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# Light Scattering from Polymer–Mixed Solvent Systems. 1. Selective Adsorption Phenomena of Poly(*N*-vinylpyrrolidone)

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ABSTRACT: The behavior of poly(vinylpyrrolidone) (PVP) in the mixed solvents $H_2O$/THF, $H_2O$/acetone, and ethanol/*n*-hexane is studied by the method of static light scattering. $H_2O$ and ethanol are good solvents for PVP. THF, acetone, and *n*-hexane are precipitants. A PVP coil first swells as the mass fraction of the precipitant is increased. Above a critical composition of the mixture the coil contracts. The nature of this change is studied on the basis of the excluded-volume theory and the Flory–Huggins theory. We find that the transition is attributed to a change in the selective adsorption. $H_2O$ and ethanol are preferentially adsorbed by PVP with regard to the systems PVP + $H_2O$/acetone and PVP + ethanol/*n*-hexane, respectively. The system PVP + $H_2O$/THF shows both normal and inverse adsorption. The interpenetration function $\Psi$ segregates into two branches, one for each type of adsorption. With increasing temperature the number of adsorbed solvent molecules per PVP monomer unit decreases slightly. As a consequence, a PVP molecule precipitates at a higher mass fraction of the precipitant. The adsorption is not affected by a change in the molecular mass of PVP. This implies that adsorption occurs in a uniform manner along the PVP chain. Looking on the $\Theta$ state, the radii of gyration are different for each system. Longitudinally acting intramolecular repulsive forces are present, which are distinct in their strength and interaction range. They are caused by selective adsorption of one of the solvent components to the polymer.

## Introduction

The investigation of the physicochemical properties of macromolecules in mixed solvents is of major importance for a number of reasons: (1) Some macromolecules do not dissolve molecularly in single solvents, but molecular solutions can be obtained in mixed solvents; (2) a certain property of the solvent, a definite value of the second virial coefficient, or a particular value of the refractive index, for instance, is more often found in mixed than in single solvents; (3) such an investigation leads to a better knowledge of the respective affinity of each solvent with regard to the macromolecule and its influence on the molecular dimensions of the polymer.

A dilute polymer solution can be taken on as a two-phase system, the microphase being the polymer coil highly swollen with the solvent and the other phase the surrounding polymer-free solvent. In a mixed solvent, the ratio of the two solvent components, A and B, is different in each phase, due to the fact that the polymer generally has a higher affinity to one of the solvent components. Therefore the concentration of this component is higher within the domain of the polymer molecules than in the surrounding polymer-free solvent. This phenomenon, first observed by Ewart et al.,[1] is called preferential or selective adsorption. Another characteristic feature of the ternary system polymer plus mixed solvent can be observed if one of the solvents is a good solvent (A) and the other a nonsolvent (B) of the polymer. In such a case[2] the macromolecule swells to a critical point as the concentration of B is increased. Above the critical composition of the mixture the polymer P contracts. The nature of this phase transition[3-5] is complex. It seems[6] that the transition is more easily achieved when the B chain is larger and sharper when the length of the B chain relative to P becomes smaller.

In this paper, we study the physicochemical properties of the ternary systems PVP + $H_2O$/THF, PVP + $H_2O$/acetone, and PVP + ethanol/*n*-hexane by the method of static light scattering. PVP is poly(*N*-vinylpyrrolidone). $H_2O$ and ethanol are good solvents of PVP, whereas THF, acetone, and *n*-hexane are nonsolvents.

Light scattering yields the radius of gyration $\langle S\rangle_z$ and the second virial coefficient $A_2$. At various compositions of the mentioned solvent mixtures, these quantities are determined for distinct temperatures and molecular masses of PVP. The observed phenomena are discussed on the basis of the excluded volume theory[7] and of the lattice theory, developed by Flory and Huggins.[8] An analysis concerning the hydrodynamic properties of the present systems will be given in a subsequent paper.

## Theory

Rigorous theories of light scattering from multicomponent systems were developed by Stockmayer[9] and Kirkwood.[10] A detailed analysis of this topic, together with an extensive collection of relevant formulas, can be found in the treatise by Casassa and Eisenberg.[11] Two different experimental procedures may be used to obtain the weight-average molecular mass $M_w$, the *z*-average radius of gyration $\langle S\rangle_z$, and the second virial coefficient $A_2$. It is possible to operate either at constant solvent composition or at constant chemical potential of the mixed solvent. The easiest and most direct method for obtaining the physicochemical properties of the polymer is to measure the difference of the Rayleigh ratio, $\Delta R(\theta)$, of the solution and of the mixed solvent after having determined the refractive index increment $\partial n/\partial C|_\mu$ at constant chemical potential. This is experimentally achieved when solvent and solution are in dialysis equilibrium through a semipermeable membrane that can be crossed by the solvent molecules but not by the solute. Under these experimental conditions the Zimm equation is written

$$(\partial n/\partial C)|_\mu{}^2(KC/\Delta R(\theta)) = (1/M_w)(1 + {}^1/_3\langle S^2\rangle_z q^2) + 2A_2C + \ldots \quad (1)$$

with $K = 4\pi^2 n_0{}^2/(N_A\lambda_0{}^4)$ and $q = ((4\pi n_0)/\lambda_0)\sin(\theta/2)$. $\theta$ denotes the scattering angle. $n_0$ and $n$ are the refractive indexes of solvent and solution, respectively. $N_A$ is

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**Table I**
**Radii of Gyration $\langle S\rangle_z$ (nanometers) for PVP in Various Mixed Solvents at $M_w = 7.5 \times 10^5$ g/mol**

A: $H_2O$ + Tetrahydrofuran (THF)

| | $w_{THF}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T/°C | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.55 | 0.60 |
| 10 | 41.8 | 42.8 | 43.3 | 42.2 | 38.9 | 32.3 | 27.6 | – |
| 20 | 43.9 | 44.7 | 45.1 | 44.1 | 40.7 | 33.8 | 28.7 | 22.3 |
| 30 | 44.8 | 45.8 | 46.2 | 45.1 | 41.6 | 34.5 | 29.5 | 22.7 |
| 40 | 46.3 | 46.6 | 46.8 | 45.8 | 42.4 | 35.4 | 30.1 | 23.0 |
| 50 | 47.2 | 47.7 | 47.9 | 46.9 | 43.3 | 36.2 | 30.9 | 23.3 |

B: $H_2O$ + Acetone

| | $w_{Ac}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| T/°C | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.78 |
| 10 | 41.8 | 43.9 | 45.7 | 47.2 | 47.5 | 46.0 | 42.0 | 34.7 | 26.0 |
| 20 | 43.9 | 45.4 | 47.3 | 48.8 | 49.2 | 47.6 | 43.5 | 35.9 | 26.9 |
| 30 | 44.8 | 46.8 | 48.7 | 50.3 | 50.7 | 49.0 | 44.8 | 36.9 | 27.7 |
| 40 | 46.3 | 47.9 | 49.9 | 51.5 | 51.9 | 50.3 | 45.9 | 37.9 | 28.8 |
| 50 | 47.2 | 48.9 | 50.9 | 52.6 | 53.0 | 51.3 | 46.8 | 38.7 | 29.5 |

C: Ethanol + n-Hexane

| | $w_{Hex}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| T/°C | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.75 |
| 20 | 44.9 | 46.0 | 47.4 | 48.4 | 48.0 | 47.3 | 43.9 | 37.9 | 26.4 |

Avogadro's number, and $\lambda_0$ is the wavelength of the incident light in vacuum. $C$ denotes the concentration of the polymer.

By extrapolation to zero angle, a plot of the quantity on the left-hand side of eq 1 against $C$ yields an intercept $1/M_w$ and a slope of $2A_2$. $\langle S^2\rangle_z$ is given by an extrapolation to zero concentration.

This is the procedure usually employed for polyelectrolyte solutions containing a salt. On the other hand, it is also possible to determine the refractive index increment $\partial n/\partial C|_{\bar{\phi}}$ at constant volume fraction $\bar{\phi}$ of the solvent, thus referred to as the main solvent and here called the A solvent. Thereby the experimental determination of $\partial n/\partial C|_{\bar{\phi}}$ is made as if dealing with polymer–single solvent systems. However the Zimm equation must be modified due to the phenomenon of the selective adsorption of one of the two solvents. Now, it holds[12] that

$$(\partial n/\partial C)|_{\bar{\phi}}^2((KC)/\Delta R(\theta)) = (1/M_a)[1 + {}^1/_3\langle S^2\rangle_z q^2] + 2(M_w/M_a)A_2C \quad (2)$$

The quantity $M_a$ is called apparent molecular mass and generally differs from the true molecular mass $M_w$. $M_a$ is directly determined experimentally and relates to well-defined parameters such as $M_w$ and the selective adsorption coefficient $\alpha_a$, as can be seen by eq 3.

$$M_a = M_w[1 + \alpha_a(\partial n_0/\partial\bar{\phi})/(\partial n/\partial C)|_{\bar{\phi}}]^2 \quad (3)$$

The calculation of $M_w$ from eqs 2 and 3 is possible if all the other parameters are known. $M_a$ is obtained by light scattering. The variations of the solvent refractive index with composition $\partial n_0/\partial\bar{\phi}$ and the refractive index increment of the solution $\partial n/\partial C|_{\bar{\phi}}$ are obtained easily by refractometry, but the selective adsorption parameter $\alpha_a$ is not directly accessible experimentally. However, there is no difficulty in molecular mass determination when the refractive indexes of the two solvents, A and B, are identical, so that the term $\partial n_0/\partial\bar{\phi}$ is zero and $M_a$ is equal to $M_w$ whatever the selective adsorption may be. Such a solvent mixture can be treated as if it was a single solvent. In practice the solvent mixture is isorefractive if $n_A - n_B < 0.025$.

It is quite evident that simpler systems, such as a polymer dissolved in a single solvent, are preferable when the molecular mass is the only desired parameter. The points of interest in considering ternary systems lie rather in the search for and the studies of $\Theta$ solvents obtained by adding a precipitant, here B, to the main solvent. Moreover, such studies give a better insight into polymer–solvent interactions by determination of the selective adsorption parameter $\alpha_a$, which characterizes the variation of the solvent composition in the vicinity of the polymer. $\alpha_a$ can be derived from eq 3 if $M_w$ is obtained by light scattering in a single solvent. A positive value of $\alpha_a$ indicates a preferential adsorption of the main solvent A. The bad solvent or the precipitant B is adsorbed if $\alpha_a$ is negative. The second phenomenon is called inverse adsorption. An example is given by the system PMMA + benzene (A)/methanol (B), where methanol is adsorbed by a PMMA molecule.[13]

## Experimental Section

**Materials.** Poly(N-vinylpyrrolidone) (PVP)[14,19] was purchased from Fluka. The water content, estimated by elemental analysis, is nearly 12%. The molecular masses of the samples, determined by light scattering according to n-butanol at 25 °C are $3.5 \times 10^5$, $7.5 \times 10^5$, and $1.0 \times 10^6$ g/mol, respectively. Butanol was dried over anhydrous potassium carbonate and distilled before use. The purity of the samples was controlled by GPC. The molecular mass distributions are of the Schulz–Flory type, and the nonuniformity coefficients $U$ are of the order of $1.8 \pm 0.3$. Ethanol and acetone (both Merck) were distilled twice on a laboratory column. THF (free of water) and n-hexane (both Aldrich) were of purity grade.

**Refractive Index Increment.** A differential refractometer of the Brice Phoenix type was operated at 633 nm by a He–Ne laser in accordance with the light-scattering measurements. The instrument was calibrated for aqueous solutions of potassium chloride, for which refractometric data have been reported.[15] Refractive index increments $\partial n/\partial C|_w$ were measured at various compositions $w$ of the mixtures A/B, where $w = m_B/(m_A + m_B)$ is the mass fraction of the precipitant B in the mixture. To determine the increment $\partial n/\partial C|_{\bar{\phi}}$ at constant volume fraction, $\bar{\phi}$ was estimated by the relationship

$$\bar{\phi} = 1/[1 + [w/(1 - w)][\rho_A/\rho_B]]$$

$\rho_A$ and $\rho_B$ are the densities of the good solvent and the precipitant,

**Table II**
**Second Virial Coefficients $A_2$ ($10^{-4}$ cm$^3$ mol g$^{-2}$) for PVP in Various Mixed Solvents at $M_w = 7.5 \times 10^5$ g/mol**

A: $H_2O$ + THF

| | $w_{THF}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $T$/°C | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.55 | 0.60 |
| 10 | 2.97 | 3.75 | 4.16 | 4.05 | 3.26 | 1.59 | 0.38 | −1.13 |
| 20 | 3.68 | 4.68 | 5.15 | 4.47 | 3.99 | 2.05 | 0.67 | −1.00 |
| 30 | 4.32 | 5.51 | 6.04 | 5.79 | 4.62 | 2.43 | 0.91 | −0.92 |
| 40 | 4.94 | 6.30 | 6.86 | 6.54 | 5.21 | 2.79 | 1.14 | −0.83 |
| 50 | 5.32 | 6.78 | 7.37 | 6.99 | 5.57 | 3.02 | 1.28 | −0.76 |

B: $H_2O$ + Acetone

| | $w_{Ac}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$/°C | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.78 |
| 10 | 2.97 | 2.99 | 3.34 | 3.73 | 3.92 | 3.62 | 2.53 | 0.37 | −3.00 |
| 20 | 3.68 | 3.71 | 4.14 | 4.63 | 4.87 | 4.52 | 3.16 | 0.85 | −2.34 |
| 30 | 4.32 | 4.36 | 4.76 | 5.32 | 5.61 | 5.24 | 3.87 | 1.34 | −2.02 |
| 40 | 4.94 | 5.02 | 5.24 | 5.91 | 6.10 | 5.82 | 4.30 | 1.60 | −1.82 |
| 50 | 5.32 | 5.32 | 5.55 | 6.26 | 6.47 | 6.11 | 4.57 | 1.97 | −1.61 |

C: Ethanol + *n*-Hexane

| | $w_{Hex}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$/°C | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.75 |
| 20 | 4.71 | 5.11 | 5.22 | 5.33 | 5.17 | 5.00 | 4.58 | 2.06 | −3.20 |

**Table III**
**Extrapolated Values of the Θ Temperature $T_{\Theta,ex}$ and the Θ Radius of Gyration $\langle S_{\Theta,ex}\rangle_z$ for PVP in Various Mixed Solvents at $M_w = 7.5 \times 10^5$ g/mol**

| $H_2O$ + THF | | | $H_2O$ + acetone | | |
|---|---|---|---|---|---|
| $w_{THF}$ | $T_{\Theta,ex}$/°C | $\langle S_{\Theta,ex}\rangle_z$/nm | $w_{Ac}$ | $T_{\Theta,ex}$/°C | $\langle S_{\Theta,ex}\rangle_z$/nm |
| 0.00 | −21.4 | 34.9 | 0.00 | −21.4 | 34.9 |
| 0.10 | −20.2 | 36.5 | 0.10 | −19.4 | 38.3 |
| 0.20 | −21.0 | 37.0 | 0.20 | −20.1 | 39.7 |
| 0.30 | −21.9 | 35.7 | 0.30 | −20.2 | 41.1 |
| 0.40 | −22.9 | 32.3 | 0.40 | −19.5 | 41.3 |
| 0.50 | −16.9 | 28.3 | 0.50 | −18.1 | 40.5 |
| 0.55 | −1.1 | 26.3 | 0.60 | −12.0 | 38.0 |
| 0.60 | +132 | 26.3 | 0.70 | −0.05 | 33.4 |
| | | | 0.78 | +33.6 | 33.6 |

respectively. Values of $\rho_A$ and $\rho_B$ for different temperatures are reported by Huglin.[15]

**Static Light Scattering.** Light-scattering measurements were made with an ALV-3000 spectrometer as described previously.[17] To determine $M_a$, $A_2$, and $\langle S^2\rangle_z$, five polymer concentrations $C$ were used in the range 1–6 g/L for each PVP sample. The concentrations were corrected according to the temperature, and the solutions were centrifuged for 1 h at 10 000 rpm.

## Results and Discussion

**Extra- and Interpolated Θ Radii of Gyration.** The radii of gyration $\langle S\rangle_z$ and the second virial coefficients $A_2$, obtained for the systems PVP + $H_2O$/THF, PVP + $H_2O$/acetone, and PVP + ethanol/*n*-hexane, are summarized in Tables I and II, respectively. $M_w$, determined by static light scattering in *n*-butanol at $T$ = 25 °C, is 7.5 × $10^5$ g/mol. The same value was obtained for the mixtures $H_2O$/acetone and ethanol/*n*-hexane. These solvents are isorefractive, whereas the mixture $H_2O$/THF is nonisorefractive. The analyses were done by eqs 2 and 3, respectively.

The $\langle S\rangle_z$ and $A_2$ data are both dependent on the mass fraction $w$ and on the temperature $T$. In all cases, $A_2$ and $\langle S\rangle_z$ increase slowly with $w$ near the mark of $w = 0$, which presents the good solvent. The PVP molecules swell, and their conformation may be well described as a coil. A maximum is reached at a definite mass fraction $w_m$, which is different for each system. $w_m$ does not depend on the temperature. Beyond the maximum, $\langle S\rangle_z$ and $A_2$ decrease very rapidly. At high $w$ the second virial coefficient becomes much less than 0, and $\langle S\rangle_z$ is nearly half as large when $w = 0$. A PVP coil converts to a contracted coil state. Finally, at very high $w$ the PVP molecules precipitate. With increasing temperature both $A_2$ and $\langle S\rangle_z$ increase. The solvatation of PVP improves, and the point of precipitation rises slightly.

**Table IV**
**Interpolated Values of the Θ Composition $w_{\Theta,int}$ and the Θ Radius of Gyration $\langle S_{\Theta,int}\rangle_z$ for PVP in Various Mixed Solvents at $M_w = 7.5 \times 10^5$ g/mol**

| | $H_2O$ + THF | | $H_2O$ + acetone | |
|---|---|---|---|---|
| $T$/°C | $w_\Theta$ | $\langle S_{\Theta,int}\rangle_z$/nm | $w_\Theta$ | $\langle S_{\Theta,int}\rangle_z$/nm |
| 10 | 0.564 | 26.1 | 0.707 | 34.0 |
| 20 | 0.570 | 26.3 | 0.719 | 33.9 |
| 30 | 0.576 | 26.1 | 0.734 | 33.4 |
| 40 | 0.580 | 26.1 | 0.741 | 33.6 |
| 50 | 0.582 | 26.3 | 0.746 | 33.6 |

The mass fraction at which $A_2$ vanishes is called the Θ mass fraction $w_\Theta$; the corresponding temperature is termed the Θ temperature $T_\Theta$. Two methods can be applied to estimate $w_\Theta$ and $T_\Theta$. At a fixed value of $w$, $A_2$ can be extrapolated to zero, yielding the Θ point ($w_{\Theta,ex}$, $T_{\Theta,ex}$). The suffix "ex" indicates that the Θ temperature is obtained by extrapolation. An appropriate extrapolation formula for $A_2(T)|_w$ is a polynomial of the second order. Values of $T_{\Theta,ex}$ and $\langle S_{\Theta,ex}\rangle_z$ calculated by this method are summarized in Table III. $\langle S_{\Theta,ex}\rangle_z$ is obtained by the second-order fit $\langle S(T)\rangle_z|_w = a + bT + cT^2$, where $T$ is set to be $T_{\Theta,ex}$. $a$, $b$, and $c$ are constants. Obviously, the choice of the extrapolation formula is somewhat arbitrary. More reliable values concerning the Θ state are obtained while working at fixed temperatures, and the mass fraction $w_{\Theta,int}$ is determined at the point where $A_2$ vanishes. In this case, the Θ point ($w_{\Theta,int}$, $T_{\Theta,int}$) is found by interpolation. Values of $w_{\Theta,int}$ and $\langle S_{\Theta,int}\rangle_z$, obtained by interpolation with regard to a polynomial of the third order, are given in Table IV. Figure 1 shows a plot of $\langle S_\Theta\rangle_z$ against $w$. The extrapolated data are presented by open symbols, and the interpolated data are symbolized by filled symbols. Both types of data complement the other remarkably well. Thus, the somewhat arbitrary choices of the extrapolation and interpolation formulas, respectively, are reasonable.

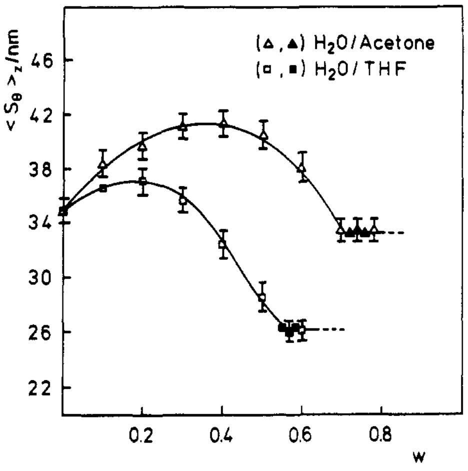

**Figure 1.** Θ radii of gyration of PVP for different solvent mixtures at $M_w = 7.5 \times 10^5$ g/mol. Extrapolated data are presented by open and interpolated data by filled symbols.

However, the Θ radius of gyration $\langle S_\Theta \rangle_z$ is not a constant, as could be expected from the Flory–Huggins theory.[8] $\langle S_\Theta \rangle_z$ is both a function of the nature of the solvent mixture and a function of their composition. This feature is often reported in the literature. It may be interpreted by the theorem of Oberthür et al.,[18] which is discussed below.

Generally, a segment of a polymer is influenced by both intra- and intermolecular forces. According to Oberthür,[18] the intramolecular forces can be divided into transversal and longitudinal forces. Transversal forces act between segments of the same macromolecule, which are not adjacent. On the contrary, longitudinal intramolecular forces act along the polymer chain between directly neighboring segments. The intermolecular forces, e.g., forces between segments of different macromolecules, and the transversal intramolecular forces are zero at the Θ state. The longitudinal forces, on the other hand, are generally larger than zero both in the Θ and in the non-Θ state. $\langle S_\Theta \rangle_z$ is strongly influenced by longitudinal forces. Thus, different Θ radii of gyration are physically reasonable if the longitudinal acting forces are different for the same kind of polymer at each Θ condition. Such an effect may be observed here, as will be shown later.

**Influences of the Molecular Mass $M_w$ on $\langle S \rangle_z$.** Light-scattering measurements are time consuming. Thus, we confine our investigations on the system PVP + $H_2O$/THF. Three different molecular masses, $M_w = 3.5 \times 10^5$, $7.5 \times 10^5$, and $= 1.0 \times 10^6$ g/mol, are considered in detail. The experiments are carried out at 20 °C. Figure 2 shows a plot of $\langle S \rangle_z$ against the mass fraction $w$. The data can be reasonably well expressed by power laws of the form $\langle S \rangle_z = KM_w^{\bar{a}}$. $K$ and $\bar{a}$ are parameters that can be evaluated by the method of least squares. The results are summarized in Table V.

Figure 3 shows a plot of the exponent $\bar{a}$ against $w$. Two regions denoted I and II may be distinguished, where $\bar{a}$ is nearly constant. With regard to the theory,[15] $\bar{a}$ is 0.8 for a rod, and $\bar{a}$ is 0.5 for a Gaussian coil in the Θ state. $\bar{a}$ becomes 0.33 as the polymer presents a globule. The mean value of $\bar{a}$ is 0.529 in region I and 0.485 in region II. Thus, in both cases a PVP molecule is in the coil state. With respect to the Θ state a PVP coil of region I is expanded and a PVP coil of region II is contracted. At the Θ state $\bar{a}$ becomes 0.5 within an experimental error of 4% regardless to whether $\bar{a}$ is obtained by using the extra- or interpolated radii of gyration. This result may be considered as a further proof that the derived Θ conditions are correct.

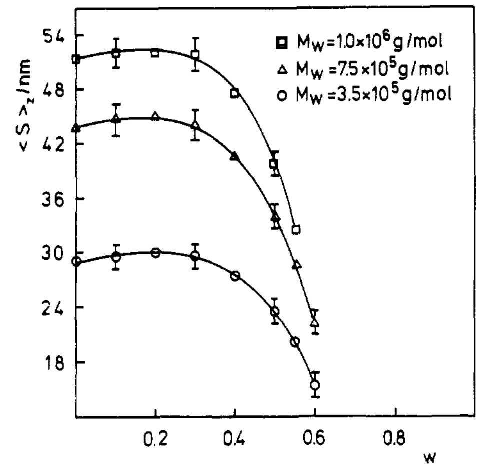

**Figure 2.** Radii of gyration of PVP for different molecular masses at $T = 20$ °C. The solvent mixture is $H_2O$/THF.

**Correlations between the Expansion Factor and the Second Virial Coefficient.** The theory of excluded volume[7] was originally elaborated for systems of linear polymer plus single solvent. Thus, it is relevant to use this theory for a comparative study to reveal the characteristic feature due to a mixed solvent.

Yamakawa et al.[7] have proposed a procedure for examining the agreement between theory and experiment that is based on the correlation between the expansion factor $\alpha = \langle S \rangle_z / \langle S_\Theta \rangle_z$ and the second virial coefficient $A_2$. Two criteria of validity of the theory must be fulfilled: (1) The values of a parameter $z$ determined from observed data of $\alpha$ and from observed values of the interpenetration function $\Psi$, which is defined by

$$\Psi = (A_2 M_w^{\,2})/(4\pi^{3/2} N_A \langle S^2 \rangle_z^{\,3/2}) \qquad (4)$$

should be equal to those estimated by using the theoretical expressions for $\alpha$ and $\Psi$. (2) A plot of $z$, determined from observed data of $\alpha$ by using its theoretical expression, against $M_w^{0.5}$ should be linear. There have been various approximate theories of $\alpha$ and $\Psi$ developed, but there are very few expressions for $\Psi$ that can be chosen for a given theory of $\alpha$ if one insists on the self-consistency of intramolecular and intermolecular theories of interaction. According to Yamakawa,[7] there are only three such self-consistent combinations:

$$\text{combination 1: } \Psi(\bar{z}) = \ln(1 + 2.30\bar{z})/2.30$$

$$z = (\alpha^5 - \alpha^3)/2.60$$

$$\text{combination 2: } \Psi(\bar{z}) = \ln(1 + 5.75\bar{z})/5.73$$

$$z = (\alpha^5 - \alpha^3)/1.28$$

$$\text{combination 3: } \Psi(\bar{z}) = 0.55(1 - (1 + 3.90\bar{z})^{-0.47})$$

$$z = 0.17[((\alpha^2 - 0.54)/0.46)^{2.17} - 1]$$

$\bar{z}$ is defined by $\bar{z} = z/\alpha^3$. $\Psi$ can be considered to be a function of $\alpha$ as $\bar{z}$ or $z$ is eliminated from $\Psi$ or $\alpha$, respectively. Thus theoretically obtained values of $\Psi$ are available according to the above three combinations. Comparative experimental data of $\Psi$ are obtained, if the light-scattering data $M_w$, $A_2$, and $\langle S \rangle_z$, summarized in Tables I and II, are inserted into eq 4.

**Table V**
**$K$ and $\hat{a}$ Parameters of the Power Law $\langle S\rangle_z = K(M_w/M_\#)^{\hat{a}}$, Estimated for the System PVP + $H_2O$/THF at $T = 20$ °C[a]**

| | $w_{THF}$ | | | | | | | | Θ state, interpolated |
|---|---|---|---|---|---|---|---|---|---|
| | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.55 | 0.60 | |
| $10^2K$/nm | 3.04 | 3.25 | 3.77 | 3.66 | 3.45 | 4.50 | 5.31 | 3.12 | 3.13 |
| $\hat{a}$ | 0.538 | 0.534 | 0.523 | 0.525 | 0.523 | 0.490 | 0.480 | 0.486 | 0.498 |

[a] $M_\# = 1$ g/mol.

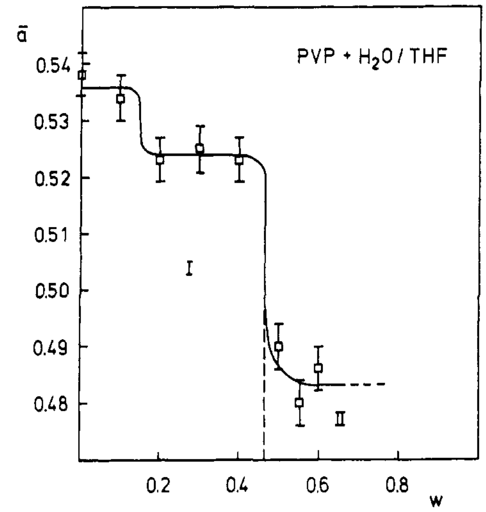

**Figure 3.** Plot of the exponent $\bar{a}$ against the mass fraction of THF at $T = 20$ °C. Region I presents the expanded coil state and region II the contracted coil state of PVP.

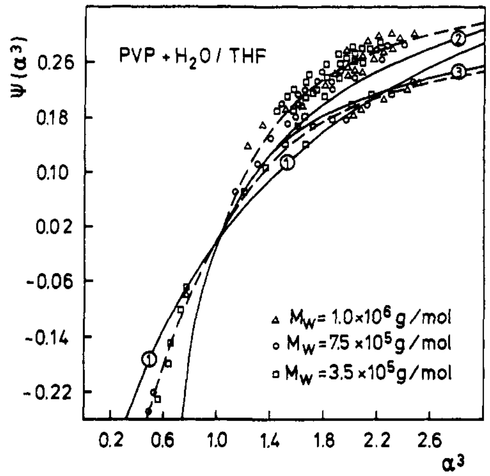

**Figure 4.** Plot of the interpenetration function $\Psi$ against the third power of the expansion factor $\alpha$ for the system PVP + $H_2O$/THF.

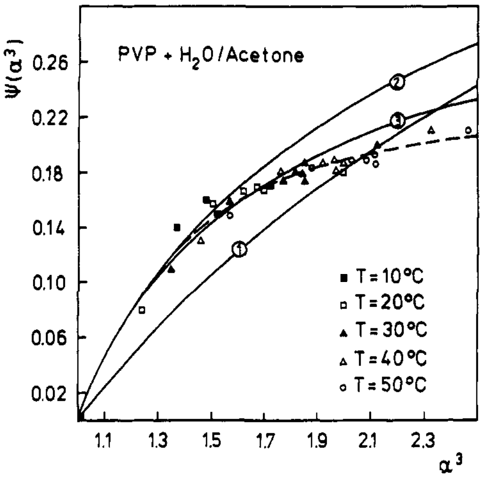

**Figure 5.** Plot of the interpenetration function $\Psi$ against the third power of the expansion factor $\alpha$ for the system PVP + $H_2O$/acetone.

**Table VI**
**Θ Radii of Gyration, Defined by Flory and Huggins**

| $M_w$/ (g/mol) | $\langle S_{\Theta,FH}\rangle_z$/nm | | |
|---|---|---|---|
| | $H_2O$/ acetone | $H_2O$/ THF | ethanol/ $n$-hexane |
| $3.5 \times 10^5$ | | 18.0 | |
| $7.5 \times 10^5$ | 33.6 | 26.2 | 32.6 |
| $1.0 \times 10^6$ | | 30.4 | |

Usually, $\Psi$ is plotted against $\alpha^3$. Figure 4 shows such a plot obtained for the system PVP + $H_2O$/THF. Interestingly, $\Psi$ builds up to branches. One branch characterizes the system PVP + $H_2O$; the other branch describes the situation where THF is present as well. Figure 5 shows the equivalent plot for the system PVP + $H_2O$/acetone. Here, the data points form a single composite curve, irrespective of whether acetone is present or not. The theoretical curves of $\Psi$ are numbered 1–3 according to the three possible combinations, listed above. It is seen that none of these curves fits the experimental data very well. Only combination 3 is particularly satisfactory. Thus, a proof of criterion 2 is not possible. It is remarkable, on the other hand, that the experimental data points $(\Psi,\alpha^3)$ form composite structurated curves. Consequently, criterion 1 is fulfilled, and the observed dependence of the coil size on $w$ may be considered as a change due to the exluded volume. Agreement between theory and experiment can be obtained by an intramolecular theory of interaction that takes into account the effect of preferential adsorption. A subsequent paper will represent such a theory.

**Flory's Interaction Parameters.** The observed change in the coil size of PVP with increasing $w$ can be studied theoretically on the basis of the Flory–Huggins expansion factor $\alpha_{FH}$. According to Tanaka[6] et al.

$$\alpha^5_{FH} - \alpha^3_{FH} - (q(\phi)/\alpha^3_{FH}) = N^{0.5}p(\phi) \qquad (5)$$

$N$ denotes the degree of polymerization of the macromolecule. $\phi$ is the volume fraction of the precipitant in the mixture. $q(\phi)$ and $p(\phi)$ are functions that depend on the five parameters $\chi_{AB}$, $\chi_{AP}$, $\chi_{BP}$, $n$, and $\phi$. The exact expressions of $q(\phi)$ and $p(\phi)$ are given in the Appendix. $\chi_{AB}$, $\chi_{AP}$, and $\chi_{BP}$ are Flory's interaction parameters, where, e.g., $\chi_{AP}$ characterizes the interaction between a solvent molecule A and a segment of the polymer P. The parameter $n$ denotes the degree of polymerization of the precipitant B. While A is always assumed to be a monomolecular solvent, B is allowed to be a polymer with $n < N$. The Flory–Huggins expansion factor $\alpha_{FH} = \langle S\rangle_z/\langle S_{\Theta,FH}\rangle_z$ is related to a Θ state, where both the transversal and the longitudinal intrasegmental forces are zero. Values of $\langle S_{\Theta,FH}\rangle_z$ are listed in Table VI.

A comparison between the experimentally estimated data of $\alpha_{FH}{}^3(\phi)$ with the theoretical ones, calculated with eq 5, is problematic. First, we have to determine a value for $n$, the degree of polymerization of the precipitant B. According to Flory and Huggins,[8] the volume occupied by

**Table VII**
**Interaction Parameters for Different PVP Systems at $M_w$ = 7.5 × $10^5$ g/mol and $T$ = 20 °C**

| | H₂O/THF | | | H₂O/acetone | | | ethanol/*n*-hexane | | |
|---|---|---|---|---|---|---|---|---|---|
| *n* | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$ | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$ | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$ |
| 1 | 1.052 | 0.869 | 0.019 | 1.210 | 0.854 | −0.011 | 1.210 | 0.857 | $10^{-5}$ |
| 2 | 0.775 | 0.355 | 0.232 | 0.723 | 0.293 | 0.000 | 0.719 | 0.295 | $10^{-4}$ |
| 3 | 0.691 | 0.187 | 0.315 | 0.559 | 0.109 | 0.009 | 0.557 | 0.109 | 0.002 |
| 4 | 0.660 | 0.107 | 0.370 | 0.499 | 0.018 | 0.021 | 0.479 | 0.016 | 0.005 |
| 5 | 0.625 | 0.053 | 0.383 | 0.463 | −0.035 | 0.034 | 0.436 | −0.038 | 0.010 |
| 6 | | | | 0.451 | −0.066 | 0.057 | 0.420 | −0.071 | 0.028 |

[a] Calculated under the condition that $\chi_{AB}$ is independent of $M_w$.

**Table VIII**
**Interaction Parameters of the System PVP + H₂O/THF at $T$ = 40 °C**

| | $M_w$/(g/mol) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3.5 × $10^5$ | | 7.5 × $10^5$ | | 1.0 × $10^6$ | | |
| *n* | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$[a] |
| 1 | 1.016 | 0.855 | 1.027 | 0.863 | 1.036 | 0.865 | 0.034 |
| 2 | 0.798 | 0.362 | 0.811 | 0.372 | 0.819 | 0.373 | 0.323 |
| 3 | 0.698 | 0.187 | 0.710 | 0.198 | 0.719 | 0.199 | 0.385 |
| 4 | 0.673 | 0.107 | 0.685 | 0.118 | 0.692 | 0.121 | 0.445 |
| 5 | 0.653 | 0.061 | 0.664 | 0.071 | 0.675 | 0.073 | 0.478 |

[a] $\partial\chi_{AB}/\partial M_w = 0$.

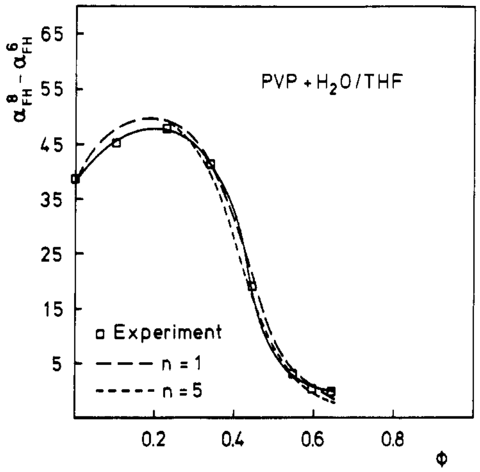

**Figure 6.** Comparison between theory and experiment. $M_w$ is 7.5 × $10^5$ g/mol and $T$ is 20 °C.

a monomer unit of the polymer should be as large as the volume occupied by a unit of the solvent mixture. The domain of one PVP unit is approximately as large as the domain of one THF or one *n*-hexane molecule. Two acetone molecules, connected by hydrogen bonding, need nearly the same volume as one PVP segment. Thus, the values $n$ = 1 and $n$ = 2 are useful. On the other hand, as suggested by Tanaka,[6] a C–C or a C–O group can be considered to be the monomer unit of component B. Thus, $n$ is 5 for THF, $n$ is 3 for acetone, and $n$ becomes 6 for *n*-hexane. Consequently, we have a rather puzzling situation, and it seems best to work with various values of $n$ in order to examine the consequences.

The calculation of the interaction parameters $\chi_{AB}$, $\chi_{AP}$, and $\chi_{BP}$ is done according to eq 5 by using a least-squares fit. Attention was paid to the fact that always the parameter $\chi_{AB}$ was independent of the molecular mass $M_w$. Thus, the fit is done under the boundary condition that $\partial\chi_{AB}/\partial M_w$ is zero. Figure 6 shows a plot of $\alpha^8_{FH} - \alpha^6_{FH}$ against the volume fraction $\phi$ of THF for various $n$. $M_w$ is 7.5 × $10^5$ g/mol, and $T$ is 20 °C. Quantitative agreement between theory and experiment is attained in the interval of $\phi \in$ [0.25–0.45] for all $n$. At very low and high values of $w$ there is some discrepancy, which may be caused by the deficiency of experimental data points. The best fit is given when $n$ is 1, but the differences are very small. The interaction parameters, obtained for each system, are listed together with the belonging values of $n$ in the Tables VII–IX.

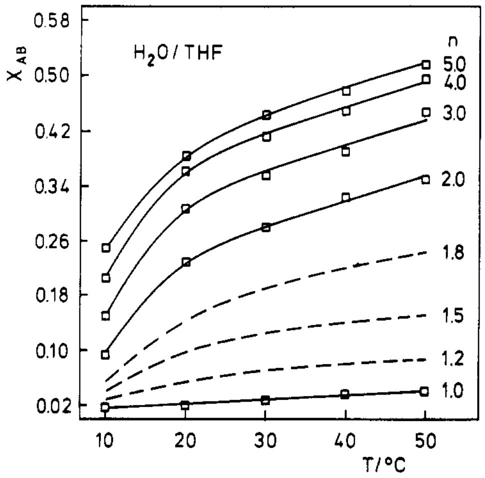

**Figure 7.** Plot of the interaction parameter $\chi_{AB}$ against the temperature $T$ for various $n$. Component A is H₂O and component B is THF.

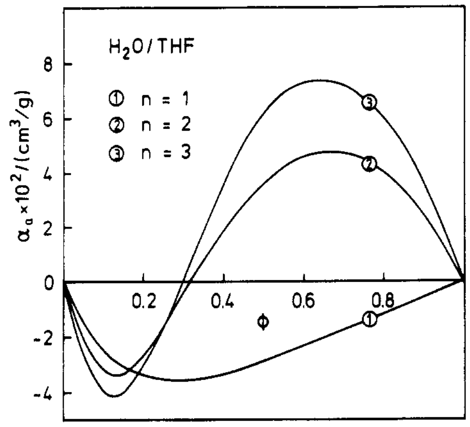

**Figure 8.** Influence of the degree of polymerization $n$ of the precipitant upon the selective adsortion parameter $\alpha_a$ for the mixture H₂O/THF. $M_w$ is 7.5 × $10^5$ g/mol and $T$ is 20 °C.

The theory[6] predicts that component B is compatible with the polymer P when $\chi_{BP} > 1/(2n)$ and incompatible when $\chi_{BP}$ is larger than $1/(2n)$. Table VII shows that $\chi_{BP}$ is larger than $1/(2n)$ when $n_{THF}$ = 1, $n_{Ac}$ = 2, and $n_{Hex}$ = 1, which are the most realistic values of $n$ for the three systems. Thus component B is always incompatible with a PVP molecule. For higher values of $n$, $\chi_{BP}$ is smaller than $1/(2n)$ and the situation becomes unphysical.

Figure 7 shows a plot of the interaction parameter $\chi_{AB}$ against the temperature $T$ for various $n$. It can be seen that $\chi_{AB}$ is not a constant as could be expected. $\chi_{AB}$ can

**Table IX**
**Interaction Parameters of the System PVP + $H_2O$/THF for $M_w = 7.5 \times 10^5$ g/mol**

| | $T$/°C | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10 | | | 30 | | | 50 | | |
| $n$ | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$[a] | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$[a] | $\chi_{AP}$ | $\chi_{BP}$ | $\chi_{AB}$[a] |
| 1 | 1.074 | 0.879 | 0.017 | 1.045 | 0.866 | 0.028 | 1.018 | 0.857 | 0.039 |
| 2 | 0.687 | 0.323 | 0.086 | 0.801 | 0.363 | 0.283 | 0.820 | 0.371 | 0.352 |
| 3 | 0.576 | 0.147 | 0.141 | 0.708 | 0.192 | 0.354 | 0.750 | 0.208 | 0.453 |
| 4 | 0.549 | 0.070 | 0.202 | 0.682 | 0.113 | 0.414 | 0.715 | 0.124 | 0.498 |
| 5 | 0.543 | 0.025 | 0.250 | 0.660 | 0.064 | 0.443 | 0.684 | 0.072 | 0.515 |

[a] $\partial\chi_{AB}/\partial M_w = 0$.

**Table X**
**Number of Adsorbed A Molecules per Monomer Unit of PVP[a]**

| | $H_2O$/THF[b] | | | | | $H_2O$/acetone[c] | | ethanol/hexane[d] |
|---|---|---|---|---|---|---|---|---|
| $w$ | $T$ = 10 | $T$ = 20 | $T$ = 30 | $T$ = 40 | $T$ = 50 | $T$ = 20 | $T$ = 40 | $T$ = 20 |
| 0.2 | 0.25 | | | | | 0.22 | 0.18 | 0.04 |
| 0.4 | 0.57 | 0.32 | 0.18 | 0.10 | 0.05 | 0.24 | 0.22 | 0.06 |
| 0.6 | 0.63 | 0.60 | 0.60 | 0.63 | 0.64 | 0.19 | 0.18 | 0.05 |
| 0.8[e] | 0.42 | 0.46 | 0.48 | 0.52 | 0.54 | 0.10 | 0.12 | 0.03 |

[a] $M_w = 7.5 \times 10^5$ g/mol; $T$ is in °C. [b] $n = 5$. [c] $n = 2$. [d] $n = 6$. [e] Hypothetical values.

be expressed as[8]

$$\chi_{AB} = Z(\epsilon_{AB} - [\epsilon_{AA} + \epsilon_{BB}]/2)/kT \qquad (6)$$

$Z$ is the lattice coordination number. $\epsilon_{ij}$ is the interaction energy between a monomer of $i$th species and a monomer of $j$th species when they sit on the nearest neighboring lattice cells. Therefore $\chi_{AB}$ should decrease with $T$ if $\epsilon_{AB}$, $\epsilon_{AA}$, and $\epsilon_{BB}$ are constants. Now it is believed that the entropy change must be included by replacing $\epsilon_{ij}$ by the free energy $f_{ij} = \epsilon_{ij} - Ts_{ij}$. Then the resultant temperature dependence of $\chi_{AB}$ is given by $\chi_{AB} = A_{AB} + B_{AB}/T$, where $A_{AB}$ and $B_{AB}$ are constants. The sign of $A_{AB}$ and $B_{AB}$ depends on the special combination of the two species. However, this problem will be discussed in more detail in a forthcoming paper.

**Selective Adsorption.** The relation between the selective adsorption parameter $\alpha_a$ and the volume fraction $\phi$ is given by[20]

$$\alpha_a = [v_3\phi(1-\phi)]([\chi_{AB}V_r(2\phi - 1) + \chi_{BP} - \chi_{AP}V_r + V_r - 1]/[(1-\phi) + V_r\phi - 2\chi_{AB}V_r\phi(1-\phi)]) \qquad (7)$$

$\alpha_a$ depends not only on the interaction parameters $\chi_{ij}$ as expected but also on the bulkiness of the solvent molecules through the ratio of their molar volume, $V_r$, where $V_r = V_B/V_A$. Values of $V_A$ and $V_B$ are reported in the literature.[16] $v_3$ denotes the partial specific volume of PVP. Values of $v_3$ are obtained by density measurements.[21]

According to eq 7 all parameters are known, and thus $\alpha_a$ can be calculated without difficulty. Figure 8 shows a plot of $\alpha_a$ against $\phi$ for the system PVP + $H_2O$/THF, where $M_w$ becomes $7.5 \times 10^5$ g/mol and $T$ is 20 °C. At low values of $\phi$, $\alpha_a$ is negative for all $n$, which are considered to be physically reasonable. The best agreement between the experiment, manifested by eq 3, and the theory, presented by eq 7, is achieved when $n$ becomes 5, as can be seen from Figure 9. This implies that at low $\phi$ the precipitant, THF, is adsorbed preferentially by PVP.

Thus the adsorption is inverse, which is contrary to the expected result that THF is incompatible with PVP.

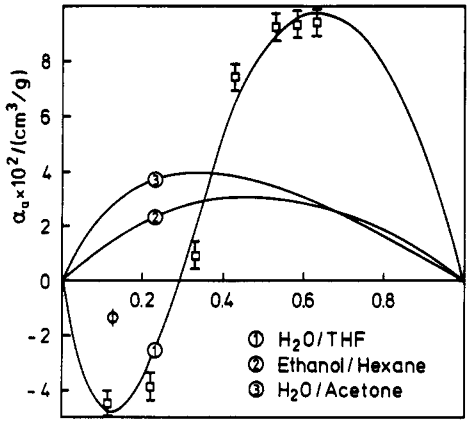

**Figure 9.** Plot of the adsorbtion parameter $\alpha_a$ against the volume fraction $\phi$ of the precipitant. The experimental data, obtained for the system PVP + $H_2O$/THF, are presented by squares. The two other systems are isorefractive. $M_w$ is $7.5 \times 10^5$ g/mol and $T$ is 20 °C. (1) $n = 5$, (2) $n = 6$, and (3) $n = 2$.

At higher values of $\phi$ the adsorption becomes normal, $\alpha_a$ takes on positive values, and consequently $H_2O$ is adsorbed preferentially by PVP. It is remarkable that $\alpha_{FH}$ has its maximum at a position ($\phi_m = 0.2$) where $\alpha_a$ is minimal. Thus, the expansion of a PVP molecule is attributed to an adsorption of THF molecules. However, THF is not capable of solvatating PVP, which is the task of $H_2O$. Possibly $H_2O$ and THF build a complex, and this complex is then adsorbed by PVP. If this is true, we are faced with a new situation. The solvent is now a mixture of two good solvents, namely, $H_2O$ and the $H_2O$/THF complex. Accordingly, it should be proved whether eq 7 can be applied or not. This will be investigated in the immediate future.

The two systems PVP + $H_2O$/acetone and PVP + ethanol/$n$-hexane give no problems. In the whole range of $\phi$ the selective adsorption parameter, $\alpha_a$, is positive for each $n$. Thus, the good solvent, $H_2O$ or ethanol, is adsorbed preferentially by PVP. The parameters $\alpha_a$ and $\alpha_{FH}$ have maximal values at nearly identical positions of $\phi$. This implies that the swelling of a PVP molecule is predominantly caused by an adsorption of the good solvent.

The adsorption parameter $\alpha_a$ is also calculated for the various molecular masses considered here. Figure 10 shows that $\alpha_a$ is practically independent of $M_w$, a result that holds for all $n$. This seems to indicate that the adsorption occurs in a uniform manner along the PVP chain as the binary solvent is $H_2O$/THF. A similar result was obtained for the system polystyrene + benzene/cyclohexane by Strazielle[22] et al.

Finally, the $\alpha_a$ values can be used to describe the phenomenon of adsorption by the number $X_A$ of solvent

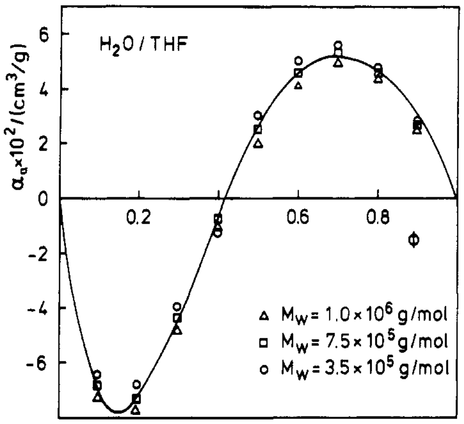

**Figure 10.** Influence of the molecular mass $M_w$ upon the adsorption parameter $\alpha_a$. $T$ is 40 °C and $n$ is 2.

A molecules, which are adsorbed preferably per monomer unit of a PVP molecule with respect to the solvent environment. $X_A$ vanishes as $\phi$ becomes zero. It holds[20] that

$$X_A = \alpha_a(M_0/\bar{V}_A)$$

where $M_0$ is the molecular mass of a monomer unit and $\bar{V}_A$ the partial molar volume of solvent A. In most cases, the molar volume $V_A$ can be used instead of $\bar{V}_A$. Values of $X_A$ are given in Table X. $X_A$ does not exceed 0.65, which corresponds to nearly two solvent A molecules adsorbed by three monomer units. It seems that the affinity of selective adsorption is highest for the mixture $H_2O$/THF and smallest for the system ethanol/*n*-hexane. However, it cannot be concluded that the PVP affinity for adsorption is higher for $H_2O$ than for ethanol. To prove this hypothesis, the system PVP + $H_2O$/ethanol has to be investigated. The influence of temperature upon $X_A$ is somewhat ambiguous. Below the point of precipitation the number of adsorbed A molecules decreases with increasing $T$. As can be expected, the opposite is found as PVP begins to precipitate. However, this result should be considered with caution because $X_A$ may be affected by an error of more than 10%.

## Conclusions

We have studied poly(*N*-vinylpyrrolidone) dissolved in various mixed solvents consisting of a good solvent and a nonsolvent. It could be shown that the mixing of two such solvents leads to completely new phenomena that do not exist if only the good solvent is used. Mainly two phenomena are observed: (1) a swelling of the PVP coil near a definite volume fraction $\phi$ of the nonsolvent; (2) a strong contraction when $\phi$ exceeds this fraction. The swelling is caused by a selective adsorption of the good solvent or by an adsorption of a complex that consists of the good solvent and the precipitant. Competition between the PVP and the nonsolvent for the good solvent induces the contraction.

The mentioned phenomena are not affected by a change in the temperature or the molecular mass of the PVP sample. Changes concern only the point of precipitation. For a lower molecular mass a PVP molecule precipitates at a higher concentration of the nonsolvent. Beyond the precipitation region the adsorption parameters $\alpha_a$ are practically independent on the molecular mass. The solvent molecules are adsorbed in a uniform manner along the PVP chain. At a fixed value of $M_w$, the precipitation point rises to a higher value of $\phi$ at an increase in temperature. This is due to the fact that the degree of adsorption is slightly lowered and consequently the degree of solvatation rises.

The PVP systems considered here possess various Θ radii of gyration. This is due to the fact that the longitudinally acting intramolecular forces are different for each system at the Θ point. The selective adsorption parameter $\alpha_a$ is positive. Thus, the intramolecular forces are mainly caused by an association of the good solvent component with the macromolecule. Thereby the radius of gyration is changed. The degree of changement depends on the degree of solvent adsorption, e.g., on the special nature of the Θ mixture. With regard to the contracted coil state of PVP, the Θ radius of gyration $\langle S_\Theta\rangle_{z,\mathrm{FH}}$ is proportional to the square root of $\alpha_a$. It holds that $\langle S_\Theta\rangle_{z,\mathrm{H_2O/THF}} < \langle S_\Theta\rangle_{z,\mathrm{H_2O/acetone}} < \langle S_\Theta\rangle_{z,\mathrm{ethanol/hexane}}$, and $\alpha^\Theta_{a,\mathrm{H_2O/THF}} < \alpha^\Theta_{a,\mathrm{H_2O/acetone}} < \alpha^\Theta_{a,\mathrm{ethanol/hexane}}$. In the expanded coil state of PVP, the Θ radius $\langle S_\Theta\rangle_{z,\mathrm{ex}}$ is nearly independent of $\alpha_a$. However, it cannot be expected that this phenomenon will generally be observed.

The excluded volume theory describes the conformational state of a PVP molecule in a mixed solvent quite well, as can be seen by the fact that the experimentally obtained interpenetration functions Ψ form composite curves. Contrary to the system PVP/$H_2O$/acetone, where a PVP molecule adsorbs only the good solvent component, namely, $H_2O$, Ψ segregates into two single branches when both solvent components are simultaneously adsorbed by the polymer. Such a case is given by the system PVP + $H_2O$/THF, where both $H_2O$ and THF are adsorbed. However, it must be proved whether this feature is a general one.

The dependence of the expansion factor $\alpha_{\mathrm{FH}}$ upon the volume fraction $\phi$ of the solvent mixture is quite well described by the Flory–Huggins theory, developed by Tanaka[6] et al. However, the concrete meaning of the interaction parameters $\chi_{ij}$ still remains unclear. For instance, the parameter $\chi_{\mathrm{BP}}$ adopts a value that states that PVP and THF are compatible with regard to the system PVP + $H_2O$/THF. The experiment, on the other hand, shows that THF is a precipitant for PVP. To solve this contradiction, it is useful to divide $\chi_{\mathrm{BP}}$ into a solvatation and an adsorption part. A detailed analysis of this topic is planned for the future.

## Appendix: Explicit Form of the Functions $q(\phi)$ and $p(\phi)$

$$p(\phi) = 4.849(-g_{02}a_1 + g_{20})$$

$$q(\phi) = 23.513(-2g_{02}a_1a_2 - g_{03}a_1^3 + g_{21}a_1 + 2g_{30})$$

$$a_1 = -(g_{11} + 0.3536g_{01})/2g_{02}$$

$$a_2 = -(3g_{03}a_1^2 + 2g_{12}a_1 + g_{21})/2g_{02}$$

$$g_{01} = -(\phi + \ln\phi)/n + \ln(1-\phi) + 1 - \chi_{\mathrm{AB}}(1-2\phi)$$

$$g_{02} = 0.3536[(2-\phi)/n + \phi/(1-\phi) - 2\chi_{\mathrm{AB}}\phi]/2$$

$$g_{03} = 0.1925[(3-2\phi)/n + (\phi/(1-\phi))^2]/6$$

$$g_{11} = 0.3536[-2(1-1/n) + (\ln\phi)/n - \ln(1-\phi) + \chi_{\mathrm{AP}} - \chi_{\mathrm{BP}} + 2\chi_{\mathrm{AB}}(1-2\phi)]$$

$$g_{12} = 0.1925[(1-1/n) - 1/(1-\phi) + 4\chi_{\mathrm{AB}}\phi]/2$$

$$g_{20} = 0.3536[\phi(2-\phi)/2n + (1-\phi)/2 - \chi_{\mathrm{AP}}(1-\phi) - \chi_{\mathrm{BP}}\phi + \chi_{\mathrm{AB}}\phi(1-\phi)]$$

$$g_{21} = 0.1925[(1-1/n)/2 - \chi_{\mathrm{AP}} + \chi_{\mathrm{BP}} - \chi_{\mathrm{AB}}(1-2\phi)]$$

$$g_{30} = 0.1925[\phi(3-2\phi)/n + 1 - \phi]/6$$

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**Registry No.** PVP (homopolymer), 9003-39-8; THF, 109-99-9; $H_2O$, 7732-18-5; $CH_3COCH_3$, 67-64-1; $CH_3CH_2OH$, 64-17-5; $H(CH_2)_6H$, 110-54-3.