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Temperature Dependence of the Phase Equilibria for the System Poly(ethylene glycol)/Dextran/Water. A Theoretical and Experimental Study

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ABSTRACT: A new mean field theory, based on the Flory–Huggins description of polymer solutions, is used to describe the temperature dependence of the phase diagram for the ternary poly(ethylene glycol)/dextran/water system. The use of this model gives a great improvement compared to the use of the conventional Flory–Huggins theory. For a fixed set of monomer interaction energies the model is able to reproduce our experimental observations for the PEG20000/Dextran(T40)/water system almost quantitatively up to 80 °C and is qualitatively correct at even higher temperatures. In both model calculations and experiments we found, at temperatures comparable to the cloud point of the poly(ethylene glycol), a three-phase area that has not been reported previously. Finally, a new interpretation for the clear solutions observed previously in the two-phase region of the phase diagram at 95 °C is given.

Introduction

The phase separation occurring when a system consisting of a solvent and two polymers separates into two isotropic polymer phases with mainly one polymer in each phase is a since long-known general phenomenon in both aqueous and organic solvents. During the last 30 years the partitioning of biological macromolecules in aqueous two-phase systems has been developed into a very powerful unit operation for enzyme and protein purification in the biochemical laboratory.[1,2] By far the most used systems for this purpose are those composed of poly(ethylene glycol), dextran, and water.

Even though a tremendous empirical know-how in using aqueous two-phase systems for partitioning purposes has been built up during these 30 years, there do not exist many studies of the fundamental physicochemical aspects of phase separation in aqueous two-polymer systems. Today, when different groups all over the world try to develop aqueous two-phase partitioning to a useful full-scale unit operation in the biotechnical industry,[3-7] the value of such fundamental studies has increased both for designing totally new two-phase systems and for optimizing already existing phase systems.

In a previous paper[8] one of us has concluded that the mechanism leading to phase separation in aqueous polymer systems has the same origin as that for polymers in organic solvents. This means that the explanation to phase separation is not to be found in some specific property of the solvent but is rather to be found in the molecular interactions between the different polymer components. As was shown[8] phase separation in aqueous polymer systems can be analyzed in terms of classical Flory–Huggins theory for a polymer 1/polymer 2/solvent system.

In this work we will study the temperature dependence of the phase equilibria in the poly(ethylene glycol)/dextran/water system by experimental and theoretical investigations and thereby get a deeper insight in the molecular interactions leading to phase separation.

Since classical Flory–Huggins theory, with temperature-independent interaction parameters, cannot describe the temperature dependence for the binary poly(ethylene glycol)/water system, we treat the poly(ethylene glycol) along the lines proposed by Karlström,[9] which leads to a somewhat different treatment compared to Scott's[10] treatment of a polymer 1/polymer 2/solvent system.

With this new model, the theoretical description of the poly(ethylene glycol)/dextran/water system has been greatly improved relative to a conventional Flory–Huggins description. The model calculations can predict the decreased solubility above 90 °C. In this model phase separation at low and moderate temperatures is due to poly(ethylene glycol)–dextran interactions, and at temperatures above ≈90 °C the phase separation is also due to poly(ethylene glycol)–water interactions.

In the experimental section phase diagrams for the system poly(ethylene glycol)/dextran/water are given at

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different temperatures. The two following sections present our Flory–Huggins based theory and the model calculations made with this model. Finally, the experimental and theoretical results are compared.

Materials and Methods

Poly(ethylene glycol) (trade name PEG20000) with a molecular weight of 17 000–20 000 was obtained from Serva, Heidelberg, FRG. Dextran (trade name Dextran(T40)) with an average molecular weight of 40 000 was obtained from Pharmacia AB, Uppsala, Sweden.

Before stock solutions of poly(ethylene glycol) were prepared, the polymer was completely dried over phosphorus pentoxide for at least 1 week. The dried polymer was used without further purification, and stock solutions were made by weight. Stock solutions of dextran were made directly of undried dextran, and the concentrations were determined by optical rotation on a Jasco DIP 360 polarimeter.

Phase diagrams were determined in the following way. Suitable amounts of water and stock solutions were weighed into a test tube and mixed thoroughly. The sealed test tubes were equilibrated in a thermostated water bath, and after they were mixed at the equilibration temperature the samples were kept in the water bath until the phases were totally separated.

Samples from the separated phases were taken for analysis of their polymer content. The dextran concentration was determined with optical rotation and the total polymer concentration, and thereby indirectly the poly(ethylene glycol) concentration, was determined by freeze drying a weighed sample.

Thermodynamical Treatment of Phase Separation. In a previous paper[8] one of us has concluded that polymer incompatibility in aqueous two-polymer systems is due to unfavorable segment–segment interactions between the different polymers. Since long, this has been the generally accepted explanation for nonpolar polymer systems, and from classical Flory–Huggins theory[11] Scott in 1949 derived equations for the chemical potentials in a polymer 1/polymer 2 system.[10] That treatment is independent of the solvent, and the treatment is thus applicable also to an aqueous system.[8,12]

In the Flory–Huggins theory the solvent molecules and the polymer segments (the polymers are divided into segments of the same size as the solvent molecule, usually the number of segments in one polymer molecule is assumed equal to the degree of polymerization) are placed randomly on a lattice where each lattice point can be occupied by one solvent molecule or one polymer segment. The free energy of mixing in such an approximation can be written as

$$G_{\mathrm{mix}}/RT = M_o\{\phi_1 \ln(\phi_1) + (\phi_2/M_2)\ln(\phi_2) + (\phi_3/M_3)\ln(\phi_3) + \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3\} \quad (1)$$

In eq 1 component 1 is the solvent and the two polymers are components 2 and 3 with the degrees of polymerizations M_2 and M_3, respectively. M_o is the total size of the lattice, N_i and ϕ_i, respectively, are the number of moles and the volume fraction of component i.

$$M_o = N_1 + M_2N_2 + M_3N_3 \quad (2a)$$

$$\phi_1 = N_1/M_o \quad (2b)$$

$$\phi_2 = M_2N_2/M_o \quad (2c)$$

$$\phi_3 = M_3N_3/M_o \quad (2d)$$

χ_{ij} is an effective interaction parameter describing the interaction between a segment i and a segment j.

Our experimental observations show that moderate temperature changes have only small effects on the phase diagram. The extent of the two-phase area is almost unaffected, but the slope of the tie lines are changed. When the temperature is raised above 90 °C, the two-phase region increases with increasing temperature.

The decreasing solubility of the polymers with increasing temperature can not be described by classical Flory–Huggins theory for a polymer 1/polymer 2/solvent system if the interaction energies are supposed to be temperature independent. The theory predicts that an increased temperature should also increase the polymer compatibility; this is due to the increased entropy contribution to the total free energy.

This does not hold for aqueous poly(ethylene glycol) solutions, which show a clouding phenomenon when heated.[13] This difficulty has sometimes been treated by introducing temperature-dependent interaction energies.[14-17] We have worked along another line and can reproduce the phase diagrams at different temperatures satisfactorily with only one set of temperature-independent interaction energies.

Recently, one of us presented a statistical mechanical mean field theory for the clouding phenomenon of poly(ethylene glycol) in water.[9] In this description the emphasis is put on the conformational equilibria of the poly(ethylene glycol) chain. It is possible to have different dihedral angles around the C–C and the C–O bonds in the poly(ethylene glycol) chain; thus, there are a vast number of different conformations differing in dipole moment and energy. At ambient temperatures a few low-energy polar conformations dominate,[9,18] and at higher temperatures the importance of several less polar conformations of higher energy increases. As the less polar conformations become more abundant, the polymer becomes less hydrophilic, which ultimately leads to a phase separation. For the binary system the equations for internal energy and entropy becomes

$$U = M_o\{w_{1L}P\phi_1\phi_2 + w_{1H}(1-P)\phi_1\phi_2 + w_{LH}P(1-P)\phi_2\phi_2 + w_{HH}(1-P)(1-P)\phi_2\phi_2/2\} \quad (3)$$

$$S/R = -M_o\{\phi_1 \ln(\phi_1) + (\phi_2/M_2)\ln(\phi_2) + \phi_2[P \ln(P) + (1-P)\ln((1-P)/F)]\} \quad (4)$$

In eq 3 and 4 water is component 1 and poly(ethylene glycol) is component 2. Index L stands for the polar "low-temperature" form of poly(ethylene glycol) and H for the less polar "high-temperature" form of poly(ethylene glycol). F is the statistical weight of the high-temperature form relative to that of the low-temperature form, and P is the fraction low-temperature form of poly(ethylene glycol). As before M_o is the total size of the lattice, and M_i and ϕ_i are the degree of polymerization and the volume fraction for species i, respectively. The interaction energy parameter characterizing the interactions between a segment of type i and a segment of type j is denoted by w_{ij} and is related to the ordinary χ parameters as

$$\chi_{ij} = w_{ij}/RT \quad (5)$$

On the basis of these ideas, we have combined the Flory–Huggins treatment of the two-polymer system in ref 10 with the more detailed model of the poly(ethylene glycol)/water system in ref 9 to obtain the following expression for the energy (or enthalpy when the system is assumed incompressible).

$$U = M_o\{w_{1L}P\phi_1\phi_2 + w_{1H}(1-P)\phi_1\phi_2 + w_{13}\phi_1\phi_3 + w_{L3}P\phi_2\phi_3 + w_{H3}(1-P)\phi_2\phi_3 + w_{LH}P(1-P)\phi_2\phi_2 + w_{HH}(1-P)(1-P)\phi_2\phi_2/2\} \quad (6)$$

The corresponding expression for the entropy is

$$S/R = -M_o\{\phi_1 \ln(\phi_1) + (\phi_2/M_2)\ln(\phi_2) + (\phi_3/M_3)\ln(\phi_3) + \phi_2[P \ln(P) + (1-P)\ln((1-P)/F)]\} \quad (7)$$

There the different components are, 1 for water, 2 for poly(ethylene glycol), and 3 for dextran. For a fixed set of segment–segment interactions (χ_{ij}), it is then possible to calculate the phase behavior of the system at different temperatures. The only parameter that changes during the calculation is P, which at every composition and temperature is given the value that minimizes the total free energy.

Model Calculations. Equations 6 and 7 lead directly to an expression for the free energy in the system at any given temperature and composition. Given an equation for the free energy, it is then an easy task to calculate the whole phase diagram. Gibbs' phase rule shows that the maximum number of phases in a three-component system is 3 when temperature and pressure are fixed. Even though the poly(ethylene glycol) in our model has two different forms, the polymer should only be counted as one component. The assumption that the system is a three-component system is only strictly true if the polymers are monodisperse. In our calculations we assume, for simplicity, that this is the case.

The computational procedure is as follows. An overall composition is chosen. This system is initially divided into three

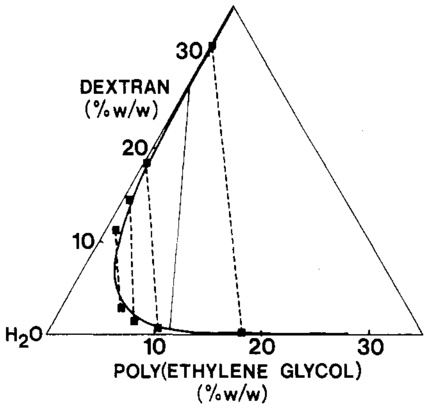

Figure 1. Calculated binodal curve (—) with tieline (—) and experimental points (■) with tielines (- - -) for the system Dextran(T40)/PEG20000/water at 20 °C. Experimental values from Table I. The model system is defined in Table V.

Table I
Coexisting Phases in the Two-Phase Region at 20 °C^a

bottom phase, % w/w		top phase, % w/w	
PEG20000	Dextran(T40)	PEG20000	Dextran(T40)
0.82	11.24	5.45	2.96
0.51	14.46	7.35	1.58
	18.40	9.95	0.79
	30.84	18.06	0.10

^{a} Experimental error ±0.1% w/w.

Table II
Coexisting Phases in the Two-Phase Region at 50 °C^a

bottom phase, % w/w		top phase % w/w	
PEG20000	Dextran(T40)	PEG20000	Dextran(T40)
1.10	10.62	6.68	1.97
0.50	14.55	9.56	0.85
0.19	17.65	12.00	0.47
0.07	20.57	14.21	0.26
0.11	24.63	17.66	0.13
0.10	28.62	20.44	0.07

^{a} Experimental error ±0.1% w/w.

phases where compositions and volumes are chosen arbitarily. Now the free energy for each phase can be calculated from eq 6 and 7. The only unknown parameter at this stage is P, the amount of low-temperature form poly(ethylene glycol), which is chosen so that the free energy is minimized for the specific composition and temperature. The value of P is usually different in the three phases. The total free energy equals a weighted sum of the free energies in the three phases and is for the start composition calculated from eq 8 where V', V'', V''', G_{mix}', G_{mix}'', and

$$G_{\text{mix}} = V'G_{\text{mix}}' + V''G_{\text{mix}}'' + V'''G_{\text{mix}}''' \qquad (8)$$

G_{mix}''' are the volumes and free energies for the three phases, respectively. The true equilibrium state of the system corresponding to the minimum of the free energy, with respect to variations in both volumes and compositions of the phases within the constraints is given by the total composition. This global free energy minimum is determined with a standard numerical procedure.

Depending on whether the overall composition is in a one-, two-, or three-phase region the calculations will end up with three different types of results. When the final result is that all three phases has the same composition, one has an overall composition in a one-phase region. When the calculation gives two phases with the same composition and a third phase with different composition, there is a two-phase region. The last possible result is that there is a three-phase region, and if the overall composition is within the three-phase triangle, the calculation gives the three corners of the three-phase area. All phases calculated are of course in equilibrium with each other, and by repeating the calculation

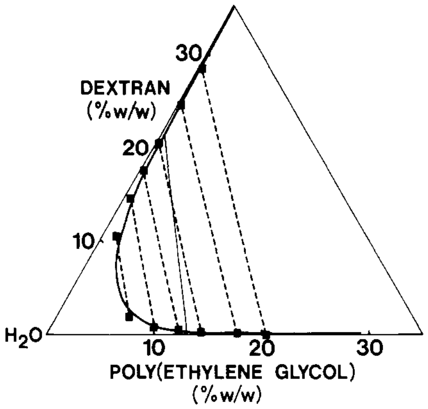

Figure 2. Calculated binodal curve (—) with tieline (—) and experimental points (■) with tielines (- - -) for the system Dextran(T40)/PEG20000/water at 50 °C. Experimental values from Table II. The model system is defined in Table V.

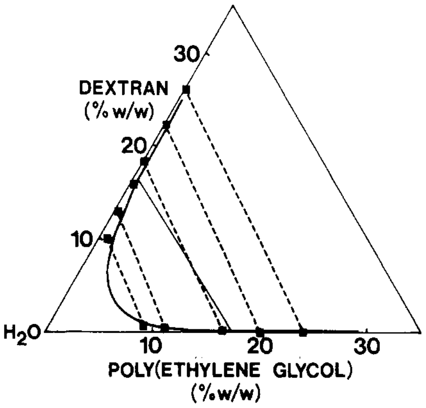

Figure 3. Calculated binodal curve (—) with tieline (—) and experimental points (■) with tielines (- - -) for the system Dextran(T40)/PEG20000/water at 80 °C. Experimental values from Table III. The model system is defined in Table V.

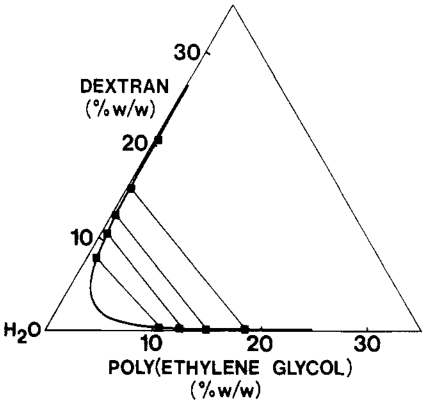

Figure 4. Experimental phase diagram for the system Dextran(T40)/PEG20000/water at 100 °C. Experimental values from Table IV.

Table III
Coexisting Phases in the Two-Phase Region at 80 °C^a

bottom phase, % w/w		top phase, % w/w	
PEG20000	Dextran(T40)	PEG20000	Dextran (T40)
0.70	10.04	8.75	0.77
0.29	13.00	11.03	0.42
0.31	15.83		
0.04	18.30	16.46	0.14
0.04	22.36	19.98	0.09
0.04	26.22	24.00	0.04

^{a} Experimental error ±0.1% w/w.

Table IV
Coexisting Phases in the Two-Phase Region at 100 °C[a]

bottom phase, % w/w		top phase, % w/w	
PEG20000	Dextran(T40)	PEG20000	Dextran(T40)
0.86	7.86	10.33	0.42
0.51	10.56	12.31	0.26
0.30	12.50	14.86	0.16
0.27	15.30	18.45	0.28
0.17	20.58		

[a] Experimental error ±0.1% w/w.

Table V
Theoretical Model System

molecular weight, g/mol	poly(ethylene glycol), 19800 dextran, 38880
interaction energies, J/mol	$w_{1L} = 650.8$ $w_{1H} = 10654$ $w_{13} = 1096$ $w_{L3} = 757.5$ $w_{H3} = 6628$ $w_{LH} = 6352$ $w_{HH} = 10172$

for different total compositions a theoretical phase diagram is easily constructed.

Phase Diagram at Different Temperatures. To describe the temperature dependence of the phase equilibria in detail in a ternary system, one uses a representation in a trigonal prism. A triangular phase diagram at constant temperature is thus a slice in such a prism, and Figures 1–4 show such phase diagrams at four different temperatures. In Tables I–IV, the experimental results for the four phase diagrams at different temperatures are given.

To give a somewhat clearer picture in what way the polymer solubility changes with the temperature, another series of experiments are shown in Figure 5. The figure shows a slice in the trigonal prism, representing the PEG20000/Dextran(T40)/water system, perpendicular to the slices shown in Figures 1–4. The poly(ethylene glycol)/dextran ratio (by weight) is 1:1 in the figure.

These results come partly from a previous work[19] and are completed with data from the phase diagrams presented in this article. The solid line represents the model calculations for the theoretical system defined in Table V. Figures 1–5 show that temperature changes at ambient temperatures have only a very small effect on the extent of the polymer incompatibility. But, as can be seen in Figure 5, when the temperature exceeds ≈90 °C, the one-phase area at the water corner decreases sharply in the phase diagram. This happens at a temperature below the cloud point for the pure poly(ethylene glycol)/water system. This is not surprising since addition of low molecular weight linear saccharides to an aqueous poly(ethylene glycol) solution lowers the cloud point.[20]

However, a general trend in phase diagrams 1–4 is that an increase in temperature makes the poly(ethylene glycol) more hydrophobic. This is the reason why the tie lines change with temperature in such a way that water is moved away from the poly(ethylene glycol)-rich upper phase to the dextran-rich bottom phase, on increasing temperature.

Results and Discussion

In Figures 1–3 a comparison between experimental and theoretical phase diagrams at 20, 50, and 80 °C is made. The calculated phase diagrams are obtained with the procedure described above.

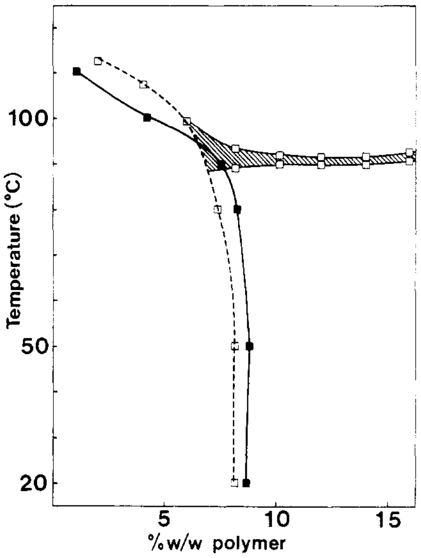

Figure 5. Visual observed (- - -) and calculated (—) phase behavior for the system Dextran(T40)/PEG20000/water. Shadowed area represents visual observed clear solutions due to identical refractive index of the two phases. Weight ratio poly(ethylene glycol)/dextran equals 1 for all samples. The model system is defined in Table V.

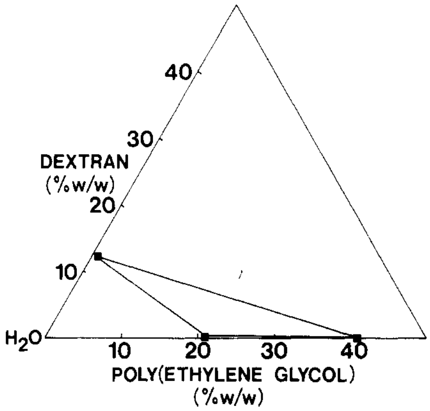

Figure 6. Calculated three-phase area for the Dextran(T40)/PEG20000/water system at 90 °C. The model system is defined in Table V.

The parameters describing poly(ethylene glycol)–water and poly(ethylene glycol)–poly(ethylene glycol) interactions are identical with the values used by Karlström.[9] The values for the interaction energy parameters involving dextran are formaly treated as fitting parameters. It is possible to get a good agreement between experimental and calculated phase diagrams at one temperature for an infinite number of combinations of w_{L3} and w_{H3}, but we have chosen a set of parameters that led to a good description of the phase behavior in the temperature 20–100 °C. This set of parameters is shown in Table V. An important feature is that the effective interaction between a high-temperature segment of poly(ethylene glycol) and dextran is more repulsive than the effective interaction between a low-temperature segment of poly(ethylene glycol) and dextran. This is a feature that is necessary in order to increase the two-phase region in the temperature range 20–85 °C. Furthermore, it is to be pointed out that the w_{ij} values in Table V correspond to rather large χ_{ij} values when compared directly with what is usual for a polymer 1/polymer 2/solvent system described by Scott's model. However, this disagreement is only apparent and is a result of the choice of zero level, and the effective interaction energies contain contributions from both high- and low-temperature forms of poly(ethylene glycol). In addition there is an entropic component to the interaction that is treated separately through the variation in P.

In Figures 6–8 the existence of a three-phase region in the poly(ethylene glycol)/dextran/water system at temperatures comparable to the clouding temperature for the binary poly(ethylene glycol) water system is shown for three different temperatures. Experimentally, this three-phase region exists roughly between 105 and 120 °C.

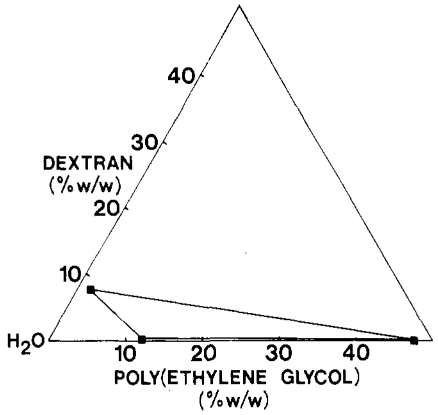

Figure 7. Calculated three-phase area for the Dextran(T40)/PEG20000/water system at 92 °C. The model system is defined in Table V.

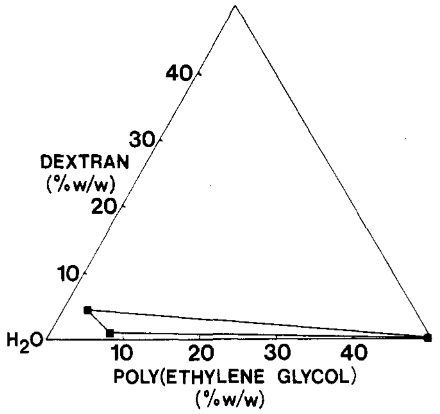

Figure 8. Calculated three-phase area for the Dextran(T40)/PEG20000/water system at 93 °C. The model system is defined in Table V.

As seen from the calculated curves the three-phase triangle shows a very strong temperature dependence, which makes it extremely difficult to prepare samples containing the three phases in equilibrium. We have succeeded in getting an approximate composition for the three-phase area at 108 °C. The polymer compositions were for the top phase 0.3% w/w dextran and 14.1% w/w poly(ethylene glycol), for the middle phase 10.5% w/w dextran and 1.6% w/w poly(ethylene glycol), and for the bottom phase 11.4% w/w dextran and 1.4% w/w poly(ethylene glycol). At the lowest temperature in the three-phase area, one expects only one dextran-rich phase, but since the phase compositions show a very strong temperature dependence, a small temperature increase is sufficient to create a situation with two dextran-rich phases, as is the case here. Further increase of the temperature would make the two dextran phases even more similar, and at somewhat higher temperature they become identical and we enter a new two-phase area. This shows a qualitative agreement with the calculated behavior.

What are the mechanisms for the formation of a three-phase region and why do the calculated and the experimentally observed temperatures for its existence not coincide? The mechanism is easily understood in our model.

Let's first look at the binary poly(ethylene glycol)/water system. When the temperature is increased, the poly(ethylene glycol) molecules become more and more hydrophobic due to the less polar conformations, which are populated to an higher extent. Just above the clouding temperature, two phases with almost identical composition are formed. If we then turn our attention to the ternary poly(ethylene glycol)/dextran/water system, there are at low temperatures mainly one dextran phase and one poly(ethylene glycol) phase in equilibrium with each other. When the temperature is increased above a certain temperature, comparable to the clouding temperature in the binary case, the poly(ethylene glycol)-rich top phase separates. At this "clouding temperature" the separated top phases are identical and neither of them is soluble in the dextran-rich bottom phase. As known from studies of poly(ethylene glycol)/water systems, only a small temperature increase above the cloud point is sufficient so that almost all of the polymer molecules should be found in one of the two phases. The same thing holds for the ternary system, and when the poly(ethylene glycol) is sufficiently unevenly distributed between the two "poly(ethylene glycol) phases", the dextran phase becomes miscible with the poly(ethylene glycol)-poor poly(ethylene glycol) phase and the three-phase region can no longer exist. The reason why the calculated three-phase region exists at a temperature lower than what is found experimentally is found already in Karlström's original paper[9] for the binary poly(ethylene glycol)/water system. In the model poly(ethylene glycol) of this particular molecular weight has a cloud point already at 95 °C, but experimentally we found that a 10% aqueous poly(ethylene glycol) solution of the batch used in this work clouds first at 112 °C.

As can be seen in Figure 5 there is a narrow area in the phase diagram just above 90 °C with clear solutions regardless of the polymer concentrations in the system Dextran(T40)/PEG20000/water. This does not signify that this is an area with a one-phase system. The reason why the solution is clear is due to the fact that there are two coexisting isotropic polymer solutions with identical refractive indices. Such a situation makes it impossible to visually determine whether there are one or two phases in the sample. Is it likely that the clear solutions are due to different phases with matching refractive indices? The answer has to be yes. Measurements at our laboratory show that the refractive indices are somewhat higher in the dextran-rich phase than those in the poly(ethylene glycol)-rich phase at 20 °C. As shown by experiment and by calculations the main effect on a poly(ethylene glycol)/dextran/water system when the temperature is increased is that solvent is moved from the poly(ethylene glycol)-rich phase to the dextran-rich phase. That is, the total polymer concentration increases in the poly(ethylene glycol) phase and decreases in the dextran phase. As a consequence of this, the different refractive indices approach each other, and at some temperature they become identical. The width of the shadowed area is then a measure of how small refractive index variations one can see. The explanation given here for the formation of clear solutions around 95 °C, in the PEG20000/Dextran(T40)/water system, has to be preferred compared to the one given earlier in ref 19.

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Registry No. PEG, 25322-68-3; dextran, 9004-54-0; water, 7732-18-5.

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Conformational Characteristics of Phenyl and Chlorophenyl Esters of 2,4-Dimethylglutaric Acid

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ABSTRACT: The dipole moments of model compounds of the dyads of phenyl- and chlorophenyl-substituted acrylate polymers (phenyl, *o*-chlorophenyl, *m*-chlorophenyl, and *p*-chlorophenyl diesters of 2,4-dimethylglutaric acid) were measured in benzene solution in the temperature range 30–60 °C. The mean-square dipole moment $\langle \mu^2 \rangle$ at 30 °C ranged from 4.36 D^2 for diphenyl 2,4-dimethylglutarate to 10.30 D^2 for bis(*p*-chlorophenyl) 2,4-dimethylglutarate. Among the chlorinated compounds, bis(*o*-chlorophenyl) 2,4-dimethylglutarate exhibits the lowest polarity. All four compounds showed positive temperature coefficients (i.e., $\langle \mu^2 \rangle$ increases with increasing T). The results were interpreted in terms of the rotational isomeric states model. The four-states model previously used in the analysis of poly(methyl acrylate), after adjustment of some of the parameters, is able to reproduce the experimental values of $\langle \mu^2 \rangle$ of these model compounds.

Introduction

The schematic substitution of the methoxy group of the repeating unit of poly(methyl acrylate) (PMA) for a phenoxy or a chlorophenoxy group may considerably alter both the structural geometry and the potentials affecting the torsional rotations about the skeletal bonds of the side groups, and consequently it will have great influence on the conformational characteristics of the resulting polymers. In this case, it is expected that the conformational energies associated to the rotational states about the skeletal bonds of the main chain will be dependent on the rotational angle (ψ) about the O–Ph group, this dependence being much more important in the cases in which the substitution of the chlorine is performed on the ortho or meta positions.[1] In addition, the spatio-configurational properties will also be dependent on the rotational angle (χ) about the C^α–C* bonds,[2-6] whose conformational energies will, of course, be affected by the location (ortho, meta, or para) of the chlorine atom on the phenoxy group.

For the reasons outlined above, the study of the statistics of poly(phenyl acrylate) (PPA) and its phenyl-halogenated derivatives requires, as a first step, studying physical properties of model compounds with structural features similar to those of the polymers indicated above and extending these studies to dimers of the polymers, in order to obtain information on the value of the conformational energies associated to the rotational states about C^α–C* and O–Ph bonds. A physical property specially suitable for this purpose is the dipole moment. Recent dielectric studies performed on phenyl and halophenyl propionates (model compounds of the repeating unit of PPA and its halophenyl derivatives) suggest the following: (a) The effect of replacing the methoxy group in methyl propionate with a less polar phenoxy group is equivalent to introducing a small contribution, $\mu_2 = 0.3$ D, along the O–Ph bond in addition to the dipole moment, μ_1, of methyl propionate. (b) Comparison of the dipole moments of *p*-chlorophenyl and phenyl propionates indicates that the dipole moment of the former compound can be obtained by simple vectorial addition of the dipole moments of phenyl propionate and chlorobenzene. (c) The rotational angles about O–Ph bonds are $\psi = \pm 60°$ and $\pm 120°$ for *m*-chlorophenyl propionate and only $\psi = \pm 75°$ for *o*-chlorophenyl propionate.[1]

The aim of the present study is to measure the dipole moment and its temperature coefficient of phenyl and chlorophenyl diesters of 2,4-dimethylglutaric acid, specifically, diphenyl 2,4-dimethylglutarate (PDG), bis(*p*-chlorophenyl) 2,4-dimethylglutarate (PCPDG), bis(*o*-chlorophenyl) 2,4-dimethylglutarate (OCPDG), and bis(*m*-chlorophenyl) 2,4-dimethylglutarate (MCPDG), which are model compounds for the dyads of poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*o*-chlorophenyl acrylate) (POCPA), and poly(*m*-chlorophenyl acrylate) (PMCPA), respectively. Also the dielectric properties will be calculated theoretically by

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