[June, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1585—1589(1972) 1585

The Determination of the Diffusion Coefficient and the Maximum Surface Concentration of Polyvinylpyrrolidone by Means of a Hanging Mercury Drop Electrode

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(Received April 20, 1971)

Subsequently to the previous work with a dropping mercury electrode (DME), the diffusion coefficient (D) and the maximum surface concentration (Γ_m) for polyvinylpyrrolidone (PVP) were determined in a 1 N sulfuric acid solution by means of a hanging mercury drop electrode (HMDE). The values of D and Γ_m for PVP were obtained separately by means of the equation for a semi-infinite spherical diffusion for HMDE. The results for D were compared with the values evaluated from the Stokes-Einstein equation or with those previously published. The results for Γ_m are also shown in comparison with those values to be expected from the data obtained by the use of DME or HMDE on the assumption of linear diffusion and D, or in comparison with the results published by Jehring. It was also confirmed that the HMDE used by the authors is almost satisfactory for the determination of D and Γ_m in this case.

In most cases, the adsorption process of organic high polymers is mainly diffusion-controlled; such a process for PVP (polyvinylpyrrolidone)1) has been discussed by the authors on the basis of the results obtained with the DME (dropping mercury electrode) in a previous paper.2) It is necessary to assume the diffusion coefficient (D) of adsorbates in order to evaluate the maximum surface concentration (Γ_m) with the Koryta equation; however, the maximum surface concentration and the diffusion coefficient may be computed separately by using a equation based on the spherical diffusion for HMDE (hanging mercury drop electrode). Moreover, the results obtained by the use of HMDE under the diffusion-controlled adsorption will be reported in this paper with reference to the values of D and Γ_m published3–5) or obtained2) by the authors with the DME.

Experimental

Apparatus. The equipment used for the HMDE was made from Pyrex glass except for some parts of the microsyringe; it is sketched in Fig. 1. The differential capacity was measured at the frequency of 1 kHz with an impedance bridge of a transformer-connected type described in the previous paper.2) A platinum wire ring6) was used as the counter electrode, and all the potentials were measured and described with reference to the saturated calomel electrode (SCE). Further, almost all the measurements with the HMDE were made at −500 mV (SCE)7) in an atmosphere of purified nitrogen kept at 20°C without stirring, except in the case shown in Fig. 3.

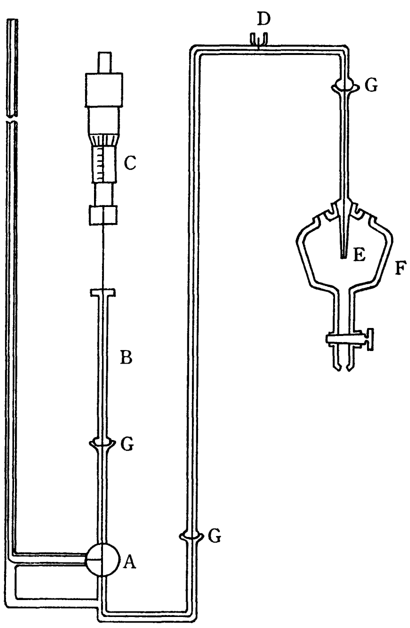

Fig. 1. Equipment for HMDE.
A: Cock, B: Microsyringe, C: Micrometer, D: Pt wire, E: Capillary, F: Cell, G: Ball-joint.

Materials. The mercury used in the present experiment was distilled twice *in vacuo* after being treated in the usual way. For the investigation, four kinds of the PVP prepared by BASF as chemical-grade reagents were used without any further purification; their mean molecular weights ($\bar{M}$) were 10000, 26000, 37000, and 750000 respectively. All the solutions were prepared with guaranteed reagents and triply-distilled water.

Purification of the Solution. Because of the fact that even a trace of impurities influences the results observed with the HMDE, the sulfuric acid solution, prepared as described above, was always standardized after treatment with granular active charcoal and then it was subjected to preelectrolysis over about 10 hours at −500 mV (SCE) in an atmosphere of purified nitrogen just before use.

Procedure for Observation with HMDE. The mercury drop ("E" in Fig. 1) of the HMDE was polarized at the potential of −500 mV (SCE) in a sulfuric acid solution which had been carefully purified and deaerated; then a definite

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1) R. L. Davidson and M. Sittig, eds., "Water-Soluble Resins," Reinhold Pub. Corp., New York 1963, p. 110.

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

3) L. E. Miller and F. A. Hamm, *J. Phys. Chem.*, **57**, 110 (1953).

4) W. Scholtan, *Makromol. Chem.*, **7**, 209 (1951).

5) H. Jehring, *Monatsber. Deut. Akad. Wiss. Berlin*, **10**, 295 (1968).

6) The ring-like electrode is prepared by winding the platinum wire which is *ca.* 50 cm in length and 0.3 mm in diameter.

7) The saturated adsorption of PVP was always attainable at this potential, as has been described in the previous paper.2)

amount of mercury was forced out by means of a micrometer connected with the microsyringe (shown as "C" and "B" in Fig. 1), just before the observation was started in pursuit of the time dependence of the differential capacity at the mercury interface, the starting time of observation being put at zero. The surface area of a mercury drop for the HMDE was determined from its differential capacity with reference to the value per unit area of mercury obtained with the DME under the same conditions; the result was also compared with that derived from the volume of mercury forced out by the microsyringe ("B" in Fig. 1). The radius of a drop was found to be 0.047 cm.

Theoretical

Relation for the Semi-Infinite Linear Diffusion. In the case of the adsorption controlled by the diffusion of adsorbates, the surface concentration (Γ_t) at the time (t) on a planar electrode is given by:[8,9]

$$\Gamma_t = (2/\pi^{1/2})D^{1/2}at^{1/2} \quad (1)$$

where Γ_t, D, a, and t are the surface concentration of adsorbates at time t in mol/cm^2, its diffusion coefficient in cm^2/sec, its bulk concentration in mol/cm^3, and the time from the beginning of its adsorption in sec respcetively. By substituting the above expression for Γ_t into the relation introduced by Frumkin,[10] we obtain:

$$\theta = \Gamma_t/\Gamma_m = (C_0-C)/(C_0-C_1) \quad (2)$$

it may be written as follows:[9]

$$C = C_0 - 1.13(C_0-C_1)D^{1/2}\Gamma_m^{-1}at^{1/2} \quad (3)$$

where C is the differential capacity per unit of area in μF/cm^2; θ, the coverage; C_0 and C_1, the differential capacities for $\theta=0$ and $\theta=1$ respectively, and Γ_m, the maximum surface concentration in mol/cm^2, that is, the value of Γ_t at $\theta=1$.

Relation for the Semi-Infinite Spherical Diffusion. Fick's law for the diffusional process on a spherical electrode is written by:[11]

$$\partial a/\partial t = D\{\partial^2 a/\partial r^2 + (2/r)(\partial a/\partial r)\} \quad (4)$$

where r is the radius distance from the center of the spherical electrode. When the initial and boundary conditions are substituted in Eq. (4), Eq. (5)[12] is obtained by the Laplace transformation:

$$\Gamma_m = (2/\pi^{1/2})D^{1/2}at_m^{1/2} + Dat_m/r_0 \quad (5)$$

where t_m is the time required to form a monolayer in sec, and r_0, the radius of the spherical electrode in cm. It follows from the rearangement of the above equation that:

$$(at_m^{1/2})^{-1} = (2D^{1/2})/(\pi^{1/2}\Gamma_m) + (Dt_m^{1/2})/(r_0\Gamma_m) \quad (6)$$

where a plot of $(at_m^{1/2})^{-1}$ against $(t_m^{1/2})$ gives a linear relation with a slope of $(D/\Gamma_m r_0)$ and an intercept of $(2D^{1/2}/\pi^{1/2}\Gamma_m)$; therefore, the slope and the intercept are denoted by "K" and "L" respectively, for convenience. The values of Γ_m and D may be computed from K and L as follows, while the values of K and L are obtainable from the experimental data:

$$\left.\begin{aligned} \Gamma_m &= (4r_0K)/(\pi L^2) = D/(Kr_0) \\ D &= (4r_0^2K^2)/(\pi L^2) \end{aligned}\right\} \quad (7)$$

Results

Purification Effect for a Solution. The sulfuric acid solution to be observed was carefully purified as has been stated previously, because of the high sensitiveness of a HMDE for contamination compared with that of a DME. An example, illustrating the wide difference between the solutions prepared with or without the treatment, is given in Fig. 2. The results shown in Fig. 2 confirm that the active charcoal treatment is very effective in the purification; the differential capacity decreases rapidly with the time in the case of the blank 1N sulfuric acid solution prepared without treatment, whereas only a slight decrease with time was observed in the case of that purified with active charcoal.

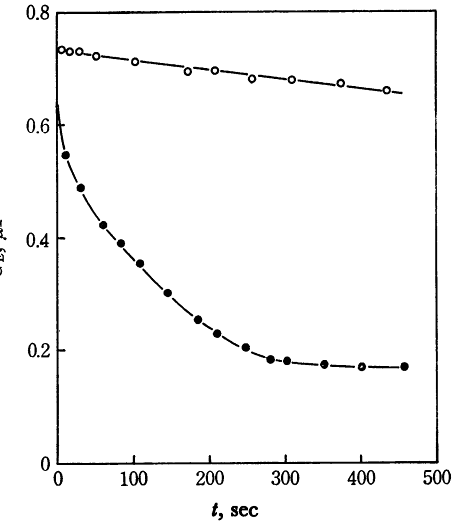

Fig. 2. Pretreatment effect with active charcoal.
20°C, Observed at −500 mV (SCE), 1N sulfuric acid solution,
-○-: Solution with pretreatment of charcoal,
-●-: Solution without pretreatment of charcoal.

Stirring Effect for a Solution. For the case observed with a 1N sulfuric acid solution containing 1.0 mg per litre of PVP ($\bar{M}=10000$), the variation in the differential capacity with the time is shown in Fig. 3, where the results were obtained with or without the stirring of the solution by nitrogen bubbling. When the bubbling was started, the differential capacity for the solution containing PVP decreased more rapidly until the minimum differential capacity was-attained than in the case without bubbling. It may be considered from the above that the process for PVP adsorption is mainly controlled by the diffusion until the saturated adsorption is achieved.

Differential Capacity vs. Time Relation. The C_E *vs.* t curves in Fig. 4-(a) were observed with extremely dilute solutions of PVP ($\bar{M}=10000$). It appears that the minimum differential capacity depends to some extent upon the bulk concentration and that the adsorp-

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[10] A. N. Frumkin, *Z. Phys.*, **35**, 792 (1926).

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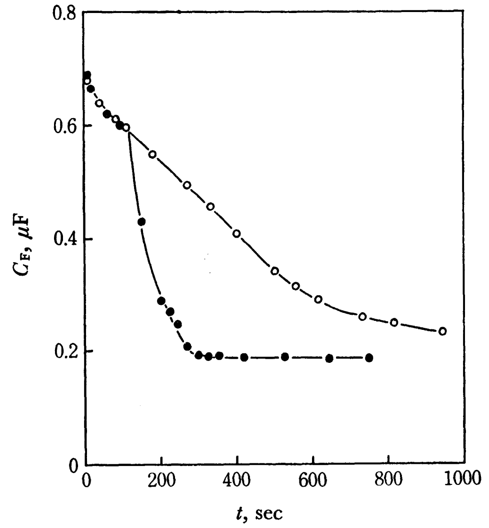

Fig. 3. Stirring effect for solution.
20°C, Observed at −500 mV (SCE), 1 N sulfuric acid solution+PVP ($\bar{M}$=10000) 1.0 mg/l,
-○-: No stirring, -●-: Stirring with nitrogen bubble after 120 sec.

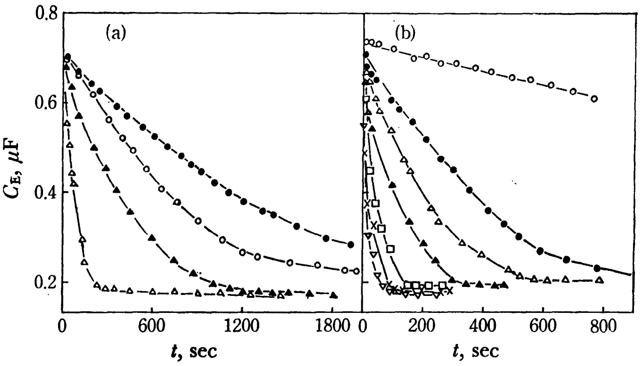

Fig. 4. Differential capacity *vs.* time curves.
20°C, Observed at −500 mV (SCE), 1 N sulfuric acid solution+PVP ($\bar{M}$=10000),
(a) -●-: 0.2 mg/l, -○-: 0.4 ml/l, -▲-: 0.8 mg/l, -△-: 4.0 mg/l
(b) -○-: 0 mg/l, -●-: 1.0 mg/l, -△-: 2.0 mg/l, -▲-: 4.0 mg/l, -□-: 6.0 mg/l, -×-: 8.0 mg/l, -▽-: 10.0 mg/l.
Where C_E is the observed differential capacity (μF/electrode surface).

tion equilibrium may take place even for the condition of $\theta < 1$ in this case. However, the minimum differential capacity for this case gradually decreased with the time. Therefore, for extremely dilute solutions of PVP, it is considered that the saturated adsorption of PVP may occur after a very long time, or that the differential capacity corresponding to an adsorption equilibrium may be slowly depressed by a trace of impurities left in the solution. On the other hand, in the case of Fig. 4-(b), observed with a relatively concentrated solution of PVP as compared with that of the above case, the minimum differential capacities were nearly constant, independently of the bulk concentration, although a slight dependence of the minimum capacity on the concentration was still observed. In a plot similar to the above, observed with PVP of $\bar{M}$=750000, the minimum differential capacities always reached a common value, regardless of the bulk concentration. The time required to attain the minimum capacity of the constant value for the PVP of $\bar{M}$=750000 was about two or three times that in the case with one of $\bar{M}$=10000, in the same bulk concentration in mg per litre.

Discussion

Application of the Semi-Infinite Linear Diffusion (C_E vs. $t^{1/2}$). Equation (3) makes it clear that the differential capacity for the solution containing adsorbates decreases linearly with $t^{1/2}$ or a. In Fig. 5, the differential capacity decreases with $t^{1/2}$, until finally it shows a constant value for the saturated adsorption, regardless of the bulk concentration. The time required to form a complete monolayer (t_m) was obtained by extrapolating these two linear relations, as has been described in the previous paper.[2] In the case of relatively concentrated solution of PVP, nearly linear plots were obtained for the diffusion process within about 100 sec, as was to be expected from Eq. (3). However, in the case of the relatively dilute solution in this case, the curves were remarkably depressed and deviated from the linear relation of Eq. (3), especially after about 100 sec. The above deviation was not due to the relation expected from a spherical diffusion, shown in Fig. 6. Consequently, such a deviation is considered to be due to the convection besides the diffusion; therefore, the effect of the convection may be neglected within a relatively short time, such as about 100 sec.

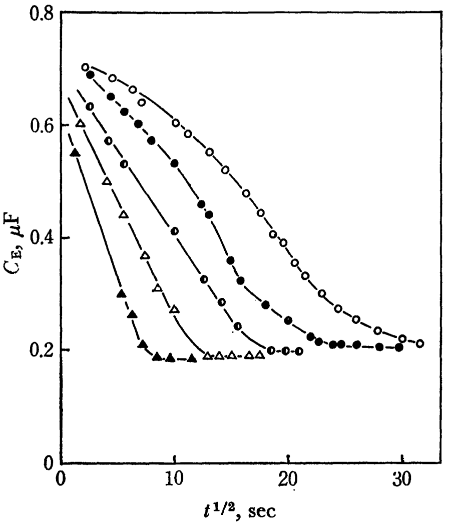

Fig. 5. Relation between differential capacity and square root of time.
20°C, Observed at −500 mV (SCE), 1 N sulfuric acid solution+PVP ($\bar{M}$=10000),
-○-: 1.0 mg/l, -●-: 2.0 mg/ml, -◐-: 4.0 mg/l, -△-: 6.0 mg/l, -▲-: 10.0 mg/l.

Accordingly, the examination was made mainly on the basis of the data observed within a relatively short time, when the effect due to the convection may be neglected.

The value of the differential capacity at the starting time of $t=0$ should be a constant, independently of the concentration of PVP. The discrepancy nevertheless observed may be due to the slight difference among mercury drops resulting from the different operations of the HMDE.

In the next place, by substituting the observed value of t_m into Eq. (3), we can evaluate Γ_m by assuming the diffusion coefficient of PVP; the results will be given later in comparison with the data derived in the other way.

Application of the Semi-Infinite Spherical Diffusion $((at_m^{1/2})^{-1}$ *vs.* $t_m^{1/2})$. As has previously been stated, the values of Γ_m and D cannot be evaluated separately by the equation for the linear diffusion process unless one of them is determined or postulated; therefore, only the ratio of (D/Γ_m^2) is obtainable in this case. However, the value either for Γ_m or D can be evaluated separately using the relation for the spherical diffusion process, as is given by Eq. (6) in relation to a HMDE.

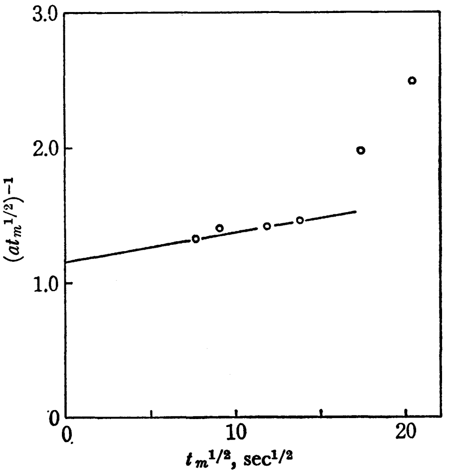

Fig. 6. Relation between $(at_m^{1/2})^{-1}$ and $t_m^{1/2}$.
20°C, Observed at -500 mV (SCE), 1N sulfuric acid solution+PVP ($\bar{M}=10000$).

The relation $(at_m^{1/2})^{-1}$ *vs.* $t_m^{1/2}$ based on Eq. (6) is illustrated in Fig. 6 for the PVP of $\bar{M}=10000$ as an example; it rises steeply from the saturation time (t_m) of about 200 sec. Such a deviation observed for a relatively long saturation time can be attributed mainly to the effect of the convection pointed out previously. Therefore, a linear relation obtained for a saturation time, of less than about 200 sec may be approximately regarded as a reasonable result for the purpose. Accordingly, the values of Γ_m and D were computed, respectively, from the slope and the intercept observed for the linear relation, as above.

Diffusion Coefficient of PVP. The diffusion coefficient of PVP has been measured by the electrophoresis[3] or diffusional sedimentation method,[4] while an approximate value for colloidal particles or large molecules was frequently estimated through the well-known Stokes-Einstein equation in the case of an unknown conductivity. Meanwhile, the Stokes-Einstein equation holds only in the case where the moving particles or molecules are nearly spherical and very large in size compared with the molecules of the solvent.

The results for D in this paper were derived from Eq. (6), related to a spherical diffusion, or from the Stokes-Einstein equation; these results are shown in Table 1 in comparison with the published values.[3,4] Further, the results obtained by Scholtan's relation[4] between D and $\bar{M}$ are also quoted in Table 1 for reference. As is shown in Table 1, the results obtained by the present authors seem to be reasonable apart from the case for the PVP of $\bar{M}=37000$.

Maximum Surface Concentration of PVP. The values of Γ_m for the PVP of several $\bar{M}$'s obtained directly by Eq. (6) are shown in Table 2 with reference to the results derived on the assumption of linear diffusion and the values of D; the D values[13] used in the previous paper[2] were also assumed for the case of the HMDE. The results by Jehring[5] are also quoted there for reference. The values resulting form the HMDE or DME[2] were always measured at -500 mV (SCE) in a 1N sulfuric acid solution at 20°C, whereas those by Jehring[5] were obtained at -1100 mV (SCE) in a 0.5M potassium chloride solution at 25°C.

TABLE 1. DIFFUSION COEFFICIENT OF PVP ($\times 10^7$ cm^2/sec)

$\bar{M}$	I[a]	II[b]	III[c]	IV[d]	V[e]
10000	10.3	10.5			10.0
12100				9.15	
13000			7.55		
21000			5.94 6.33		
23000			5.87		
25500				6.20	
26000	7.28	7.65			6.21
32000			4.81		
32500				6.00	
36000			4.24		
37000	9.52	6.78			5.21
39200				4.50	
41500			4.14		
55600				3.50	
584000				1.35	
750000	1.27	2.50			1.15
1129000				0.70	

a) The results derived from the equation for spherical diffusion [*cf.* Eqs. (5) and (6)].
b) The calculated results from the Stokes-Einstein equation, *i.e.* $D=2.96\times10^{-7}/(\eta V^{1/3})$, where η in dyn·sec·cm^{-2} and V in $\bar{M}$/density.
c) The values by the electrophoresis method (*cf.* Ref. 3).
d) The values by the sedimentation method (*cf.* Ref. 4).
e) The values calculated with $D=1.00\times10^{-4}\bar{M}^{-0.5}$ (cm^2/sec) (*cf.* Ref. 4).

It was found previously[2] that the saturated adsorption of PVP is attained promptly at -500 mV (SCE) in a 1N sulfuric acid solution in the case of a relatively high bulk concentration, while Jehring[5] also investigated the Γ_m for PVP under conditions when the saturated adsorption was achieved easily. Accordingly, the values of Γ_m reported by Jehring[5] may be compared approximately with the present authors' results.

The data in Table 2 are illustrated in Fig. 7, where the results obtained with the DME[2] are approximately in agreement with those reported by Jehring.[5]

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[13] Here $D=10.3\times10^{-7}$ (cm^2/sec) for $\bar{M}=10000$, 7.3×10^{-7} (cm^2/sec) for $\bar{M}=26000$, 5.1×10^{-7} (cm^2/sec) for $\bar{M}=37000$, and 1.2×10^{-7} (cm^2/sec) for $\bar{M}=750000$.

TABLE 2. MAXIMUM SURFACE CONCENTRATION OF PVP ($\times 10^{12}$ mol/cm^2)

$\bar{M}$	HMDE a)	HMDE b)	DME c)	Jehring d)
10000	9.98	8.10	6.67	
11500				6.06
25000				3.29
26000	3.10	2.85	2.92	
37000	2.90	1.80	2.02	
38000				1.98
750000	0.101	0.075	0.090	0.089

a) The results obtained directly with the equation for spherical diffusion.

b) The results obtained on the assumption of linear diffusion and *D* (*cf.* Ref. 13).

c) The results by the previous paper.2)

d) The values5) by A.C. polarography observed at −1100 mV (SCE) in 0.5M potassium chloride kept at 25°C.

Therefore, it may be considered for PVP that the dependence of Γ_m upon the electrolyte and the polarized potential is almost negligible under the above conditions.

In Fig. 7, with reference to the results derived from the equation for linear diffusion, the values obtained by the HMDE are approximately in accordance with those obtained by the DME.2) On the other hand, the results obtained directly by the equation of spherical diffusion with regard to the HMDE are somewhat large as compared with both results mentioned above.

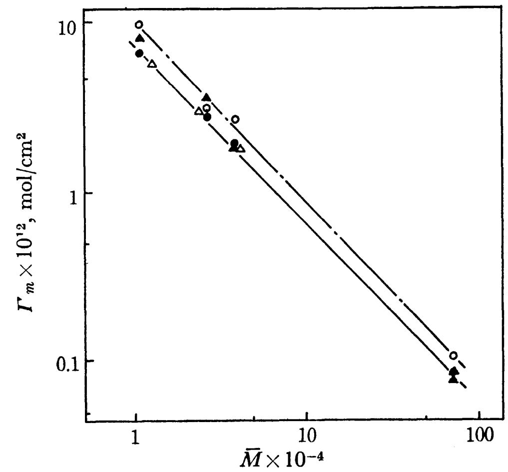

Fig. 7. Relation between Γ_m and $\bar{M}$.

-○-: Values with HMDE, derived from the equation for spherical diffusion.

▲: Values with HMDE, derived from the equation for linear diffusion.

-●-: Values with DME,2) derived from the assumption of *D* as described in the text.

△: Results by Jehring.5)

It is considered from the above results that nearly reliable values of the *D* or Γ_m of PVP were obtained by means of the HMDE shown in Fig. 1.

The authors would like to express their appreciation to Mr. Shoji Tanaka and Mr. Osamu Yoshioka for the earnest assistance.