Adsorption of *N*-Vinyl-2-pyrrolidone at the Mercury/Solution Interface

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The adsorption of *N*-vinyl-2-pyrrolidone (NV2P) or the monomer of polyvinylpyrrolidone (PVP) at the mercury/solution interface was examined by means of differential capacity *vs.* potential relations (*C-E* curves). The usual *C-E* curve obtained in 1N sulfuric acid was similar to that of the saturated aliphatic compounds. However, in 1N sodium sulfate or sodium hydroxide potential dependence of C_{min} (minimum differential capacity) was observed as a result of π-electron interaction of adsorbed molecules. The adsorption behavior in 1N sulfuric acid followed the Langmuir isotherm. The peculiar behavior in 1N sodium sulfate or sodium hydroxide was explained by means of the Frumkin isotherm with the potential dependence of interaction constant (*g*), which varied linearly with potential in a range more negative than *ca.* -0.6 V (SCE) in contrast to nearly constant values in a more positive range. At a relatively high bulk concentration, there was a slight deviation from the Frumkin isotherm and the standard free energy of adsorption (ΔG^0) *vs.* $\theta^{3/2}$ plot revealed a sharp break in the same way as pointed out by Conway and his co-worker. The C_{min} value of NV2P coincided approximately with that of its polymer of PVP in aqueous sulfuric acid, sodium sulfate or sodium hydroxide, respectively. The results are utilized for the discussion on the configuration of adsorbed PVP at the interface.

For *N*-vinyl-2-pyrrolidone (NV2P)[1] with pyrrolidone and vinyl radicals, π-electron seems to have a strong influence upon its adsorption behavior.

The role of π-electron interaction on adsorption was first pointed out by Gerovich[2] and further has been discussed by several authors.[3–6] Klyukina and Damaskin[7] investigated the Frumkin adsorption isotherm considering the potential dependence of interaction constant (*g*) among adsorbed molecules, while Conway[5] discussed the molecular orientation due to the π-electron interaction in connection with the coverage (θ) dependence of standard electrochemical free energy of adsorption (ΔG^0) obtained by means of the Langmuir adsorption isotherm.

We have investigated the adsorption of NV2P as regards the results[8,9] obtained for its polymer or polyvinylpyrrolidone (PVP) by measurement of the differential capacity at the mercury/solution interface.

Experimental

Electrodes. A dropping mercury electrode (DME) with a flow rate of *ca.* 4.5×10^{-4} g/sec was used, with a ring-like platinum wire of sufficiently large suface area as the counter electrode. The electrode potentials were measured with reference to a 3.3N calomel or mercury/mercuric oxide electrode, and the results are given against the saturated calomel electrode (SCE).

Apparatus and Materials. The differential capacity at the mercury/solution interface was determined at 22°C by

1) Molecular structural formula:

$$CH=CH_2$$
$$\diagdown N \diagup$$
$$H_2C \quad C=O$$
$$H_2C—CH_2$$
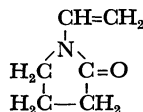
2) M. Gerovich, *Dokl. Akad. Nauk. SSSR*, **96**, 543 (1954).

3) A. Frumkin, R. Kaganovich, and E. Bit-Popova, *ibid.*, **141**, 670 (1961).

4) E. Blomgren, J. O'M. Bockris, and C. Jesh, *J. Phys. Chem.*, **65**, 2000 (1961).

5) B. Conway and R. Barradas, *Electrochim. Acta*, **5**, 319 (1961).

6) H. Nürnberg and G. Wolff, *Collect. Czech. Chem. Commun.*, **30**, 3997 (1965).

7) L. Klyukina and B. Damaskin, *Izv. Akad. Nauk SSSR Ser.*, *Khim.* **1963**, 1022; B. Damaskin, *Electrochim. Acta*, **9**, 231 (1964).

8) T. Yoshida, T. Ohsaka, and S. Tanaka, This Bulletin, **45**, 326 (1972).

9) T. Yoshida, T. Ohsaka, and S. Nomoto, *ibid.*, **45**, 1585 (1972).

the universal bridge (Yokogawa BV-Z13A) equipped with an oscilloscope as a detector and d.c. polarization circuit. The balance time (*i.e.*, time, elapsed from the beginning of a drop growth) was set at 8 sec with a sinusoidal wave of 1 kHz adjusted to a input voltage of *ca.* 10 mV$_{p-p}$ or less. Interfacial impedance was assumed as series equivalent circuit of capacitance and resistance. NV2P of pure chemical grade prepared by Tokyo Kasei Co. was used without further purification. All the solutions were prepared from triply-distilled water and pure chemicals. Observation was carried out in the atmosphere of purified nitrogen.

Results and Discussion

Variation of Differential Capacity with Potential.   The relations between differential capacity and potential (*C–E* curves) caused by the addition of NV2P were observed in 1N sulfuric acid, 1N sodium sulfate and 1N sodium hydroxide. The results are shown in Figs. 1—3.

The *C–E* curves in Figs. 1—3 can be regarded as the results of the adsorption equilibrium except for peak regions, since the capacity data per unit area are independent of the balance time exceeding 8 sec in the solution containing 1 mmol/*l* NV2P.

In the case of low bulk concentration of NV2P in 1N sulfuric acid the peak caused by ad- or desorption appears on the positive side, but none on the negative owing to hydrogen evolution. In 1N sulfuric acid with a relatively high content of NV2P, the differential capacity (*C*) attains almost a constant value in the range more negative than *ca.* −0.5 V(SCE).

In 1N sodium sulfate, the peak appears both on the positive and negative sides (Fig. 2) and the differential capacity is depressed in the adsorption range as the potential becomes negative. However, it is well-known that the potential dependence of capacity
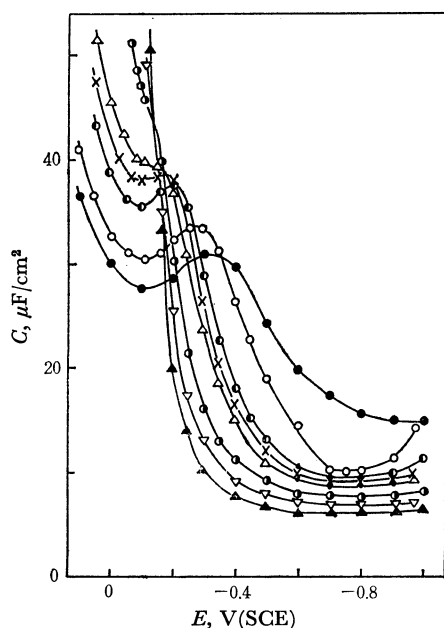
Fig. 1.   Differential capacity *vs.* potential curves.
22°C, 1 kHz, 1N sulfuric acid +NV2P (●: 0 mol/*l*, ○: 1.0× 10⁻², ◑: 5.0×10⁻², ×: 7.5×10⁻², △: 1.0×10⁻¹, ◐: 2.0× 10⁻¹, ▽: 3.0×10⁻¹, ▲: 4.7×10⁻¹).
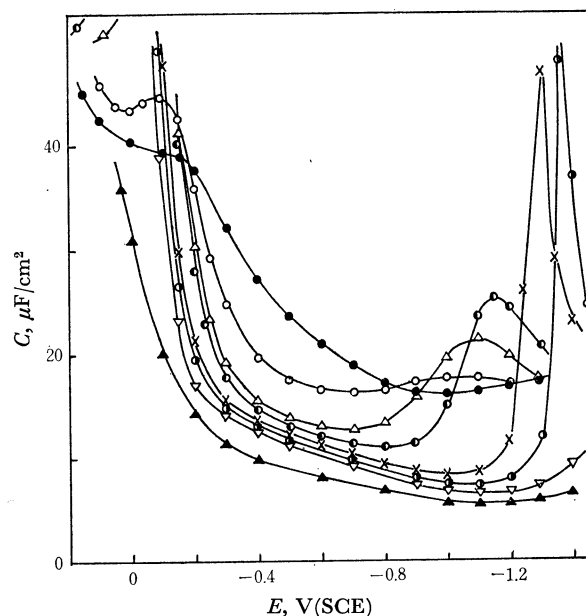
Fig. 2.   Differential capacity *vs.* potential curves.
22°C, 1 kHz, 1N sodium sulfate +NV2P (●: 0 mol/*l*, ○: 1.0×10⁻³, △: 5.0×10⁻³, ◑: 1.0×10⁻², ×: 3.0×10⁻², ◐: 5.0×10⁻², ▽: 1.0×10⁻¹, ▲: 4.0×10⁻¹).
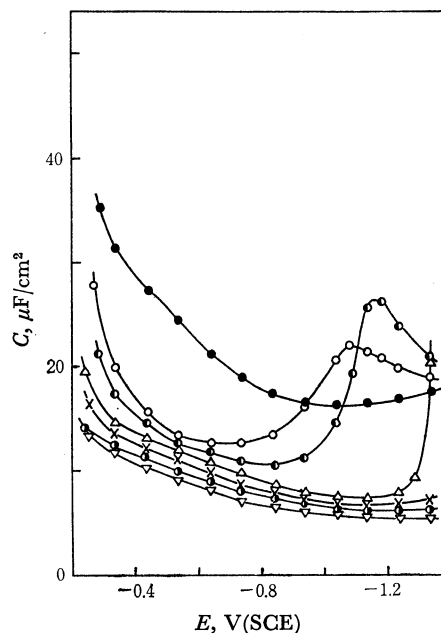
Fig. 3.   Differential capacity *vs.* potential curves.
22°C, 1 kHz, 1N sodium hydroxide +NV2P (●: 0 mol/*l*, ○: 5.0×10⁻³, ◐: 1.0×10⁻², △: 4.1×10⁻², ×: 8.4×10⁻², ◑: 1.7×10⁻¹, ▽: 3.4×10⁻¹, 5.0×10⁻¹).

is hardly observed for the adsorption range in usual cases. Both peaks are asymmetric and the cathodic peak becomes somewhat negative and sharp with the increase of bulk concentration of NV2P (Fig. 2). This tendency might be due to the attractive interaction among the adsorbed molecules. The peculiar adsorption is also found in 1N sodium hydroxide (Fig. 3). Similar behavior was discussed for pyridine in potassium chloride by Damaskin.[7] The anodic peak seems to be due to reorientation of adsorbed pyridine molecules and not to ad- or desorption. Nearly the

same values of capacity obtained by the solutions with and without pyridine in the more positive range than the anodic peak may result from the interfacial structure, not from the adsorbed layer because of the strong interaction between the π-electron and the electrode. The anodic peak in Figs. 1 and 2 might be assumed as the above. For the unusual adsorption of NV2P in 1N sodium sulfate or 1N sodium hydroxide, π-electron interaction seems to play an important role.

Potential Dependence of Coverage (θ-E Curves). The θ-E relations in sulfuric acid (Fig. 4) were given from the C–E curves (Fig. 1) by means of Frumkin's parallel condenser model. The computation was carried out for the region with a slight potential dependence of C. The θ-E curves (Fig. 4) reveal an usual bell-type form, their maximum adsorption being attained at *ca.* −0.7 V (SCE).
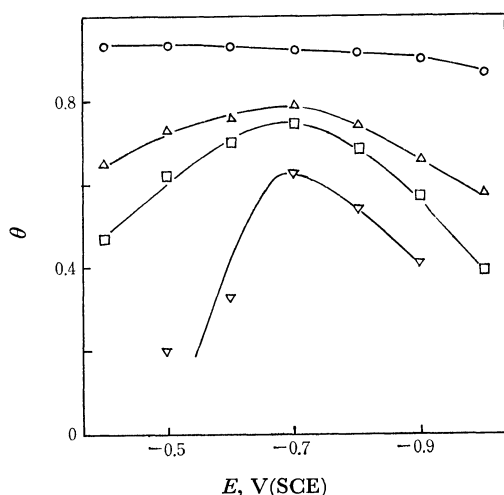

Fig. 4. Coverage *vs.* potential curves.
22°C, 1N sulfuric acid +NV2P (∇: 1.0×10^{-2} mol/l, $\square$: 5.0×10^{-2}, $\triangle$: 1.0×10^{-1}, $\bigcirc$: 3.1×10^{-1}).

It is necessary to find the minimum differential capacity (C_{min}) for determination of coverage by Frumkin's model. In the case of 1N sodium sulfate
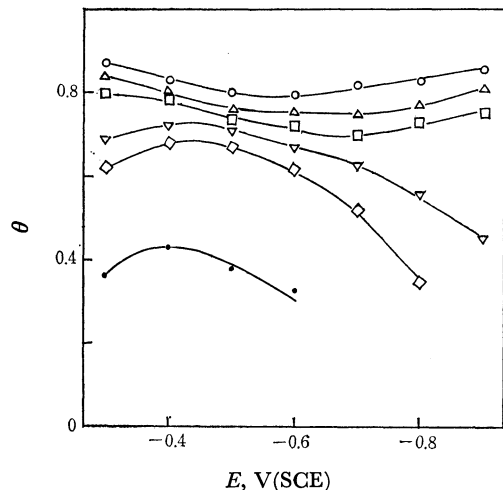

Fig. 5. Coverage *vs.* potential curves.
22°C, 1N sodium sulfate +NV2P ($\bullet$: 1.0×10^{-3} mol/l, $\diamondsuit$: 5.0×10^{-3}, ∇: 1.0×10^{-2}, $\square$: 3.0×10^{-2}, $\triangle$: 5.0×10^{-2}, $\bigcirc$: 1.0×10^{-1}).

or 1N sodium hydroxide, however, no definite value can be found for C_{min} owing to its potential dependence (Figs. 2 or 3). In these cases, the lowest value within the adsorption range may be taken, while the lowest value at each potential may be used respectively for the determination of coverage in consideration of the potential dependence of capacity due to the gradual reorientation of adsorbate. The θ-E curves in sodium sulfate solution (Fig. 5) were derived from C_{min} at each potential. At a relatively low bulk concentration (Fig. 5), the bell-type θ-E curves were obtained. The maximum coverage at *ca.* −0.45 V (SCE) increased with bulk concentration. In the case of high bulk concentration, the tendency was reversed and minimum coverage was observed contrary to the usual cases. This tendency was also shown by another θ-E plot where θ was evaluated by the lowest common capacity instead of respective C_{min} at each potential.

Adsorption Isotherm. The Langmuir adsorption isotherm was always applied to the adsorption of NV2P in 1N sulfuric acid, while the Frumkin adsorption isotherm was applied to that in 1N sodium sulfate or 1N sodium hydroxide in view of the potential dependence of interaction constant (g). The adsorption isotherm in 1N sodium sulfate is shown in Fig. 6, where the coverage is calculated with the respective C_{min} at each potential. The curve becomes somewhat S-type at the negative potential (Fig. 6), which might indicate the change from repulsive to attractive interac-
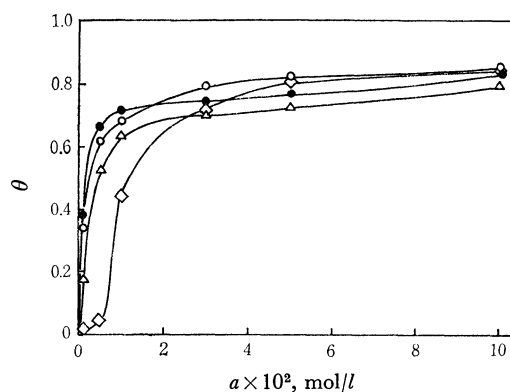

Fig. 6. Adsorption isotherms.
22°C, 1N sodium sulfate +NV2P [$\bigcirc$: −0.3 V(SCE), $\bullet$: −0.5 V, $\triangle$: −0.7 V, $\diamondsuit$: −0.9 V].

tion. In the adsorption isotherm of pyridine given by the potential dependence of interfacial tension, almost the same tendency as above was also pointed out by Gierst,[10] Conway and Barradas,[5] and Nürnberg and Wolff.[6] The adsorption isotherm of NV2P in sodium sulfate or sodium hydroxide solution is similar to that of pyridine to some extent.

Potential Dependence of Interaction Constant. The coverage of NV2P in 1N sodium sulfate or 1N sodium hydroxide solution was evaluated by Frumkin's condenser model with minimum capacity at each potential on the assumption of full coverage at each C_{min}. The

10) L. Gierst, "Transactions of the Symposium on Electrode Processes," ed. by E. Yeager, John Wiley and Sons Inc., New York, (1961), p. 294.

interaction constant (g) is given by the Frumkin isotherm

$$\beta a = \frac{\theta}{1-\theta} \exp(-2g\theta) \tag{1}$$

where β, a, θ, and g are the adsorption coefficient, the bulk concentration, the coverage, and the interaction constant, respectively. According to Frumkin and Damaskin,[11] the interaction constant (g) might be obtained by means of the adsorption isotherm.

Substituting the relative concentration $y=a/a_{\theta=0.5}$ into Eq. (1), we have

$$y = \frac{\theta}{1-\theta} \exp[g(1-2\theta)] \tag{2}$$

and

$$(dy/d\theta) = \frac{(1-2g\theta+2g\theta^2)}{(1-\theta)} \exp[g(1-2\theta)] \tag{3}$$

At $\theta=0.5$:

$$(dy/d\theta)_{\theta=0.5} = 4 - 2g \tag{4}$$

Thus, g can be determined graphically. The results are shown in Fig. 7.

The g value gives a constant of $ca. -1.3$ in the range from -0.3 to nearly -0.6 V (SCE). This might indicate a certain repulsive interaction between the molecules. In the range from -0.6 to about -0.9 V
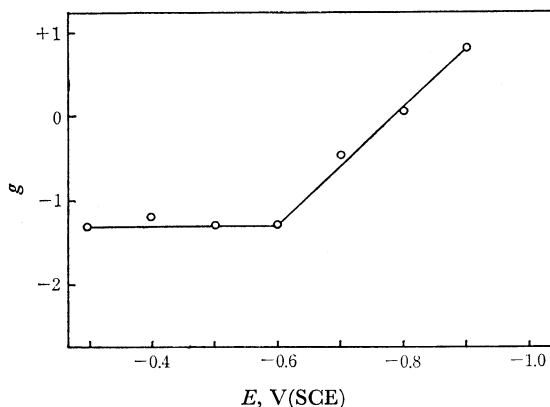

Fig. 7. Potential dependence of interaction constant.
22°C, 1N sodium sulfate +NV2P.

(SCE), the g value varies almost linearly with a slope of $ca.$ 6.7 (V^{-1}) as the potential becomes negative, and the g value turns positive at $ca. -0.8$ V (SCE). This indicates the attractive interaction between the adsorbed molecules.

Coverage Dependence of Standard Free Energy of Adsorption ($\Delta\bar{G}^0$).   For the purpose of investivating some deviations from the Frumkin isotherm in Fig. 5 or 6 (*i.e.*, the unusual shape of θ-E in Fig. 5 and the slight rise of isotherm at a relatively high concentration in Fig. 6), the results were examined in terms of the coverage dependence of $\Delta\bar{G}^{0}$ [12] after Conway.[5]

If no interaction is assumed for the adsorbed molecules at the interface, $\Delta\bar{G}^0$ is given by the Langmuir isotherm.[5]

$$\ln\left(\frac{55.5\ ^{14)}}{a} \frac{\theta}{1-\theta}\right) = -\frac{\Delta\bar{G}^0}{RT} \tag{5}$$

When the surface interaction of the adsorbates is taken into account, Eq. (5) can be written as follows:[5]

$$\ln\left(\frac{55.5}{a} \frac{\theta}{1-\theta}\right) - \ln f_\theta = -\frac{\Delta\bar{G}^0}{RT} \tag{6}$$

where the surface activity coefficient (f_θ) at a coverage θ consists of an electrostatic dipole-dipole interaction term ($\theta^{3/2}$) and van der Waals-London interaction term (θ^3).[5]

Equation (6), then, becomes:

$$\ln\left(\frac{55.5}{a} \frac{\theta}{1-\theta}\right) + \frac{P_a\theta^{3/2}-Q_a\theta^3}{RT} = -\frac{\Delta\bar{G}^0}{RT} \tag{7}$$

where P_a and Q_a are constants dependent on the characteristics of adsorbed layer. If θ is not too close to unity, the term $Q_a\theta^3$ is almost negligible and the relation between $\Delta\bar{G}^0$ and $\theta^{3/2}$ becomes approximately linear. $\Delta\bar{G}^0$ varies with $\theta^{3/2}$ as expected, although a remarkable break is revealed on each curve as shown in Fig. 8. Such a sharp inflection may be attributed to onset of extensive orientation with the increase of coverage.[5]
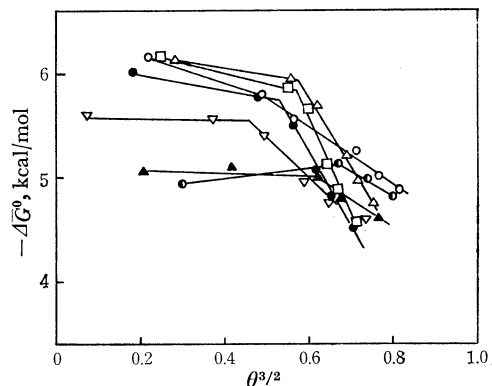

Fig. 8. Coverage dependence of $\Delta\bar{G}^0$.
22°C, 1N sodium sulfate +NV2P [○: −0.3 V(SCE), △: −0.4 V, □: −0.5 V, ●: −0.6 V, ▽: −0.7 V, ▲: −0.8 V, ◑: −0.9 V].

The Frumkin isotherm can be written as follows, where the value of 55.5 is taken for a comparison with Conway's treatment and $\beta=(1/55.5)\exp(-\Delta\bar{G}^0/RT)$ in Eq. (1)

$$\ln\left(\frac{55.5}{a} \frac{\theta}{1-\theta}\right) - 2g\theta = -\frac{\Delta\bar{G}^0}{RT} \tag{8}$$

The correction term for surface interaction on the adsorbed layer is assumed to be $-2g\theta$ instead of $(P_a/RT)\theta^{3/2}$ term in Eq. (7). $\Delta\bar{G}^0$ is expected to vary linearly with θ. This relation was verified for the adsorption of phenol by Blomgren[4] except for the case where θ is close to unity. In the case of NV2P, a sharp break was also shown in $\Delta\bar{G}^0$-θ plot. The result does not seem to be in line with the Frumkin isotherm. The Frumkin isotherm, however, is approximately applicable to the adsorption of NV2P at a relatively low coverage ($0<\theta<ca.$ 0.7), because the g values at $\theta=0.5$ derived from Eq. (8) with $\Delta\bar{G}^0$ of

11) A. Frumkin and B. Damaskin, "Modern Aspects of Electrochemistry," No. 3, eds. by J.O'M. Bockris and B. Conway, Butterworth, London, (1964), p. 182.

12) Refer to Refs. 13 and 5 for the definition of $\Delta\bar{G}^0$.

13) P. Delahay, "Double Layer and Electrode Kinetics," John Wiley and Sons Inc., New York (1965), p. 81.

14) Molar concentration of H_2O per liter given by Conway *et al.*

the Langmuir isotherm nearly coincided with the values in Fig. 7, where the g values at $\theta=0.5$ were chosen for convenience as the typical data in the range of low coverage before the appearance of the sharp break. The sharp variation of $\Delta \bar{G}^0$ with θ at relatively high coverage is considered to be mainly caused by reorientation of adsorbed molecules, although the variation might be explained by the Frumkin isotherm modified with the association number of adsorbed water molecules.[15]

Orientation of NV2P at the Interface. For NV2P in aqueous sodium sulfate or sodium hydroxide, the variation of differential capacity within the adsorption range seems to be due to π-electron interaction. The reorientation of adsorbed molecules may take place gradually in the above range, as discussed by Damaskin for the adsorption of pyridine[7] or aniline,[16] where results analogous to Figs. 2 and 3 are obtained.

g values of NV2P in Fig. 7 change with the potential in the range more negative than *ca.* -0.6 V (SCE) but they are nearly constant in the range more positive than the above. The tendency might be related to surface charge, since the point of zero charge for mercury in the solution with no adsorbates is about -0.43V (SCE).[17] In the negative range, a nearly perpendicular form of the adsorbed molecules may be expected because of the repulsion between the electrode surface and π-electron while the attractive force between adsorbed molecules is considered to increase as the potential becomes negative. In the range more positive than *ca.* -0.6 V (SCE), the repulsive force between adsorbed molecules is considered to become nearly constant because the gradual reorientation of the adsorbed molecule may be expected as the potential becomes positive, or the attraction between the electrode surface and π-electron increases. The reorientation might take place gradually as the electrode potential changes, since the differential capacity varies gradually with the potential in the adsorption range.

Examination of Minimum Differential Capacity. The relation between the minimum differential capacity (C_{min}) and the thickness (δ) of adsorbed layer is as follows:

$$C_{min} = \varepsilon/(4\pi\delta) \qquad (9)$$

where ε is the dielectric constant of adsorbed layer. The values of C_{min} of NV2P in several solutions are shown in Table 1, where almost the same values of C_{min} are given for both cases of sodium sulfate and sodium hydroxide solutions, while C_{min} value in sulfuric acid is about 1.1 times those in the above solutions. This difference of C_{min} is considered to result from the difference of δ on the assumption that ε hardly varies with supporting electrolyte.

The perpendicular/planar ratio of orientation for

TABLE 1. C_{min} OF NV2P AND PVP (μF/cm^2)

Electrolyte	C_{min} of NV2P (Monomer)	PVP (Polymer)	
		$\bar{M}$	C_{min}
1N H$_2$SO$_4$	6.4	10000	6.5
		26000	6.3
		37000	6.15
		750000	6.05
1N Na$_2$SO$_4$	5.6	10000	5.8
1N NaOH	5.7	10000	5.7
		750000	5.9

NV2P is about 2.5 from the approximate calculation with the molecular model. It appears from the C_{min} ratio 1.1 that the variation of orientation with electrolytes does not take place completely from perpendicular to planar. In the adsorption range of NV2P in sulfuric acid, the nearly constant C_{min} may be due to the alleviation of π-electron interaction by the highly concentrated hydrogen ion, but the conclusion from only C–E relations is somewhat doutful as pointed out by Damaskin[16] for the adsorption of aniline.

Adsorption Behavior of PVP Expected from That of NV2P. The adsorption behavior of PVP at the mercury interface may be discussed in reference to that of NV2P or the monomer of PVP. In Table 1 of the C_{min} values of PVP depending a little upon $\bar{M}$ (mean molucular weight), the values of C_{min} for $\bar{M}$ of 10000 are used for the discussion in view of the lieast difference between the values of PVP and its monomer.

In aqueous solutions of sulfuric acid, sodium sulfate and sodium hydroxide, C_{min} of NV2P hardly differs from that of PVP in each solution as shown in Table 1. Thus, it may be considered that the thickness of adsorbed NV2P layer is similar to that of its polymer layer adsorbed in each solution, if ε remains nearly constant.

It is interesting that C_{min} value of the polymer or PVP varies with a supporting electrolyte similarly to the case of its monomer or NV2P. However, the variation of C_{min} due to reorientation of the adsorbed polymer is almost impossible. Therefoe, the dependence of C_{min} value on the supporting electrolyte may be connected with the compactness of adsorbed layer in the case of polymer.

The dependence of inhibition effect by PVP upon the supporting electrolyte is observed[18] from the comparison of inhibition effect for some electrodeposition processes. It is considered to be also related to the compactness of adsorbed layer to a certain extent.

It appears from C_{min} value of PVP in accordance with that of its monomer that the configuration of adsorbed PVP at the interface is spread or flattened as assumed previously.[8] Strictly speading, however, the above assumption is a mere approximation in consideration of the fact that C_{min} of PVP depends slightly on $\bar{M}$.

15) B. Damaskin, *J. Electroanal. Chem.*, **23**, 431 (1969); L. Pospišil and J. Kůta, *Collect. Czech. Chem. Commun.*, **34**, 3047 (1969).
16) B. Damaskin, I. Mishutushkina, V. Gerovich, and R. Kaganovich, *Zhur. Fiz. Khim.*, **38**, 1797 (1964).
17) P. Delahay, "Double Layer and Electrode Kinetics," John Wiley and Sons Inc. (1965), p. 23; B. Conway, "Electrochemical Data," Elsevier (1952), p. 221.
18) T. Yoshida and T. Ohsaka, *Bull. Sci. Eng. Res. Lab. Waseda Univ.*, **58**, 34 (1972).