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Competitive Adsorption of Polyvinylpyrrolidone with *n*-Alkyl Alcohols at the Mercury/Solution Interface

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Competitive adsorption of polyvinylpyrrolidone (PVP, $\bar{M}=10000$) with *n*-hexanol, *n*-pentanol, or *n*-butanol was examined by observation of the differential capacity at the mercury interface in 1 N sulfuric acid. Adsorption of PVP coexistent with alcohol hardly differed from the single adsorption[1] controlled by its diffusion. The competitive adsorption curve of C (differential capacity) *vs.* $t^{1/2}$ (adsorption time) was expected from the sum of the individual capacity depressions by the single adsorption at -0.5 or -0.6 V (SCE) and the expected curve of C *vs.* $t^{1/2}$ was compared with the curve observed. The competitive behavior of alcohol coexistent with PVP was examined by the relation "$\theta_{\mathrm{Alc}}^{\mathrm{com}}$ (coverage of coexistent alcohol) *vs.* $t^{1/2}$" at -0.5 or -0.6 V (SCE), where $\theta_{\mathrm{Alc}}^{\mathrm{com}}$ was estimated from the difference between the differential capacities with and without PVP, in view of the fact that behavior of PVP is nearly independent of the coexistent alcohol. The results are discussed in terms of four types of models assumed for the competitive behavior of coexistent alcohols with different adsorbability. It is considered that the alcohol is replaced with PVP as soon as the latter reaches the interface by diffusion, the adsorption equilibrium of an alcohol being achieved immediately. The relation $\theta_{\mathrm{Alc}}^{\mathrm{com}}=(1-\theta_{\mathrm{PVP}})\theta_{\mathrm{Alc}}$ holds in the case of *n*-butanol coxistent with PVP, where θ_{PVP}, θ_{Alc}, and $\theta_{\mathrm{Alc}}^{\mathrm{com}}$ are the coverages due to the single adsorption of PVP and butanol and to the competitive adsorption of butanol, respectively. The tendency of alcohol to be replaced with PVP is inversely proportional to its adsorption coefficient. *n*-Butanol was most sensitive to the coexistence of PVP.

The adsorption of PVP(polyvinylpyrrolidone) at the mercury/solution interface was previously discussed[2] in terms of the process controlled by diffusion. We have investigated the competitive adsorption of PVP with *n*-alkyl alcohol of low molecular weight at the mercury interface with the alcohol attaining its adsorption equilibrium immediately.

Not many electrochemical studies on competitive adsorption have been published. Only the tensammetry wave for competitive adsorption has been shown by Jehring.[3] The treatment of the Flory-Huggins adsorption isotherm[4] and analyses of the reorientation of the adsorbed molecules at equilibrium[5,6] may be applied to the equilibrium of the competitive adsorption. The analyses, however, are useless for the competitive process influenced by the diffusion of PVP.

The results of competitive adsorption of PVP with an alcohol will, therefore, be discussed with respect to the behavior of the single adsorption of each compoent.

Experimental

The test electrode and counter electrode were a dropping mercury electrode (DME) with a drop time *ca.* 11 sec and a cylindrical platinum net. The potentials were referred to the saturated calomel electrode (SCE). The differential capacity was observed by a transformer impedance bridge[2] with an input of 1 kHz wave adjusted to below 10 $\mathrm{mV_{p-p}}$. PVP ($\bar{M}=10000$) prepared by BASF was used without further purification. Observation was always conducted with 1 N sulfuric acid at 22°C in the atmosphere of purified nitrogen. The DME[2] was composed of Pyrex parts and a molybdenum glass capillary with a ground glass joint, the other conditions being the same as described previously.[2]

Results and Discussion

Differential Capacity vs. Potential Curves (C-E Curves) for Competitive Adsorption. An example of C-E curves at the adsorption time (t_{B}) of 8 sec for the competitive adsorption of PVP with *n*-butanol is given in Fig. 1. 1 N sulfuric acid containing 0.1 mol/*l* *n*-butanol and various amounts of PVP ($\bar{M}=10000$) were employed. The C–E relation for the single adsorption of *n*-butanol is also shown. The adsorption process of PVP revealed at $t_{\mathrm{B}}=8$ sec is expected to be controlled by diffusion. In the case of the single adsorption of PVP, an ad- or desorption peak is revealed at *ca.* 75 mV (SCE) and the peak height increases with bulk concentration. The differential capacity is depressed by the adsorption of PVP in the more cathodic potential than the above peak. The inhibitive action of PVP on the adsorption of *n*-butanol can be seen in Fig. 1, since the adsorption or desorption peak due to *n*-butanol is depressed and the peak due to PVP grows with PVP concentration. In the competitive adsorption of PVP with *n*-pentanol or *n*-hexanol, the tendency of the C–E relation was similar to that for *n*-butanol.

Time-Dependence of Differential Capacity for Competitive Adsorption (C-t Curves). For the purpose of examining competitive adsorption accompanied by the process controlled by the diffusion of PVP, the time-dependence of differential capacity was observed at *ca.* -0.5 V (SCE), where the saturated adsorption of

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1) "Single adsorption" is used in contrast to "competitive adsorption" and means the adsorption of an organic substance contained solely in a supporting electrolyte.

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

3) H. Jehring, *J. Electroanal. Chem.*, **21**, 77 (1969).

4) L. Pospišil and J. Kůta, *Collect. Czech. Chem. Commun.*, **34**, 3047 (1969).

5) J. M. Parry and R. Parsons, *J. Electrochem. Soc.*, **113**, 992 (1966).

6) B. B. Damaskin, *J. Electroanal. Chem.*, **21**, 149 (1969).

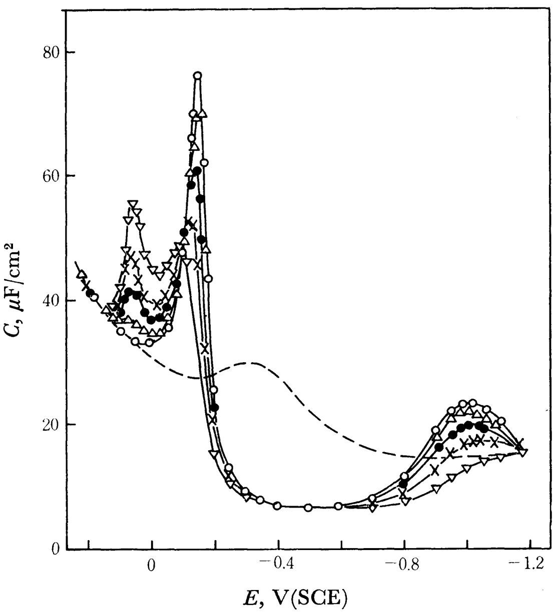

Fig. 1. Potential-dependence of differential capacity in 1N sulfuric acid solution containing 0.1M/l *n*-butanol and several amount of PVP.
1 kHz, 22°C, t_B=8 sec, $\bar{M}$ of PVP=10000, dashed line: 1N sulfuric acid solution, ○: PVP content 0 mg/l, △: PVP 2.0 mg/l, ◐: PVP 5.0 mg/l, ×: PVP 10.0 mg/l, ▽: PVP 15.0 mg/l.

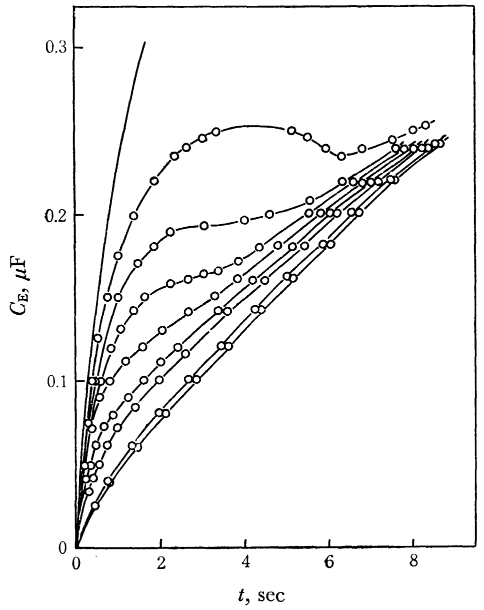

Fig. 2. Time-dependence of observed capacity at −0.5 V (SCE) in 1N sulfuric acid solution containing 30 mg/l PVP and several amount of *n*-hexanol.
1 kHz, 22°C, solid line: 1N sulfuric acid solution, *n*-hexanol content mM/l from top to the bottom: 0, 0.25, 0.50, 0.75, 1.00, 1.25, 5.00, 30.0.

PVP is always attainable.[2] Figure 2 shows typical plots of time-dependence of the observed capacity (C_E) for competitive adsorption in 1N sulfuric acid containing PVP (30 mg/l) and various amounts of *n*-hexanol, where the adsorption of PVP is controlled by diffusion.[2]

Single adsorption of PVP was found to approach saturation after the appearance of maximum value of C_E (Fig. 2). The transient range from diffusion-controlled to saturated adsorption becomes gradually ambiguous as *n*-hexanol content increases. It appears that the individual adsorption equilibrium is attained in the case of relatively high hexanol content. The C-$t^{1/2}$ plot obtained from the C_E-t relation is shown in Fig. 3, where (a) and (b) refer to the competitive adsorption of PVP with *n*-hexanol and *n*-butanol, respectively.

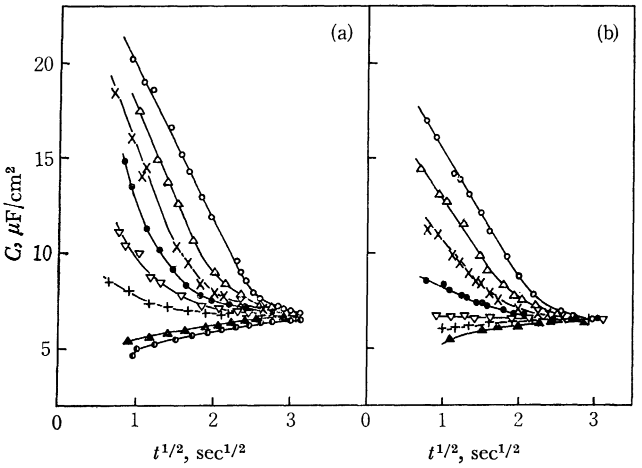

Fig. 3. Relation between differential capacity and square root of time at the competitive adsorption.
1N sulfuric acid solution, 1 kHz, 22°C, (a) PVP ($\bar{M}$=10000) +*n*-hexanol at −0.5 V(SCE): (30 mg/l PVP +*n*-hexanol mM/l, ○: 0, △: 0.25, ×: 0.5, ●: 0.75, ▽: 1.00, +: 1.25, ▲: 5.00, ◐: 30.0). (b) PVP ($\bar{M}$=10000)+*n*-butanol at −0.6 V(SCE): (35 mg/l PVP +*n*-butanol mM/l, ○: 0, △: 0.01, ×: 0.02, ●: 0.04, ▽: 0.08, +: 0.15, ▲: 0.50).

In the case of adsorption controlled by the diffusion of adsorbates, the behavior on a DME is approximately explained in terms of the Koryta equation.[7] The following equation[8] can be derived by substitution of the Koryta equation into the relation for the Frumkin parallel condenser model:

$$C = C_0 - 0.736(C_0 - C_1)D^{1/2}\Gamma_m^{-1}at^{1/2} \qquad (1)$$

where C_0 and C_1 are the differential capacities at $\theta=0$ and $\theta=1$, respectively, and D, Γ_m, and a are diffusion coefficient (cm²/sec), maximum surface concentration (mol/cm²) and bulk concentration (mol/cm³). Equation (1) holds for $t<t_m$, where t_m is the time required to attain the saturated adsorption. When $t \geq t_m$, we have

$$C = C_1 \qquad (2)$$

In Fig. 3, the linear portion of C-$t^{1/2}$ plot decreases and the transient range from diffusion-controlled to saturated adsorption increases with the content of *n*-hexanol or *n*-butanol. In each single adsorption, the minimum differential capacities of PVP ($\bar{M}$=10000), *n*-hexanol and *n*-butanol were found to be 6.5, 4.7, and 5.2 μF/cm², respectively. It is expected that the hexanol molecules are replaced gradually

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[7] J. Koryta, *Collect. Czech. Chem. Commun.*, **18**, 206 (1953).

[8] P. W. Board, D. Britz, and R. V. Holland, *Electrochim. Acta*, **13**, 1633 (1968).

by the PVP molecules which reach the interface by diffusion.

In the case of competitive adsorption of PVP with *n*-butanol shown in Fig. 3-(b), or with *n*-pentanol, a similar tendency to that in the case of hexanol was also observed in the relation C–$t^{1/2}$.

Competitive Adsorption Curves (C–$t^{1/2}$) Observed and Expected. The C–$t^{1/2}$ relation of competitive adsorption was expected from the sum of individual capacity depression[9] for PVP and alcohol. The expected behavior was compared with the result obtained from competitive adsorption in the same electrolyte. Typical cases[10] of competitive adsorption of PVP with *n*-hexanol and *n*-butanol are shown in Fig. 4-(a) and (b). The capacity due to the adsorption of hexanol decreases with time. The adsorption equilibrium is not attained but influenced somewhat by the diffusion process under such hexanol content. The expected curve of C–$t^{1/2}$ agrees approximately with that observed for competitive adsorption in the initial stage of the linear portion. The observed curve, however, approaches the minimum differential capacity due to the saturated adsorption of PVP. Results nearly analogous to the above were obtained for the competitive adsorption of PVP with *n*-pentanol. With *n*-butanol, however, the expected curve is relatively isolated from the observed one [Fig. 4-(b)].

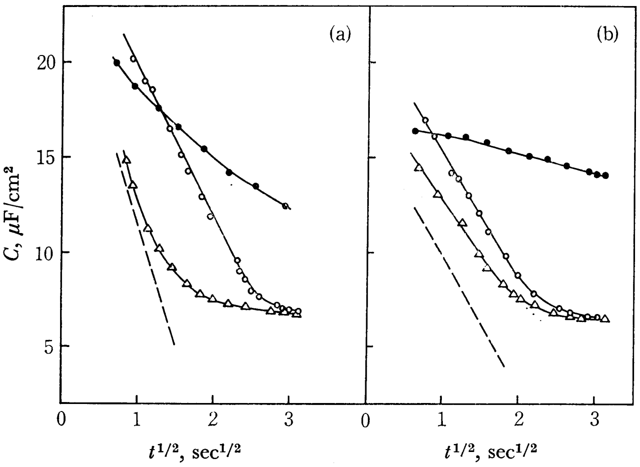

Fig. 4. Relation between differential capacity and square root of time at the competitive adsorption.
1 N sulfuric acid solution, 1 kHz, 22°C, (a) PVP+*n*-hexanol at −0.5 V(SCE), ○: 30 mg/*l* PVP at the single adsorption, ●: 0.75 mM/*l* *n*-hexanol at the single adsorption, △: 30 mg/*l* PVP+0.75 mM/*l* *n*-hexanol at the competitive adsorption, dashed line: the curve of the competitive adsorption expected from the individual behaviour of the single adsorption. (b) PVP+*n*-butanol at −0.6 V(SCE), ○: 35 mg/*l* PVP at the single adsorption, ●: 0.01 mM/*l* *n*-butanol at the single adsorption, △: 35 mg/*l* PVP+0.01 mM/*l* *n*-butanol at the competitive adsorption, dashed line: the curve of the competitive adsorption expected from the individual behaviour of the single adsorption.

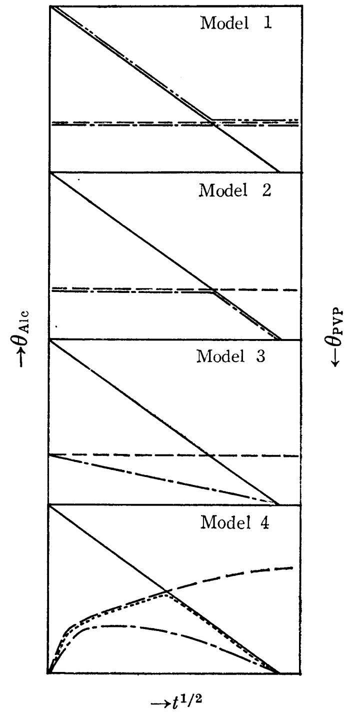

Fig. 5. Models assumed for the competitive adsorption of *n*-aliphatic alcohol with PVP.
solid line: the behaviour of diffusion-controlled adsorption of PVP at the single adsorption whose coverage is shown by θ_{PVP}, dashed line: the behaviour of adsorption equilibrium of *n*-aliphatic alcohol at the single adsorption whose coverage is shown by θ_{Alc}, dashed-two-dotted line in Model 1: the behavior of PVP at the competitive adsorption (*cf.* In the other models, the behavior of PVP at the competitive adsorption is nearly the same as that at the single adsorption.), dotted and dashed-dotted lines: the behavior of alcohol at the competitive adsorption with PVP, where the coverage of alcohol coexistent with PVP is shown by $\theta_{\mathrm{Acl}}^{\mathrm{com.}}$.

Behavior of Alcohols during Competitive Adsorption. Some models of competitive adsorption are shown in Fig. 5. One of the adsorbates (PVP) undergoes diffusion-controlled adsorption and the other (alcohol) easily attains adsorption equilibrium. In each single adsorption, the coverage of PVP and alcohol are expressed by θ_{PVP} (solid line) and θ_{Alc} (dashed line), respectively. The coverage of alcohol during competitive adsorption is expressed by $\theta_{\mathrm{Alc}}^{\mathrm{com}}$ and plotted with dashed-dotted lines. The coverage of PVP coexistent with alcohol is assumed to be nearly analogous to θ_{PVP}.

Model 1 (Fig. 5) is the case in which interaction or replacement between alcohol and PVP hardly takes place, and $\theta_{\mathrm{Alc}}^{\mathrm{com}}$ remains constant after the full coverage of ($\theta_{\mathrm{PVP}}+\theta_{\mathrm{Alc}}=1$) is established. The behavior of PVP in single adsorption, expressed by the dashed-two-dotted line, differs only for this case from that in competitive adsorption. Since the behavior of PVP in single and competitive adsorption is considered to be the same in the other models, it is always shown by a solid line. Model 1 is impractical because PVP has a higher adsorbability than that of the saturated alcohol.

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[9] The individual capacity depression is the difference between the capacity of the individual adsorbate for the single adsorption and that in the solution without adsorbates at a certain potential and adsorption time.

[10] Extrapolation of the three solid lines in Fig. 4 should coincide at $t=0$. The results of differential capacity at t less than 1 sec are not shown, an accurate estimation of the mercury drop surface being difficult.

Model 2 is the case in which the adsorbed alcohol in its equilibrium begins to be replaced by PVP arriving after the full coverage of $(\theta_{PVP}+\theta_{Alc}=1)$ is achieved. In this case, the space in the electrode is preferentially covered by PVP until the time $(\theta_{PVP}+\theta_{Alc}=1)$, the rate of the replacement being controlled by the diffusion of PVP.

Model 3 is the case in which replacement of the adsorbed alcohol with PVP takes place as soon as PVP reaches the interface by diffusion. The amount of alcohol replaced by PVP is proportional to that of the adsorbed PVP. Thus the coverage of θ_{Alc}^{com} (dashed-dotted line) is given by $\theta_{Alc}^{com}=(1-\theta_{PVP})\theta_{Alc}$.

It is necessary to assumed another model in consideration of practical cases in which the adsorption of saturated alcohol is somewhat controlled by its diffusion dependent on the adsorption isotherm. This diffusion process was discussed by Delahay[11] by means of Henry's law, by Reinmuth[12] by means of the Langmuir isotherm and by Rampazzo[13] by means of the Frumkin isotherm. In view of these discussions, Model 4 is shown qualitatively as a practical case. The dashed-dotted line corresponds to that in Model 3. The plot is also expressed by the relation $\theta_{Alc}^{com}=(1-\theta_{PVP})\theta_{Alc}$, and the dotted line corresponds to the dashed-dotted line in Model 2.

θ_{Alc}^{com} was expected from the difference between the capacity depressions for the competitive and single adsorption of PVP by means of the relation "$\theta=(C_0-C)/(C_0-C_1)$" on the assumption that the adsorption behavior of PVP coexistent with alcohol is analogous to that of the single adsorption in view of the results in Figs. 1, 2, and 3. The θ_{Alc}^{com}–$t^{1/2}$ relations expected for the competitive adsorption of PVP with *n*-hexanol, *n*-pentanol, and *n*-butanol are shown by the dashed-dotted lines in Figs. 6, 7, and 8, respectively. θ_{Alc} given by the dashed lines is obtained from the capacity depression observed for the single adsorption.

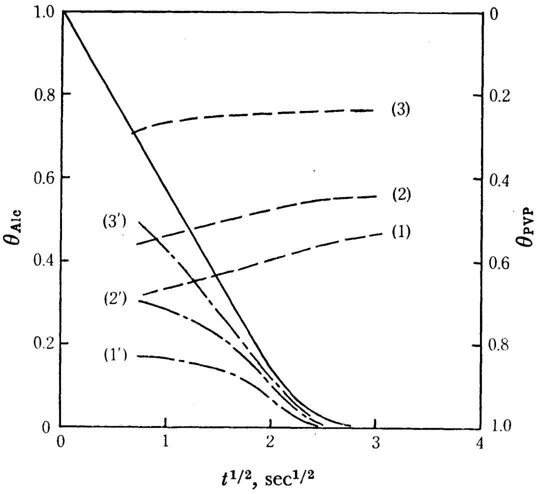

Fig. 6. Relation between coverage and square root of time in the case of hexanol.

1N sulfuric acid solution, −0.5 V(SCE), solid line: the single adsorption of PVP 30 mg/*l*, dashed lines; the single adsorption of *n*-hexanol mM/*l*: [(1): 0.25, (2): 0.50, (3) :0.75], dashed-dotted lines: the competitive adsorption of *n*-hexanol expected from the capacity depression, PVP 30 mg/*l* +*n*-hexanol mM/*l*: [(1)′: 0.25, (2)′: 0.50, (3)′: 0.75].

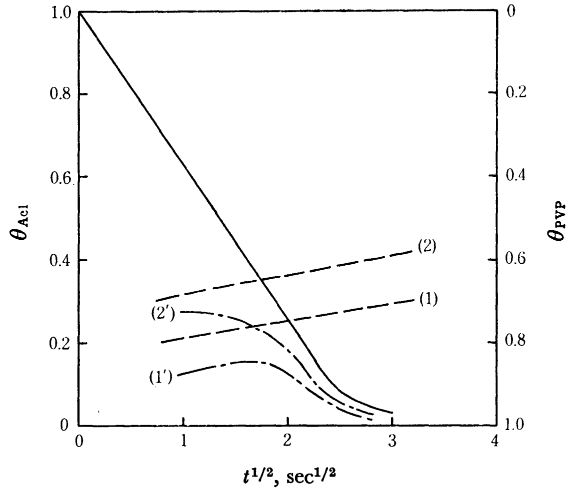

Fig. 7. Relation between coverage and square root of time in the case of pentanol.

1N sulfuric acid solution, −0.5 V(SCE), solide line: the single adsorption of PVP 30 mg/*l*, dashed lines: the single adsorption of *n*-pentanol mM/*l*: [(1): 2.0, (2) : 3.0], dashed-dotted lines: the competitive adsorption of *n*-pentanol expected from the capacity depression, PVP 30 mg/*l* +*n*-pentanol mM/*l*: [(1)′: 2.0, (2)′: 3.0].

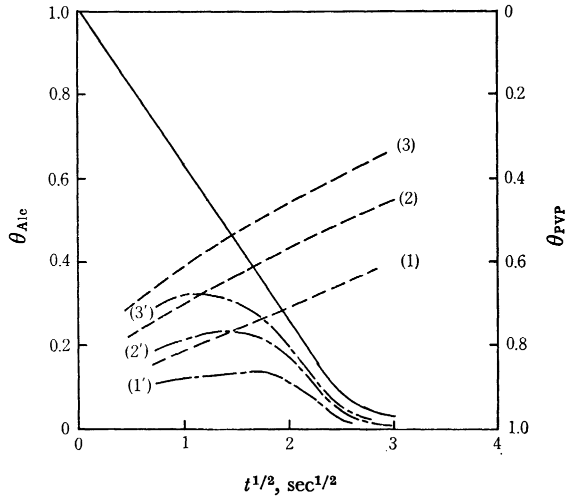

Fig. 8. Relation between coverage and square root of time in the case of butanol.

1N sulfuric acid solution, −0.6 V(SCE), solid lines: the single adsorption of PVP 35 mg/*l*, dashed lines: the single adsorption of *n*-butanol M/*l*: [(1): 0.01, (2): 0.02. (3): 0.04], dashed-dotted lines: the competitive adsorption of *n*-butanol expected from the capacity depression, PVP 35 mg/*l*+*n*-butanol M/*l*: [(1)′: 0.01, (2)′: 0.02, (3)′: 0.04].

The values of θ_{Alc}^{com} somewhat deviates from θ_{Alc} in the early stage of the adsorption for *n*-hexanol (Fig. 6), the deviation becoming greater at lower bulk concentration. The θ_{Alc}^{com} plots come closer to the θ_{PVP} curve with increasing adsorption time. The

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[11] P. Delahay and I. Trachtenberg, *J. Amer. Chem. Soc.*, **79**, 2355 (1957); P. Delahay and C. T. Fike, *ibid.*, **80**, 2628 (1958).

[12] W. H. Reinmuth, *J. Phys. Chem.*, **65**, 473 (1961).

[13] L. Rampazzo, *Electrochim. Acta*, **14**, 733 (1969).

tendency shows the gradual replacement of the adsorbed alcohol with PVP which reaches the interface. This behavior of *n*-hexanol coexistent with PVP is explained in terms of the intermediate type between the dashed-dotted and dotted lines in Model 4, *viz.*, between Models 2 and 3.

The value of θ_{Alc} for *n*-pentanol (Fig. 7) shows a relatively smaller dependence on *t* than that for *n*-hexanol. The adsorption behavior of *n*-pentanol, coexistent with PVP is similar to that of *n*-hexanol.

The plot of $\theta_{\mathrm{Alc}}^{\mathrm{com}}$ for butanol (Fig. 8) approaches the θ_{PVP} curve in a relatively early stage and the effect of the coexistence of PVP is remarkable as compared with the other cases. This behavior might correspond to that shown by the dashed-dotted line in Model 4 or 3, since the values agree approximately with those of $\theta_{\mathrm{Alc}}^{\mathrm{com}}$ derived from the relation $\theta_{\mathrm{Alc}}^{\mathrm{com}}=(1-\theta_{\mathrm{PVP}})\theta_{\mathrm{Alc}}$.

The adsorption behavior of alcohol coexistent with PVP is considered to be dependent on its adsorbability. The adsorption coefficients of *n*-butanol, *n*-pentanol, and *n*-hexanol were found to be 1.25×10^2, 5.00×10^2, and 2.20×10^3 (*l*/mol), respectively, assuming the Langmuir isotherm. These are approximately in agreement with those published by Delahay,[11] Lorenz,[14] and Kalvoda,[15] and the order of the magnitude of the adsorbability is as *n*-hexanol>*n*-pentanol>*n*-butanol. Thus, it is considered that the influence of coexistent PVP with high adsorbability is the largest for *n*-butanol and relatively small for *n*-hexanol during the course of competitive adsorption.

Models 1—3 (Fig. 5) are shown in the order of magnitude of the adsorbability of alcohol. It is natural that the relation $\theta_{\mathrm{Alc}}^{\mathrm{com}}=(1-\theta_{\mathrm{PVP}})\theta_{\mathrm{Alc}}$ holds in the case of *n*-butanol because of its low adsorbability. In conclusion, the behavior during competitive adsorption of *n*-butanol is explained by Model 3, and that of *n*-hexanol and *n*-pentanol by an intermediate type between Models 2 and 3 due to their somewhat higher adsorbability.

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[14] W. Lorenz and F. Möckel, *Z. Electrochem.*, **60**, 507 (1956).

[15] R. Kalvoda and A. Vaškelis, *Collect. Czech. Chem. Commun.* **32**, 2206 (1967).