Dielectric Relaxation of N-Methyl-2-Pyrrolidone in Polyvinylpyrrolidone

E. Dachwitz

Institut für Physikalische Chemie der Universität Münster

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Frequency dependent permittivity measurements on liquid mixtures of both substances in the relaxation region of N-methyl-2-pyrrolidone (MPy) show two spectral components originating from MPy. Pure MPy, on the other hand, exhibits only one component. The components are discussed as due to the microheterogenity of the mixtures.

Interactions of small molecules with polymers can be studied by observation of their dielectric relaxation. Small molecules other than water, however, have scarcely been investigated. Here we report on results on liquid mixtures of polyvinylpyrrolidone (PVP) and N-methyl-2-pyrrolidone (MPy) obtained by dielectric relaxation spectroscopy. These substances were chosen since the monomeric unit of PVP is similar to MPy in its chemical character. In liquid solutions, PVP is known to exhibit its relaxation region at fairly low frequencies [1].MPy, on the other hand, relaxes moderately fast, so that we are able to cover the relaxation region of that substance (as pure liquid) experimentally. For mixtures one expects clearly separable relaxation contributions, and from measurements in the latter region one might gain information on the relaxation behaviour of MPy as modified by the presence of PVP. Previous work [2–4] has shown that MPy behaves as a quasi rigid, monomeric molecule simply relaxing by rotational tumbling and exhibiting only one Debye type spectral component, even in polar solvents. It should therefore be a suitable probe molecule.

PVP ("K 30") with a mean molecular weight of 40000 and MPy were obtained from Aldrich and Merck and were used without further purification. The mole fraction range of the liquid mixtures (as related to monomeric units of PVP) was between $x_{\mathrm{MPy}} = 0.75$ and 1.00. Their complex permittivity was measured at 8 spot frequencies between 30 MHz and 36 GHz at 20 °C. The experimental error is a few percent at all frequencies. In addition, the viscosity of all mixtures was determined.

In order to describe the relaxation behaviour formally, the imaginary part of the permittivity (the dielectric loss), $\varepsilon''(\omega)$, already corrected for the conductivity contribution, was fitted by a sum of elementary Debye type spectral components C_i according to

$$\varepsilon''(\omega) = \sum_i S_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} . \qquad (1)$$

For all mixtures, two components were sufficient within a 5% error range.

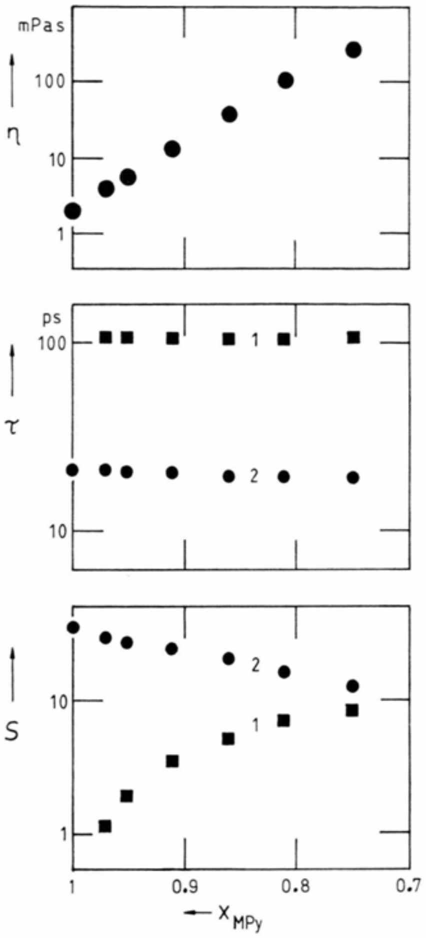

Fig. 1. Relaxation parameters τ_i, S_i and viscosity η (log scales) versus mole fraction x_{MPy}.

The relaxation parameters τ_i and S_i may be altered within a certain variability range, which, however, can be reduced by the following assumption: Usually the relaxation times increase with increasing viscosity, and since the present systems show a viscosity increase with decreasing MPy, it is unlikely that any τ should decrease at the same time. Therefore τ_i values shorter than the relaxation time of pure MPy ($\tau^* = 20$ ps) have not been accepted in the fitting procedure. With that restriction, the two spectral components remain clearly separable. Their parameters are represented in Figure 1. In view of the relaxation features of MPy, as mentioned above, the components should be ascribed to two distinguishable physical processes.

The discussion of the spectral components shall be based on the supposition that both components merely reflect the fluctuation of MPy molecular moments, but do not comprise contributions from PVP moments. This assignment is straightforward since the sum of observed dispersion steps, $\sum S_i = S_1 + S_2$, equals (within experimental uncertainties) the dispersion step of pure MPy, S^*, reduced to S_v by the volume fraction v_{MPy}, that is

$$S_v = S^* \cdot v_{\mathrm{MPy}} . \qquad (2)$$

Reprint requests to Dr. E. Dachwitz, Institut für Physikalische Chemie der Universität, Schlossplatz 4, D-4400 Münster (FRG).

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Table 1. Comparison between dispersion steps $\sum S_i$ and S_v after (2), and the fraction of MPy molecules involved in C_1 estimated as $\psi_1 = S_1/\sum S_i$.

x_{MPy}	$\sum S_i$	S_v	ψ_1
1.00	30.0	30.0	0.00
0.97	28.2	28.8	0.05
0.95	28.0	28.2	0.09
0.91	26.8	26.7	0.15
0.86	25.2	25.2	0.23
0.81	23.2	23.4	0.32
0.75	21.6	21.6	0.41

For comparison, values of $\sum S_i$ and S_v are given in Tab. 1.

The relaxation times both stay practically constant over the investigated concentration range ($\tau_1 \simeq 105$ ps; $\tau_2 \simeq 20$ ps), viz. they are independent of viscosity. This unusual behaviour points towards a microheterogenity of the mixtures, which probably consist of regions where MPy experiences two differing kinds of environment. Since the dispersion step S_1 increases with increasing PVP concentration, while the opposite holds for S_2, the spectral component C_1 may be attributed to regions where MPy is influenced by PVP, while C_2 should be due to regions where MPy is in a state similar to the pure liquid.

As mentioned above, MPy was found to behave as "normal" species without specific self interactions like hydrogen bonding [2–4]. Those interactions are also unlikely between MPy and the similar PVP. Therefore C_1 should result from some kind of weaker interaction.

The following simple model is suitable to explain the observations [5]. When solved in the molecular liquid, the polymer may swell by binding solvent molecules. The rotational fluctuations of the involved solvent molecules will be slowed down. Provided that there are enough solvent molecules, two kinds of regions may be formed:

Those with direct contact of MPy to the polymer (gel particles) and those without direct influence of the polymer. These obviously are observed in our experiment as C_1 and C_2, respectively.

Assuming again that the molecular moment of MPy stays unchanged in the different environments, we can determine the concentration ratio of "free" and "gel bonded" MPy molecules since then S_i is proportional to the respective concentration. Results are listed in Table 1. Formal extrapolation of the linear dependence yields $x_{\mathrm{MPy}} \approx 0.39$ as the concentration where all MPy molecules are "bonded". (Unfortunately, experimental difficulties prevented us from measuring in that concentration range.)

Our results my finally be compared to those obtained by Kaatze [1] on the PVP/H_2O system. Rather than two distinguishable spectral components, only one component could be resolved in the H_2O case, which probably is due to self associated water, resembling the behaviour of water in (low molecular) pyrrolidones as mixture partner [4].

Acknowledgements

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