Density Measurement in Dilute Aqueous Solution of Polyvinyl Alcohol

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Precise determination of solution density has an important bearing on the measurements of various physicochemical properties of high polymers in dilute solution. Fragmentary data can be found in literature, but the density measurement itself was scarcely ever chosen as the subject of studies on dilute high polymer solutions, except in the case of a few studies concerning polystyrene[1-5].

Recently a suggestion was made by Kobatake[6] on the possibility of elucidating the polymer-solvent interaction from the density data of dilute solution. According to an equation proposed by Kobatake[6], the polymer-solvent interaction B_{12} can be best estimated from the molecular weight dependence of the solution density. An analysis of Schulz and Hoffmann's data[5] on the apparent specific volume of polystyrene and polymethyl methacrylate was carried out by Kobatake and Inagaki[7] along with this line of approach. Some interesting data concerning molecular interactions in solution were obtained from the values of B_{12}. It would seem, therefore, that systematic accumulation of density data should contribute to the problems in dilute high polymer solutions.

In this paper, the density of an aqueous solution of polyvinyl alcohol (PVA) is measured by the use of well defined and fractionated samples, and some analysis

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[1] D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951).

[2] W. Heller and A. C. Thompson, *J. Colloid Sci.*, **6**, 57 (1951).

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of the results are made on the basis of Kobatake's equation[6,7].

In order to determine the solution density, the authors adopted the method of floating equilibria which is the same as that used for the quantitative analysis of heavy water concentration[8,9]. This method was proved to be applicable also to polymer solution. It was rather easy to obtain the solution density and polymer concentration with the same accuracy as that obtained by other methods[2,3,5].

Experimental

Preparation of Materials.—The PVA fractions were obtained by the saponification of polyvinyl acetates which were polymerized in solution under various conditions and fractionated in acetone-water system. Acetyl group content in the resulting PVA samples was less than 0.2%.

The molecular weight of PVA samples was determined from the intrinsic viscosity in water. The viscosity average molecular weight calculated from Nakajima's equation[10] is shown in Table I. In the same table, experimental conditions for polymerization are also tabulated since they have an important bearing on the molecular weight dependence of density.

Unfractionated samples of PVA were also used in the preliminary experiments.

Water as solvent was obtained by the careful distillations of conductivity water.

Apparatus and Float.—The apparatus used for the measurement of floating equilibria is based on the one described by Harada[9] for the quantitative analysis of heavy water. The float, made of silicate glass, is spindle-shaped and 2~3 cm. long. The upper spherical part of the float is hollowed, and the apparent specific weight of the whole float is adjusted to a value of the solvent density (water, in this case) near room temperature. The temperature at which the measurements run is always regulated within the accuracy of 0.005°C by a large outer thermostat.

The motion of the float in the sample liquids was followed by a traveling microscope and the equilibrium temperature of the float was read on a Beckmann thermometer.

Density Measurement. — (*a*) *Preparation of sample solution.* — The PVA samples, after the saponification, were purified by extraction with methanol in a Soxhlet extractor for three days or longer and dried in vacuo. These samples were dissolved into water in a flask which was placed on a boiling water bath for more than eight hours and about 1% solution was prepared. The solution was then filtered through the glass filters Nos. 2 and 4, and again heated on a boiling water bath. This stock solution was diluted by weight and/or by volume to obtain required concentrations and each solution was stored in a closed tube. Before use, each solution was kept overnight in a thermostat at 80°C. Concentrations of the solution were determined by evaporating the solvent and drying in vacuo at 60°C to constant weight.

(*b*) *Measurement of equilibrium temperature.*— The equilibrium temperature, T_0, of the float in water—the temperature which keeps the float both from sinking and floating—is first measured for each float. The "apparent density" of the float is next obtained by comparing this temperature with the density-temperature curve of water (chain-dotted line in Fig. 1). Thus, when the equilibrium temperature in solution, T, is again measured for each float of known density, the density-temperature curve of the solution (solid line in Fig. 1) is immediately obtained. The density of solution at any temperature is also determined from this curve.

In practice, the sensitivity of the float to

TABLE I. EXPERIMENTAL CONDITIONS IN POLYMERIZATION, FRACTIONATION AND MOLECULAR WEIGHT OF POLYVINYL ALCOHOL

	B-5	T-2	E-2	U-1	U-2	U-5
Polymerization						
Solvent	Benzene	Toluene	Ethanol	Commercial sample		
Initiator	0.1% BPO	0.1% BPO	1.0% BPO			
Monomer, wt.%	60	60	30			
Temp., °C	80	80	70			
Time, hr.	12	13.5	25			
Yield, %	74	44	60			
Fractionation						
Solvent/precipitant	Acetone/water			Unfractionated		
Fractions	8	5	5			
Temp., °C	25	25	25			
Molecular weight						
$M_w (\times 10^{-3})$	70.4	24.2	8.4	107	96.8	57.2
P	1600	550	190	2430	2200	1300

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[8] T. W. Richards, J. H. Shipley and G. W. Harris, *J. Am. Chem. Soc.*, **34**, 599 (1912).

[9] M. Harada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **56**, 811 (1935).

[10] A. Nakajima and K. Furutati, *Chemistry of High Polymers* (*Kobunshi Kagaku*), **6**, 460 (1949).

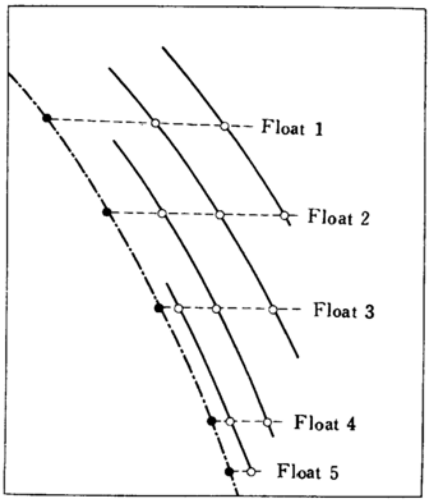

Fig. 1. The method of floating equilibria —— a schematic representation.
● T_0 in Eq. 2, ○ T in Eq. 2

temperature variation was higher than the constancy of the thermostat. The equilibrium temperature was then measured in the following two ways; namely, the "quasi-static" and the "dynamic" method[11]. In the former, floating equilibrium is determined directly by a fine adjustment of temperature, while the latter is based on the interpolation of the floating and sinking velocity of the float near the equilibrium temperature.

When the difference between the equilibrium temperature of the solution and that of the solvent is large, a correction for the thermal expansion of the float is required. In this case, the following equation was used,

$$d_t = d_0/(1+\alpha\cdot\Delta T) \tag{1}$$

$$\Delta T \equiv T - T_0 \tag{2}$$

where d_t and d_0 are the density of the float at T and T_0, respectively, and α is the coefficient of cubic expansion of silicate glass[12].

(*c*) *Apparent and partial specific volumes*.—Following the procedure given above, the solution density d_{12} can be obtained as a function of polymer concentration c_2 (g./cc.) and temperature. For the discussion of experimental data, however, it is convenient to use the apparent specific volume ϕ_2 (cc./g.) and the partial specific volume V_2 (cc./g.) of solute polymer in solution. They can be calculated from the solution density by the following equations,

$$\phi_2 = 1/d_1 - d_{\mathrm{sp}}/c_2 \tag{3}$$

$$V_2 = \phi_2 + w_2(1-w_2)\cdot\partial\phi_2/\partial w_2 \tag{4}$$

$$V_2 \cong \phi_2 + c_2\cdot\partial\phi_2/\partial c_2 \quad \text{(for dilute aqueous solution)} \tag{5}$$

where d_1 is the density of solvent (g./cc.), w_2 is the weight fraction of solute polymer and $d_{\mathrm{sp}} = (d_{12}-d_1)/d_1$.

Discussion of the Experimental Error.—Although the float is sensible to the temperature change of 0.001°C, fluctuation in excess of 0.003°C is inevitable in the determination of equilibrium temperature in both the two methods, quasi-static and dynamic. The error in the density determination, even when the work is very carefully done, is accordingly expected to be about $\pm 2\times 10^{-6}$. In practice, such a degree of precision was easily obtained in the measurement with water in which the "apparent density" of the float was quite stable.

While in PVA solutions, the "apparent density" of the float becomes somewhat unstable, though the cause is uncertain. PVA may be adsorbed to the float and sometimes an insoluble film may be formed on the surface. Under this circumstance, calibration with water is frequently required. Thus, the actual error found in PVA solution was not in excess of $\pm 4\times 10^{-6}$.

Finally, it was often observed that foam grows on the surface of the float and that the quasi-equilibrium of the float is attained especially in the measurement near 20°C. In the temperature region from 25 to 30°C with which the authors' experiment is concerned, however, the appearence of foam was rare and there was practically no experimental difficulty.

Results and Discussion

Equilibrium Temperature as Function of Polymer Concentration. — Fig. 2 shows the temperature difference (ΔT) vs. concentration relationship of PVA aqueous solution up to 1.0 g./100 ml. Each curve in the figure corresponds to the values obtained with using different floats. It is seen at once that the ΔT vs. concentration relationship can be regarded as almost linear below 0.5 g./100 ml., but convex in the more concentrated region. It can be also observed that the larger the "apparent density" of the float is (namely, the lower the T_0 of the float is), the more magnified the temperature difference is for the same sample solution. The molecular weight of PVA affects ΔT, though very minutely and can not be seen in the figure. This point will be discussed later.

The ΔT vs. concentration curve in Fig. 2 may be used as a calibration curve for the determination of polymer concentration in dilute solution. The temperature difference ΔT for PVA aqueous solution of 1.0 g./100 ml. reaches to about 9~10°C, while the equilibrium temperature itself can be obtained with a precision of 0.003°C. In this case, accordingly, a concentration difference of at least 0.003 g./100 ml. (i. e.

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[11] H. Akamatsu, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **61**, 470 (1940).

[12] G. W. Morey, "Properties of Glass", Reinhold Publishing Corp., New York (1954), p. 275.

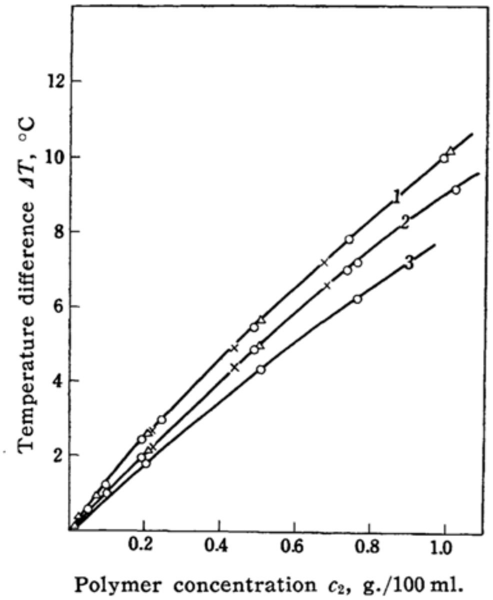

Fig. 2. Equilibrium temperature difference vs. polymer concentration relationship.
○ P=1300 × P=2200 △ P=2430
1 Float 6 (T_0=18.47°C)
2 Float 1 (T_0=21.29°C)
3 Float 9 (T_0=26.21°C)

0.003 wt. %) will be detectable by the present method.

Solution Density as Function of Polymer Concentration and Molecular Weight.—In Fig. 3, the solution density vs. polymer concentration relationship is shown for aqueous solution of fractionated PVA.

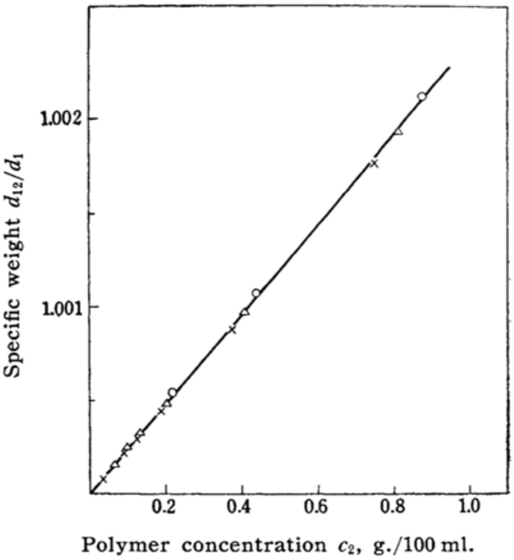

Fig. 3. Solution density vs. polymer concentration relationship for dilute solution of fractionated PVA at 30°C.
○ B-5 P=1600 △ T-2 P=550
× E-2 P=190

The data of d_{12}/d_1 (specific weight to solvent water) vs. c_2 fall on a straight line at least below the polymer concentration of 1.0 g./100 ml., and are slightly dependent on the molecular weight of PVA.

For a clear detection of this dependence, it is convenient to calculate the apparent specific volume ϕ_2 of PVA in solution. Fig. 4 shows the experimental values of

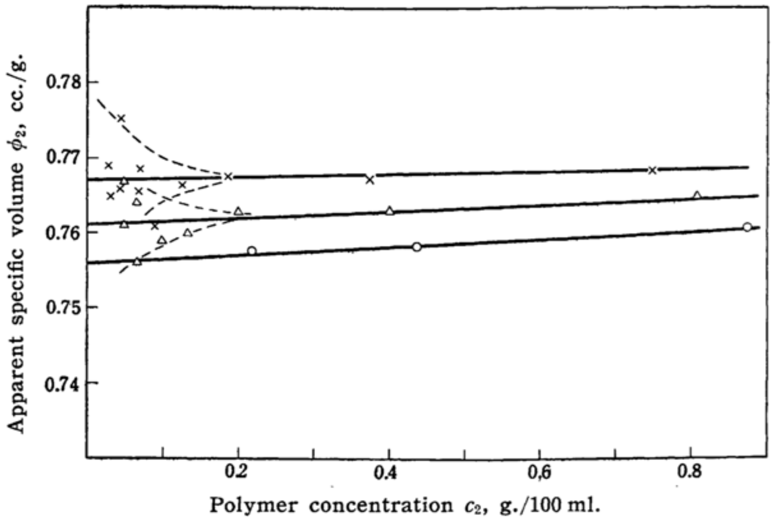

Fig. 4. Apparent specific volume of PVA in aqueous solution, as function of polymer concentration, c_2, at 30°C.
○ B-5 P=1600 △ T-2 P=550 × E-2 P=190

ϕ_2 calculated by Eq. 3 at each concentration. It is seen from the figure that ϕ_2 increases slightly with c_2 for every case concerned, though the data at extreme dilution are somewhat uncertain. It may be thus concluded that a negative second order term, though very small, does exist, if the d_{12} vs. c_2 relationship, as usual, is represented by a power series (see Eq. 6).

Another remarkable result seen on Fig. 4 is the clear dependence of ϕ_2 on the molecular weight of PVA. This dependence is expected from the simple qualitative consideration that the presence of the end-group which is different from the intermediate segment will affect the spatial configuration of the polymer molecule. It is seen that ϕ_2 decreases with increasing molecular weight, and the fifth decimal place of the solution density d_{12} is influenced by the molecular weight of the solute polymer. As is shown immediately after, ϕ_2 and the partial specific volume V_2 seem to be inversely proportional to the molecular weight of PVA. Taking this molecular weight dependence into account, the experimental formula for the solution density of a dilute solution of PVA at 30°C is proposed as follows:

$$\frac{d_{12}}{d_1} = 1+\left(0.249-\frac{2.47}{P}\right)\cdot c_2 -\left(0.64-\frac{88}{P}\right)\cdot c_2^2 \tag{6}$$

where P is the polymerization degree of PVA and c_2 is the polymer concentration in g./cc. This equation could reproduce the experimental data very well.

Eq. 6 should prove useful for predicting the density of an aqueous solution of PVA, irrespective of the origins of the PVA samples, if the polymerization degree is not too low. However, it is to be remarked here that, if P is lower than 500, the solution density of PVA which is polymerized under different initiators may not be represented by this equation.

From Eq. 4 or 5, the partial specific volume V_2 of PVA is easily obtained. Because of scattering in the observed values of ϕ_2, the accurate determination of V_2 and its concentration dependence becomes difficult at concentrations lower than 0.2 g./100 ml., and V_2 only at the concentration of 0.5 g./100 ml. was estimated by interpolation. Plotting the experimental values of V_2 against $1/P$, a nearly linear relationship is obtained as in Fig. 5.

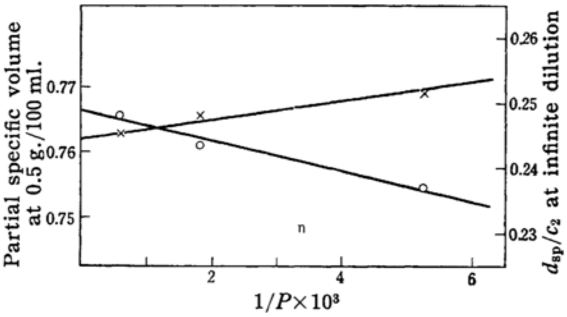

Fig. 5. Molecular weight dependence of $(d_{sp}/c_2)_{c_2\to0}$ and V_2 at 0.5 g./100 ml., at 30°C.

○ $\left(\frac{d_{sp}}{c_2}\right)_{c_2\to0}$ × V_2 at 0.5 g./100 ml.

In the same figure, the values of d_{sp}/c_2 at infinite dilution $(d_{sp}/c_2)_{c_2\to0}$ are also plotted against $1/P$. A linear relationship is observed here. This dependence of $(d_{sp}/c_2)_{c_2\to0}$ on P must be the same as that of $\phi_{2(c_2\to0)}$ as is easily seen from Eq. 3. Thus, one may write

$$\phi_2 = \phi_{2(P\to\infty)}+K/P \tag{7}$$

at infinite dilution. Here, $\phi_{2(P\to\infty)}$ is the apparent specific volume of the polymer whose polymerization degree P is infinity and K is a constant.

Estimation of Polymer-Solvent Interaction.—If the end-segments in the polymer molecule are different in size from the intermediate segments, it is to be expected that ϕ_2 (or V_2) may change inversely proportional to the molecular weight of the polymer.

In fact, Kobatake[6] has derived theoretically an equation which is quite the same in form as Eq. 7. According to his theory, two constants in Eq. 7 can be correlated with the parameters of intermolecular potential as follows:

$$\phi_{2(P\to\infty)} = -\beta_{12}/m_2 \tag{8}$$

$$K = -2\beta'_{12}+\frac{2\rho_1 B_{11}+1}{\rho_1} \tag{9}$$

$$B_{12} = 2\beta'_{12}+P\beta_{12} \tag{10}$$

where B_{11} is the excluded volume (or McMillan-Mayer's "irreducible integral"[13]) between two solvent molecules, B_{12} is the excluded volume between solvent- and polymer molecules, β_{12} is the excluded volume between solvent molecule and intermediate segment, β'_{12} is the excess excluded volume representing the end-group effect, m_2 is the molecular weight

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[13] W. G. McMillan, Jr. and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

TABLE II. EXPERIMENTAL VALUES OF APPARENT AND PARTIAL SPECIFIC VOLUMES AND POLYMER-SOLVENT EXCLUDED VOLUMES

P	$(d_{sp}/c_2)_{c_2\to 0}$	$\phi_{2(c_2\to 0)}$	V_2	$-B_{12}(\times 10^{-3})$	$-\beta_{12}$	$-\beta'_{12}$
1600	0.248	0.756	0.763	1.21		
550	0.243	0.761	0.766	0.415	0.755	1.20
190	0.237	0.767	0.769	0.143		

of monomer, and ρ_1 is the density (number density) of the solvent.

According to Orstein and Zernike[14], the B_{11} in Eq. 9 is correlated with the isothermal compressibility κ_1 as follows:

$$\frac{2\rho_1 B_{11}+1}{\rho_1} = \boldsymbol{k}T\kappa_1 \tag{11}$$

where $\boldsymbol{k}$ is the Boltzmann constant and T is the absolute temperature in °K. One can then calculate β_{12} and β'_{12} by Eqs. 8 and 9, and finally B_{12} by Eq. 10.

The authors will first estimate the second term $(2\rho_1 B_{11}+1)/\rho_1$ in Eq. 9. Using Eq. 11, the value of $(2\rho_1 B_{11}+1)/\rho_1$ for water is estimated to be 0.068 cc./g. from the experimental data of κ at ordinary pressure[15]. Thus, Eq. 9 can be reduced to

$$K = -2\beta'_{12}+0.068 \tag{12}$$

Using the experimental results of $\phi_{2(c_2\to 0)}$ (extrapolated values of ϕ_2 to infinite dilution) and its molecular weight dependence, the authors calculate the values of β_{12}, β'_{12} and B_{12}, which are listed in Table II.

The value of β_{12} represents the "free volume" of PVA molecule per monomer unit, while β'_{12} is related to the excess contribution by end-segments. It may be concluded from the comparison between them that the contribution of the end-group in the polymer molecule to total interaction differs markedly from that of the intermediate segment and can not be neglected.

Furthermore, it is to be remarked here that a linear relationship between ϕ_2 and $1/P$ can also be expected from Eq. 9 even when the end-group effect is negligible. However, for the present case, β'_{12} have a large value in comparison with the second term in Eq. 9; the experimental value of K is estimated to be 2.47 cc./g., $-2\beta'_{12}$ is thus estimated to be 2.40 cc./g. which is to be compared with 0.068 cc./g. for the second term. Therefore, a greater part of molecular weight dependence of ϕ_2 may be attributed to the end-group effect.

Finally, the authors will make a comparison between V_2 (see Table II) and the specific volume of solid PVA, V_2°. The specific volume of completely amorphous PVA is estimated to be 0.787 from the extrapolation of the experimental values for PVA-film having different crystallinity[16]. A volume contraction in solution is clearly observed in the present case.

Summary

The solution density of polyvinyl alcohol dilute aqueous solution is measured by the use of the method of floating equilibria. This method is proved to be useful for the purpose of precise density and concentration determination of PVA dilute solution. An experimental formula for the density of PVA aqueous solution both as a function of the concentration and polymerization degree of PVA is proposed. The excluded volumes between solute and solvent are estimated from the molecular weight dependence of apparent and partial specific volumes obtained.

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[16] I. Sakurada, Y. Nukushina and N. Mori, *Chemistry of High Polymers* (*Kobunshi Kagaku*), **12**, 302 (1955).