The Partial Specific Compressibility of Polyvinylpyrrolidone

By Hiroyasu NOMURA and Yutaka MIYAHARA

Department of Chemical Engineering, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

(Recieved October 18, 1965)

In our previous papers[1-4] it has been shown that, in the study on the solution properties of high polymers, the compressibility of the solution can be used as a valuable parameter. In our treatment, the data of the compressibility of a dilute solution were extrapolated to an infinite dilution to give a quantity which limits the partial specific compressiblity (LC). So far the LC values of such polymers as polyvinyl acetate,[1,2] polystyrene,[3] and dextran[4] have been determined under various conditions. In the organic solvents, the LC was intimately related to the intrinsic viscosity. The LC of dextran in the aqueous solution was negative as a result of the hydration, and the amount of hydration water was estimated from the LC value.

In the present note, the LC of polyvinylpyrrolidone (PVP) was determined at various temperatures by ultrasonic velocity measurements. The details of the experimental procedure have been reported previously.[1,3] The PVP used was a commercial product, PVP K-30, supplied by the Tokyo Kasei (Chemical) Industrial Co., Ltd., the noted molecular weight was 40000. The sample was used without further purification.

TABLE I.

t°	$\kappa_1\times 10^{12}$ cm^2/dyn.	$\bar{v}_{20}$ cc./g.	$\bar{\kappa}_{20}\times 10^{12}$ cm^2/dyne	ω cc./g.	$[\eta]$ cc./g.
5	49.14	0.783	−18.2	0.458	24.5
15	46.53	0.793	−8.2	0.230	24.5
25	44.84	0.794	−1.1	0.033	24.5
35	43.57	0.806	8.1		21.8
45	42.81	0.808	20.7		23.5
55	42.40	0.821	24.0		25.5

The experimental results are summarized in Table I, where κ_1 is the compressibility of the solvent; $\bar{v}_{20}$, the partial specific volume of the solute at infinite dilution; $\bar{\kappa}_{20}$, the LC; ω, the amount of hydration, and $[\eta]$, the intrinsic viscosity. The methods of the determination of these quantities were given in the previous papers. In the table, it should be noted that the LC increases from a negative value to a positive with the rise in temperature. As was discussed in the previous paper,[4] the negative value of LC can be ascribed to the hydration in the present case. The amount of hydration decreases with the increase in temperature, as in the cases of sucrose[5] and dextran,[4] as a result of the exothermic nature of the hydration process.

It is interesting to see that the value of LC becomes positive above 30°C. The temperature rise breaks the structure of water to some extent, and at the same time it reduces the amount of hydration. Then the behavior of dehydrated bare molecules of PVP becomes similar to that of a synthetic chain polymer, such as polystyrene in an organic solvent, and the LC becomes positive.

The intrinsic viscosities at various temperatures are also listed in the table. It may be seen that the variation in the intrinsic viscosity with the temperature is not so remarkable. This result is in contrast to the linear relationship between the intrinsic viscosity and the LC for the such synthetic chain polymers as polystyrene and polyvinyl acetate in the organic solvents.

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[1] Y. Miyahara and Y. Masuda, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **81**, 692 (1960).

[2] Y. Masuda, T. Hasegawa and Y. Miyahara, ibid., **82**, 1131 (1961).

[3] H. Nomura and Y. Miyahara, *J. Appl. Polymer Sci.*, **8**, 1643 (1964).

[4] H. Nomura, S. Yamaguchi and Y. Miyahara, ibid., **8**, 2731 (1964).

[5] H. Shiio, *J. Am. Chem. Soc.*, **80**, 70 (1958).