

Studies of Polymer Solvation by Dielectric Relaxation Spectroscopy IV: Polyvinylpyrrolidone in Urea Derivatives at Different Temperatures

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The dielectric spectrum is measured up to 72 GHz of solutions of polyvinylpyrrolidone (PVP) in tetramethylurea (TMU), dimethylethylene urea and dimethylpropylene urea. Concentrations are up to a monomole fraction of 0.65 (PVP 1200) or 0.5 (PVP 40 000). Measuring temperatures are 20 °C for all systems and additionally 40 and 60 °C for the TMU solutions. For the description of the results a superposition of Debye type components is used, which are discussed in particular with respect to the solvent contributions. These can be distinguished into three regions: (i) Unaffected bulk-type; (ii) loosely affected, relaxation time and activation enthalpy increasing with increasing polymer content; (iii) quasi bound and moving together with the polymer. The solvation numbers (total of affected solvent per repeat unit of polymer) are about 1.5 to 2.

Introduction

Dielectric relaxation spectroscopy observes in principle the stochastic motion of molecular dipole moments and is therefore a suitable tool to study both solvent and solute dynamics in binary liquid mixtures. This method was applied in some previous publications [1–5] particularly to polymer solutions in order to gain information on the solvent rather than the polymer behaviour. It was found that those solutions can be characterized by dielectric relaxation times which are more or less independent of the polymer content, although the viscosity is remarkably increased in many cases. This finding, which contrasts sharply with the observations usually made with solutions of small molecules, may be considered as an expression of microheterogeneity in polymer solutions. It allows for a distinction of bulk type (unaffected) solvent contributions and those slowed down in their relaxation, thus obviously being affected by the polymer. The physical origin of the latter contribution may in a general sense be termed solvation.

As polymeric solute we had recently studied polyvinylpyrrolidone (PVP) with a number of different solvents [2, 3, 5]. Aqueous solutions of this polymer

are widely applied, and their dielectric relaxation properties have attracted interest because of their similarity to protein solutions [6, 7]. For an interpretation of the rather broad relaxation spectra, however, solvents of “simple” relaxation behaviour are advantageous, meaning aprotic liquids without self-association effects, which preferably should consist of quasi rigid molecules. With those substances the distinction of up to three states of the solvent (free, loosely affected and tightly bound) was inferred from the dielectric behaviour of PVP solutions, a model which then appeared to be applicable also to PVP solutions in associating solvents (alcohols, water) [5].

In the present communication we revert to the application of a “simple” solvent, namely tetramethylurea (TMU). In continuation of our previous studies we have now carried out temperature dependent measurements on PVP-TMU solutions over an increased concentration range in order to find out whether the proposed solvation picture may still be applicable. For the same purpose, the series of solvents is extended by two other urea derivatives, dimethylethylene urea (DMEU) and dimethylpropylene urea (DMPU). These are five and six-membered rings, respectively, and are presumably flexible to a certain degree. All three solvents, however, are “simple” liquids with respect to their dielectric relaxation behaviour inasmuch as there is no hint at self-association.

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Experimental

Solvents and polymers from Aldrich, BASF, and Fluka were used as obtained. Two PVPs were studied which had mean relative molar masses of 1200 and 40 000. Solutions were prepared up to the highest concentrations which could be handled with the measuring cells in view of their viscosity. Expressed as mole fraction x_{mPVP} of PVP monomeric repeat units, the upper concentration limit was $x_{\text{mPVP}}=0.65$ for PVP 1200 and 0.40 ... 0.50 for PVP 40 000.

The complex permittivity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of the pure solvents and of the solutions was measured at frequencies ranging between 2 MHz and 72 GHz employing different spot frequency apparatus. The accuracy is a few percent in ε'' . In a few cases, measurements were also made at 138 GHz. All systems were studied at 20 °C, the solutions in TMU furthermore at 40 and 60 °C.

Results

The relaxation behaviour of the polymer solutions exhibits some common features which first of all may be illustrated in Fig. 1 by a representative absorption spectrum $\varepsilon''(\omega)$, where ε'' stands for the (negative) imaginary part of the permittivity as already corrected for the conductivity contribution. Typically there is a high frequency absorption resembling that of the pure solvent but being broader and less intense. In addition there is a broad low frequency shoulder which increases as the polymer content.

The absorption of the pure solvents can roughly be described by Debye curves. The TMU absorption is actually of Debye character to within experimental uncertainty [8, 9], while the DMEU and DMPU absorption regions are slightly broadened possibly due to internal motions in these molecules [9]. Here we have chosen a description by Cole-Cole (CC) and Cole-Davidson (CD) functions though discrete Debye terms could be used as well. The relaxation parameters, viz. τ^* (relaxation time), S^* (relaxation strength) and CC or CD distribution parameter, are given in Table 1.

In order to obtain now a formal description of the solution spectra, it was first assumed that a spectral component of the same character as with the respective pure solvent persists in solution, i.e. a term with adjustable τ_i and S_i but fixed distribution parameter

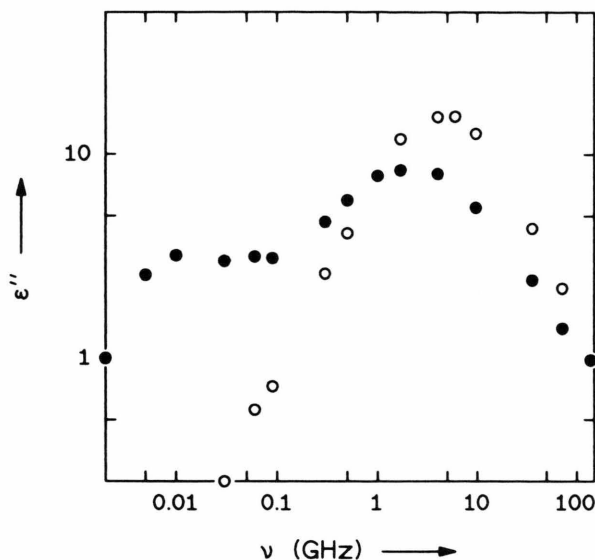


Fig. 1. Dielectric loss ε'' versus frequency ν for a representative example. Full symbols: PVP 1200-DMEU solution ($x_{\text{mPVP}}=0.29$, 20 °C), open symbols: Pure solvent DMEU.

Table 1. Pure solvents. Relaxation parameters τ^* , S^* and distribution parameters α or β (CC or CD, respectively).

	τ^* (ps)	S^*	
DMEU	36.5	34.2	$\alpha=0.04$
DMPU	88.6	32.1	$\beta=0.82$
TMU (20 °C)	28.2	21.6	
(40 °C)	21.0	19.3	
(60 °C)	16.3	17.7	

Distribution parameters are defined such that for the Debye case there is $\alpha=0$ but $\beta=1$.

according to Table 1 was introduced. A sum of this and additional Debye type spectral components C_i was fitted to the data, using the minimum number of terms necessary. Thus for TMU solutions the fitting function reads

$$\varepsilon''(\omega) = \sum S_i \frac{\tau_i \omega}{1 + \tau_i^2 \omega^2}, \quad (1)$$

while for the other two solvents one of the Debye components is replaced by a CC or CD component. Altogether up to five spectral components were needed. It was found that their relaxation times τ_i vary relatively little within each concentration series, so we made use of the variability range of the fitting procedure to keep them as constant as possible. The relaxation parameters τ_i and S_i obtained in that manner are

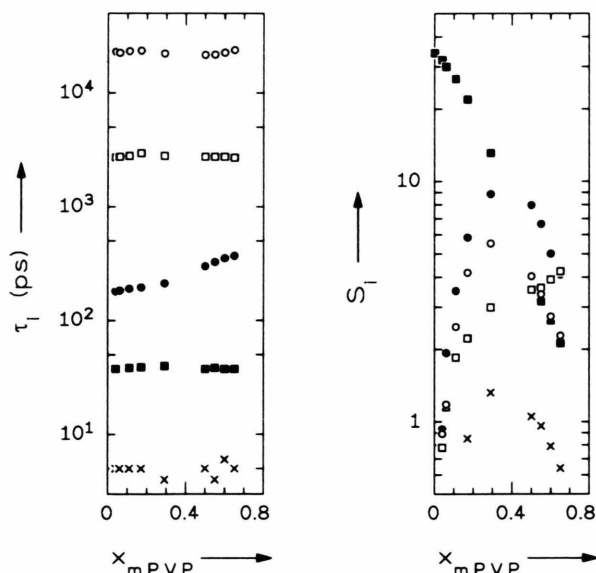


Fig. 2. System PVP 1200-DMEU (20°C). Relaxation parameters τ_i and S_i versus polymer mole fraction x_{mPVP} (referring to monomeric units). Symbols for spectral components: $\circ$ C_1 , $\square$ C_2 , $\bullet$ C_3 , $\blacksquare$ C_4 , $\times$ C_5 . Here, the DMEU component C_4 is a CC term with $\alpha=0.04$.

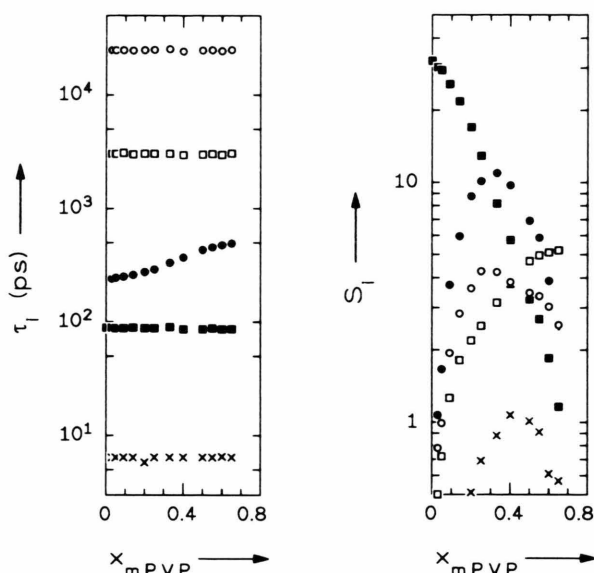


Fig. 4. System PVP 1200-DMPU (20°C), relaxation parameters. Symbols as Figure 2. Here, the DMPU component C_4 is a CD term with $\beta=0.82$.

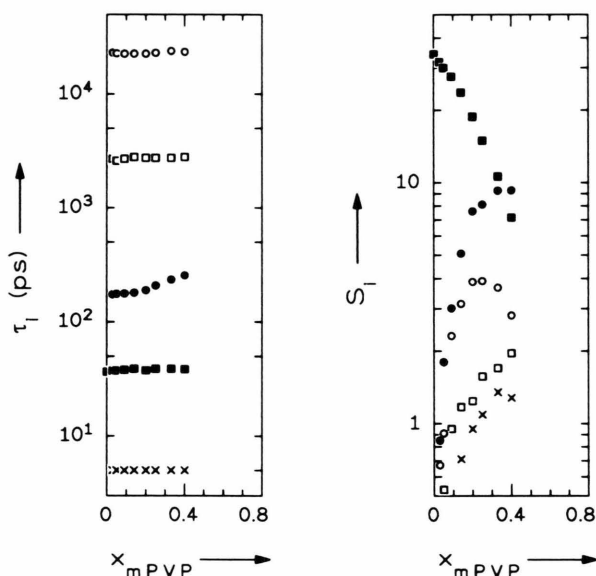


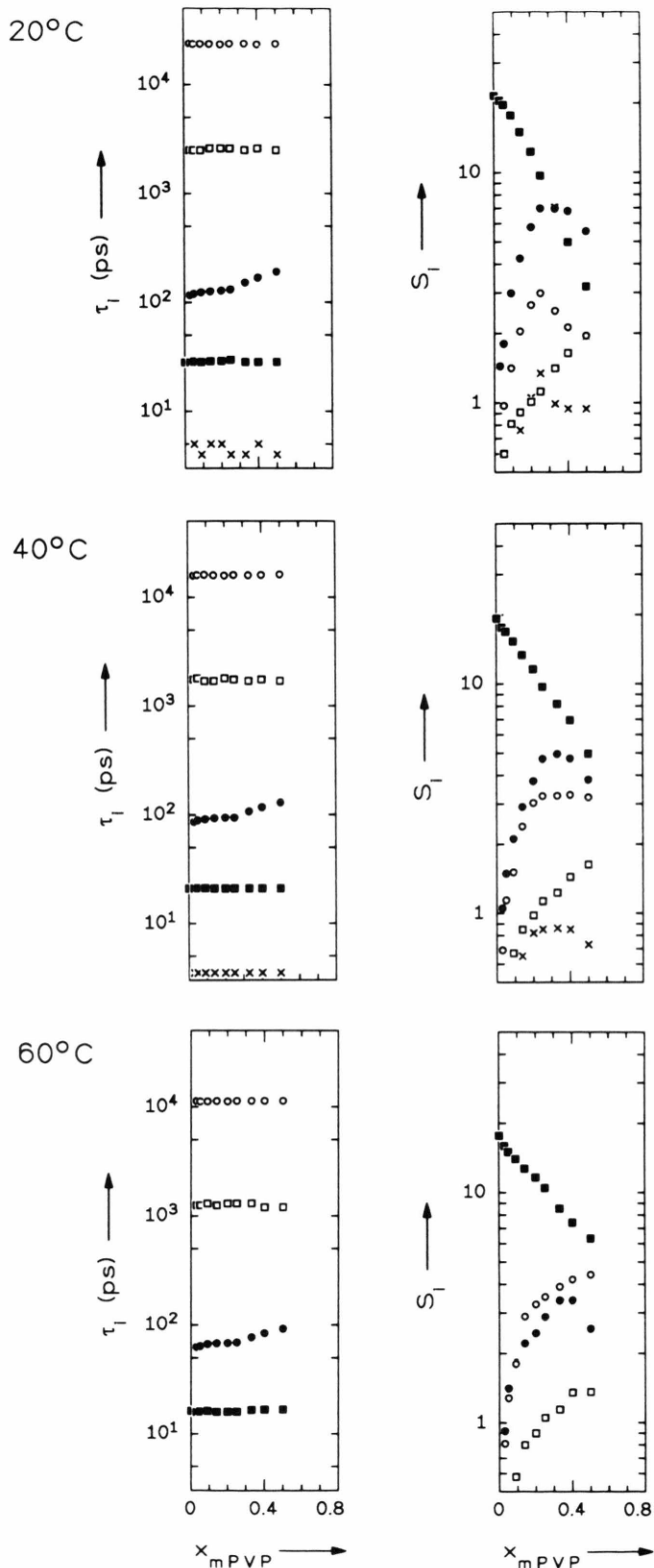
Fig. 3. System PVP 40000-DMEU (20°C), relaxation parameters. Symbols as Figure 2.

represented summarily for all the systems investigated in Figures 2–5.

One may notice the similarity of the present results to those previously found on other PVP solution systems [2, 3, 5]. This allows for an according assessment

of the spectral components, just as it might be gained from a cursory inspection of the qualitative features of the absorption curves. The following preliminary assignment is suggested (terming the components in the order of increasing frequency): C_1 and C_2 are likely to be due to the polymer. This assignment was previously substantiated by results on PVP solutions with nonpolar solvents [5]. The intermediate component C_3 , which by the way is the only one with a noticeable relaxation time alteration, is probably caused by affected solvent molecules, while C_4 , which stays at the pure solvent relaxation time, is doubtless due to unaffected solvent. The origin of the weak high frequency component C_5 , which was also observed in previous work, is still unclear. The underlying motion, however, is so fast than an involvement of solvent seems most probable.

Adopting that assignment, some further quantities shall be derived from the relaxation strengths S_i in order to show tendencies more clearly. For substances as the present solvents, which do not exhibit self-association effects, one can reckon with an approximate proportionality between total solvent relaxation strength and actual solvent concentration c_s . Thus gathering up the spectral components ascribed to the solvent, the total solvent relaxation strength $S_s=$



$S_3 + S_4 + S_5$ is expected to be

$$S_s^e = S_s^* \frac{C_s}{C_s^*} \quad (2)$$

(where the asterisk denotes the pure solvent). The ratio

$$V = S_s / S_s^e \quad (3)$$

is depicted in Figure 6. A corresponding argumentation for the polymeric solute is not permissible. Therefore only the relative intensity of the polymer spectral component C_1 is given as

$$W = S_1 / (S_1 + S_2) \quad (4)$$

in Figure 6.

Regarding the temperature dependent properties of the TMU solution systems, an activation enthalpy for the relaxation mechanism responsible for each of the spectral components can be obtained by formally applying an Arrhenius equation to the relaxation times τ_i ,

$$\tau_i = A e^{\Delta H_{\tau_i} / RT} \quad (5)$$

Taking into account the uncertainties of the τ_i values, that equation is found to be well obeyed. The relaxation times except for τ_3 are practically independent of the polymer concentration, and so are the respective ΔH_{τ_i} values, while ΔH_{τ_3} increases with increasing polymer content. Results are given in Table 2. For comparison the activation enthalpy for viscous flow in the pure solvent TMU, ΔH_η^* , is included in Table 2.

Discussion

Molar Mass Effects

First of all the influence of the PVP chain length on the relaxation parameters may be briefly regarded by comparing the two DMEU solution series containing PVP 1200 and PVP 40 000. Corresponding relaxation times of both series are closely alike. Concerning the relaxation strengths, however, there is a different influence on the components ascribed to the polymer, C_1 and C_2 , on the one hand, and on those assigned to the solvents C_3 to C_5 , on the other hand. At higher concentrations S_1 and in particular S_2 are tending to become

Fig. 5. System PVP 40000-TMU (20, 40, and 60 °C), relaxation parameters. Symbols as Figure 2.

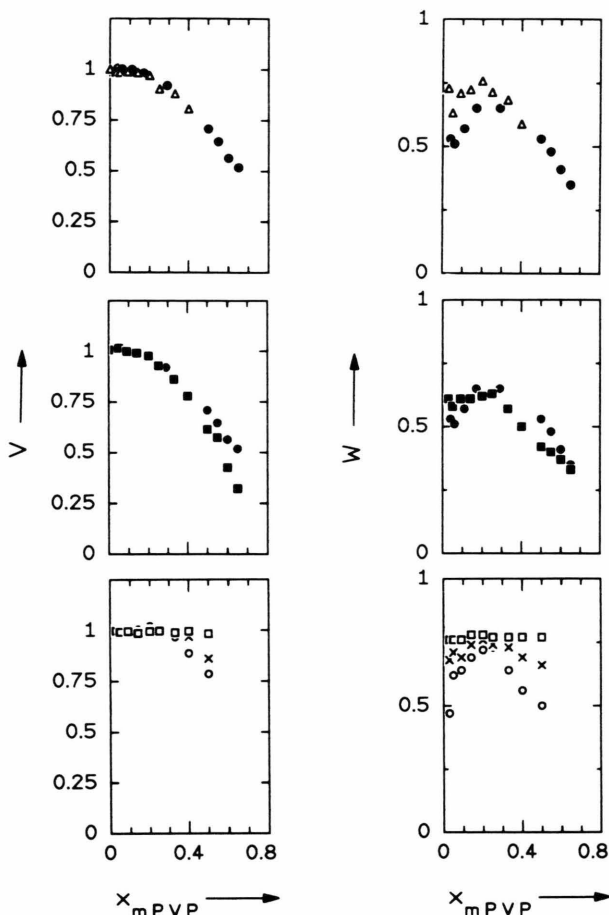


Fig. 6. Quantities V and W after (3, 4) versus polymer mole fraction x_{mPVP} . – Above: PVP 1200-DMEU (●) and PVP 40000-DMEU (Δ). – Middle: PVP 1200-DMEU (●) and PVP 40000-DMEU (Δ). – Below: PVP 40000-TMU at different temperatures, 20°C (○), 40°C (×), and 60°C (□).

Table 2. PVP 40 000-TMU system. Activation enthalpies ΔH_{τ_i} of spectral components C_i , and ΔH_{η}^* from viscosity of pure TMU.

ΔH_{τ_1}	ΔH_{τ_2}	ΔH_{τ_3} (kJ/mol)	ΔH_{τ_4}	ΔH_{η}^*
15.1 ±0.5	14.3 ±0.5	12.5–14.7	11.4 ±0.3	11.9

larger for PVP 1200 than for PVP 40 000 solutions, though the ratio W (Fig. 6) does only insignificantly differ between both series. In contrast, S_3 to S_5 do not exhibit any significant chain length effect, as may be seen from the quantity V also in Figure 6. It should be mentioned that significant chain length effects haven't

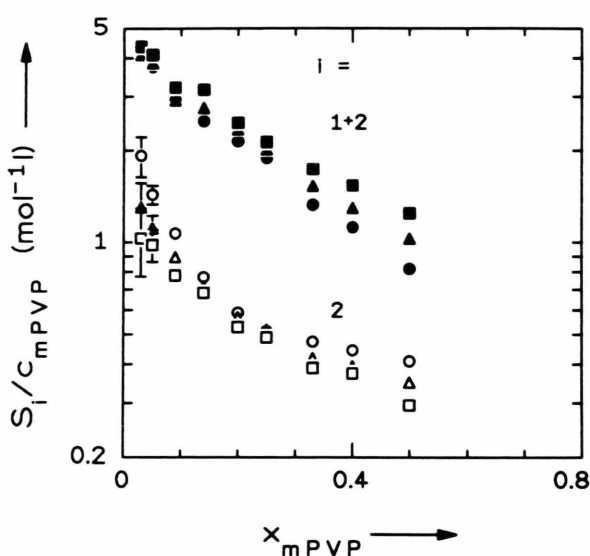


Fig. 7. System PVP 40 000-TMU. Normalized relaxation strengths S_i/c_{mPVP} of spectral components ascribed to the polymer versus polymer mole fraction x_{mPVP} . Temperatures 20°C (●, ○), 40°C (▲, △), and 60°C (■, □).

yet been observed with PVP in other solvents, so possibly the present finding may be peculiar to DMEU. However, here we want to direct attention to the solvent behaviour, and it can be stressed that the respective components C_3 to C_5 appear to be independent of the polymer chain length anyhow.

Polymer Relaxation Contribution

In view of the just-mentioned scope of this study a cursory glance at the relaxation contributions of the polymer (C_1 and C_2) will be sufficient.

The concurring relaxation times observed for the PVP 1200 and PVP 40 000 polymer components (τ_1 as well as τ_2) give evidence that the underlying motion cannot be the reorientation of whole macromolecules but is very probably a segmental motion. A plain suggestion is that longer and shorter chain segments may cause C_1 and C_2 , respectively, although these formally obtained two spectral components must not necessarily correspond to just two distinct physical processes but may stand for a distribution.

With reference to the TMU solutions, both the concentration and the temperature dependence of S_1 and S_2 can be considered. Normalized relaxation strengths S_i/c_{mPVP} are depicted for that purpose in Figure 7. For low polymer contents these are slightly larger than

estimated for independently oriented side group moments [5]. The general decrease of S_i/c_{mPVP} with increasing concentration (tending roughly towards the value expected for pure PVP) is thus indicative of structural alterations causing the moments of the groups to change from a perhaps constructive to an increasingly destructive orientational correlation. The total relaxation strength is altered in the same sense by either increasing the polymer concentration or decreasing the temperature, which both should be accompanied by the contraction of the polymer coils when gradually changing towards the drained state.

It is a noteworthy feature with respect to the following that at least at the lower temperatures (in particular 20°C) the magnitude of the slope of S_2/c_{mPVP} (Fig. 7) becomes clearly smaller when the polymer mole fraction exceeds $x_{\text{mPVP}} = 0.2 \dots 0.3$ (at higher temperatures, that effect seems to vanish). Correspondingly W (Fig. 6) decreases above that concentration at 20°C, while it is practically constant at 60°C.

Solvent Relaxation Contribution

From the relaxation parameters it is perfectly obvious that spectral component C_4 represents an unaffected portion of solvent. We reasoned already that the present solvents because of their "simple" dielectric behaviour can be expected to contribute in total the solvent relaxation strength S_s^e according to (2). Therefore the fraction of solvent removed from its unaffected relaxation region C_4 can simply be estimated to be $(S_s^e - S_4)/S_s^e$. We shall first consider this fraction disregarding for the moment what has become of it.

It may be more informative to consider instead of the above ratio the number of affected solvent molecules per repeat unit of polymer, called the solvation number Z . If generally α denotes all kinds of affected solvent and β refers to unaffected [4, 5], then

$$Z = \frac{S_\alpha}{c_{\text{mPVP}}} \left(\frac{S_\alpha + S_\beta}{c_s} \right)^{-1}. \quad (6)$$

In the present case, we put $S_\alpha = S_s^e - S_4$ and $S_\alpha + S_\beta = S_s^e$. Figure 8 shows Z for the PVP-TMU systems at different temperatures as an example. For $x_{\text{mPVP}} \rightarrow 0$ there is $Z_0 \approx 2$ at all temperatures. For the other systems studied the following Z_0 values are obtained: About 1.5 for both DMEU series (i.e. with PVP 1200 and 40 000) and about 2 for DMPU (PVP 1200). Similarly low solvation numbers are known e.g. for DMSO and methylpyrrolidone solutions of PVP, in

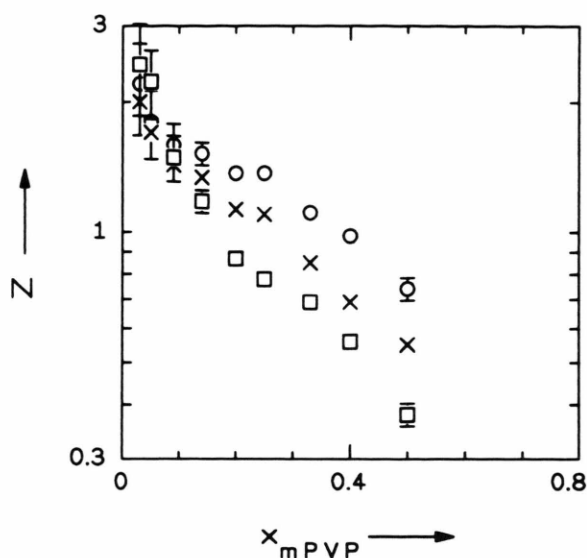


Fig. 8. System PVP 40 000-TMU. Solvation number Z after (6) versus polymer mole fraction x_{mPVP} . Temperatures 20°C (○), 40°C (×), and 60°C (□).

contrast e.g. to aqueous solutions where Z_0 is considerably larger [3].

What can now be learned about the whereabouts of the solvent contribution missing in C_4 ? So far, in particular the spectral component C_3 was claimed for affected solvent. However, including this and even C_5 , the total of C_3 to C_5 cannot account for the expected solvent contribution (at least at lower temperatures) except for sufficiently small polymer concentrations. A "disappeared" portion is left at higher polymer concentrations since there $V < 1$, see Figure 6. As this figure shows, it is $V \approx 1$ at 20°C only up to $x_{\text{mPVP}} = 0.2 \dots 0.3$, but at 60°C this is the case over the whole concentration range covered experimentally. In this respect the above-mentioned relative intensification of S_2/c_{mPVP} (or the relative decrease of S_1/c_{mPVP} , which is equivalent to the decrease of W) seems to parallel the reduction of V . It may thus be conjectured that the "disappeared" solvent contributes in any way to the polymer spectral components, either by reducing the apparent dipole moment appearing in C_1 or by enhancing that belonging to C_2 . Note that, however, both relaxation times characterizing the dynamical behaviour of the polymer (τ_1 and τ_2) stay practically constant and that there is no need to introduce another (resolvable) spectral component. The "disappeared" solvent portion may therefore be pictured as to tightly bound to the polymer that it follows its motions.

Concerning the affected solvent represented by C_3 it remains to be stressed that not only τ_3 but (so far as measured, i.e. in case of the PVP-TMU system) also ΔH_{τ_3} increases with increasing polymer content, the latter in a manner resembling the variation of the above-mentioned parameters (i.e. beginning with zero slope at low concentrations and increasing only for $x_{\text{mPVP}} > 0.2$). Note that at high concentrations there becomes $\Delta H_{\tau_3} \approx \Delta H_{\tau_{1,2}}$ (Table 2) to within experimental uncertainty. Altogether this suggests that C_3 originates in a process which is not at all independent of concentration. The respective solvent portion appears to be affected such that it is hindered in its reorientational motion to a gradually increasing extent as concentration increases. Accordingly C_3 might virtually be replaceable by a continuous succession of components representing increasingly "bound" solvent.

Summing up, we arrive at a three state solvation picture, including free solvent (C_4), solvent affected to a degree which increases with the polymer content (C_3), and tightly bound solvent (deduced indirectly). It is reasonable to take into consideration an equilib-

rium between those states. The temperature dependence of the observed parameters is consistent with such an assumption. E.g., an increase of T at high enough polymer content leads to an intensity increase of the unaffected solvent contribution, S_4 , in its absolute magnitude as well as relative to S_3 , meaning that bound solvent is released to the free state.

In comparison to the previous measurements, the extended concentration range and the temperature variation did allow to round off the incomplete information gained before. The present interpretation is in accordance with that given for PVP dissolved in methylpyrrolidone [5], so it may be applicable more generally to the solvation behaviour of nonassociating solvents and may be helpful for the assessment of polymer solutions in associating solvents.

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