-

ately obtained by using the linear sweep and differential pulse voltammetry. This yielded linear plots as shown in Figure 8. Figure 8a shows a dynamic range when linear sweep voltammetry was used. In this case, the linear plot was yielded before the concentration was over $\sim 10^{-4}$ M. However, the plot has a different slope over $\sim 1 \times 10^{-4}$ M. Least-squares treatment of the data of phenol obtained in the range between 1×10^{-5} M and 1×10^{-4} M yielded the equation of $I(\mu\text{A}) = 2.44 \times C(\times 10^{-5} \text{ M}) + 6.50 \mu\text{A}$ and $r = 0.999$ (See Figure 8a). The detection limit for phenol using the linear sweep voltammetry was 8.0×10^{-6} M. Also, the least-squares treatment of p-cresol obtained by using the differential pulse voltammetry yielded the equation of $I(\mu\text{A}) = 0.245 \times C(\times 10^{-6} \text{ M}) + 0.270$ and $r = 0.993$ (See Figure 8b). The detection limit was 5.0×10^{-7} M and the relative standard deviation was $\pm 5.6\%$ in 3.0×10^{-6} M (four repetitions). The other cresol isomers and phenol showed the similar results and responded as p-cresol. Conclusively, this method could apply to the analysis of the total content of phenol derivatives in an aqueous sample.

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A New Substituent Constant, σ^{c+} ; a Fit for π -Participation in Modified Hammett-Brown Equation

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A set of substituent constants, σ^+ , has been widely used comparing the stability of carbocation in super acid condition. Plotting of ^{13}C chemical shifts of cationic carbon ($\Delta\delta^{c+}$) against σ^+ constants yields an excellent correlation with a good correlation coefficient ($r=0.999$) for a cyclopentyl cation system. But these σ^+ constants show poor linearity in norbornenyl cations that well known to show homoallylic stabilization in a cationic condition. We calculated the new substituent constant, $\sigma^{c+\pi}$, and found that the new substituent constants give an excellent correlation in π - and $\pi\sigma$ -participating cation systems.

Introduction

The correlation of ^{13}C chemical shifts with Hammett-Brown σ^+ constants has received considerable attention over past few years. On the assumption that ^{13}C chemical shifts were linearly proportional to charge density, it was not unreasonable to expect the σ^+ constants to correlate ^{13}C chemical shifts of the fully formed carbocations in superacids. Accordingly, numerous attempts seeking to correlate the ^{13}C chemical shifts of the cationic carbons with Hammett-Brown σ^+ constants have been reported.

For example, Olah and co-worker¹ originally reported approximated linearity in the plot of C^+ chemical shifts of the substituted *tert*-cumyl cations ($\Delta\delta^{c+}$) against Hammett-Brown σ^+ constants. In a reinvestigation of the behavior of the substituted *tert*-cumyl cations, Kelly and Spear² observed an even lower correlation coefficient, $r=0.967$.

The use of Hammett-Brown σ^+ constants have shown to be inappropriate for this purpose. Thus Brown and coworkers³ developed the following modified Hammett-Brown equation,

$$\Delta\delta^{c+} = \rho^{c+} \cdot \sigma^{c+}$$

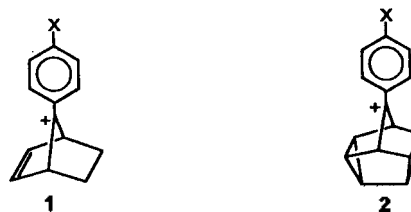
where ρ^{c+} is the slope obtained from the plot of $\Delta\delta^{c+}$ against σ_m^+ values of the *tert*-cumyl cations. Using this equation, their calculated the new substituent constants σ^{c+} .

A plot of σ^{c+} values against $\Delta\delta^{c+}$ values of the 1-aryl-1-cyclopentyl cations revealed an excellent correlation, with a correlation coefficient $r=0.999$.⁴ Therefore, a set of substituent constants, σ^{c+} , has been widely used for investigation of structure-reactivity relationship in acyclic, cyclic, and polycyclic cation systems.⁵

However, these new σ^{c+} constants reveals only a fair fit

in cation systems with neighboring π -participating groups. For example, when plotted against σ^{c+} , the cationic carbon substituent chemical shifts ($\Delta\delta^{c+}$) of 7-arylnorbornenyl cations **1** give a poor correlation ($r=0.961$), in which the cation **1** was well-known the presence of π -participation.⁶

We wish now to report the calculated the new σ^{c+} s constants and examined on their ability to correlate $\Delta\delta^{c+}$ values for π - and $\pi\sigma$ -participating cations such as 7-aryl-norbornenyl and 9-aryl-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}] cation **2**.



Results and Discussion

7-Arylnorbornen-7-ol derivatives were prepared by the addition of the ketone to the *Grignard* reagents that were prepared from the *m*-CH₃, *m*-F, *m*-Cl, *m*-CF₃, *m*-OCH₃, *p*-CH₃, *p*-OCH₃, *p*-Cl, *p*-F and *p*-H substituted bromobenzenes. The cations **1** were prepared by adding a measured quantity of the corresponding alcohol to the FSO₃H/SO₂ClF solution at $-120\text{ }^\circ\text{C}$, and ^{13}C NMR spectra of the cations were recorded at $-90\text{ }^\circ\text{C}$ and $-100\text{ }^\circ\text{C}$. The ^{13}C NMR chemical shifts of cationic carbon in these cations and $\Delta\delta^{c+}$ values summarized in Table 1 and 2.

When the $\Delta\delta^{c+}$ values for the *para*-substituted 7-arylnorbornenyl cations are plotted against the substituent constants σ^{c+} , the results are unsatisfactory with $r=0.961$, $\rho^{c+} =$