

# Thermodynamics of the Solubilization of 2-Undecanone in Aqueous Solutions of Poly(sodium styrenesulfonate-co-2-vinylnaphthalene)

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**ABSTRACT:** Poly(sodium styrenesulfonate-co-2-vinylnaphthalene) (PSSS-VN) displays a pseudomicellar conformation in aqueous solution. Such a conformation enables the solubilization of large hydrophobic organic compounds. A two-phase model is proposed to describe the solubilization of 2-undecanone in aqueous solutions of PSSS-VN. Thermodynamic parameters for the solubilization of 2-undecanone in aqueous solutions of PSSS-VN have been determined. Two approaches, based on mole fraction and weight fraction as reference functions, for the determination of the distribution coefficients of 2-undecanone between water and polymer pseudophase are presented. The values of the distribution coefficients of 2-undecanone between polymer pseudophase and water are high. Solubilization is a spontaneous process ( $\Delta G^\circ = -33.9$  kJ mol<sup>-1</sup>). The influence of ionic strength and pH on the solubilization efficiency has also been studied. An increase in the ionic strength causes a decrease in solubilization. The solubilizing ability of PSSS-VN has been found to be highest at neutral pH and decreased with increased acidity and basicity of the solution. Ionic strength and pH effects have been explained in terms of induced changes in the effective hydrodynamic volume of the polymer.

## Introduction

It is well-known that the solubility of many sparingly water-soluble organic compounds can be enhanced considerably by the addition of a surfactant. The surfactant solution at a concentration above the critical micelle concentration (cmc) consists of micelles with a hydrophobic interior into which hydrophobic solute molecules can be easily dissolved. The formation of similar types of aggregates has been observed in some polymer systems such as partially N-alkylated poly(tertiary amines) with pendant amino groups.<sup>1</sup>

Interestingly, some synthetic polyelectrolytes consisting of hydrophobic and hydrophilic groups can form hydrophobic microdomains within a single polymer coil in aqueous solution.<sup>2-6</sup> This behavior resembles that of surfactant micelles. For example, some water-soluble poly(carboxylic acids) containing hydrophobic side chains<sup>3</sup> and their copolymer with alkyl vinyl ethers<sup>4</sup> as well as with styrene<sup>5</sup> exhibit a pH-induced conformational transition. At a low degree of ionization a compact coil exists in solution while with an increase in the ionization the polymer undergoes a conformational change to an unfolded random coil.

The equilibrium between a tight globular and extended macromolecule is controlled by electrostatic repulsive forces between polar groups, hydrophobic interactions between apolar groups, and interactions between hydrophobic groups and water. The solubilizing ability of most polymer systems based on poly(carboxylic acids) is restricted to conditions at which the degree of carboxyl group ionization is low (low pH values). This limits the practical applications of such polymer systems.

On the basis of studies of the photophysical properties of copolymers of 1-naphthyl methacrylate and acrylic acid terminated with anthracene, Guillet and co-workers<sup>2,6</sup> found that these polymers in aqueous solution adopt a "hypercoiled" structure. The hydrophobic aromatic groups form the interior of the coil while the carboxyl groups,

with their counterions nearby, form an outer "shell".

Recently, it has been shown that a new type of synthetic water-soluble polyelectrolyte, poly(sodium styrenesulfonate-co-2-vinylnaphthalene) (PSSS-VN), solubilized large hydrophobic organic molecules such as polynuclear aromatic compounds and long-chain aliphatic ketones at neutral pH. The polymer has also been found to have interesting photocatalytic activity,<sup>7,8</sup> analogous to the "photon-harvesting" phenomenon that plays such an important role in photosynthesis.<sup>9</sup> PSSS-VN is able to absorb light in the near-UV-visible spectral region. Energy transfer from the pendant excited naphthalene groups to the solubilized probe induces photochemical reactions of the solute.

In order to give a quantitative description of the photophysical and photochemical processes occurring in the system, information regarding the concentration of the probe solubilized in the polymer hydrophobic microdomains and the distribution of the probe between water and polymer pseudophase is needed. Thus an understanding of the nature of the solubilization phenomenon and a determination of the thermodynamic parameters that govern the solubilization process seem to be very important.

This paper deals with studies of the solubilization of 2-undecanone in aqueous solutions of PSSS-VN.

## Experimental Section

**Materials.** Poly(sodium styrenesulfonate-co-2-vinylnaphthalene) (PSSS-VN) containing 60 mol % vinylnaphthalene and 40 mol % sodium styrenesulfonate was used in these studies. The preparation and purification of the polymer are described elsewhere.<sup>10</sup> The weight-average molecular weight,  $\bar{M}_w$ , was determined on a Beckman Model E analytical ultracentrifuge equipped with an RTIC temperature measurement system and an electronically controlled drive. The sedimentation equilibrium work was performed according to the high-speed meniscus depletion method of Yphantis.<sup>11</sup> Samples of PSSS-VN (0.03% in 0.10 M NaCl) were analyzed at 25 °C at a speed of 11 000 rpm by using Rayleigh interference optics. A partial specific volume of 0.75 cm<sup>3</sup> g<sup>-1</sup> was assumed in calculating molecular weight. The value of  $\bar{M}_w$  was found to be 310 000. The number-average molecular weight of the polymer was estimated (assuming

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a polydispersity of 2.0) to be 155 000.

2-Undecanone (Eastman Organic Chemicals) was purified by vacuum distillation. The purity of 99.96% was confirmed by gas chromatography. Aqueous polymer solutions were prepared with deionized water.

The ionic strength of the aqueous polymer solutions was adjusted by addition of appropriate amounts of a standard NaCl solution. The pH was changed by using standard HCl and NaOH solutions.

**Solubilization of 2-Undecanone.** The equilibrium concentrations of 2-undecanone in each system studied were determined at saturation conditions. Microliter quantities of 2-undecanone were slowly added to 10 mL of the aqueous PSSS-VN solutions. The mixture was shaken for 5 min, tumbled for 20 h, and filtered through fine filter paper (Whatman no. 42). In a control experiment, the time of equilibration was prolonged to 150 h, but no change in the concentration of the solubilized ketone was observed.

**Gas Chromatography Analysis.** The quantitative analyses of the aqueous polymer systems were carried out on a Varian Aerograph Series 1700 gas chromatograph. The instrument contained a flame ionization detector (FID) and a 6 ft  $\times$  2 mm OV17 glass column fitted with a glass wool precolumn. The function of the precolumn was to remove the polymer from the samples analyzed.

The GC analysis was done with a programmed temperature from 50 to 250 °C at 10 °C min<sup>-1</sup>.

The peak areas were measured by a disk integrating unit attached to the chromatograph recorder.

**Viscosity Measurements.** The viscosities of the polymer solutions at various polymer concentrations, ionic strengths, pHs, and temperatures were determined with an automatic viscometer described elsewhere.<sup>12</sup> The values of the intrinsic viscosity,  $[\eta]$ , were calculated from the experimentally determined dependence  $(\eta_{sp}/c)^{-1}$  vs  $c^{1/2}$  analytically described by the Fuoss empirical equation:<sup>13</sup>

$$\eta_{sp}/c = [\eta]/(1 + Bc^{1/2}) \quad (1)$$

where  $\eta_{sp}/c$  is the reduced viscosity,  $c$  is the concentration of the aqueous polymer solution, and  $B$  is an empirical constant.

## Results and Discussion

**1. Determination of the Distribution Coefficient and Standard Thermodynamic Functions of 2-Undecanone Solubilized in an Aqueous Solution of PSSS-VN.** By assuming that the aqueous solution of PSSS-VN can be treated as consisting of two phases (a water phase and a polymer core pseudophase), one can define the distribution coefficient of 2-undecanone between these two phases ( $K$ ) as

$$K = a_U^c/a_U^{aq} \quad (2)$$

where  $a_U^c$  and  $a_U^{aq}$  are the activities of 2-undecanone in the polymer "core" and water phase, respectively. Equation 2 can be rewritten in the form

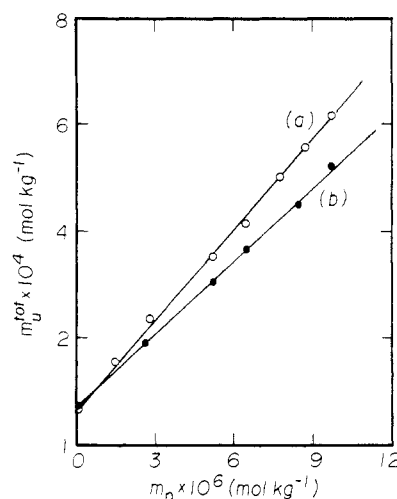
$$K = (x_U^c/x_U^{aq})(\gamma_U^c/\gamma_U^{aq}) \quad (3)$$

where  $x_U^c$  and  $x_U^{aq}$  are the mole fractions of 2-undecanone in the polymer pseudophase and in the water phase, respectively, and  $\gamma_U^c$  and  $\gamma_U^{aq}$  are the activity coefficients of 2-undecanone in their respective phases.

Taking into account that the aqueous solution of 2-undecanone is dilute and assuming ideal interactions between hydrocarbon polymer core and 2-undecanone, both activity coefficients,  $\gamma_U^c$  and  $\gamma_U^{aq}$ , can be assumed to be approximately equal to unity. Thus the expression for the distribution coefficient can be simplified to

$$K = x_U^c/x_U^{aq} \quad (4)$$

Considering the relationship between the mole fraction of 2-undecanone in the aqueous and polymer phases and



**Figure 1.** Total concentration of 2-undecanone in aqueous PSSS-VN solution as a function of the copolymer concentration (a) at 26 °C and (b) at 55 °C.

the total molal concentration in the system, one can obtain the following expression:

$$m_U^{\text{tot}} = x_U^{\text{aq}}(10^3/M_{\text{H}_2\text{O}}) + [x_U^c/(1 - x_U^c)]m_p^c \quad (5)$$

where  $m_U^{\text{tot}}$  and  $m_p^c$  represent the total molal concentrations of 2-undecanone and polymer microdomains in the system, respectively, and  $M_{\text{H}_2\text{O}}$  is the molecular weight of water.

Assuming that for the polymer being studied

$$m_p^c \approx m_p \quad (6)$$

where  $m_p$  is the molal concentration of the polymer, one can write eq 5 in the form

$$m_U^{\text{tot}} = (x_U^c/K)(10^3/M_{\text{H}_2\text{O}}) + [x_U^c/(1 - x_U^c)]m_p \quad (7)$$

Figure 1 shows the dependence of the total molal concentration of 2-undecanone on the concentration of polymer at two chosen temperatures, 26 and 55 °C. It can be observed that in the concentration range  $(0-1) \times 10^{-5}$  mol kg<sup>-1</sup>, calculated based on the number-average molecular weight of PSSS-VN, the total concentration of 2-undecanone in the system is linearly dependent on the concentration of polymer. The solubilization of 2-undecanone decreases with increasing temperature, while its solubility in water increases slightly in this temperature range ( $m_U^{\text{aq}} = 6.6 \times 10^{-5}$  mol kg<sup>-1</sup> at 26 °C and  $m_U^{\text{aq}} = 7.4 \times 10^{-5}$  mol kg<sup>-1</sup> at 55 °C). Values of the mole fraction of solubilized ketone and distribution coefficient  $K$  at several temperatures were determined by using eq 7 and the experimentally determined dependence of the total concentration of 2-undecanone in aqueous solutions of PSSS-VN on the concentration of copolymer (see Figure 1).

From a knowledge of the values of the distribution coefficient one can determine the thermodynamic functions for the solubilization process. If one assumes ideal behavior of the 2-undecanone in both phases, the standard molar Gibbs free energy of transfer of 2-undecanone from water to the polymer core can be calculated as follows:

$$\Delta G^\circ = \mu_U^{\circ, \text{core}} - \mu_U^{\circ, \text{aq}} = -RT \ln K \quad (8)$$

where  $\mu_U^{\circ, \text{core}}$  and  $\mu_U^{\circ, \text{aq}}$  are the chemical potentials of 2-undecanone in the polymer core and water phase, respectively,  $T$  is absolute temperature, and  $R$  is the gas constant.

The corresponding standard enthalpy of transfer  $\Delta H^\circ$

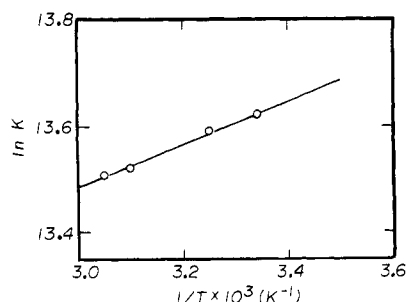


Figure 2. Plot of the distribution coefficient vs temperature.

Table I  
Values of the Distribution Coefficient ( $K$ ) and Standard Thermodynamic Functions for Solubilization of 2-Undecanone in Aqueous Solutions of PSSS-VN

temp, °C	$K \times 10^{-5}$	$\Delta G^\circ$ , kJ mol <sup>-1</sup>	$\Delta H^\circ$ , kJ mol <sup>-1</sup>	$\Delta S^\circ$ , kJ mol <sup>-1</sup> K <sup>-1</sup>
26	8.27 ± 0.17	-33.9 ± 0.1	-3.3 ± 0.1	0.10 ± 0.01
35	8.02 ± 0.16	-34.8 ± 0.1		0.10 ± 0.01
50	7.45 ± 0.15	-36.3 ± 0.1		0.10 ± 0.01
55	7.35 ± 0.15	-36.8 ± 0.1		0.10 ± 0.01

Table II  
Mole Fraction ( $x_U^c$ ) and Molal Concentration ( $m_U^c$ )<sup>a</sup> of 2-Undecanone Saturated in Aqueous Solutions of PSSS-VN at Various Temperatures

temp, °C	$x_U^c$	$m_U^c$ , mol <sup>-1</sup> kg <sup>-1</sup>
26	0.983 ± 0.001	0.37 ± 0.02
35	0.981 ± 0.001	0.33 ± 0.02
50	0.978 ± 0.001	0.30 ± 0.02
55	0.978 ± 0.001	0.29 ± 0.02

<sup>a</sup> The molal concentration was calculated by using the relationship  $m_U^c = 10^3 x_U^c / [(1 - x_U^c) M_p]$ , where  $x_U^c$  is the mole fraction of 2-undecanone in the polymer core and  $M_p$  is the number-average molecular weight of the polymer.

can be derived from the temperature dependence of the standard free energy of solubilization  $\Delta G^\circ$  or the distribution coefficient,  $K$ :

$$\Delta H^\circ = \frac{\partial}{\partial(1/T)} (\Delta G^\circ / T) = - \frac{\partial}{\partial(1/T)} (R \ln K) \quad (9)$$

Thus from the slope of the plot  $\ln K$  as a function of  $1/T$  (Figure 2) one can calculate  $\Delta H^\circ$ . The entropy of transfer can be estimated by using the expression

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \quad (10)$$

The values of the distribution coefficients as well as the standard thermodynamic functions for the solubilization of 2-undecanone in aqueous solution of PSSS-VN at four different temperatures are summarized in Table I.

The experimentally determined values of the mole fraction of 2-undecanone saturated in aqueous solutions of PSSS-VN ( $x_U^c$ ) at four temperatures and the molal concentration of 2-undecanone in the polymer pseudophase ( $m_U^c$ ) are summarized in Table II.

In the thermodynamic treatment of the system presented above, the mole fraction was used as a reference function. With such an approach one can compare the solubilizing ability of PSSS-VN with that of low molecular weight systems, e.g., surfactants. A disadvantage of this method is that it requires a precise determination of the molecular weight of the polymer. This problem is avoided when the weight fraction is chosen as a reference function. The distribution coefficient  $K^*$  is now

Table III  
Values of the Distribution Coefficient  $K^*$ , Weight Fraction  $x_{w,U}^c$ , and Molal Concentration  $m_U^c$  of 2-Undecanone Saturated in Aqueous Solutions of PSSS-VN at Various Temperatures<sup>a</sup>

temp, °C	$K^* \times 10^3$	$x_{w,U}^c$	$m_U^c$ , mol kg <sup>-1</sup>
26	5.20 ± 0.26	0.059 ± 0.005	0.37 ± 0.02
35	4.70 ± 0.24	0.053 ± 0.005	0.33 ± 0.02
50	3.90 ± 0.20	0.049 ± 0.005	0.30 ± 0.02
55	3.80 ± 0.19	0.047 ± 0.005	0.29 ± 0.02

<sup>a</sup> The molal concentration was calculated by using the relationship  $m_U^c = 10^3 x_{w,U}^c / [(1 - x_{w,U}^c) M_U]$ , where  $x_{w,U}^c$  is the weight fraction of 2-undecanone in the polymer core and  $M_U$  is the molecular weight of 2-undecanone.

defined by

$$K^* = x_{w,U}^c / x_{w,U}^{aq} \quad (11)$$

where  $x_{w,U}^c$  and  $x_{w,U}^{aq}$  represent the weight fraction of 2-undecanone in the polymer pseudophase and water, respectively.

It can be shown that the total amount of 2-undecanone solubilized in the aqueous polymer solution is a linear function of the amount of polymer present in the system:

$$w_U^{\text{tot}} = w_U^{aq} + \frac{K^* w_U^{aq}}{10^3 - K^* w_U^{aq}} w_p \quad (12)$$

where  $w_U^{\text{tot}}$ ,  $w_U^{aq}$ , and  $w_p$  are the total concentration of 2-undecanone in the system, the concentration of 2-undecanone saturated in the aqueous phase, and the concentration of polymer (all concentrations are expressed in grams per kilogram of water), respectively.

From eq 12 and the experimental data, the values of the distribution coefficient of 2-undecanone between water and polymer pseudophase  $K^*$ , weight fraction  $x_{w,U}^c$ , and molal concentration of 2-undecanone in the polymer pseudophase were calculated (Table III).

A comparison of the data collected in Tables II and III shows that although the values of the distribution coefficients calculated using mole fraction are different from those calculated using a weight fraction as a reference function, the local concentrations of 2-undecanone in the polymer pseudophase ( $m_U^c$ ) (the value of practical importance) determined by both methods are the same.

From an analysis of the data presented in Figures 1 and 2 and collected in Tables I-III the following can be concluded.

1. The linear dependence of the total amount of solubilized 2-undecanone on the polymer concentration in the range  $(0-1) \times 10^{-5}$  M ( $0-1.5$  g kg<sup>-1</sup>) indicates that the two-phase model proposed for the description of the system is valid.

2. The values of the distribution coefficients are high, which indicates that PSSS-VN is a very good medium for the solubilization of relatively large hydrophobic molecules.

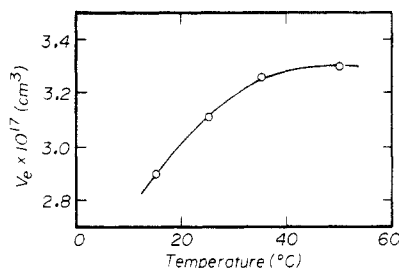
3. The negative values of the Gibbs standard free energy indicate that the solubilization process is spontaneous.

4. The positive values of the free entropy of solubilization can be explained by taking into account the changes in the structure of water surrounding the hydrophobic solubilized molecules. (The release of the compact iceberg structure of water surrounding hydrophobic molecules during solubilization in surfactant micellar systems is suggested.<sup>14</sup>)

5. The negative value of  $\Delta H$  indicated that the negative enthalpy of hydrophobic interactions between 2-undecanone and hydrocarbon polymer core is greater than

**Table IV**  
Intrinsic Viscosity  $[\eta]$ , Effective Hydrodynamic Volume  $V_e$ , and Effective Radius of the Sphere  $R_{eff}$  for PSSS-VN in Aqueous Solution at Four Chosen Temperatures

temp, °C	$[\eta]$ , dL g <sup>-1</sup>	$V_e \times 10^{18}$ , cm <sup>3</sup>	$R_{eff}$ , Å
15	2.82 ± 0.01	29.03 ± 0.58	191 ± 1.0
25	3.03 ± 0.01	31.20 ± 0.62	195 ± 1.3
35	3.17 ± 0.01	31.63 ± 0.65	198 ± 1.3
40	3.20 ± 0.01	32.34 ± 0.66	199 ± 1.5



**Figure 3.** Dependence of the effective hydrodynamic volume of the polymer core on temperature.

the positive enthalpy of release of the compact structure of water.

6. The decrease in the values of the distribution coefficient with increasing temperature is probably caused by the decrease of the dielectric constant of water as the temperature is raised. A decrease in the dielectric constant lowers the hydrophobic-hydrophilic interaction forces between water and hydrophobic solute molecule as well as between water and the hydrophobic part of the macromolecule. The previously mentioned phenomenon was verified by a comparison of the effective hydrodynamic volumes,  $V_e$ , and the effective radius of the polymeric sphere,  $R_e$ , at various temperatures (compare Table IV and Figure 3).

The effective hydrodynamic volume of the spherical polymer particle was calculated from the equation<sup>15</sup>

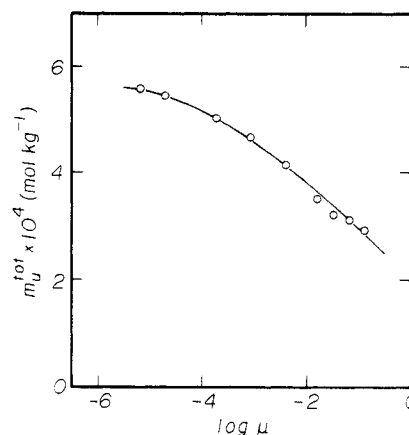
$$V_e = M[\eta]/0.025N \quad (13)$$

where  $M$  is the viscosity-average molecular weight,  $[\eta]$  is the intrinsic viscosity of the polymer, and  $N$  is Avogadro's number. The observed increase in the hydrodynamic volume of the polymer coil with increasing temperature reflects the lowering of the hydrophobic-hydrophilic interactions between polymer and water as well as an increase in the chain mobility at higher temperatures. Both of these phenomena result in a decrease in the compactness of the polymer chain with an increase in temperature, which may in turn reduce the solubilization of 2-undecanone in PSSS-VN solution.

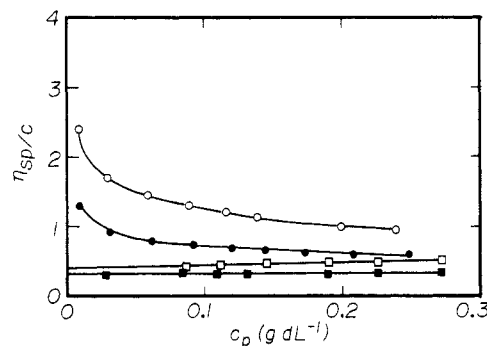
**2. Effect of the Ionic Strength and pH on the Solubilization of 2-Undecanone in Aqueous PSSS-VN Solution.** The physical properties of polyelectrolytes are known to be drastically influenced by the ionic strength of the solution. It was of interest to determine if the addition of salt would effect solubilization in the present system.

Figure 4 shows the dependence of the total molal concentration of 2-undecanone in PSSS-VN ( $c_{pol} = 1 \times 10^{-5}$  M) on the ionic strength. It can be observed that although solubilization of 2-undecanone decreases with an increase in the ionic strength, this effect is not very large. An increase in the ionic strength of 5 orders of magnitude has only decreased the amount of solubilized ketone by a factor of  $\sim 2$ .

In order to explain the dependence of the solubility of 2-undecanone on the ionic strength, the influence of added electrolyte on the size of the polymer coil was studied.



**Figure 4.** Total concentration of 2-undecanone solubilized in aqueous PSSS-VN solution as a function of ionic strength.



**Figure 5.** Dependence of the specific viscosity on the concentration of the polymer solution at various values of the ionic strength ((○)  $2 \times 10^{-6}$ , (●)  $1 \times 10^{-4}$ , (□)  $1 \times 10^{-3}$ , (■)  $1 \times 10^{-2}$ ).

**Table V**  
Intrinsic Viscosity  $[\eta]$ , Effective Hydrodynamic Volume  $V_e$ , and Effective Spherical Radius of PSSS-VN at Various Ionic Strengths of the Aqueous Solution

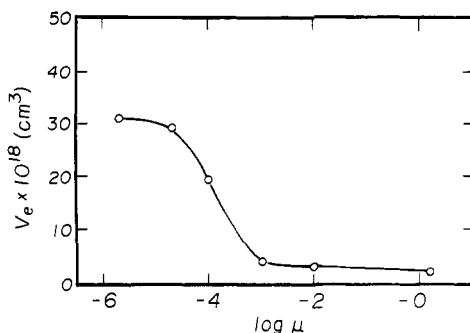
ionic strength	$[\eta]$ , dL g <sup>-1</sup>	$V_e \times 10^{18}$ , cm <sup>3</sup>	$R_{eff}$ , Å
$2 \times 10^{-6}$	3.03 ± 0.01	31.20 ± 0.62	195 ± 1.3
$2 \times 10^{-5}$	2.86 ± 0.01	29.44 ± 0.50	192 ± 1.2
$1 \times 10^{-4}$	1.91 ± 0.01	19.66 ± 0.39	167 ± 1.0
$1 \times 10^{-3}$	0.40 ± 0.01	4.12 ± 0.10	99 ± 0.5
$1 \times 10^{-2}$	0.30 ± 0.01	3.09 ± 0.06	90 ± 0.5
1.5	0.20 ± 0.01	2.06 ± 0.04	79 ± 0.5

The dependence of the specific viscosity of the polymer on the concentration of PSSS-VN at different values of the ionic strength is shown in Figure 5. An increase in the concentration of added electrolyte suppressed the electroviscous effect observed for polyelectrolytes at low ionic strengths.

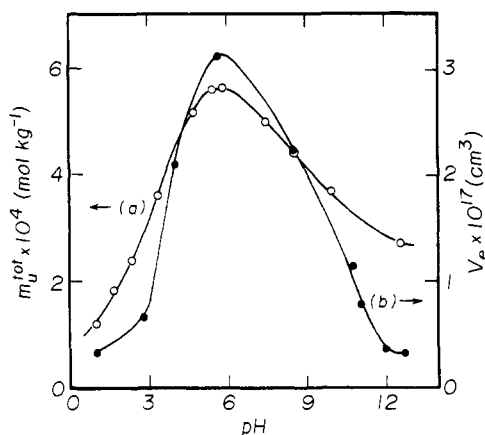
The values of the intrinsic viscosity, determined from the Fuoss empirical equation (eq 1), and the effective hydrodynamic volume ( $V_e$ ) of the macromolecule coil showed that an increase of the ionic strength resulted in a more compact conformation of the polymer (compare Table V and Figure 6).

From a comparison of the data shown in Figures 4 and 6, it can be concluded that (1) an increase in the ionic strength leads to a decrease in the effective hydrodynamic volume of the polymer core, (2) an increase in the ionic strength lowers the solubility of 2-undecanone in the aqueous PSSS-VN solution, and (3) the changes in both  $V_{eff}$  and  $m_U^{tot}$  are quite small compared with the ionic strength range ( $2 \times 10^{-6}$  to  $1 \times 10^{-1}$ ), although the change in particle volume is greater (about 15 times) than the observed change in the solubility (about 2 times).

**3. Effect of pH on the Solubilization of 2-Undecanone in Aqueous PSSS-VN Solution.** As previ-



**Figure 6.** Effective hydrodynamic volume of PSSS-VN as a function of the ionic strength of the solution (polymer concentration  $c = 1 \times 10^{-5}$  M).

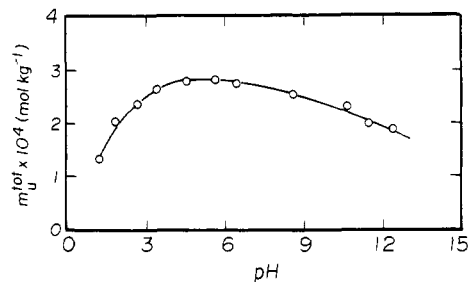


**Figure 7.** Dependence of the molal concentration of solubilized 2-undecanone (curve a) and effective hydrodynamic volume of the polymer (curve b) on the pH of the solution (polymer concentration  $c = 1 \times 10^{-5}$  M).

ously mentioned, some polyelectrolytes can undergo drastic conformational transitions at a given degree of ionization. This is followed by an abrupt drop in the solubilizing efficiency of the polymer. Thus it was reasonable to study the effect of pH on the solubilizing ability of PSSS-VN in aqueous solutions. Figure 7 shows the dependence of the total molal concentration of 2-undecanone solubilized in aqueous solutions of PSSS-VN on the pH.

The solubilization of 2-undecanone is relatively low in acidic solutions. It increases with increasing pH in the range  $1 < \text{pH} < 6$ , reaches a maximum at  $\text{pH} \approx 5.4$ , and decreases gradually to  $\text{pH} \approx 13$ . The observed phenomenon may be explained by taking into account the changes in the dimensions of the polymer coil. It has been found that the effective hydrodynamic volume of the polymer core also depends on the pH of the solution (Figure 7, line b). A comparison of the data presented in Figure 7 (lines a and b) indicates that there is a correlation between the dimensions of the polymer core and the efficiency of the solubilization process. Interestingly, the solubilization of 2-undecanone is more effective when the coil is in a more expanded form. The opposite trend was observed during studies of the solubilization of polynuclear aromatic compounds in aqueous solutions of PSSS-VN at different values of pH and ionic strength.<sup>8</sup> This difference is probably due to two factors: the size of the solubilized molecule and its ability to penetrate the interior of the polymer coil.

It should be stressed, however, that even when the polymer coil is in its most compact conformation, solubilization of 2-undecanone is still efficient. The real decrease in 2-undecanone solubility was observed in the region  $\text{pH} < 2.3$  where protonation of the pendant sulfonate



**Figure 8.** Total concentration of 2-undecanone in aqueous PSSS-VN solution as a function of pH at constant ionic strength ( $\mu = 1 \times 10^{-1}$ , polymer concentration  $c = 1 \times 10^{-5}$  M).

groups commences.

It was recognized that the dependence of the solubilization on pH could be distorted by changes in the ionic strength of the solutions at different pH values. In order to isolate the effect of pH on the solubilization process, separate experiments were performed at a constant ionic strength ( $\mu = 1 \times 10^{-1}$ ). Although the same general behavior was observed, the effect of pH on the magnitude of the solubilization process was considerably suppressed (see Figure 8).

## Conclusions

The results of this study have shown that aqueous solutions of PSSS-VN are very efficient at solubilizing 2-undecanone. The solubilization process is spontaneous. The values of the distribution coefficients are high. The pH and ionic strength effects are relatively small and reflect changes in the dimensions of the polymer coil. Hence, in an aqueous solution, PSSS-VN forms hydrophobic microdomains within the polymer coil regardless of the pH and ionic strength. This feature is very promising for possible practical applications of the system.

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