

minated trialkylamine groups of the macrocycle. The formation of the octahedral species accompanied by the protonation is also affected by the coordinating ability of the anion.

Acknowledgment. This work was supported by the Basic Science Research Program (1994), the Ministry of Education of the Republic of Korea.

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Determination of Nitrate in Chromium Plating Solution with Nitrate-Selective Electrodes

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Received November 10, 1994

A method for determining nitrate in post treatment chromium plating solutions with PVC-based nitrate-selective electrodes is described. PVC-based nitrate-selective membranes which contain TDMANO₃ ion-exchanger in PVC/NPOE, PVC/DOA or PVC/DBP matrices, and a commercially available Corning electrode (No. 476134) have been compared in respect of their detection limits, response slopes, selectivities at various pHs, and dynamic response to the hydrochromate ion in basic condition. The PVC/DBP/TDMANO₃ membrane electrode was chosen as the ISE detector for the determination of nitrate in the presence of hydrochromate interference. The amount of nitrate in real post treatment chromium plating solution could be determined successfully with this electrode in both static and flow-injection measurements when the sample was properly diluted with an alkaline buffer.

Introduction

Nitrate is commonly monitored for environmental, ecological and agricultural investigations, and for the control of some industrial processes.^{1,2} The amounts of nitrate in various samples, such as in foods, industrial effluents, wastes, soil and water, have been determined with numerous methods.¹⁻⁶ Among many analytical methods developed to date nitrate-selective electrodes have emerged as one of the

most promising tool for those purposes, especially for *in situ* monitoring of industrial samples.⁶⁻¹⁵

Ion-selective electrodes offer many advantages over other analytical techniques in the analysis of industrial samples or in the control of a particular chemical species in a process stream.² ISEs have high selectivities over a wide dynamic range (typically from 10⁻¹ to 10⁻⁵ M), exhibit fast response times (seconds to few minutes) and can be adapted easily to a flow through analysis system. Unlike most photometric

methods, sample color, turbidity and viscosity, which are commonly varying parameters of many industrial samples, rarely affect the performance of electrode detectors. Aside from the functional advantages of electrode detectors, analytical methods involving ISEs are relatively simple and economical to develop, install and operate.

In this article, a method for determining nitrate in post treatment chromium plating solutions using nitrate-selective electrode as the detector for a flow-injection analysis (FIA) system is described. Post treatment of electrogalvanized steel sheets with chromate is an important finishing process in steel industry.¹⁶⁻¹⁹ The chromate film on an electrogalvanized steel sheet not only increases its resistance against corrosion, but also improves its surface appearance.¹⁷ A post treatment chromium plating solution may contain Cr (VI) complex, nitric acid, sulfuric acid and some organic compounds: the exact composition which in many cases is a proprietary information varies largely depending on the purpose of plating.^{16,17} The time variations of all chemical constituents including nitrate in plating baths are closely monitored to control the quality of electroplating and waste effluents, and to make an efficient management plan.¹⁷⁻¹⁹

For our application we have chosen PVC-based nitrate-selective electrodes prepared with tridodecylmethylammonium nitrate (TDMANO₃) ion-exchanger,²¹ and a commercial one from Corning (Corning No. 476134).⁸ Since the selectivity patterns of typical ion-exchange type nitrate-selective electrodes are dictated by the Hofmeister series,²⁰ a successful determination of nitrate with ISE depends more on the sample pretreatment than the type of the electrodes employed;² the anion interferents which are more selective than nitrate should be suppressed or removed by adding an appropriate reagent. Such sample pretreatment procedure can be implemented easily in an FIA setup.² In this work, we carefully examined the response behavior of typical nitrate-selective electrodes to possible interferents present in post treatment chromium plating solutions and developed an optimal ISE-FIA nitrate determination method for chromium plating industries.

Experimental

Reagents. The reagents used to prepare the buffers (citric acid, TRIS and boric acid buffers) of different pH values and standard solutions for various anions (hydrochromate, nitrate, nitrite, chloride, sulfate and acetate) were of analytical-reagent grade. The real post treatment chromium plating solutions which contain 0.01 M~0.1 M of chromium (VI) complex, 1.0 M~10 M of nitrate, less than 0.02 M of sulfate and small amount of some organic compounds were obtained from POSCO (Pohang, Korea).¹⁷ All solutions were prepared with deionized water (18 M Ω cm).

Nitrate-Selective Electrodes. Poly(vinyl chloride), 2-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl) adipate (DOA), and tridodecylmethylammonium nitrate (TDMANO₃) from Fluka AG (Buchs, Switzerland), and dibutyl phthalate (DBP) from Scientific Polymer Products Inc. (Ontario, NY) were used to cast the nitrate-selective membranes. Typical membrane composition was 4 wt% TDMANO₃, 29 wt% PVC and 67 wt% plasticizer (NPOE, DOA or DBP). The electroactive membranes were prepared and mounted in Phillips elec-

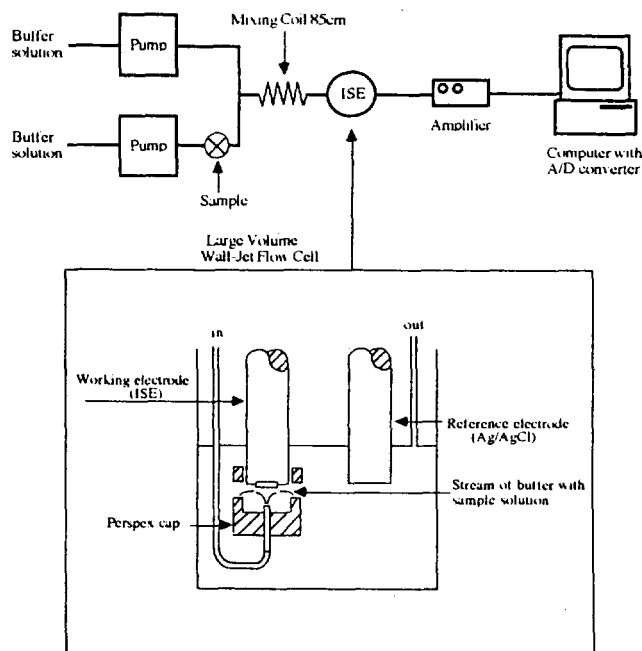


Figure 1. Schematic diagram of a flow injection system and a wall-jet flow cell.

trode bodies (IS-561; Glasblaserei Moller, Zurich, Switzerland) as described in reference 22. The internal filling solution for the electrodes were 0.01 M NaCl and 0.1 M NaNO₃. A commercial nitrate-selective electrode (Corning No. 4761 34) was purchased from Corning (Corning, NY). All nitrate-selective electrodes were preconditioned overnight in buffer solutions before use. The external reference electrode was an Orion Sleeve-type double-junction Ag/AgCl electrode (Model 90-82).

Static Mode potentiometric Measurements. Initial potentiometric evaluation of nitrate-selective electrodes was conducted by employing a static arrangement: the indicator and reference electrodes immersed in a magnetically stirred buffer solution were connected through a high-impedance amplifier to an IBM AT-type computer equipped with an A/D converter.²² Calculated amounts of various anion standard solutions were injected every 100 s to the measuring system and the corresponding potentiometric responses to the anions were recorded successively from 10⁻⁶ M to 10⁻¹ M at 32 °C. Recovery study on the real chromium plating solutions was also carried out in the static mode. The data obtained here were then used to evaluate the selectivities and dynamic responses for various nitrate-selective electrodes employed in this study and to determine the optimal sample pretreatment condition for the following FIA system.

Flow-Injection Measurements. FIA measurements were made in the wall-jet configuration as shown in Figure 1. Two variable speed peristaltic pumps (Ismatech Model 7331-00, Zurich, Switzerland), a Rheodyne four-way rotary valve (Model 5042) equipped with a sample loop and 80 cm teflon mixing-coil (i.d.=0.056 inch) before the electrode detectors completed the flow-injection setup. The arrangement of electrodes in a large volume wall-jet cell was the same configuration as was used in our previous study.²² The reagent buffer consisting of 0.1 M boric acid and 0.01 M KCl,

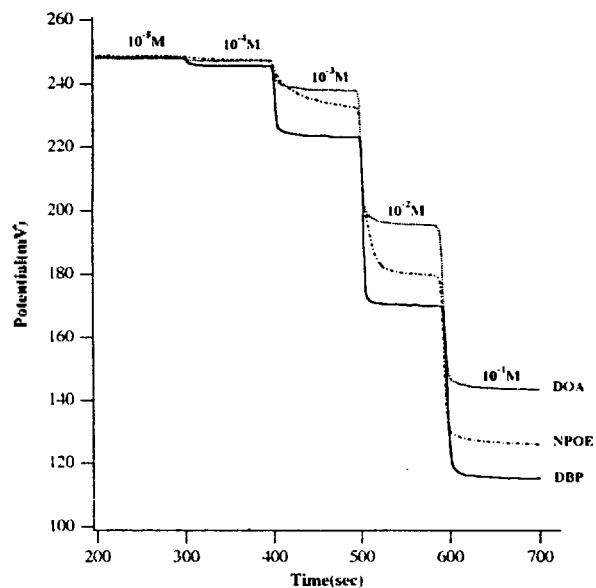


Figure 2. Dynamic response characteristics of three nitrate-selective membranes containing TDMANO₃ as an ion-exchanger in PVC/NPOE, PVC/DOS or PVC/DBP matrices at pH 3.

adjusted with NaOH solution to pH 9 (boric acid buffer) was used in a large volume beaker. Injected sample was carried by a boric acid buffer and thoroughly mixed with another stream of the same buffer solution at the mixing-coil. The dilution ratio (1 : 100) was adjusted by varying the relative speed of the two peristaltic pumps and the size of tubings that carry the sample and mixing solutions. The emf values were recorded every 0.5 s at 32 °C, using the same data acquisition system as described in the previous section.

Results and Discussion

Nitrate-Selective Electrodes. The PVC-based nitrate-selective membranes containing TDMANO₃ ion-exchanger were fabricated with three different plasticizers (NPOE, DOA or DBP) and their potentiometric responses to nitrate were evaluated at pH 3.0. The results are displayed in Figure 2: the membrane prepared with DBP exhibits lower detection limit and faster response times at low concentration than the other two membranes. Thus, we conducted the rest of this study with the membrane fabricated with 29 wt% PVC, 67 wt% DBP and 4 wt% TDMANO₃.

The potentiometric responses of these membranes may be improved by varying the composition of plasticizers and/or employing different type of ion-exchangers.⁷⁻¹⁵ However, we have not pursued such possibilities, since the concentration of nitrate in post treatment chromium plating solution (greater than 1 M in usual) is expected to be much higher than the detection limits of the membranes tested in this study. Instead, we evaluated the Corning No. 476134 electrode, which is also a PVC-based liquid ion-exchange type electrode.⁸ Its detection limit is claimed to be 10⁻⁵ M, about a decade lower than that of the PVC/DBP/TDMANO₃ membrane electrode.

The Effect of pH. The effect of pH on the response of the PVC/DBP/TDMANO₃ membrane was examined at four

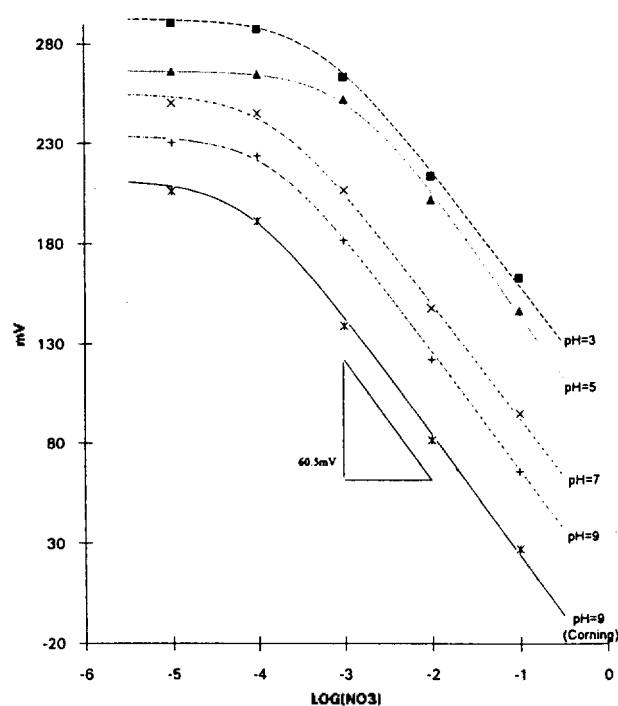


Figure 3. The effect of pH on the PVC/DBP/TDMANO₃ membrane electrode at 32 °C. The potentiometric response of the Corning No. 476134 electrode was compared at pH 9. For the sake of comparison, experimental E₀ values are adjusted to an appropriate level to separate each line by 20-30 mV.

different pH values (3, 5, 7 and 9). The response characteristics for the PVC/DBP/TDMANO₃ membrane improved as the pH of the sample solution increased: the response slope and the detection limit were 59.8 mV/decade (Nernstian slope: 60.5 mV/decade at 32 °C) and 1.6 × 10⁻⁴ M, respectively, at pH 9, while they were 58.0 mV/decade and 5.0 × 10⁻⁴ M, respectively, at pH 3. The response slope and detection limit for the Corning electrode were 60.5 mV/decade and 6.9 × 10⁻⁵ M, respectively, at pH 9. These results are summarized in Figure 3: the variation of pH influences little on the response slope, but changes the linear dynamic range of the PVC/DBP/TDMANO₃ membrane electrode to some extent. Apparently, the PVC/DBP/TDMANO₃ electrode exhibits better potentiometric response in basic conditions.

The chromium complexes in post treatment chromium plating solutions are usually derived from chromium trioxide. In acidic solutions below pH values < 1, CrO₃ forms H₂CrO₄; between pH 2 and 6, HCrO₄⁻ and Cr₂O₇²⁻ are in equilibrium; and at pH values > 6 the main species is CrO₄²⁻.²⁴ As can be seen from Figure 4, the PVC-based nitrate-selective electrodes exhibited a large interference from the hydrochromate ion in acidic condition (pH 3). However, in basic condition (pH 9) the interference from the chromate ion was not as serious as that from the hydrochromate ion. Thus, the measurement of nitrate in post treatment chromium plating solutions should be made by diluting the sample solution with a basic buffer. In this study, we used a buffer solution consisting of 0.1 M boric acid and 0.01 M KCl, and its pH value was adjusted to 9 by titrating with a NaOH solution.

When the standard chromium trioxide solutions were ad-

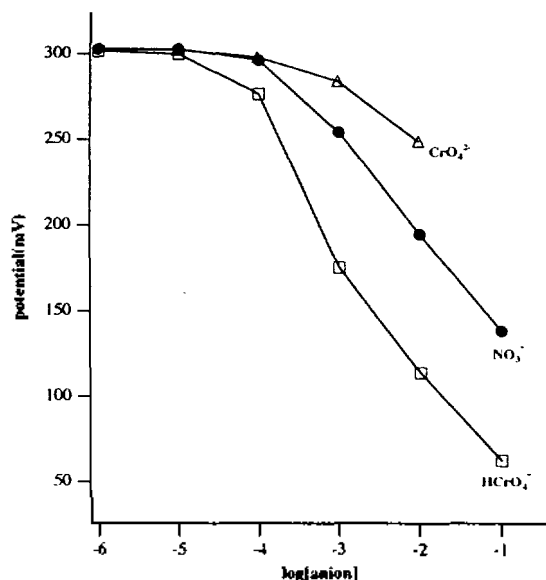


Figure 4. Comparison of potentiometric responses to nitrate (pH 9), chromate (pH 9) and hydrochromate (pH 3).

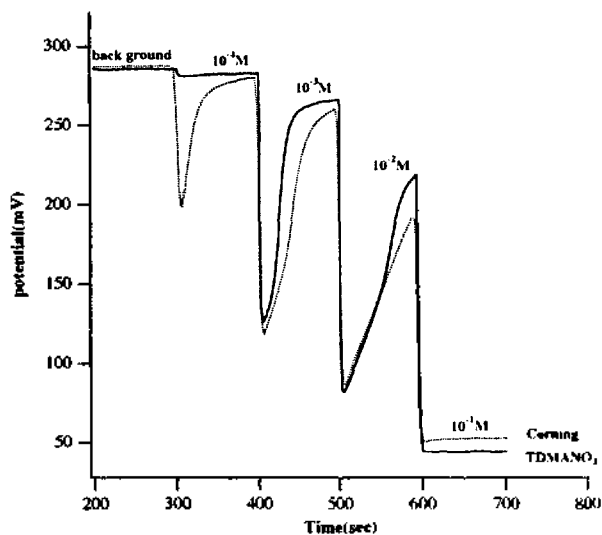


Figure 5. Dynamic response of two PVC-based nitrate selective electrodes to the change in going from HCrO_4^- to CrO_4^{2-} in basic condition (pH 9): —, PVC/DBP/TDMANO₃ membrane electrode; ----, Corning No. 476134 electrode.

ded to a pH 9 boric acid buffer with stirring, both the PVC/DBP/TDMANO₃ membrane and the Corning electrodes quickly responded first to the hydrochromate ion and then gradually reached the equilibrium potential as chromate is formed in basic condition (see Figure 5). Although the PVC/DBP/TDMANO₃ membrane and the Corning electrodes exhibited a similar potentiometric response to the chemical change, $\text{HCrO}_4^- \rightarrow \text{CrO}_4^{2-}$, at pH 9, the PVC/DBP/TDMANO₃ membrane electrode responded to chromate ions faster than the Corning electrode did. The PVC/DBP/TDMANO₃ membrane electrode also exhibited a negligible response to a low concentration of hydrochromate (10^{-4} M) at pH 9. Based on these results, we selected the PVC/DBP/TDMANO₃ mem-

Table 1. Selectivity coefficients ($\log K_{\text{NO}_3}^{\text{pot}}$) for nitrate-selective electrodes measured by separate solution method in a pH 9 boric acid buffer

$j =$	NO_3^-	Cl^-	SO_4^{2-}	NO_2^-	CrO_4^{2-}	acetic acid
TDMANO ₃	0	-2.59	-2.90	-1.97	-1.69	-2.92
Corning	0	-2.91	-3.83	-2.14	-1.97	-3.58

No. 476134

Table 2. Analytical recovery data for nitrate added to real post treatment chromium plating solution as determined by the PVC/DBP/TDMANO₃ electrode: the real sample was diluted by 100 times with a pH 9 boric acid buffer

Spike (10^{-2} /M)	Amount found (10^{-2} /M)	Percentage Recovered
sample	1.63	—
0.35	2.00	105.5
0.96	2.58	98.9
1.47	3.09	99.2

NO_3^- in real sample = 1.63 M

brane electrode as the detector for an FIA setup.

Selectivity. Table 1 shows the logarithmic selectivity coefficients ($\log K_{\text{NO}_3}^{\text{pot}}, X^-$) for few possible anion interferences that might present in post treatment chromium plating solutions. Separate solution method was used to estimate those values.²³ The logarithmic selectivity coefficient for the chromate ion was -1.69 for the PVC/DBP/TDMANO₃ membrane electrode and -1.97 for the Corning electrode in a pH 9 boric acid buffer. If we dilute the post treatment chromium plating solution by 100 times with a basic buffer, the concentration of chromate would be less than 10^{-3} M, while the concentration of nitrate would be in the 10^{-1} – 10^{-2} M range. Using these information and the Nikolskii-Eisenman formalism, the level of interference for 10^{-2} M of nitrate in the presence of 10^{-3} M of chromate was estimated to be about 6% (worst case). The second most abundant anionic interferent in post treatment chromium plating sample is sulfate (<0.02 M). However, the selectivity coefficient for the sulfate ion ($\log K_{\text{NO}_3}^{\text{pot}}, \text{SO}_4^{2-} = -2.90$ for the PVC/DBP/TDMANO₃ membrane electrode) is smaller than that for the chromate ion, and thus the level of interference from sulfate would be negligible (less than 0.2% for 10^{-2} M of nitrate).

Recovery Study The analytical recovery of nitrate added to the real plating sample obtained from POSCO was examined. The results of this study are summarized in Table 2. It can be seen that the added nitrate can be recovered with satisfactory accuracy; the results ranged from 98.9 to 105.5%, with an average of 101.2%. It indicates that the PVC/DBP/TDMANO₃ membrane electrode does not experience any significant matrix effects from the real plating sample diluted with a pH 9 boric acid buffer. The concentration of nitrate in POSCO's post treatment chromium plating solution was determined to be 1.63 M.

Flow-Injection Analysis (FIA). As discussed in the previous sections, the PVC-based nitrate-selective electrodes

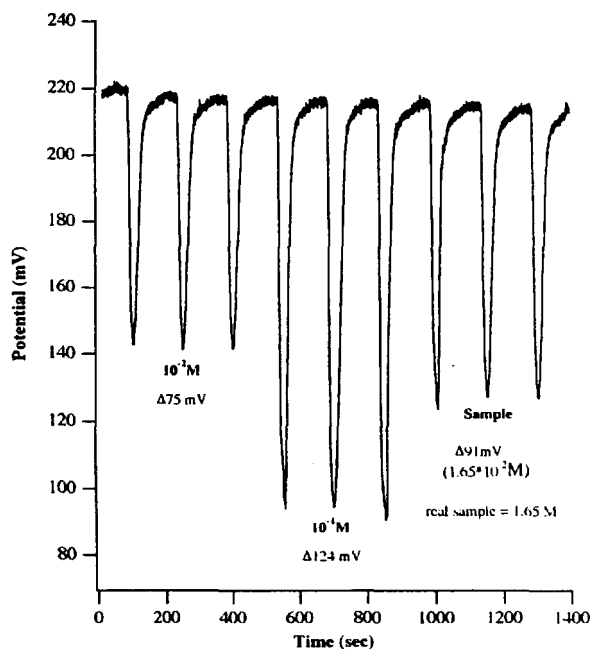


Figure 6. Potentiometric response obtained for injections of nitrate standards (10^{-1} M and 10^{-2} M) and real post treatment chromium plating sample with the PVC/DBP/TDMANO₃ membrane electrode detector.

exhibit a large interference from hydrochromate at the early stage of measurement when the sample containing hydrochromate is added to a basic buffer. Thus, in order to eliminate such a problem the FIA setup shown in Figure 1 was designed in a way that the injected sample solution be thoroughly mixed with the diluting buffer solution and equilibrated in the mixing coil before the ISE detection.

Figure 6 shows the typical flow-injection response to nitrate when an electrode prepared with PVC/DBP/TDMANO₃ is used as the detector in the FIA arrangement shown in Figure 1. The sample throughput of the system (about 20 samples/h) is limited by the time required to return completely to baseline potential. There were neither significant drift in baseline nor peak heights for a series of injected samples. The concentration of nitrate in real sample determined using FIA method was 1.65 M. This result is highly comparable to the value obtained from recovery study.

Conclusion

The aim of this study was to develop an efficient analytical method for the determination of nitrate in post treatment chromium plating solution and in its waste effluent. Considering sample throughput, cost of analysis and the simplicity of the measurement system, a flowinjection analysis system that utilizes a PVC-based nitrate-selective electrode was investigated.

We first evaluated the potentiometric performance of PVC-based nitrate-selective electrodes containing TDMANO₃ as an ion-exchanger in PVC/NPOE, PVC/DOA or PVC/DBP matrices, and the commercial Corning, No. 476134 electrode. After carefully examining the detection limits and response slopes for nitrate, and the dynamic response behavior to the

chemical change, $\text{HCrO}_4^- \rightarrow \text{CrO}_4^{2-}$, in basic condition, the PVC/DBP/TDMANO₃ membrane electrode was chosen as the FIA detector.

The analytical recovery of nitrate added to the real plating sample obtained from POSCO was examined in static mode prior to the FIA experiment. The added nitrate could be recovered with satisfactory accuracy (101.2% on the average), indicating that the PVC/DBP/TDMANO₃ electrode does not experience any significant matrix effect from the real sample if it is diluted by an appropriate proportion with a basic buffer. Based on these results, an FIA setup was designed in a way that the injected sample solution be thoroughly mixed with the diluting buffer solution and equilibrated in the mixing coil before the ISE detection. The FIA determination of nitrate in real plating sample gave essentially the identical result to that from static mode measurement.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (Project No. 94-0800-07-01-3), and in part by the Ministry of Education through the program of Basic Science Research (BSRI-94-3439). The authors thank Mr. Jae Chun So of the Research Institute of Industrial Science and Technology (Pohang, Korea) for supplying post treatment chromium plating solutions used in this work.

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MO Studies on C₆₀ and Its Pt-Derivatives

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Received November 2, 1994

The electronic structures of the C₆₀, (H₃P)₂Pt(η²-C₂H₄) and (H₃P)₂Pt(η²-C₆₀) are calculated by using the EHMO method with the fragment analysis. We have modified the EHT parameters so as to yield the orbital energy level correlation and to fit the optical transition gap to the previous theoretical results of C₆₀. In Pt-derivatives, our FMO results with the modified parameters show that the carbon-carbon double bonds of C₆₀ and ethene react like those of electron-poor arenes and alkenes, and also that C₆₀ is more electron-susceptive than C₂H₄.

Introduction

In 1985, a soccer ball carbon structure, C₆₀ or BF (Buckminsterfullerene), was obtained through laser vaporization of graphite in a high-pressure supersonic nozzle (Smalley *et al.*¹). Since the development of the large-scale synthesis of fullerenes, a variety of studies of the cluster have been promoted in order to discern chemical and physical properties.^{2,3} The stability of the C₆₀ has been calculated using MNDO,⁴ *ab initio* SCF⁵ and Hückel⁶ methods. The 3D-Hückel,⁷ DV-Xα⁸ and Linear Muffin-Tin Orbitals (LMTO)⁹ calculations have been represented for the orbital energy levels of this compound.

The interaction of fullerenes with molecules has been of fundamental interest, so several papers showed the chemical reactivity between metal (Os, Pt, Ir) complexes and C₆₀ *via* solution chemistry forming metal-C₆₀ bonds. Hawkins *et al.*¹⁰ have synthesized a one-to-one C₆₀-osmium tetroxide adduct, C₆₀(OsO₄)(4-*tert*-butylpyridine)₂, in which osmium was connected through a pair of oxygen atoms to the exterior of the C₆₀.

Balch *et al.*¹¹ have shown that addition of an equimolar amount of a purple solution of C₆₀ in benzene to a yellow benzene solution of Ir(CO)Cl(PPh₃)₂ immediately forms a deep brown solution from which black-brown crystals of (η²-C₆₀)Ir(CO)Cl(PPh₃)₂·5C₆H₆ precipitate.

Fagan *et al.*¹³ have shown that the addition of C₆₀ to (Ph₃P)₂Pt(η²-C₂H₄) results in displacement of ethylene and formation of (η²-C₆₀)Pt(PPh₃)₂. For the platinum complex [(C₆H₅)₃P]₂Pt(η²-C₆₀), the reactivity of C₆₀ is not like that of relatively electron-rich planar aromatic molecules such as benzene, that is, the carbon-carbon double bonds of C₆₀ behave chemically like those of very electron-deficient arenes and alkenes. In terms of the platinum coordination sphere, it was found that

this C₆₀ complex formed at the junction of two fused 6-MRs in C₆₀ closely resembles the structures seen for other platinum alkene complex,^{13b} [(C₆H₅)₃P]₂Pt(η²-ethylene). Also, using NMR spectra and X-ray crystallographic results of the hexa-substituted platinum derivative [(C₆H₅)₃P]₂Pt)₆C₆₀, Fagan *et al.*¹⁴ have shown that the molecule has a multiply-substituted buckminsterfullerene with an octahedral array of platinum atoms.

Their structural studies for metal complexation suggest that the bonds between two fused six-membered rings in C₆₀ are the most reactive, these bonds being shorter and having the most double bond character. The fact that low-valent metal centers like Ir(I) and Pt(0) add to the carbon atoms at 6-6 membered ring fusions in C₆₀ was consistent with the predictions of bond localization energy calculations.¹²

Fann *et al.*¹⁵ have calculated for C₆₀ and the bunnyballs (Os-C₆₀, Ru-C₆₀ and Mn-C₆₀ complexes) by the Extended Hückel (EH) method. The energy level correlation of C₆₀ in his work is similar to Figure 1 in this paper, but it is very different from those of 3D-Hückel,⁷ DV-Xα,⁸ and CNDO/S.³ *Ab initio* molecular orbital calculations¹⁹ for (η²-C₂H₄)Pt(PH₃)₂ and (η²-C₆₀)Pt(PH₃)₂ have shown that charge transfer from Pt fragment is 0.347 to C₂H₄ and 0.926 to C₆₀, and binding energy (eV) with Pt(PH₃)₂ is 0.32 for C₂H₄ and 0.95 for C₆₀.

Therefore, it suggests that it is interesting and important to choose proper EH parameters for calculations of the intermediate size cage cluster like C₆₀ between molecule and surface. EH method with and without Carbon parameter modification is used to see a detailed molecular orbital (MO) description of the effect of addition of C₆₀ to (Ph₃P)₂Pt(η²-ethylene) which results in displacement of ethylene and formation of (η²-C₆₀)Pt(PPh₃)₂. All calculations are simplified by substituting the phenyl groups (C₆H₅-) in each complex with hydrogen atoms.