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ORIGINAL CONTRIBUTION

Self-diffusion in poly(*N*-vinyl pyrrolidone) – poly(ethylene glycol) systems

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Abstract We have applied the PFG NMR technique to investigate the translational mobility in the PVP-PEG system as a function of composition and temperature at the stages of PVP-PEG complex formation, its swelling, and dissolution in excess of liquid PEG. It has been found that the variations of the spin-echo attenuation with PEG content, water amount, and temperature reflect the different stages. The first two stages are characterized by a distribution of the self-diffusion coefficients of PEG involved in the network. The dissolution shows two diffusion coefficients; the fast one is attributed to PEG molecules, the slow one to the associates of PEG and PVP. The temperature dependencies can be described by an Arrhenius law with an activation energy depending on the composition of the blend. The concentration dependence of the PEG self-diffusion coefficients in the blend occurred to be independent of the molecular weight of PVP. The results are discussed in terms of the Mackie-Meares model.

Key words Polymer blends · Self-diffusion · Complex formation

Introduction

Polymer blends usually demonstrate properties intermediate between those of the unblended components. New properties arise, as a rule, when the components of mixtures form an intermolecular complex that is in fact a new chemical entity with new characteristics [1]. This is the case for hydrogen bonding of short-chain poly(ethylene glycol) (PEG) terminal hydroxyl groups to the carbonyls in poly(*N*-vinyl pyrrolidone) (PVP) repeating units, which results in a stoichiometric complex formation [2, 3]. Poly(ethylene oxide) (PEO) and PVP with close molecular masses (M_w = 24,000–35,000 g/mol) have been shown to be incompatible [4], because both PVP and PEO have only electron-donating groups in their repeating units. At the same time, the glassy PVP is easily soluble in excess of liquid PEG of low molecular mass (less than 1000 g/mol at room temperature) [5]. This behavior implies the contribution of proton-donating hydroxyl groups at the ends of PEG chains to the miscibility with PVP. As recent studies have shown [6–8], the PVP mixing with liquid PEG (M_w = 400 g/mol) is a two-stage process. As only a comparatively small amount of plasticizer (PEG400) is added to PVP the glass transition temperature T_g falls dramatically ($T_g \approx 200$ K). This stage, demonstrating the large negative deviations in T_g from weight-average magnitudes, is consummated as the blend composition attains nearly

15 PEG400 macromolecules per 100 PVP monomer units (about 36 vol.% PEG, $\varphi_{PEG} = 0.36$). The large T_g deviations are generally regarded as a sign of a strong interaction between polymer components under mixing [9]. Actually, the mechanism of hydrogen bonding in PVP-PEG blends has been established by FTIR spectroscopy [2, 3]. Due to the location of reactive hydroxyl groups at the ends of PEG short chains, the PVP-PEG hydrogen bonding is accompanied by crosslinking of longer PVP macromolecules. The PVP-PEG complex has therefore a network-like structure [2]. Owing to their appreciable length and flexibility the PEG crosslinks act as spacers creating a free volume between the PVP chains [10]. Subsequent adding of plasticizer is not accompanied by an essential drop of T_g in the blend and can be understood as PVP-PEG network swelling and dissolution in excess of PEG. The flexible network structure of the hydrogen-bonded PVP-PEG complex imparts to the blend a rubber-like viscoelasticity [2, 11] and a pressure-sensitive character of adhesion towards different substrates [12–14]. Since these properties are also coupled with the enhanced molecular mobility of PVP-PEG blends, which is a result of free volume formation, the PVP-PEG adhesive hydrogels have found increasing applications in medicine as a universal diffusional matrix designed for controlled drug delivery [15, 16].

The present work is a first attempt to evaluate directly the molecular dynamics in PVP-PEG mixtures with the Pulsed Field Gradient (PFG) NMR method.

Experimental

PEG ('ALDRICH', Germany) with $M_w = 200$ and 400 g/mol and PVP K-17 (BASF) and K-90 ('Fluka', Germany) with $M_w = 8000$, and 1,000,000 g/mol, respectively, have been used after preliminary drying at $T = 378$ K until termination in weight loss. Since PVP is soluble only in excess of PEG, over the entire composition range the blends have been prepared by dissolving both polymeric components in water followed by drying the solution. In order to remove water, the blend of a certain composition was evacuated inside the NMR tube at 378 K. Following this procedure, the 'dry' PEG400-PVP mixtures contained no more than 1–5 wt% of residual water while PEG200-PVP blends retained 20–30% of water. In some experiments, the dry samples were moistened by a certain amount of water, up to 10 wt% of water content. Two samples of PVP blends with PEG200 content of $\varphi_{PEG} = 0.83$ were studied. The first sample was prepared by using water as a solvent and the second one by dissolving PVP in excess of liquid PEG200. The former retained 29 wt% of water. (Table 1)

The PFG NMR diffusion measurements were carried out by means of the home-built NMR spectrometer FEGRIS 400 [17, 18], operating at a proton resonance frequency of 400 MHz. We used the conventional stimulated echo rf-pulse sequence $\pi/2$-τ_1-$\pi/2$-τ_2-$\pi/2$-τ_1-echo with two identical pulses of magnetic field gradient applied after the first and the third rf $\pi/2$-pulse [19].

In a conventional pulsed field gradient NMR experiment the information about the self-diffusion processes is obtained from the analysis of the dependence of the spin echo amplitude $A(q,t_d)$ on the generalized scattering vector $q = \gamma\delta g$, with γ, δ, and g – denoting the gyromagnetic ratio, the duration and amplitude of the gradient pulses, and the observation time $t_d = \tau_1 + \tau_2$.

Table 1 Water contents of samples

Sample	Water content (%)
Dried mixture PEG400-PVP (K-90)	1–5
PEG400-PVP (K-90) with retained water	11
Wetted PEG400-PVP (K-90)	10
PEG400-PVP (K-17)	0
PEG200-PVP (K-90)	20–30
83% PEG200-PVP (K-90)	0

The normalized spin echo amplitude

$$S_{inc}(q, t_d) = A(q, 2\tau_1 + \tau_2)/A(0, 2\tau_1 + \tau_2) \quad (1)$$

is often considered as an incoherent intermediate dynamic structure factor [20], where

$$A(0, 2\tau_1 + \tau_2) = \frac{1}{2} A_0 \exp\left(-\frac{2\tau_1}{T_2}\right) \exp\left(\frac{\tau_2}{T_1}\right) \quad (2)$$

where A_o is the initial amplitude of the free induction decay after the first rf $\pi/2$-pulse, and T_1 and T_2 denote the spin-lattice and spin-spin relaxation times.

$S_{inc}(q,t_d)$ obeys the relation

$$S_{inc}(q, t_d) = \int \exp(iq(r)) P(r, t_d) \mathrm{d}r \quad (3)$$

where $P(r, t_d)$ denotes the propagator, i.e., the probability density for molecular displacements r during observation time t_d [18]. For free diffusion, the propagator is a Gaussian function with the mean square displacement given by Einstein's equation

$$\langle r^2 \rangle = 6Dt_d \quad (4)$$

where D is the self-diffusion coefficient.

The diffusion decay of the spin echo is then found to be

$$S_{inc}(q, t_d) = \exp(-q^2 D t_d) \quad (5)$$

For a multiphase system with a Gaussian propagator and identical relaxation behavior in each phase, the diffusion decay can be presented as a sum of exponential terms or by introducing a spectrum $p(D)$ of self-diffusion coefficients by the integral representation

$$S_{inc}(q, t_d) \int_0^\infty p(D) \left[\exp(-q^2 t_d D)\right] \mathrm{d}D \quad (6)$$

In many cases, the log-normal distribution

$$p(D) = \frac{1}{\sqrt{2\pi \ln^2 \sigma}} \exp\left(\frac{\ln^2(D/D^*)}{2 \ln^2 \sigma}\right) \quad (7)$$

may be used [21, 22], where ln σ is the width of the spectrum and D^* the median of the distribution. The distribution may be characterized by two mean values, namely, the average self-diffusion coefficient [23]

$$D_{av} = D^* \exp(0.5 \ln^2 \sigma) \quad (8)$$

and the most probable self-diffusion coefficient

$$D_{mp} = D^* \exp(-\ln^2 \sigma) \quad (9)$$

In our investigations the narrow-pulse approximation ($t_d \gg \delta/3$) holds, which means that strict validity of Eq. (2) is given. The interval τ_1 was limited to 3 ms. The duration δ of the gradient pulses was chosen between 0.2 ms and 1.85 ms. The maximum gradient amplitude g was 25 T/m.

We have analyzed the experimentally observed diffusion decays using the log-normal distribution at Eq. (5). In some measurements, the resulting curves $S_{inc}(q, t_d)$ were fitted by a sum of two exponentials:

$$S_{inc}(q, t_d) = p_1 \exp(-q^2 t_d D_1) + p_2 \exp(-q^2 t_d D_2) \quad (10)$$

where $p_{1,2}$ are the relative fractions of resonating species characterized by $D_{1,2}$, and hence $p_1 + p_2 = 1$.

The measurements were carried out in a temperature interval of 293–373 K with an accuracy of ± 1 K. The uncertainties of the self-diffusion measurements were not more than 10%.

Results and discussion

According to previous studies [2, 3], the stoichiometric complex PEG400-PVP is characterized by a constant composition of 15 macromolecules of PEG400 to 100 monomer units of PVP, that corresponds to $\varphi_{PEG} = 0.36$. It is interesting to follow the changes of mobility of the molecules while the complex is formed.

In the PEG-PVP blend PVP molecules are very immobile with transverse proton magnetic relaxation times much shorter than the experimental values of τ_1 [24]. As a consequence, the observed signal is due to PEG. Only in the case of dilute solutions does PVP contribute to the signal.

The short values of T_2 in the samples with $\varphi_{PEG} < 0.36$ did not allow us to perform the diffusion measurements in this concentration range.

In the sample PEG400-PVP with $\varphi_{PEG} = 0.36$ it was possible for us to follow the complex formation by observing the change of the diffusion over 4 weeks, following the preparation of the blend.

Figure 1a shows $S_{inc}(q, t_d)$ measured at different instants of time after the preparation of the blend. Over nine days the spin-echo attenuation $S_{inc}(q, t_d)$ with a log-normal distribution of self-diffusivities with a distribution width of $\sigma = 4.8$ ($D_0 = 2.3 \times 10^{-13}$ m^2/s) evolves to biexponential behavior ($D_{min} = 3.4 \times 10^{-14}$ m^2/s, $p_{min} = 0.75$; $D_{max} = 5.6 \times 10^{-12}$ m^2/s, $p_{max} = 0.25$). During the following period of 32 days, the relative fraction of slow protons in the signal increased with time from 0.75 up to 0.87, and the corresponding value of the self-diffusion coefficient from 3.4×10^{-14} m^2/s to 1.5×10^{-13} m^2/s, respectively. The observed change of $S_{inc}(q,t_d)$ reflects the processes of redistribution of PEG molecules in the blend and of PEG immobilization by complex formation with PVP macromolecules. The increase in the values of the minimum self-diffusion coefficient is caused by the growth of free volume for diffusion of the PEG-PVP complex segments.

Note that the amplitude of the spin-echo decreases with time after preparation as a consequence of the decrease of the relaxation time.

The spin-echo attenuation of the blend of the same content of PEG, but retaining 10% water occurred to be practically constant in time ($D^* = 4.9 \times 10^{-13}$ m^2/s, $\sigma = 1.16$ after 4 days, and $D^* = 4.6 \times 10^{-13}$ m^2/s, $\sigma = 1.2$ after 26 days) (Fig. 1b), so that water can be considered as a mediator of complex formation.

Figure 2a represents the diffusion decays $S_{inc}(q, t_d)$ observed in the samples PEG400-PVP with $\varphi_{PEG} = 0.36$ retaining 11% water and with $\varphi_{PEG} = 0.63$ and 0.9 for $t_d = 13$ ms at T = 303 K. The increase of PEG400 content induces the changes of $S_{inc}(q, t_d)$. The samples with $\varphi_{PEG} = 0.36$ (+11% water) and 0.63 exhibit diffusion decays $S_{inc}(q, t_d)$, which may be described by log-normal distributions with $\sigma = 1.16$ and 1.68, respectively. The log-normal fitting failed in describing the diffusion decay $S_{inc}(q, t_d)$ for $\varphi_{PEG} = 0.9$, so that we used the biexponential function with two self-diffusion

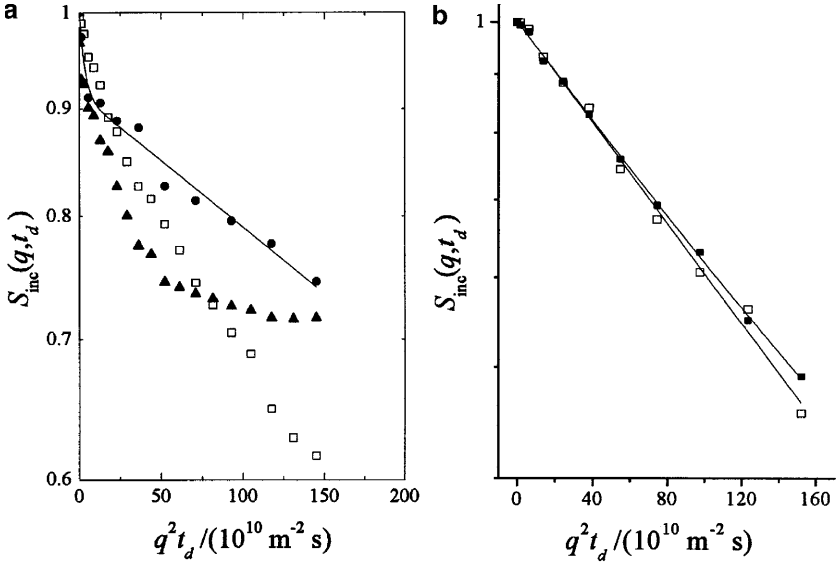

Fig. 1 **a** $S_{inc}(q,t_d)$ observed in dried PVP400-PVP1,000,000 blends, $\varphi_{PEG} = 0.36$, T = 303 K; 2 days (□), 9 days (▲), and 41 days (●) after blend preparation. *Solid lines* are the fitting curves. **b** The spin echo attenuations observed in the sample PVP400-PVP1,000,000–11% water, $\varphi_{PEG} = 0.36$, T = 303 K; 4 (□) and 26 (■) days after blend preparation. *Solid lines* are the fitting curves

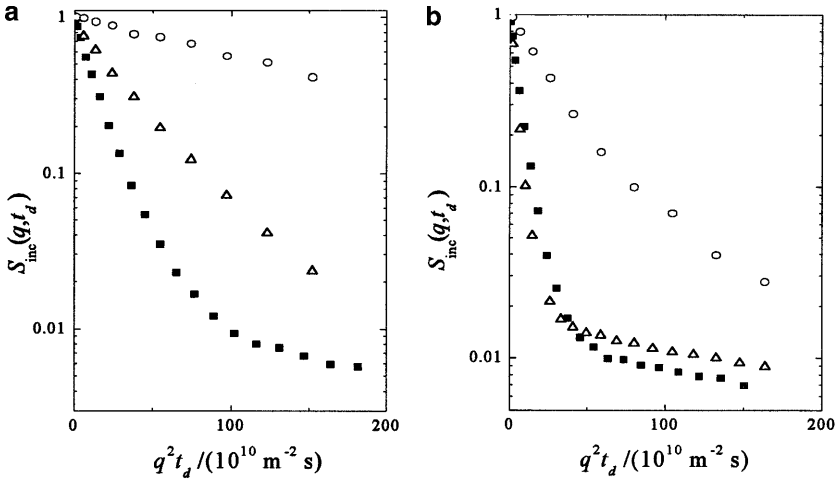

Fig. 2a, b PFG NMR diffusion decays of the stimulated echo observed in the samples PEG400-PVP1,000,000, $\varphi_{PEG} = 0.36$ with retained 11% water (○); $\varphi_{PEG} = 0.63$ (■) and $\varphi_{PEG} = 0.9$ (△) at: **a** T = 303 K; **b** 333 K. The observation time is equal to 13 ms

coefficients. Figure 2a shows the experimental results for $S_{inc}(q, t_d)$ with $\varphi_{PEG} = 0.9$ with the results of fitting ($D_{max} \sim 10^{-12}$ m^2/s ($p_{max} = 0.98$) and $D_{min} \sim 10^{-13}$ m^2/s ($p_{min} = 0.02$)). We denote the value of volume of PEG content corresponding to the appearance of two diffusivities as φ^*_{PEG}.

The tendency to phase separation (i.e., to two different diffusivities) increased with increasing temperature. Figure 2b shows $S_{inc}(q, t_d)$ at 333 K for the same systems. We observed two diffusion coefficients $D_{max} \sim 10^{-12}$ m^2/s ($p_{max} = 0.99$) and $D_{min} \sim 10^{-13}$ m^2/s ($p_{min} = 0.01$) for the sample with $\varphi_{PEG} = 0.63$. The change in the state of the complex appears in the variation of $S_{inc}(q, t_d)$ with increasing φ_{PEG} and temperature. Indeed, according to the results obtained by different methods [2, 3, 6, 7] (DSC, FTIR-spectroscopy, WAXS, and rheology) the increase of PEG content from 0.36 to 0.5 is known to lead to complex swelling and at $\varphi_{PEG} > 0.5$ to a dissolution of the complex in excess of liquid PEG. For elevated temperatures the onset of these processes are shifted to lower values of φ_{PEG}.

The component with $D_{min} \sim 10^{-13}$ m^2/s ($p = 0.01$–0.02), observed in the samples with $\varphi_{PEG} = 0.63$ and 0.9, is attributed to the PVP macromolecules associated with PEG. The unbound PEG molecules are moving with $D_{max} \sim 10^{-11}$ to 10^{-12} m^2/s. The appearance of the second component with φ^*_{PEG} indicates the crossover between complex swelling and dissolution at 303 K.

Analogous trends in the temperature dependence of $S_{inc}(q, t_d)$ are obtained for the sample PEG200/PVP with $\varphi_{PEG} = 0.83$ retaining 29% of water (Fig. 3). The increase of the amplitude of the component with $D_{min} \sim 10^{-13}$ m^2/s for higher temperature is due to the increase of the corresponding relaxation time with temperature (see Eq. 2).

Figure 4 shows the dependencies of the diffusivities of PEG on the composition of the dried mixtures for two molecular masses of PVP (8000 and 1,000,000) at 293 K, 333 K, and 353 K. Also represented are the data for the

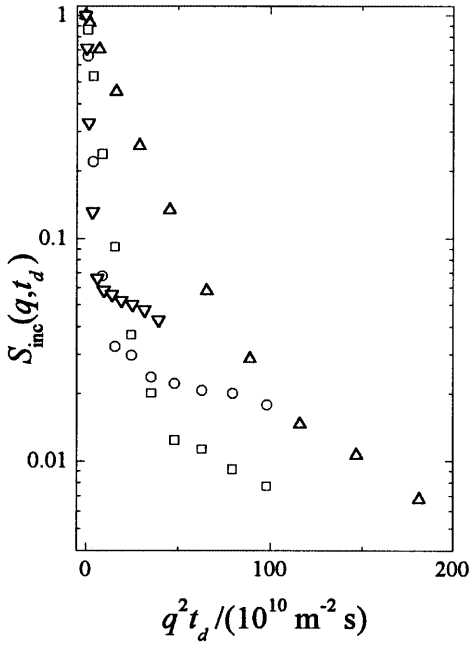

Fig. 3 Diffusion decays of the sample PEG200-PVP1,000,000, $\varphi_{PEG} = 0.83$, with 29% water retained at T = 293 (△), 313 (□), 333 (○), and 353 (▽) K. The observation time is 13 ms

wet samples at 293 K. The data for the dried blend PEG400-PVP with $\varphi_{PEG} = 0.36$ are the last observable after 41 days after preparation. The others were found to be unchanged over 2 months. Note that the self-diffusivities refer to PEG molecules bound in the complex in the interval of contents from 0.36 up to φ^*_{PEG} and unbound PEG for contents larger than φ^*_{PEG}. For the dried samples the extrapolation to zero concentration of PVP are in reasonable agreement with the diffusivities of bulk PEG400, $D_0 = 9.4 \times 10^{-12}$ m^2/s, 6.2×10^{-11} m^2/s, and 1.3×10^{-10} m^2/s, at 293 K, 33 K, and 353 K, respectively. In the wet samples (10% water

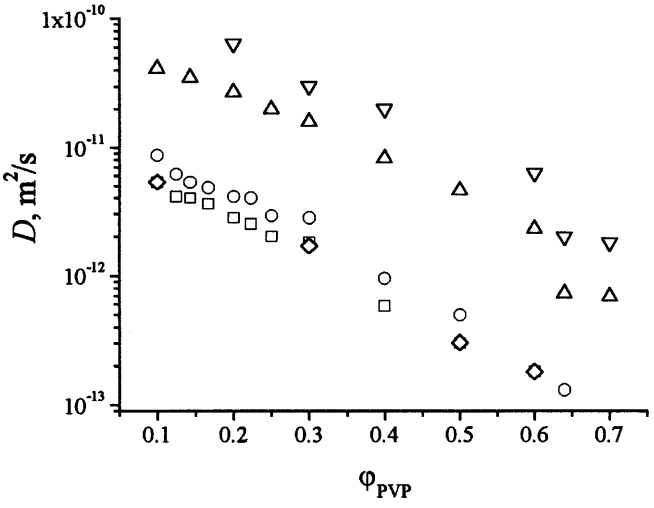

Fig. 4 The self-diffusion coefficients of PEG molecules in the mixture PEG400-PVP1,000,000 as a function of PVP concentration at the temperatures 293 K (□), 333 K (△) and 353 K (▽). The data for the blend with 36% PEG400 in PVP1,000,000 are the last observable (41 days after preparation). The symbols (○) represents the data for the samples, containing 10% of water at 293 K, symbols (◇) denote the self-diffusion coefficients in the samples PEG400-PVP8,000 at 293 K

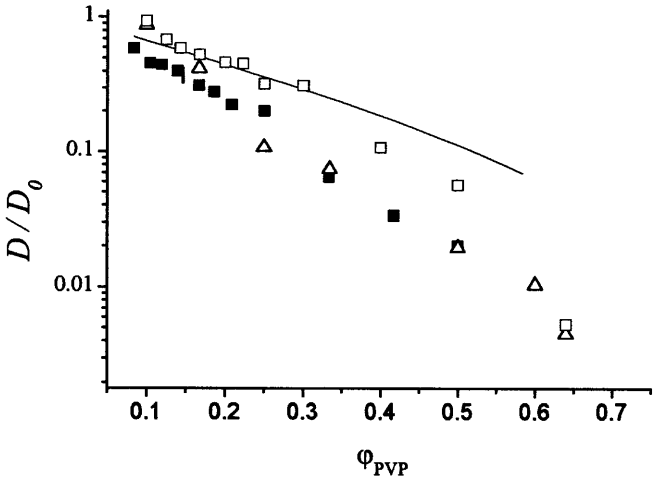

Fig. 5 The experimental data of self-diffusion coefficients of PEG in blend PEG-PVP1,000,000 as a function of PVP content. The symbols (■) represents the data for the dry samples, (□) – the samples containing 10% of water, (△) – samples with PEG200 retaining 20–29% of residual water. The *solid line* is calculated according to Eq. (11)

with respect to the whole blend) the diffusivities are enhanced by a factor of 1.5. It is seen that the self-diffusion coefficients of the PEG molecules in blends with PVP of different molecular masses (8000 and 1,000,000) coincide. Thus, primarily the interaction with the carbonyl groups of PVP, rather than the size of PVP-macromolecules controls the mobility of the PEG molecules. The logarithmic plots of D vs φ_{PVP} happened to be close to linear at 293 K, both for dried and wet samples. The increasing temperature causes a slight deviation from the linear behavior at high content of PVP.

The model of Mackie and Mears [25] has been successfully applied to rationalize the self-diffusion coefficient of water in macromolecular environment of different chemical structure [26]. This model is based on the obstruction effect by the polymer chains. They are considered as motionless and impenetrable obstacles that increase the tortuosity of the solvent. The Mackie-Mears [25] relation reads

$$D = D_0((1 - \varphi_{PVP})/(1 + \varphi_{PVP}))^2 \quad (11)$$

where in our case D characterizes the mobility of PEG molecules blended with PVP, D_0 is the bulk value of PEG diffusivity, and φ_{PVP} is the fraction of PVP.

Figure 5 represents D/D_0 vs φ_{PVP} plots for the dried and wet samples of the blends PEG400/PVP and PEG200/PVP with residual water, as well as the calculated curve. For the wet samples, D_0 is the most probable self-diffusion, measured in the aqueous solution of PEG. The data happened to be closed to the

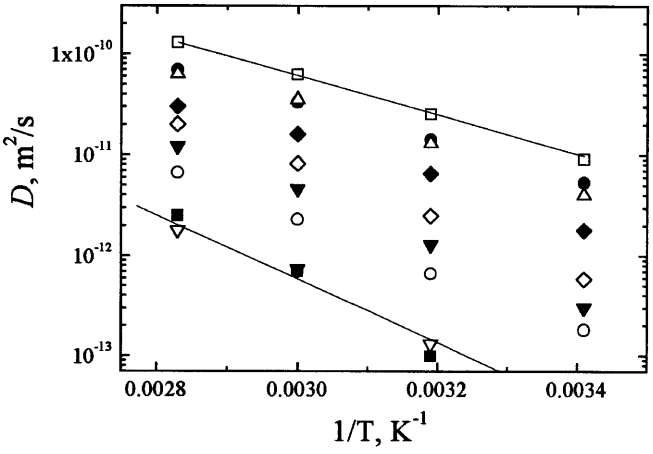

Fig. 6 The Arrhenius plots of PEG-400 self-diffusion coefficients in bulk (□) and in the blends with PVP at $\varphi_{PEG} = 0.9$ (●); 0.86 (△) ; 0.7 (◆) ; 0.6 (◇) ; 0.5 (▼); 0.4 (○) ; 0.36 (▽) ; 0.3 (■)

calculated curve in the interval of small content of PVP, while for the large values of φ_{PVP} the ratio D/D_0 deviates systematically from the model predictions.

For rationalizing the observed discrepancy between the calculated and measured curves, let us consider the data of the temperature measurements. In Fig. 6, Arrhenius plots of the self-diffusion coefficients of the PEG molecules are shown for the different values of φ_{PEG}. The data are well described by straight lines following the Arrhenius dependence

$$D = D' \exp(-E_a/RT) \quad (12)$$

where D' stands for a pre-exponential factor.

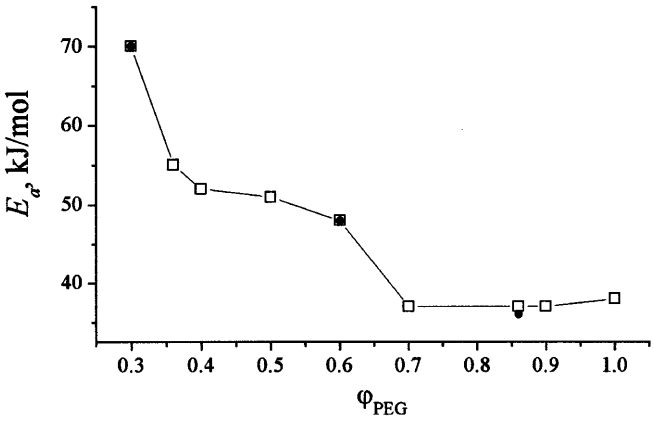

Fig. 7 The plot of the activation energy for PEG400 self-diffusion in the blends with PVP1,000,000 against the blends composition. The symbols (□) represent the data for the dry samples, (●) – the samples containing 10% of water. The *solid lines* are the result of fitting according to the Arrhenius law

The activation energies E_a of self-diffusion of PEG obtained from the corresponding slopes are represented in Fig. 7. As PEG content increases, E_a reduces from 70 kJ/mol for $\varphi_{PEG} = 0.3$, to ≈38 kJ/mol for $\varphi_{PEG} \geq 0.7$. The bulk value E_a^0 is 38 kJ/mol.

The observed dependence of E_a on the blend composition shows that for blends with $\varphi_{PEG} < 0.7$ (cf. Fig. 7) the influence of PVP is revealed in increased values of the activation energy, i.e., the decrease of self-diffusion coefficients is caused by the second factor of relation at Eq. (12). For $\varphi_{PEG} \geq 0.7$ (that corresponds to $\varphi_{PEG} < 0.3$; Fig. 4) the variations of D are caused by the pre-exponential factor in Eq. (12).

This indicates that the Mackie-Mears model may be used only for large φ_{PEG} values.

It has been found that the addition of 10% of water (with respect to the whole sample) to the blend with $\varphi_{PEG} = 0.30$, 0.60, and 0.86 did not influence the values of the activation energy. For these samples, the obtained values of $E_a = 70$ kJ/mol, 48 kJ/mol, and 36 kJ/mol coincide with the values for the dry sample (Fig. 7).

Conclusions

We have studied the molecular mobility in the system PEG-PVP as a function of composition and temperature in the stages of complex formation, swelling, and dissolution. It has been found that the variation of the patterns of spin echo attenuation with PEG content and temperature reflects the different stages. The first two stages are characterized by the spectrum of the self-diffusion coefficients of PEG involved in the network. During complex dissolution, we have observed two self-diffusion coefficients, the lowest one being attributed to PEG-PVP associates.

The concentration dependence, represented as log D vs φ_{PVP} plot, occurred to be approximately linear, being independent of the molecular mass of PVP. The Mackie-Mears model considering macromolecules as the obstacles for the motion of PEG molecules fails especially in the range of large PVP content.

The Arrhenius plots are linear and yield an activation energy of self-diffusion of PEG molecules depending on the composition of the system. We have found that for the formed complexes the activation energy is – by a factor of 2 – larger than in the complex solution and the bulk, respectively.

The concentration dependence of the self diffusion coefficients of PEG molecules can be explained by the interaction with the PVP segments and free volume effects of the network structure in the formed and swollen complex, while in diluted solutions the PVP-PEG associates are to be considered as the immobile obstacles.

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