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# Adsorption Behavior of N-Containing Heterocycles at a Mercury/Water Interface

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Adsorption behavior of 1-methylimidazole and 1-methylbenzimidazole at a mercury/water interface were investigated by electrocapillary measurement. These heterocycles showed a horizontal orientation at lower surface excesses, but at higher surface excesses a vertical one complicated by the presence of the horizontal one. In positive surface charge density, 1-methylbenzimidazole showed an anomalous behavior in which the potential drops across the inner layer, $\Delta_2^M\phi$ does not change with adsorption through the displacement of the water molecules on the electrode. The analysis of the electrosorption valency indicated the absence of a partial charge transfer between the electrode and the adsorbate. This anomalous behavior was interpreted by the compensation effect between the polarization of the water molecules due to the permanent dipoles and that of the 1-methylbenzimidazole molecules due to the dipoles induced in the electric field.

It has been observed that organic compounds with $\pi$-electron system show unique adsorption behavior, compared to the compounds lacking $\pi$-electron system. Gerovich *et al.*[1–4] studied adsorption of nonpolar organic compounds with $\pi$-electrons, such as benzene, anthracene, phenanthrene and chrysene, and found that the adsorbability of these compounds at positive surface charges increases with an increase in the number of benzene ring in the molecule and at the same time the potential of zero charge (p.z.c) shifts toward the negative potentials. They considered that these characteristics are due to a strong interaction between $\pi$-electrons and the positive charges. Similar consideration has also been given by Blomgren and Bockris,[5] and Conway and Barradas.[6,7] Damaskin *et al.* studied adsorption of aniline molecules[8] and anilinium cations[9] by the differential capacity measurement. They found that the capacity-potential curves at highly positive potentials measured in pure electrolyte solution and solution containing aniline or anilinium cation approximately coincide, and that the anode peak is caused by the reorientation process not the adsorption-desorption process. These results were explained as following: the aniline and the anilinium cations lie horizontally on the electrode surface with the positive charges and constitute a kind of extension of the metallic surface toward the solution; the double layer capacity changed very slightly.

Thereafter, the negative shift of the p.z.c due to adsorption of organic compounds with $\pi$-electron system has been attributed to the extension of the metallic surface[10] or the partial charge transfer.[11] However, the partial electron transfer from the adsorbed molecules to the electrode should increase the negative charge on the electrode, and as the result, the p.z.c seems to shift toward the positive direction. The possibility of this partial charge transfer was discussed in this study.

Furthermore, in the previous report[12] in which the adsorption behaviors of various N-containing heterocycles were studied, it was pointed out that imidazole adsorbed through aggregates due to intermolecular association,[13] because it did not take a vertical orientation owing to the large dipole moment.[14] It was also found that on positive surface charges the potential drop across the inner layer $\Delta_2^M\phi$ was not changed with adsorption of imidazole. This anomalous behavior was considered to result from an interaction between positive charges on the electrode and the aggregates at the outer layer without displacement of the water molecules adsorbed. In order to clarify the above two phenomena, namely the formation of aggregates and the anomalous adsorption behavior of a constant $\Delta_2^M\phi$, 1-methylimidazole (1-MI) without a possibility of intermolecular association,[15] and 1-methylbenzimidazole (1-MBI) with larger $\pi$-electron system were chosen, and their adsorption behavior at the mercury/water interface was studied. Besides the above two compounds which are classified into $\pi$-excessive heterocycles, quinoxaline, which is a $\pi$-deficient heterocycle, was also studied, but the adsorption equilibrium was not observed in the measurement of interfacial tension.

## Experimental

All chemicals were analytical grade materials. 1-Methylimidazole (1-MI) was purified by distillation in a vacuum. 1-Methylbenzimidazole (1-MBI) was prepared by the methylation of benzimidazole,[16] and recrystallized twice from petroleum ether. Mercury was purified by treatment with dilute nitric acid, then triply distilled in vacuum. Nitrogen gas, after passing through a purification line, was used for deaeration of the solution. As the supporting electrolyte 0.099 M (1 M = 1 mol dm$^{-3}$) $NaClO_4$ containing 0.001 M NaOH was prepared from triply distilled water, and treated with purified active charcoal before use. The 0.001 M NaOH was used to depress the ionization of the adsorbates.

Adsorption behavior of 1-MI and 1-MBI was estimated from the analysis of the electrocapillary curves, which were measured by the maximum bubble pressure method.[17,18] The interfacial tension was measured at 50 mV intervals, except for positive and negative extrema where 25 mV intervals were chosen. The error of the measurement was $\pm 0.1$ mN m$^{-1}$ near the electrocapillary maximum, and $\pm 0.3$ mN m$^{-1}$ at positive and negative extrema. The measurement was carried out in a water bath thermostated at $25 \pm 0.1$ °C, and the potentials were measured against a normal calomel electrode (NCE).

Most of the parameters essential to adsorption were derived by analyzing the electrocapillary curves with a computer program. In the analysis, no corrections were made for the medium effect on the activity coefficient of the supporting electrolyte[19,20] and the activity coefficient of the adsorbate.[21]

## Results and Discussion

*Electrocapillary Curves.* The electrocapillary data for 1-methylimidazole (1-MI) and 1-methylbenzimidazole (1-MBI) are summarized in Table 1. The interfacial tension, $\gamma$ for 1-MBI dropped gradually with an increase in the concentration, $C_{\mathrm{org}}$. However, such a change was not observed in quinoxaline (QX). Figure 1 shows the plot of $\gamma$ at $-0.5$ V against log $C_{\mathrm{org}}$ with respect to 1-MBI and QX. The surface excess, $\Gamma$ can be obtained by a differentiation of the above plot

$$(\partial\gamma/\partial \ln C_{\mathrm{org}})_E = -RT\Gamma. \qquad (1)$$

The interfacial tension for QX was nearly constant up to 1 mM, but fell abruptly beyond 2 mM, and then gradually at more than 5 mM. The surface excess obtained from the constant slope at higher concentrations is considered to be a saturated value of the surface excess, $\Gamma_{\mathrm{s}}$. These values were $3.4\times10^{-10}$ mol cm$^{-2}$ for 1-MBI and $2.9\times10^{-10}$ mol cm$^{-1}$ for QX, which are in fair agreement with $2.9$—$3.0\times10^{-10}$ mol cm$^{-2}$ estimated from the projected areas assuming a horizontal orientation for both compounds, though somewhat large with 1-MBI.

Table 1. Electrocapillary data for 1-methylimidazole and 1-methylbenzimidazole

| $C_{\mathrm{org}}$ / M | $\gamma_{\mathrm{ecm}}$[a)] / mN m$^{-1}$ | $-E_{\mathrm{ecm}}$ *vs.* NCE[b)] / V |
|---|---|---|
| 0(base soln)[c)] | 425.1 | 0.504 |
| 1-Methylimidazole | | |
| 0.005 | 423.7 | 0.505 |
| 0.007 | 423.2 | 0.504 |
| 0.010 | 422.7 | 0.507 |
| 0.015 | 421.8 | 0.510 |
| 0.020 | 421.2 | 0.511 |
| 0.030 | 419.8 | 0.510 |
| 0.040 | 418.8 | 0.510 |
| 0.050 | 417.9 | 0.512 |
| 0.070 | 416.3 | 0.505 |
| 0.100 | 414.4 | 0.502 |
| 0.150 | 412.2 | 0.501 |
| 0.200 | 410.2 | 0.499 |
| 0.300 | 307.2 | 0.491 |
| 1-Methylbenzimidazole | | |
| 0.00010 | 424.7 | 0.503 |
| 0.00015 | 424.2 | 0.506 |
| 0.00020 | 423.8 | 0.505 |
| 0.00030 | 422.9 | 0.505 |
| 0.00040 | 421.7 | 0.506 |
| 0.00050 | 420.6 | 0.508 |
| 0.00060 | 419.4 | 0.506 |
| 0.00070 | 418.4 | 0.515 |
| 0.00085 | 417.0 | 0.517 |
| 0.00100 | 415.7 | 0.528 |
| 0.00150 | 412.4 | 0.533 |
| 0.00200 | 409.9 | 0.540 |
| 0.00300 | 406.7 | 0.534 |

a) $\gamma_{\mathrm{ecm}}$ is the interfacial tension at the electrocapillary maximum. b) $E_{\mathrm{ecm}}$ is the potential of the electrocapillary maximum. c) Base solution consists of 0.099 M $NaClO_4$ and 0.001 M NaOH.

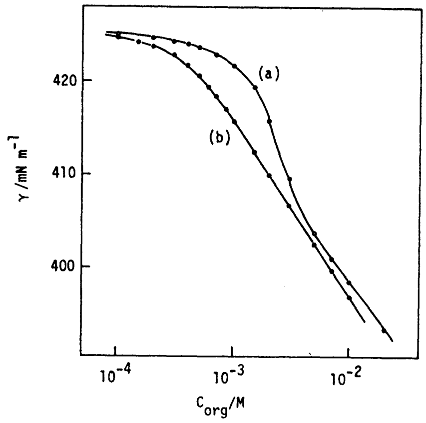

Fig. 1. Plot of $\gamma$ at $-0.5$ V against log $C_{\mathrm{org}}$ for quinoxaline (a) and 1-methylbenzimidazole (b).

The relation for QX in Fig. 1 is similar to that in the presence of a diffusion limit, which was observed in the interfacial tension measurement due to drop time.[22)] However, the concentration of $10^{-3}$ M where $\gamma$ changes abruptly, is considered to be higher than that of $10^{-4}$ M observed for the diffusion limit. Probably, micelle formation[23)] or polymeric aggregate formation due to an interaction with water molecules seems to be the cause.

*Evaluation of $\Gamma_{\mathrm{s}}$.* The valuation of $\Gamma_{\mathrm{s}}$ is necessary to elucidate the adsorption state qualitatively. When adsorption can be described by a Langmuir isotherm, $\Gamma_{\mathrm{s}}$ is evaluated from the slope of the plot of $x/\Gamma$ against $x$, where $x$ is the molar fraction. If this is not the case, $\Gamma_{\mathrm{s}}$ can be evaluated simply from the extrapolation of the plot of $1/C_{\mathrm{org}}$ against $1/\Gamma$ to $1/C_{\mathrm{org}}=0$. From the nature of this plot, $\Gamma_{\mathrm{s}}$ obtained in this way reflects $\Gamma_{\mathrm{s}}$ at higher surface excesses. Therefore, the validity of the $\Gamma_{\mathrm{s}}$ at $\Gamma_{\mathrm{s}}$ should be confirmed by a fit to the isotherm molecular model.

The values of $\Gamma_{\mathrm{s}}$ evaluated by the above simple method are shown in Fig. 2 for 1-MI and 1-MBI. Various orientation parameters expected for 1-MI and 1-MBI were estimated using the CPK molecular model; these are shown in Fig. 3 for 1-MI and in Fig. 4 for

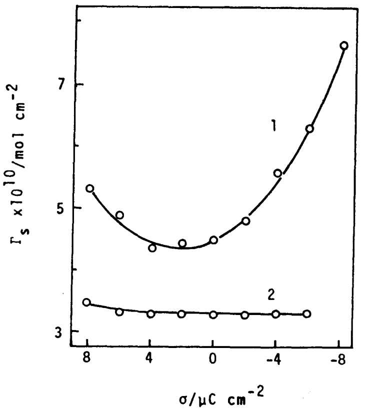

Fig. 2. Saturated value of surface excess as a function of surface charge density. (1) 1-Methylimidazole and (2) 1-methylbenzimidazole.

Table 2. Orientation parameters for 1-methylimidazole and 1-methylbenzimidazole

| | 1-Methylimidazole | | 1-Methylbenzimidazole | |
|---|---|---|---|---|
| | Horizontal | Vertical | Horizontal | Vertical |
| $A_s$/Å$^2$ | 35.7 | 21.5 | 54.6 | 29.7 |
| $\Gamma_s$/mol cm$^{-2}$ | $4.7\times10^{-10}$ | $7.7\times10^{-10}$ | $3.0\times10^{-10}$ | $5.6\times10^{-10}$ |
| $d_1$/Å | 3.4 | 6.6 | 3.4 | 6.6 |

Here $A_s$ and $d_1$ are the projected area and the molecular height from the electrode, respectively.

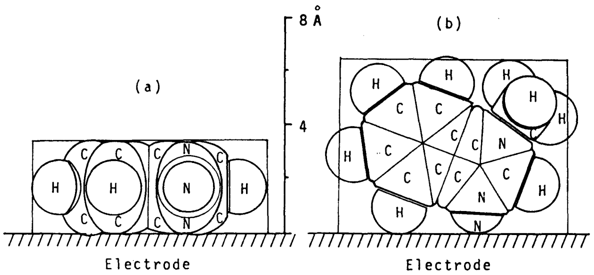

Fig. 3. Scale drawings of a 1-methylimidazole molecule adsorbed on the electrode through the horizontal orientation (a) and the vertical orientation (b). The area of rectangles enclosing the molecule in (a) and (b) correspond to the projected area of the vertical and the horizontal orientation, respectively.

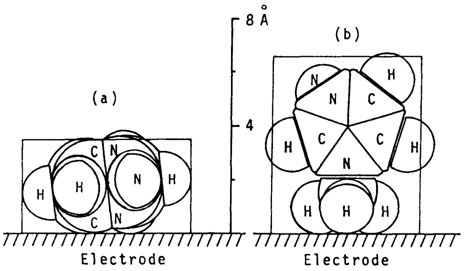

Fig. 4. Scale drawings of a 1-methylbenzimidazole molecule adsorbed on the electrode through the horizontal orientation (a) and the vertical orientation (b). The area of rectangles enclosing the molecule in (a) and (b) correspond to the projected area of the vertical and the horizontal orientation, respectively.

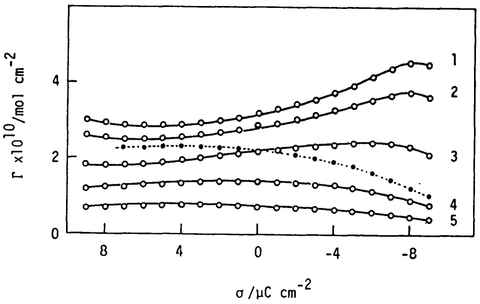

Fig. 5. Relations between surface excess and the surface charge density at various concentrations of 1-methylimidazole. The concentrations in M: (1) 0.3, (2) 0.2, (3) 0.1, (4) 0.03, and (5) 0.01. The broken line is for the 0.2 M imidazole.[12)]

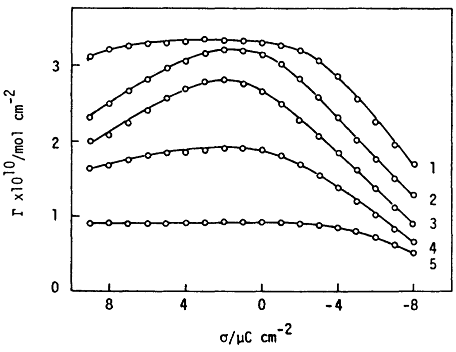

Fig. 6. Relations between surface excess and the surface charge density at various concentrations of 1-methylbenzimidazole. The concentrations in mM: (1) 3.0, (2) 1.0, (3) 0.6, (4) 0.4, and 0.2.

1-MBI. The paramenters obtained for a horizontal and a vertical orientation are summarized in Table 2.

*Surface Excess.* Figures 5 and 6 show the relations between $\Gamma$ and surface change density $\sigma$ with respect to 1-MI and 1-MBI, respectively. The broken line in Fig. 5 is the result for 0.2 M imidazole[12)] obtained previously. Adsorption behavior of 1-MI is somewhat similar to that of imidazole at positive charges, but at negative charges it is quite different. From the results in Fig. 2 and Table 2, 1-MI is considered to take a horizontal orientation at lower surface excesses, but change to a vertical orientation at higher surface excesses, owing to the large dipole moment[24)] and the absence of the intermolecular association.[15)]

The difference in the adsorption behavior of imidazole and 1-MI supports the previous consideration[12)] that imidazole adsorbs in an aggregate form. On the other hand, the adsorbability of 1-MBI is similar to that of imidazole, as can be seen from Fig. 6. This result also supports the formation of aggregate for imidazole, whose structure resembles that of 1-MBI with a large $\pi$-electron system and planarity.

*Potential Drop across the Inner Layer, $\Delta_2^M\phi$.* Figures 7 and 8 show the relations between $\Delta_2^M\phi$ at constant charge and $\Gamma$, with respect to 1-MI and 1-MBI, respectively. The values of $\Delta_2^M\phi$ were determined by the following equation

$$\Delta_2^M\phi = E - E_z - \phi_2, \tag{2}$$

where $E$ is the measured potential against NCE, $E_z$ is the potential of zero charge obtained in the electrolyte without specific adsorption of ions (−0.472 V *vs.* NCE[25)]), and $\phi_2$ is the potential drop ascross the diffuse layer, which was determined using the Gouy-Chapman theory.[26)]

The results in Fig. 7 also show that 1-MI changes its orientation from horizontal to vertical above a certain value of $\Gamma$. The change in the slope indicates that 1-MI at negative charges takes a vertical orientation with the positive pole of the dipole toward the electrode, but at positive charges it takes a vertical orientation with the

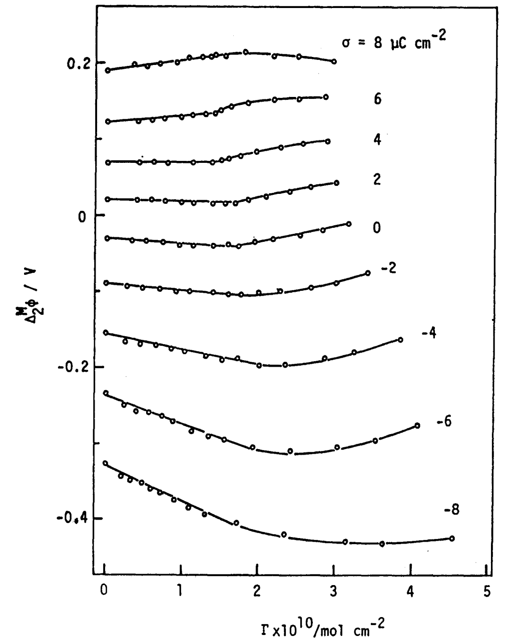

Fig. 7. Change in $\Delta_2^M\phi$ due to adsorption of 1-methylimidazole. Charge densities are indicated by each line.

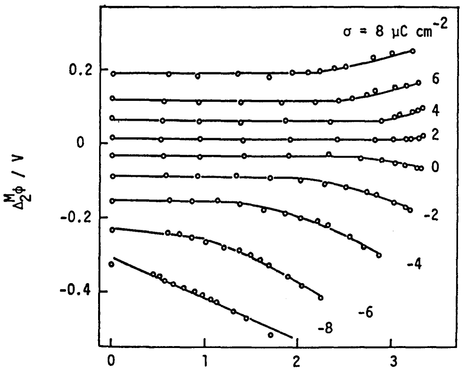

Fig. 8. Change in $\Delta_2^M\phi$ due to adsorption of 1-methylbenzimidazole. Charge densities are indicated by each line.

negative pole of the dipole towards the solution side.

The results in Fig. 8 show the presence of the region where $\Delta_2^M\phi$ does not change due to adsorption of 1-MBI, especially in $\sigma \geq -2$ μC cm$^{-2}$. This is similar to the results obtained in imidazole.[12)] In general, organic compounds without a net dipole moment, such as pyrazine, exhibit a constant $\Delta_2^M\phi$ around $\sigma = -4$ μC cm$^{-2}$,[27)] where the orientation of water molecules on the electrode becomes most disordered, they show linear lines with a positive or negative slope at more positive or negative charges than $-2$—$-4$ μC cm$^{-2}$, respectively. An example is shown in Fig. 9 for pyrazine. This was obtained in the previous experiment[12)] and was nearly same as that reported by Conway *et al.*[28)]

The anomalous adsorption behavior of 1-MBI appears to result from an adsorption without displacement of the adsorbed water molecules. However, such an adsorption seems to be unreasonable, because

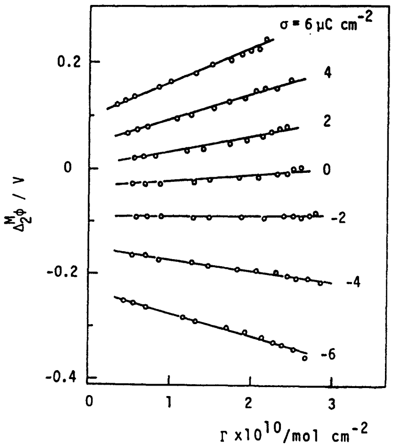

Fig. 9. Change in $\Delta_2^M\phi$ due to adsorption of pyrazine. Charge densities are indicated by each line.

adsorption due to the displacement of water actually occurs at fairly negative charges, as can be seen from Fig. 8; generally organic compounds without a net dipole moment adsorb strongly at low electric fields. This behavior of 1-MBI will be discussed precisely in the following sections.

The constancy of $\Delta_2^M\phi$ disappeared at higher surface excesses. The cause is not clear at the present time. However, note the following: (1) $\Gamma_s$ of 1-MBI at the holizontal orientation was estimated from the projected area to be $3.0\times10^{-10}$ mol cm$^{-2}$, which is somewhat smaller than that of $3.4\times10^{-10}$ mol cm$^{-2}$ determined from the experiment. A vertical orientation contributing to a change in $\Delta_2^M\phi$ through the dipole moment will be mixed with the horizontal orientation at higher surface excesses. (2) Specifically adsorbed perchlorate ions will be desorbed at higher surface excesses.

*The Adsorption Isotherm and Free Energy of Adsorption.* The determination of the adsorption isotherm and the free energy of adsorption at infinite dilution, $\Delta\bar{G}^\circ$, was carried out in the region where the change in the orientation was considered to be negligible, namely at lower surface excesses for 1-MI and that showed a constant $\Delta_2^M\phi$ for 1-MBI.

By examining a fit to various isotherms, 1-MI and 1-MBI were found to obey the Langmuir (Fig. 10) and the Frumkin isotherm (Fig. 11) with $\Gamma_s = 3.0\times10^{-10}$

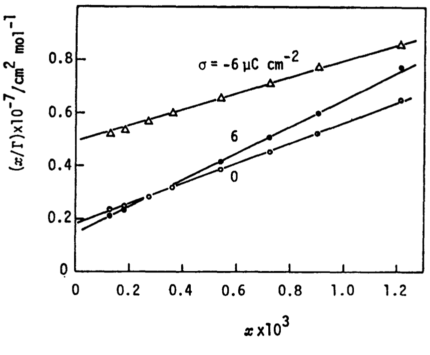

Fig. 10. Test of the Langmuir isotherm for adsorption of 1-methylimidazole at various charge densities. Charges are indicated by each line.

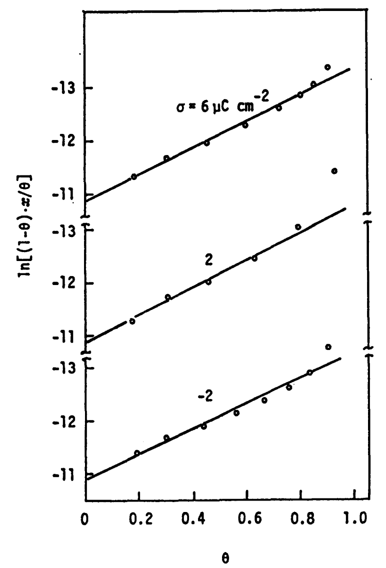

Fig. 11. Test of the Frumkin isotherm with $\Gamma_s=3.0\times10^{-10}$ mol cm$^{-2}$ for adsorption of 1-methylbenzimidazole at various charge densities. Charges are indicated by each line.

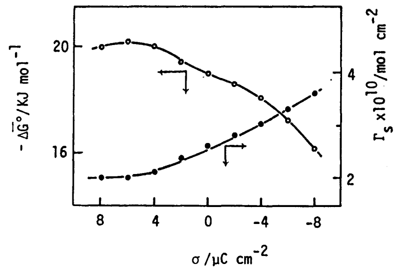

Fig. 12. Variation of $\Delta\bar{G}^\circ$ and $\Gamma_s$ for 1-methylimidazole due to surface charge density.

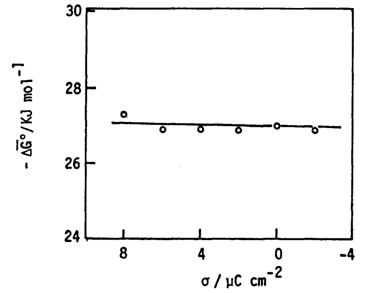

Fig. 13. Variation of $\Delta\bar{G}^\circ$ for 1-methylbenzimidazole due to surface charge density.

mol cm$^{-2}$ and the interaction parameter $2a=2.5$, respectively.

$\Gamma_s$ and $\Delta\bar{G}^\circ$ obtained for 1-MI are shown in Fig. 12. $-\Delta\bar{G}^\circ$ was increased with an increase in the surface charge, and the maximum was observed at highly positive charges. This behavior is typical to that of organic compounds with $\pi$-electrons. On the other hand, $\Delta\bar{G}^\circ$ for 1-MBI was charge independent, as shown in Fig. 13. If the isotherms are congruent to charge the slopes of linear lines in Fig. 8 are related to the change in $\Delta\bar{G}^\circ$ due to surface charge[29]

$$(\partial \Delta_2^M\phi/\partial\theta) = -RT\Gamma_s(\partial \ln\beta/\partial\sigma), \quad (3)$$

where $\beta=\exp(-\Delta\bar{G}^\circ/RT)$. Since both $(\partial\Delta_2^M\phi/\partial\theta)$ and $(\partial\ln\beta/\partial\sigma)$ are nearly zero, Eq. 3 is set up for adsorption of 1-MBI. This indicates that the experimental results are reliable and the final picture is consistent.

*Quantitative Interpretation of Adsorption.* From the fit to the adsorption isotherm, the horizontal orientation was approximately confirmed for both 1-MI and 1-MBI at lower surface excesses. Further to verify this, evaluation of the dipole moment at the adsorbed state was made at $\sigma=0$ μC cm$^{-2}$, to simplify the calculation.

In general, if the adsorption of an organic compound is charge congruent, the change in $\Delta_2^M\phi$ can be described by the following equation[30]

$$\Delta(\Delta_2^M\phi)/\theta = (\Gamma_s P_1/\varepsilon_1 - \Gamma_s n P_0/\varepsilon_0) + \sigma(1/C_1 - 1/C_0), \quad (4)$$

where $P$, $\varepsilon$, and $C$ are the effective normal dipole moment, the permittivity of the inner layer and the inner layer capacity, respectively, $n$ is the number of water molecules displaced by adsorption of one adsorbate molecule, and subscripts 1 and 0 denote the surface layer saturated with the adsorbate and water. The potential drop due to water dipoles, $\Delta g^{W}_{\text{dipole}}$ can be represented by Eq. 5

$$\Delta g^{W}_{\text{dipole}} = -\Gamma_s n P_0/\varepsilon_0. \quad (5)$$

The $\varepsilon_1$ can be obtained from $C_1$ using the relation, $C_1=\varepsilon_1/d_1$, where $d_1$ is the thickness of the adsorption layer. Further, the values of $C_1$ can be obtained by the extrapolation of the linear relation between $1/C^i$ and $\Gamma$ at $\sigma=0$ μC cm$^{-2}$, as shown in Fig. 14, to the corresponding to $\Gamma_s$. They were 32.5 μF cm$^{-2}$ for 1-MI and 40.0 μF cm$^{-2}$ for 1-MBI.

One can obtain 30 mV as $\Delta g^{W}_{\text{dipole}}$ at $\sigma=0$ μC cm$^{-2}$ from Bockris and Habib's water adsorption model,[31] and 3.4 Å as $d_1$ from Table 2, and −20 mV for 1-MI and −13 mV for 1-MBI as $\Delta(\Delta_2^M\phi)/\theta$ from Figs. 7 and 8. By introducing the above values into Eq. 4, the effective normal dipole moment at $\sigma=0$ μC cm$^{-2}$, $P_1$ was found to be −1.1 Debye for 1-MI and −1.0 Debye for 1-MBI. The negative value of $P_1$ means an orientation with the negative pole of the dipole of the adsorbate toward the electrode. However, the above values seem to be too large, compared with the value

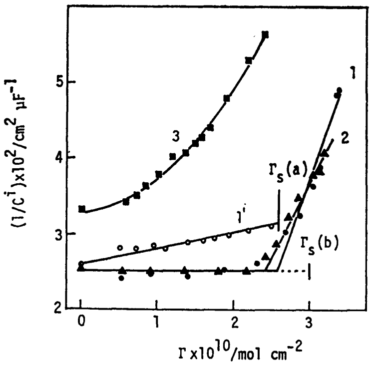

Fig. 14. Plot of $1/C^i$ against $\Gamma$ at various charge densities. Open and closed symbols correspond to 1-methylimidazole and 1-methylbenzimidazole, respectively. Charge density in μC cm$^{-2}$: (1) and (1′) 0, (2) 6 and (3) −6. $\Gamma_s$ (a) and $\Gamma_s$ (b) represent $\Gamma_s$ of 1-methylimidazole and 1-methylbenzimidazole at the horizontal orientation, respectively.

expected for the horizontal orientation, $P_1=0$ Debye, The cause of the large negative values is probably the presence of the specifically adsorbed perchlorate anions, which contribute to the negative dipole moment. Therefore, the effect of the specific adsorption of perchlorate anion was taken into consideration in the calculation of the true $P_1$. In this calculation, the data obtained by Payne[32] in the mixed solution of 0.1 M $NH_4ClO_4$ and 0.9 M $NH_4F$ was used. The procedures are as follows: (i) If the specific adsorption of $ClO_4^-$ is deducted, $\Delta_2^M\phi$ shifts towards a positive direction by 31 mV, which is the difference between $\Delta_2^M\phi$ at $\sigma=0$ $\mu C\ cm^{-2}$ in the base solution of 0.099 M $NaClO_4+$ 0.001 M NaOH, $-0.031$ V and that in the 0.1 M NaF,[33] 0 V. (ii) In the absence of the specific adsorption of $ClO_4^-$, true surface charge density at $-0.504$ V. which is the p.z.c for the base solution, can be estimated to be $-0.64$ $\mu C\ cm^{-2}$ from the result on 0.1 M NaF,[33] then $\Delta g_{\text{dipole}}^{W}$ at that charge amounts to 24 mV.[31] (iii) True value of $C_1$, $C_1^t$ is given by the following relation derived using the data of Payne[32]

$$1/C_1^t = 1/C_1^a + 4.73\times 10^{-3}, \tag{6}$$

where $C_1^a$ is the apparent value of $C_1$ in the presence of specifically adsorbed perchlorate ions. After the above treatment, the true $P_1$ was calculated to be $-0.2$ Debye for 1-MI and $-0.1$ Debye for 1-MBI. These values are reasonable for the horizontal orientation.

*Electrosorption Valency.*[11] It was discussed on the basis of the electrosorption valency whether the constancy of $\Delta_2^M\phi$ observed clearly in 1-MBI results from a partial charge transfer or not. Figure 15 shows a change in $\sigma$ at constant $\Delta_2^M\phi$ due to adsorption of 1-MBI. The electrosorption valency, $r$ is defined by Eq. 7

$$r = (1/F)(\partial\sigma/\partial\Gamma)_{\Delta_2^M\phi}, \tag{7}$$

where $F$ is the Faraday constant. Further, $r$ at $\Delta_2^M\phi=0$, $r_N$ is represented by Eq. 8 with respect to neutral organic compounds

$$r_N = -\lambda(1-g) + K^{ad} - nK^{w}, \tag{8}$$

where $\lambda$ is the partial charge transfer coefficient, $g$ is the geometric factor defined as $(X_0-X_a)/X_0$, $X_0$, and $X_a$ are the distance of the outer Helmholtz plane and the adsorption plane from the electrode, respectively, $K_{ad}$ and $K_w$ are the dipole terms of the adsorbate and water, and $n$ is the same as used in Eq. 4. The value of $r$ is plotted as a function of $\Delta_2^M\phi$ in Fig. 16, from which $r_N$ was estimated to be 0.0035.

As can be seen from Fig. 14, and as Eq. 4 and the result in Fig. 8 predict, $C_1$ and $C_0$ for 1-MBI are nearly equal in the region where the constancy of $\Delta_2^M\phi$ is observed. This implies compensation between $(\Gamma_s P_1/\varepsilon_1)$ and $(-\Gamma_s n P_0/\varepsilon_0)$. Therefore, $(K_{ad}-nK_w)$ in Eq. 8 becomes also zero. If $X_0$ and $X_a$ can be represented by the sum of $d_1$ and the ionic radius of $Na^+$(0.96 Å), and the half of $d_1$, respectively, $g$ is calculated to be 0.61. Finally one obtains $\lambda$ near 0.01. However, this value is too small to be considered a partial charge transfer between the electrode and the adsorbed 1-MBI molecules.

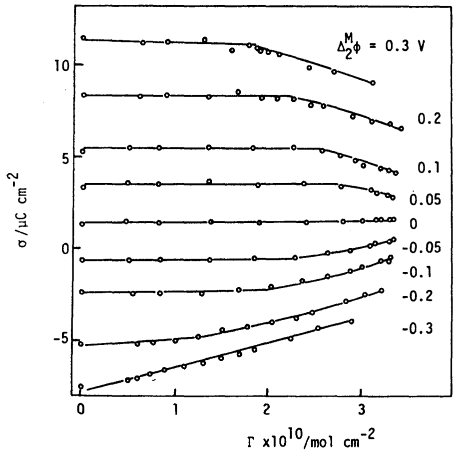

Fig. 15. Change in $\sigma$ at constant $\Delta_2^M\phi$ due to adsorption of 1-methylbenzimidazole. The values of $\Delta_2^M\phi$ are indicated by each line.

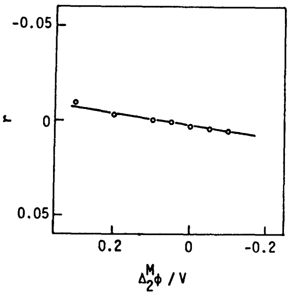

Fig. 16. Variation of electrosorption valency due to $\Delta_2^M\phi$.

What is the compensation between $(\Gamma_s P_1/\varepsilon_1)$ and $(-\Gamma_s n P_0/\varepsilon_0)$? If this effect results from a partial charge transfer, it corresponds to the increased negative dipole moment or charge in 1-MBI. That means the partial electron transfer from the electrode to the adsorbed 1-MBI molecules. Since the compensation is observed even at fairly positive charges, the above deduction is hard to accept. The most reasonable consideration will be an electronic polarization effect. Thus, the dipole moment of 1-MBI induced in the electric field compensates for the dipole moment of the water molecules displaced. Further, this effect is valid at positive charges and seems to disappear at highly negative electric field because of increased repulsion between $\pi$-electrons and the negative charges on the electrode surface.

The compensation effect observed in this study correlates with the constant adsorbability in positive charges. Such an adsorbability was clearly observed for heterocycles classified into $\pi$-excessive type, for example 1-MI and 1-MBI in this study, and imidazole and pyrazole,[12] but not so clearly observed for those classified into $\pi$-deficient type, for example pyrazine, pyrimidine and pyridazine.[12] These results are also considered to support the compensation effect observed in 1-MBI which has easily polarizable $\pi$-electrons. Recently, King *et al.*[34] explained the enormous intensity enhancement observed for Raman scattering from pyridine adsorbed on the electrode on the basis of a classical electrostatic theory, namely electronic polarization.

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