Preparation and Electrochemical Characterization of Poly(*N*-isopropylacrylamide-*co*-acrylic acid) Gels Swollen by Nonaqueous Solvents: Alcohols

Wojciech Hyk[†] **and Malgorzata Ciszkowska***

Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York 11210-2889

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Preparation and electrochemical characterization of poly(*N*-isopropylacrylamide-*co*-acrylic acid), NIPA-AA, gels swollen by organic solvents are described. Five simple alcohols, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, were chosen for these studies. Transport properties of gels swollen by alcohols for several NIPA-AA concentrations were investigated using steady-state voltammetry at microelectrodes with 1,1′-ferrocenedimethanol as an electroactive probe. Diffusion coefficients of 1,1′-ferrocenedimethanol determined over the temperature range 5−55 °C were used to evaluate the activation energy of the probe diffusion and to estimate the local microscopic viscosity of the gels using the Arrhenius equation and the Stokes−Einstein relation, respectively. It was found that an increase in the solvent viscosity is accompanied by an increase in the macroscopic viscosity of the gel; however, an enormously large value of macroscopic viscosity has an insignificant effect on the transport parameters for uncharged species. Diffusion of an uncharged probe in gels was almost as fast as in corresponding liquid media (alcohols). Change in the composition of NIPA-AA/alcohol gels from 2.5 to 4.0% polymer concentration influenced the diffusion coefficient value at 25 °C and activation energy of diffusion by less than 18% and 13%, respectively. No volume phase transition of NIPA-AA gels was observed while swollen by alcohols, a phonomenon well-known for NIPA-AA gels swollen by water, indicating a key role of hydrogen bonds in that process. The strength of hydrogen bonds at amide groups of the NIPA-AA polymer swollen by alcohols and water was examined by Fourier transform infrared spectroscopy, FT-IR.

Introduction

Polymeric hydrogels consisting of poly(*N*-isopropylacrylamide) and acrylic acid, NIPA-AA, have been studied extensively in recent years.[1−3] Much attention has been paid to the volume phase transition and transport properties of these gels because of their potential applications in drug delivery systems, separation techniques, and construction of sensors. It is known that NIPA-AA gels undergo temperature- or pH-induced reversible volume phase transition while swollen by water or aqueous solutions. Because these gels exhibit dramatic changes in their structure by responding to environmental changes, they have been increasingly studied as vehicles for applications such as drug delivery, separation media, and the construction of sensors.

Two effects are essential in understanding the thermally induced volume phase transition of *N*-isopropylacrylamide hydrogels. The first is attributed to thermal destruction of hydrogen bonds between water molecules and hydrophilic groups such as −CO− or −NH− in *N*-isopropylacrylamide units,[4,5] while the second one is due to the hydrophobic interactions between water molecules and nonpolar, hydrophobic segments of the polymeric chain.[6] To demonstrate the significance of these two effects for the temperature-induced volume phase transition, the swelling agent should be changed for a nonaqueous solvent. Such a replacement could also lead to the new information on the transport properties of NIPA-based gels swollen by organic solvents.[7]

In this work, we present a new method of preparing NIPA-AA gels swollen by nonaqueous solvents with a well-defined concentration of an electroactive probe. It should be emphasized that the procedure proposed here allows one to prepare new polymeric gel materials. The unique feature of these materials such as "solid-state" storage of organic solvents and solutions provides an alternative environment for kinetic and physical studies in organic phases as well as organic synthesis.

We study transport properties of the prepared gels under various experimental conditions of polymer concentration and temperature. Five simple alcohols (methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol) were chosen for the examination and 1,1′-ferrocenedimethanol served as a probe molecule.

One of the physical quantities that characterize transport properties of any medium is the diffusion coefficient of a probe in that medium. Recently, it has been shown that steady-state voltammetry at microelectrodes is a very convenient method for the determination of the diffusion coefficient of electroactive probes in gels.[8−11] This parameter can be determined from the steady-state current, I_s, which for disk microelectrodes is given by the following expression:

$$I_s = 4nFDc^b r_e \qquad (1)$$

where n denotes the number of electrons transferred per molecule, F is the Faraday constant, D and c^b are diffusion coefficient and bulk concentration of the probe, respectively, and r_e is the radius of the disk microelectrode.

Diffusivity of a probe determined over a wide temperature range allows calculation of the activation energy of diffusion, E_a, according to the Arrhenius equation:

$$D = Ae^{-E_a/RT} \qquad (2)$$

* Corresponding author. E-mail: malgcisz@brooklyn.cuny.edu.
† Permanent address: Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland. E-mail: wojhyk@chem.uw.edu.pl.
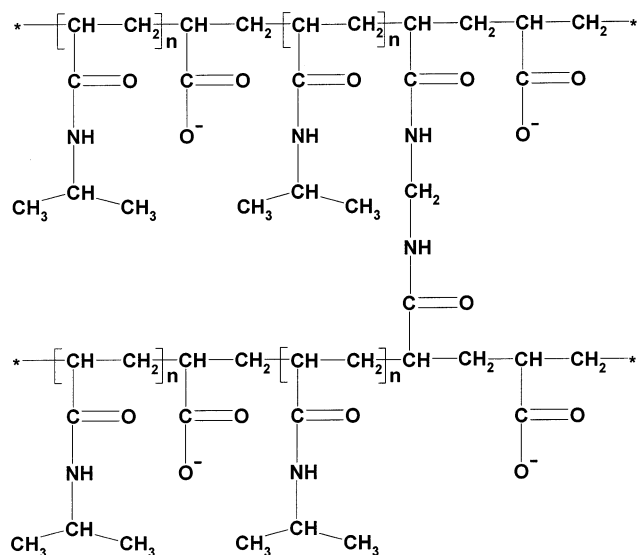
11470 *J. Phys. Chem. B, Vol. 106, No. 44, 2002*

Hyk and Ciszkowska

Figure 1. Schematic structure of *N*-isopropylacrylamide-*co*-acrylic acid polymer cross-linked with *N,N′*-methylenebisacrylamide.

where *A* is the preexponetial factor, *R* is the gas constant, and *T* denotes absolute temperature.

Finally, local viscosity of the NIPA-AA/alcohol gel network can be determined from the diffusion coefficient of a probe using the Stokes−Einstein relation:

$$\eta = \frac{kT}{a\pi D r_h} \tag{3}$$

where *k* is the Boltzmann constant, *a* corresponds to 6 (hard-sphere relation for sticking boundary conditions) or 4 (slip boundary conditions), and r_h denotes the hydrodynamic radius of the diffusing species.

Experimental Section

Chemicals. All solvents, methanol (MeOH, anhydrous, 99.8%), ethanol (EtOH, anhydrous, 99.5+%), 1-propanol (PrOH, anhydrous, 99.7%), 1-butanol (BuOH, anhydrous, 99.8%), and 1-pentanol (PnOH, anhydrous, 99+%) were purchased from Aldrich. The probe, 1,1′-ferrocenedimethanol (Fe(C_5H_4)$_2$(CH_2-OH)$_2$ or Fc(MeOH)$_2$, 98%) was purchased from Aldrich. High-purity lithium perchlorate (LiClO$_4$, 99%, Fluka) was chosen as the supporting electrolyte. All chemicals were used as received.

Poly(*N*-isopropylacrylamide-*co*-acrylic acid) polymer cross-linked with *N,N′*-methylenebisacrylamide (BIS) was synthesized and purified according to the previously described procedure.[10] The mole fraction of each monomer was 0.94:0.05:0.01 for NIPA, AA, and BIS, respectively. The schematic structure of the cross-linked NIPA-AA polymer is shown in Figure 1.

Fourier Transform Infrared Spectroscopy (FT-IR) Measurements. FT-IR spectra were obtained using a Nicolet Impact 410 FTIR spectrometer controlled with OMNIC software (Nicolet). We have found that Parafilm may serve as a convenient material for the gel sample container. A very small gel sample was spread between two pieces of Parafilm and then was placed in the IR instrument. The spectra were recorded at room temperature and were background-corrected.

Voltammetric Measurements. Electrochemical measurements were performed using an AMETEK PARC model 283 potentiostat, controlled via software by a PC. All experiments were carried out in a three-electrode system consisting of a platinum wire counter electrode, a silver/silver chloride reference

electrode, and a 5 *μ*m radius platinum disk microelectrode (Project Ltd., Warsaw, Poland). The electrode system was placed in a water-jacketed glass cell. The temperature of that cell was controlled using a refrigerated circulator (Isotemp model 1016P, Fisher Scientific). Before each experiment, the microelectrode was polished with diamond suspension (0.1 *μ*m, Buehler) on a wet pad, rinsed with water, and then dried using ethanol. The surface of the microelectrode was inspected optically with a Nikon model Epiphot 200 inverted microscope for reflected light.

Steady-state voltammetry experiments were performed at a scan rate of 10 mV/s over the temperature range 5−55 °C. Five replicates of voltammograms were taken at each temperature.

Viscosity Measurements. Measurements of gel viscosity were performed at room temperature (23 °C) using a Brookfield digital viscometer (model DV-E) with a HA/HB spindle set. The spindle no. 29 was selected for the measurements. The rotational speed of the spindle was set to 3 rpm. The instrument was calibrated with Brookfield viscosity standard of 5080 mPa s at 25 °C.

Gel Preparation. The newly synthesized NIPA-AA hydrogel was carefully purified. The purification procedure consisted of collapsing the gel at the temperature of approximately 80 °C, which is well above the gel volume phase transition temperature of 45 °C. The released solution was poured off, and several hundred milliliters of ultrapure water (Milli-Q, Millipore) was added to the collapsed gel. The gel was allowed to swell at room temperature for several hours. This procedure was repeated at least three times.

After the purification, the collapsed gel was placed in an oven for several days at 60 °C. During this period of time the gel was dehydrated and a soft, milky polymeric substance was transformed into transparent very hard material. The latter was ground to a fine powder using a laboratory grinder (Micro-Mill, Bel-Art Products, Pequannock, NJ). The powder was further dried until the changes in its mass were less then 0.5%.

The preparation of NIPA-AA gels swollen by alcohol consisted of mixing a known amount of dry, ground NIPA-AA polymer with alcohol solution, containing a known concentration of 1,1′-ferrocenedimethanol (approximately 2 mM) and LiClO$_4$ (approximately 5 mM). The solution was left overnight at room temperature in a calibrated cylinder to form a transparent gel. The change of the volume during the swelling process was negligible (less than 0.5%). The concentration of the supporting electrolyte was sufficiently small not to change the viscosity of the solvent, either as a bulk phase or trapped in the gel structure.

Results and Discussion

FT-IR Spectroscopic Studies. To verify an importance of the role of hydrogen bonds in the swelling behavior and volume phase transition phenomenon of NIPA-AA gels, samples of gels swollen by five alcohols, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol and water were examined by FT-IR spectroscopy. The obtained spectra are presented in Figure 2 and they are focused on the position of absorption maxima of amide groups (i.e., amide I: C=O stretching and amide II: N−H bending) of poly(*N*-isopropylacrylamide-*co*-acrylic acid). We have found that for all alcohols the absorption maxima of amide I of the polymer are located between 1651 and 1653 cm^{-1} while those of amide II are between 1550 and 1552 cm^{-1}. For the hydrogel, the wavenumbers for amide I and II are 1640 and 1560 cm^{-1}, respectively. It has been reported that the stretching and bending peaks are shifted to the lower and higher frequencies, respectively, as hydrogen bonding strength increases.[5] As
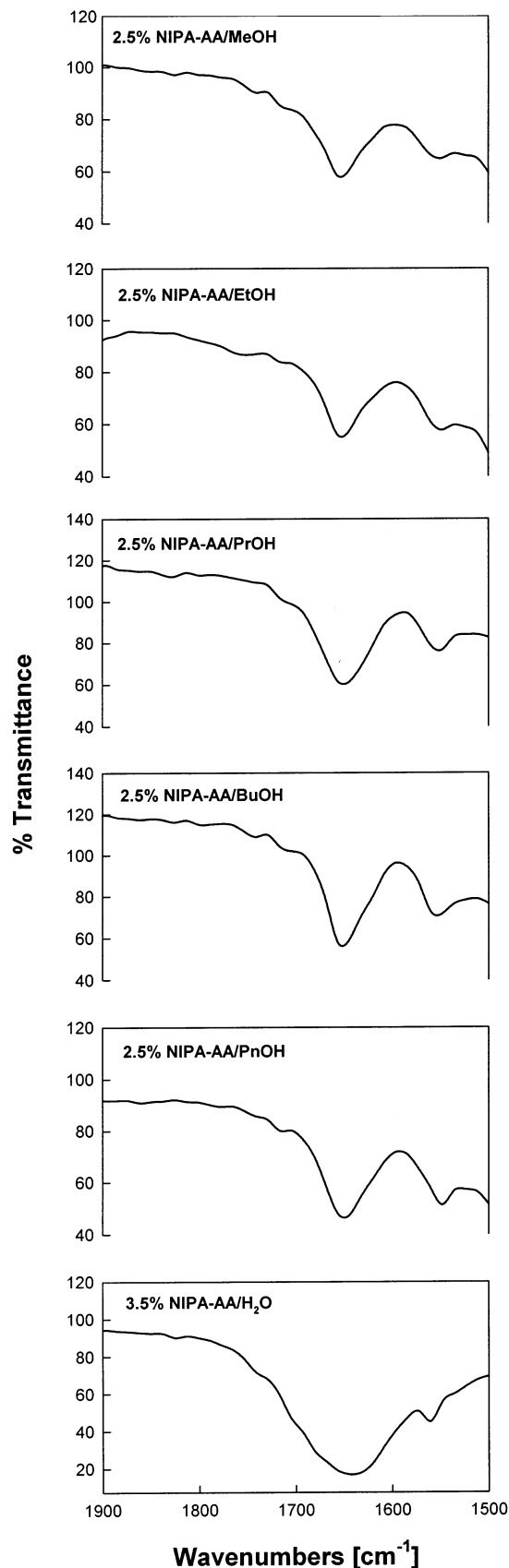
NIPA-AA Gels Swollen by Nonaqueous Solvents

J. Phys. Chem. B, Vol. 106, No. 44, 2002 **11471**

Figure 3. Linearized temperature dependencies of diffusion coefficient of 1,1′-ferrocenedimethanol in 1-propanol solution with 5 mM $LiClO_4$ (1) and in 2.5 (2), 3.5 (3), and 4.0% (4) NIPA-AA/PrOH gels with 5 mM $LiClO_4$. The inset shows the set of voltammograms at 5.2 (curve a), 14.8 (b), 25.0 (c), 35.0 (d), 45.0 (e), and 55.0 (f) °C for 3.5% NIPA-AA/1-propanol gel.

NIPA-AA polymer and water is much larger than that between polymer and alcohols.

It should be mentioned here that the hydrogen bonding in NIPA-AA gel structure plays an important role in the process of the volume phase transition of the gel. No volume phase transition of NIPA-AA gels, as determined visually, was observed over the temperature range 5−85 °C while swollen by alcohols.

Probe Diffusion in the NIPA-AA/Alcohol Gels. 1,1′-Ferrocenedimethanol, used as a probe, gives one-electron, reversible anodic response at Pt microelectrodes in all tested alcohols.[12] Voltammograms for the oxidation of this redox system in alcohol solutions and NIPA-AA/alcohol gels of 2.5, 3.5, and 4.0% polymer concentration were well reproducible over the temperature range 5−55 °C with the coefficient of variation less than 3%. Diffusion coefficients of the probe were determined from the steady-state limiting currents, I_s, according to eq 1 for both liquid and gel media. The exemplary set of the linearized temperature dependencies of the probe diffusion coefficient for 1-propanol solution and NIPA-AA gel swollen by 1-propanol is presented in Figure 3.

As shown in Figure 3, temperature dependencies of diffusivities of the probe were analyzed in terms of the linearized Arrhenius relation given by eq 2. In all cases linear correlation between $\ln(D)$ and $1/T$ was good and the correlation coefficient departed from 1 by less than 0.005. The slopes of these dependencies were used to calculate the activation energy of diffusion in both liquid and gel media.

Experimentally determined values of diffusion coefficients at 25 °C ($D^{(25)}$) and the calculated values of activation energy of diffusion (E_a) of 1,1′-ferrocenedimethanol in both liquid and gel media are listed in Table 1 for all studied alcohols. As one can see, the differences between D- and E_a-values in the gel and the corresponding alcohol solution are relatively small. The change in the composition of NIPA-AA/alcohol gels from 2.5 to 4.0% resulted in no more than 18% and 13% changes in the diffusion coefficient value at 25 °C and activation energy of diffusion, respectively. It can be noted that the higher the polymer concentration is, the larger differences between probe diffusivity determined in the gel and the corresponding alcohol solution are observed. In other words, the magnitude of the probe diffusion coefficient is inversely proportional to the polymer concentration. However, for the largest concentration of NIPA-

Figure 2. IR spectra of amide group bands of NIPA-AA gels swollen by methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and water.

one can see from Figure 2, the amide I and II peaks shift to lower and higher frequencies, respectively, as alcohols are exchanged for water. This indicates, as expected, that the strength of hydrogen bonds between C═O and N−H groups of
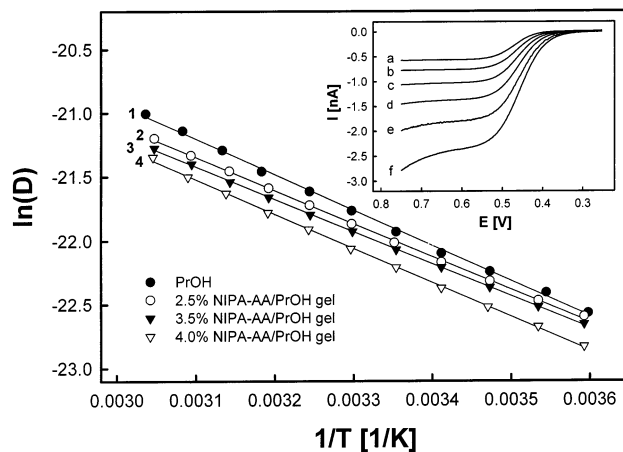
TABLE 1: Diffusion Coefficient at 25 °C, $D^{(25)}$, Activation Energy of Diffusion, E_a, of 1,1′-Ferrocenedimethanol in Alcohol Solutions and NIPA-AA/Alcohol Gels[a]

NIPA-AA concentration	$(D^{(25)} \pm s(D^{(25)})) \times 10^{10}$ [m²/s]	$E_a \pm s(E_a)$ [kJ/mol]	$\eta^{\prime(25)} \pm s(\eta^{\prime(25)})$ [mPa s]
	Methanol		
0	9.49 ± 0.08	13.2 ± 0.3	0.54[b]
2.5%	9.18 ± 0.05	11.5 ± 0.3	0.56 ± 0.01
3.5%	8.99 ± 0.01	11.4 ± 0.2	0.58 ± 0.09
4.0%	8.70 ± 0.02	10.1 ± 0.1	0.59 ± 0.01
	Ethanol		
0	5.30 ± 0.01	15.5 ± 0.4	1.07[b]
2.5%	4.87 ± 0.09	13.9 ± 0.2	1.17 ± 0.02
3.5%	4.64 ± 0.06	13.8 ± 0.3	1.23 ± 0.01
4.0%	4.29 ± 0.05	14.7 ± 0.3	1.33 ± 0.02
	1-Propanol		
0	2.99 ± 0.02	23.1 ± 0.3	1.95[b]
2.5%	2.75 ± 0.01	21.5 ± 0.2	2.12 ± 0.01
3.5%	2.60 ± 0.03	21.0 ± 0.1	2.24 ± 0.03
4.0%	2.26 ± 0.01	22.3 ± 0.2	2.57 ± 0.02
	1-Butanol		
0	2.19 ± 0.01	24.3 ± 0.2	2.54[b]
2.5%	1.91 ± 0.01	23.5 ± 0.1	2.92 ± 0.01
3.5%	1.84 ± 0.01	24.8 ± 0.2	3.03 ± 0.02
4.0%	1.59 ± 0.01	25.8 ± 0.3	3.52 ± 0.02
	1-Pentanol		
0	1.68 ± 0.04	24.7 ± 0.2	3.62[b]
2.5%	1.57 ± 0.02	25.3 ± 0.1	3.85 ± 0.11
3.5%	1.51 ± 0.02	27.0 ± 0.3	4.02 ± 0.11
4.0%	1.46 ± 0.02	25.2 ± 0.3	4.15 ± 0.12

[a] Microscopic viscosities of the media, $\eta^{\prime(25)}$, at 25 °C are calculated using the Stokes−Einstein relation and assuming no-slip boundary conditions. [b] Viscosity of pure solvent.[15]
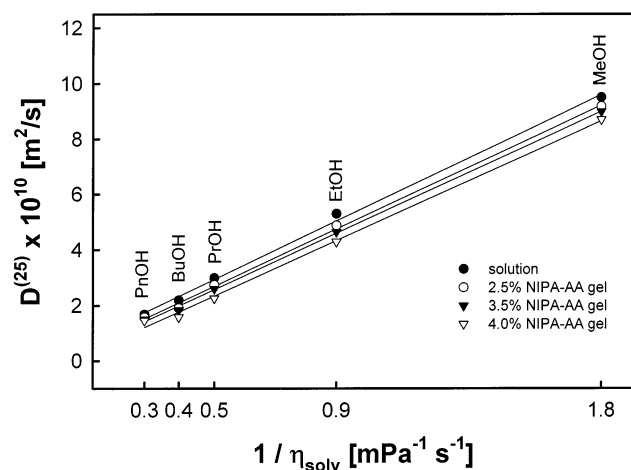
Figure 4. Diffusion coefficient of 1,1′-ferrocenedimethanol at 25 °C versus reciprocal of the solvent viscosity for 5 mM LiClO₄ alcohol solutions and 2.5, 3.5, and 4.0% NIPA-AA gels with 5 mM LiClO₄ swollen by methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol.

AA studied, i.e., 4% NIPA-AA gels, these differences do not exceed 28%. The results for the activation energy of diffusion are less correlated with the percentage of NIPA-AA.

Figures 4 and 5 show that both transport parameters for the probe change linearly with respect to the reciprocal and logarithm of the solvent viscosity, respectively. As expected, Figures 4 and 5 demonstrate that the increase in the solvent viscosity, in the sequence from methanol to 1-pentanol, leads to the larger activation barrier in the transport of the probe molecules in alcohol solutions (Figure 5) and, as a result, the values of diffusion coefficients decrease (Figure 4). Interestingly, the changes in $D^{(25)}$- and E_a-values determined in gels of various NIPA-AA concentrations follow those for liquid media.
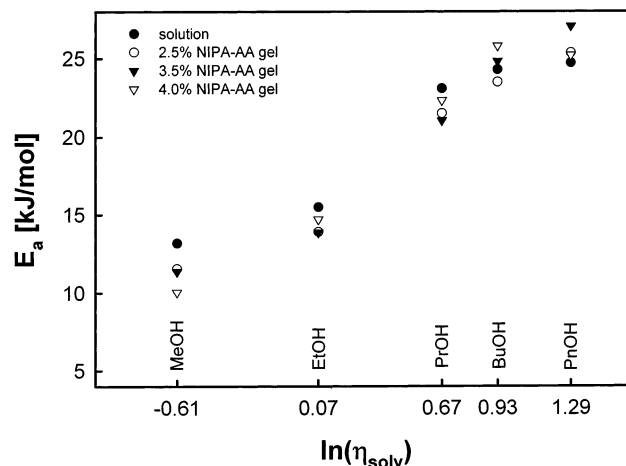
Figure 5. Activation energy of diffusion of 1,1′-ferrocenedimethanol versus logarithm of the solvent viscosity for 5 mM LiClO₄ alcohol solutions and 2.5, 3.5, and 4.0% NIPA-AA gels with 5 mM LiClO₄ swollen by methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol. The values of solvent viscosity refer to 25 °C.

Changes of the probe diffusion coefficient, $D^{(25)}$, as a function of the reciprocal of the pure solvent viscosity at 25 °C, η_{solv}, can be described by the following regression equations: $D^{(25)} = 5.03/\eta_{solv} + 0.35$ ($r^2 = 0.997$), $D^{(25)} = 4.93/\eta_{solv} + 0.16$ ($r^2 = 0.998$), $D^{(25)} = 4.85/\eta_{solv} + 0.08$ ($r^2 = 0.999$), $D^{(25)} = 4.77/\eta_{solv} - 0.11$ ($r^2 = 0.997$) for liquid alcohols and 2.5, 3.5, and 4.0% NIPA-AA gels swollen by those alcohols, respectively. In all these cases, zero value is located inside the confidence interval of the experimentally determined intercept ($b \pm t \, s(b)$, where b denotes intercept of the linear relation, t is the critical value of Student's t distribution at 95% confidence level, and $s(b)$ is the standard deviation of the intercept). This, first of all, validates applicability of the Stokes−Einstein relation to gel media. Additionally, the comparable values of the $D^{(25)}\eta_{solv}^{(25)}$ products for both gel and the corresponding liquid imply that the hydrodynamic friction of the fluid that is experienced by a probe molecule is similar in these systems. This indicates that probe molecules are transported through the channels filled with the solvent and shows that there are no significant specific interactions between probe molecules and the polymeric network. Note that both the slope and the intercept vary monotonically with the percentage of NIPA-AA polymer.

To fully understand the results presented in Table 1 and Figures 4 and 5 it is necessary to distinguish between the local microscopic viscosity, $\eta^{\prime}_{gel}$, that is experienced by probe molecules, and extremely large macroscopically observed viscosity, η_{gel}, of the gel. The former may be estimated on the basis of the hard-sphere version of the Stokes−Einstein relation (coefficient a in eq 3 equal to 6). This version of the Stokes−Einstein relation seems to be appropriate for the gel and liquid systems under studies, because 1,1′-ferrocenedimethanol molecules are larger than molecules of studied alcohols, and therefore, no-slip boundary conditions apply.[13] Assuming that the hydrodynamic radius of the diffusing uncharged species in the liquid medium is comparable to that in the liquid trapped in the gel structure, and employing the Stokes−Einstein equation, one obtains the following relation used for the $\eta^{\prime}_{gel}$ determination:

$$\eta^{\prime}_{gel} = D_{gel} \, \eta_{solv} = D_{soln} \qquad (4)$$

where D_{gel} is the diffusion coefficient of a probe in NIPA-AA/alcohol gel, η_{solv} and D_{soln} are the viscosity of a solvent and the

NIPA-AA Gels Swollen by Nonaqueous Solvents

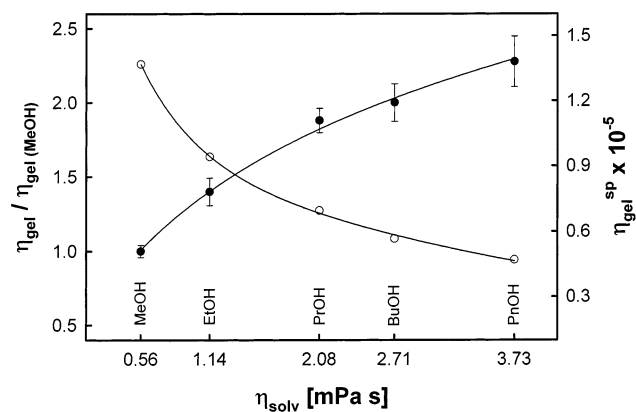*J. Phys. Chem. B, Vol. 106, No. 44, 2002* **11473**

Figure 6. Macroscopic viscosity (left axis, ●) and specific viscosity (right axis, ○) Of 2.5% NIPA-AA gels swollen by methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol containing 5 mM LiClO$_4$ versus pure solvent viscosity. Error bars represent standard deviations. $T = 23$ °C.

diffusion coefficient of a probe in the alcohol solution, respectively. The values of η'_{gel} obtained for 2.5, 3.5, and 4.0% NIPA-AA/alcohol gels are presented in Table 1.

Viscosity Measurements. Although the gelation process does not change significantly, the local microscopic viscosity of NIPA-AA gels swollen by alcohols, the macroscopic viscosity of these systems, η_{gel}, becomes extremely large. The results of the viscosity measurements for 2.5% NIPA-AA gels plotted as a function of pure solvent viscosity are presented in Figure 6. Since NIPA-AA gels exhibit strong non-Newtonian behavior, their viscosity changes with shear rate, the viscosities of the gels are made dimensionless with respect to the viscosity of the 2.5% NIPA-AA gel swollen by methanol. As one can see in Figure 6, an increase in the viscosity of the swelling agent (alcohol) results in an increase in the gel viscosity and in a decrease in the specific viscosity of the gel, defined as ($\eta_{gel} - \eta_{solv})/\eta_{solv}$. These changes are due to the decrease in the fractional volume occupied by NIPA-AA polymeric particles in the gel structure, because the volume occupied by the solvent molecules increases in the sequence from methanol to 1-pentanol. The changes in the specific viscosity of a polymeric system can be described by the following expression:[14]

$$\frac{\eta_{gel} - \eta_{solv}}{\eta_{solv}} = b \frac{V_{polymer}}{V_{solv}} \tag{5}$$

where $V_{polymer}$, V_{solv} are molar volumes of polymeric macromolecules and solvent ($V_{polymer} + V_{solv} = V_{total} = 1$), respectively, and b is the proportionality constant (it equals 2.5 for spherical macromolecules).

Inspection of eq 5 reveals that the product of the specific viscosity of the gel and the molar volume of the corresponding alcohol, $[(\eta_{gel} - \eta_{solv})/\eta_{solv}]V_{solv}$, should remain constant. We have found that for all NIPA-AA/alcohol gels studied in this work the mean value of this product is $5332/b$ dm^3/mol with the coefficient of variation 4%. The number obtained may be

treated as an average molar volume occupied by the polymer. Its relatively small value may suggest that the gel prepared in a way proposed by us, in fact, consists of many gel particles which are formed by swollen polymer grains.

Concluding Remarks

The procedure of preparing NIPA-AA gels swollen by nonaqueous solvents described in this paper has been examined for the series of five simple, aliphatic alcohols. It can also be successfully applied to other nonaqueous solvents, such as acetonitrile, formamide, dimethyl sulfoxide, acetone, etc., or their mixtures, and the corresponding projects are now underway in our laboratory.

The transport properties of such materials as NIPA-AA gels, characterized by the probe diffusion coefficient, can be easily measured using steady-state voltammetry at microelectrodes. The results for NIPA-AA gels swollen by alcohols and 1,1′-ferrocenedimethanol probe revealed that the viscosity, which is experienced by the probe molecules, is close to that of the solvent used as a swelling agent. The extremely large macroscopic viscosity of the gels has a small effect on transport parameters of the uncharged probe.

Characterization of NIPA-AA gels should also include the studies on volume phase transition phenomenon, since these gels are known to undergo temperature-induced volume phase transition while swollen by water. Interestingly, no volume phase transition of those gels was observed over the temperature range 5 −85 °C while swollen by alcohols. This observation may support the key role of hydrogen bonds, which are thermally destructed during the process of the volume phase transition.

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