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Mesophase Formation and Polymer Compatibility. 2. Cellulose Acetate/(Hydroxypropyl)cellulose/Diluent System

Enrico Marsano, Estella Bianchi, and Alberto Ciferri*

Istituto di Chimica Industriale, Università di Genova, Genoa, Italy.
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ABSTRACT: The phase diagram of the system cellulose acetate (CA)/(hydroxypropyl)cellulose (HPC)/*N,N*-dimethylacetamide (DMAc) at 20 °C was investigated. The CA and HPC samples chosen have similar size and semirigid conformation composed, respectively, of ~14 and ~12 Kuhn statistical segments ~140 Å long. The binary systems CA/DMAc and HPC/DMAc exhibit a cholesteric mesophase above polymer volume fractions $v_2' \sim 0.33$ and $v_3' \sim 0.35$, respectively. Ternary systems exhibit a single isotropic phase only when the combined volume fraction is below ~0.05. When $(v_2 + v_3)$ is between ~0.1 and ~0.35, two isotropic phases exist, one containing prevalently CA and the other HPC. This incompatibility in the isotropic phase is in line with an evaluation of enthalpy parameters for the CA/HPC pair. Above the critical volume fraction, there is a composition range, which roughly corresponds to the biphasic gap of the corresponding binary systems, in which *three* phases coexist. The volume fraction of the anisotropic phase of HPC increases at the expense of the isotropic HPC phase in the presence of the anisotropic phase of CA. All compositions are invariant until all isotropic phases disappear. Henceforth, two anisotropic phases are stable, each containing pure polymer. It appears that compatibility between polymers forming similar mesophases may not be often observed, in contrast to the case of low molecular weight liquid crystals.

In a previous paper[1] we discussed the phase behavior of ternary systems composed of a rodlike polymer, a flexible polymer, and a solvent. The systems were poly(*p*-benzamide) (PBA)/polyterephthalamide of *p*-aminobenzhydrazide (X-500)/*N,N*-dimethylacetamide (DMAc) + 3% LiCl, and PBA/poly(acrylonitrile) (PAN)/DMAc + 3% LiCl. The results showed complete exclusion of the flexible coils from the mesophase formed by the rodlike solute. An analysis of the role of polymer compatibility, as conventionally defined by enthalpy parameters in the case of an isotropic mixture of two random coiled polymers,[2] was performed. The results showed that no demixing should have been expected for the PBA/X-500/DMAc + 3% LiCl and for the PBA/PAN/DMAc + 3% LiCl systems in the composition range investigated. Thus, in line with theoretical prediction,[3] the exclusion of the flexible polymer from the mesophase is an entropy effect related to the interference of random coils with the mutual orientation of rodlike molecules.

Rodlike molecules, able to form mesophases in binary polymer/solvent systems, should not exhibit the latter type of repulsive interference when suitably dissolved in ternary systems. Indeed, theory[4] predicts that two rodlike polymers having different axial ratios, and not necessarily the same chemical composition, should form a single anisotropic phase at sufficiently high concentration. The expectation concerning chemically different polymers is apparently verified by the not too extensive data reported in the literature.[5,6] Indeed, in the case of low molecular weight liquid crystals, the well-known compatibility rule between mesogens forming similar mesophases is used as a test for mesophase identification.[7] Lack of miscibility between low molecular weight mesogens forming similar mesophases has also been observed, but it is the exception rather than the rule. Gross differences in chemical constitution, resulting in large unfavorable mixing enthalpies, may be advocated in the latter cases.

In the case of two mesogenic polymers, the expected compatibility of the mesophases may, however, not be observed on account of the poor compatibility generally exhibited by polymers in isotropic phases and of differences in the conformation of the mesogens. In the present paper we investigate the role of compatibility in the isotropic phase for two polymers exhibiting similar conformations. The two polymers are cellulose acetate (CA) and (hydroxypropyl)cellulose (HPC) dissolved in DMAc. It will be shown that CA and HPC are not compatible in both isotropic and anisotropic solutions, giving rise to situations involving *three* coexisting phases which have not yet been theoretically predicted.

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Experimental Section

Materials. The HPC sample (Klucel EF, MS ~ 4) is similar to that used and described in a previous investigation.[8] Its intrinsic viscosity in ethanol at 25 °C was 1.26 dL/g, corresponding to $M_w \cong 132\,000$ in terms of the $[\eta]$–M_w relationship given by Wirich and Waldam.[9] The CA sample was supplied by Eastman Kodak (Eastman 4655, acetyl content 39.4 ± 0.5, DS ≅ 2.4). Its intrinsic viscosity in acetone at 25 °C was 1.66 dL/g, corresponding to $M_w \cong 105\,000$ in terms of the $[\eta]$–M_w relationship given by Kamide et al.[10] The solvent was analytical grade DMAc.

Ternary mixtures were prepared by dissolving in the solvent weighed amounts of the two polymers. From the weight of HPC, CA, and solvent present in the mixture, C_p of the overall system is given by the sum of HPC [(g of HPC)/(g of HPC + g of CA + g of solvent)] × 100 and of CA [(g of CA)/(g of CA + g of HPC + g of solvent)] × 100. Concentrations are alternatively given as polymer volume fraction. These were calculated from the corresponding C_p by using the partial specific volumes of HPC ($\bar{v}_{HPC}$) and CA ($\bar{v}_{CA}$) and the specific volume of the solvent (V_1) and assuming additivity. These quantities were determined pycnometrically at 25 °C. As previously reported[8] $\bar{v}_{HPC} = 0.821$ mL/g. $\bar{v}_{CA}$ was found to be equal to 0.730 mL/g ($V_1 = 1.068$ mL/g). Mixtures were highly viscous and were stirred by very slow rotation at room temperature (~20 °C) for about 2–3 weeks. In order to verify the attainment of equilibrium, the temperature was increased to cause disappearance of at least one phase and then decreased again, observing the re-formation of the original phases. Separation of the coexisting phases was achieved by centrifugation at 44 000 rpm using polyallomer tubes at room temperature. Up to a total of ~300 h of centrifugation was needed for the most viscous samples. Separation was achieved by alternating 24-h centrifugation periods with 24-h rest periods. The volume of each phase was determined by calibration of the centrifuge tube. The composition of the individual phases in the polyphase regions was determined by using two weighed aliquots of each phase. The first aliquot was used for the determination of the overall C_p by drying the sample under vacuum at 80 °C. The second aliquot was diluted with solvent and the CA precipitated with water (HPC is soluble in water). The precipitate was washed and dried, and the weight of CA was determined. From the above results the composition in grams of each polymer per 100 g of ternary solution of each phase was determined. A test performed with a mixture with known amounts of the two polymers gave quantitative separation. Very good reproducibility was shown by the analytical data when duplicate measurements on different solutions having the same overall C_p were performed.

The critical concentration C_p^* for the appearance of the anisotropic phase at room temperature for binary solutions of CA, or HPC, in DMAc was determined with a polarizing microscope (Reichert Zetopan) using a technique similar to that described in previous work.[8] The occurrence of anisotropy within the ternary systems was likewise monitored with the polarizing microscope and confirmed with the ORD technique performed as reported elsewhere.[8] The latter revealed a large optical rotation above the critical concentration.

Results and Discussion

Optical determination on binary CA/DMAc and HPC/DMAc solutions yielded $C_p' = 41.4\%$ and $C_p' = 41.7\%$, respectively, as the critical concentration at which an anisotropic phase appears. The figure for HPC is in line with data previously reported.[8] These data[8] also indicate that the composition, C_p'', of the conjugated anisotropic phase for the HPC/DMAc system is ~50% ($C_p''/C_p' \sim 1.2$). The determination of the width of the biphasic gap for the binary CA/DMAc system is complicated by the difficulty of isolating the conjugated phases even after extensive centrifugation. In this respect we note that the viscosity of the CA/DMAc system is much greater than that of the HPC/DMAc system. For instance, at $C_p \sim 35\%$ and $T = 25$ °C, $\eta \cong 80\,000$ P for the former and $\eta \cong 5000$ P for the latter. This problem has also been encountered by other investigators. Meeten and Navard[11] suggested that no biphasic gap exists, at least for CA in trifluoroacetic acid (TFA). However, Dayan et al.[12] reported viscosity–concentration curves for the CA/TFA and the HPC/H_2O systems. These exhibit the typical maximum and minimum which have been observed with a variety of liquid crystalline solutions in the biphasic gap.[13] The data of Dayan et al.[12] suggest $C_p''/C_p' \sim 1.2$ for both CA and HPC. This figure is in agreement with our own determination for the HPC/H_2O and HPC/dichloroacetic acid systems.[8,14] Thus, we believe that $C_p''/C_p' \sim 1.2$ also for the CA/DMAc system.

Table I
Overall Composition of Ternary Mixtures

mixt	CA C_p, %	CA v_2	HPC C_p, %	HPC v_3	$C_{p\,CA} + C_{p\,HPC}$, %
0	3.0	0.0208	3.0	0.0234	6.0
1	5.0	0.0351	4.9	0.0387	9.9
2	7.6	0.0542	7.5	0.0601	15.1
3	10.0	0.0723	10.1	0.0822	20.1
4	12.5	0.0917	12.6	0.1040	25.1
5	15.0	0.1117	15.3	0.1282	30.3
6	17.5	0.1323	17.5	0.1488	35.0
7	19.9	0.1528	20.2	0.1745	40.1
8	23.0	0.1799	23.0	0.2024	46.0
9	13.0	0.1007	33.0	0.2875	46.0
10	24.0	0.1889	24.0	0.2125	48.0
11	27.9	0.2257	28.1	0.2552	55.0

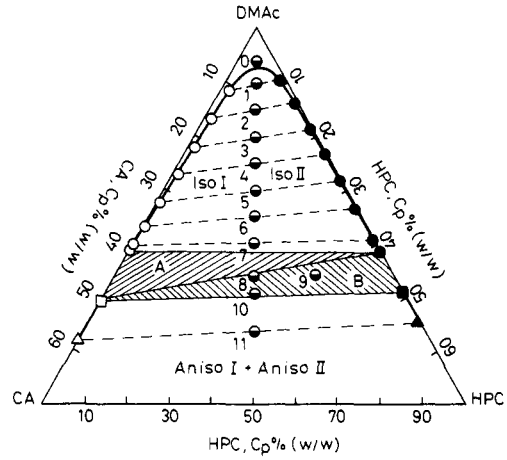

Figure 1. Ternary phase diagram for the system CA/HPC/DMAc at 20 °C: (◒) overall composition of polyphasic mixture; (○) composition of isotropic phase I; (●) composition of isotropic phase II; (□) composition of anisotropic phase I in region A; (■) composition of anisotropic phase II in region B; (△) composition of pure anisotropic phase I; (▲) composition of pure anisotropic phase II.

A series of ternary mixtures covering an overall C_p range between ~6% and 55% were prepared. The overall composition of the mixture is given in Table I and in Figures 1 and 2 (the phase diagrams have been constructed by using the same approach, and the same symbols, described in part 1[1]). All mixtures contained about equal weights of the two components with the exception of mixture 9. When the overall C_p is below ~7% (cf. mixture 0 in Figure 1; $C_p \sim 3\%$ for both CA and HPC), a single isotropic phase containing both polymers is observed. When the overall C_p is between ~10% and 40%, *two isotropic* phases, I and II, are observed. The compositions of these isotropic phases are given in Table II and in Figures 1 and 2. We observe that HPC segregates in the isotropic phase II, and CA segregates in isotropic phase I. The exclusion of CA from phase II and of HPC from phase I increases with increasing overall concentration and is practically complete above an overall $C_p \sim 30\%$ (mixture 5).

Table II
Composition of Conjugated Isotropic Phases

	isotropic I				isotropic II			
	CA		HPC		CA		HPC	
mixt	C_p, %	v_2	C_p, %	v_3	C_p, %	v_2	C_p, %	v_3
1	10.0	0.0708	1.6	0.0127	1.1	0.0077	9.2	0.7254
2	16.0	0.1155	1.0	0.0081	0.8	0.0056	13.0	0.1033
3	21.1	0.1549	1.0	0.0081	0.3	0.0021	18.2	0.1462
4	26.5	0.1981	0.8	0.0067			23.2	0.1886
5	32.2	0.2453	0.3	0.0026			28.1	0.2311
6	37.0	0.2865					33.1	0.2756
7	40.2	0.3149					39.2	0.3314
8							41.7	0.3549
9							41.5	0.3529
10							nd[a]	nd[a]

[a] Insufficient amount to perform determination.

Table III
Volume Fraction of Each Phase within the Three-Phase Region

mixt	$\Phi_{aniso\ I}$, %	$\Phi_{iso\ II}$, %	$\Phi_{aniso\ II}$, %
8	46.7	49.2	4.1
9	28.2	41.4	30.4
10	52.6	3.7	43.7

It is interesting to observe that, upon preparation, solutions with $C_p < 40\%$ appeared completely clear and homogeneous. Only upon prolonged standing or upon extensive centrifugation could two clear phases be visually detected. The phase sedimenting to the bottom was that containing CA. To confirm the occurrence of equilibrium conditions, a biphasic solution enclosed between a slide and cover slide was heated to ~70 °C under the microscope. The solution become monophasic at the higher temperature, but upon returning to room temperature and upon prolonged standing, reappearance of the two phases was detected.

When the overall C_p is greater than ~40% (mixture 7), turbidity is observed. Extensive centrifugation of mixtures with C_p between 40% and 46% (area A in Figures 1 and 2) produced a turbid solution containing CA at the bottom and a clear solution consisting of HPC at the top. Extensive centrifugation of mixtures with C_p between 46% and 48% (area B, mixtures 8–10) resulted in the separation of one clear and *two* turbid phases containing isotropic HPC (iso II) at the top, anisotropic HPC (aniso II) in the middle, and CA (aniso I) at the bottom. The volume fraction, Φ, of each of these phases (Φ = (volume phase)/(total volume)) is given in Table III and the corresponding compositions are included in Table IV and in Figures 1 and 2. Comparing data in Table III for mixtures 8 and 10, we observe a decrease of $\Phi_{iso\ II}$ and an increase of $\Phi_{aniso\ II}$ ($\Phi_{aniso\ I}$ ~ constant) when the overall C_p increases at the same ratio of the CA/HPC composition (cf. Table I). In the case of mixture 9 (which contains a larger amount of HPC than all other mixtures), $\Phi_{aniso\ I}$ is decreased, but $\Phi_{iso\ II}$ and $\Phi_{aniso\ II}$ are increased. The corresponding compositions (cf. Tables II and IV) of the three phases observed with mixtures 8–10 do not change, in spite of the variations of their volumes. These results suggest that the following equilibrium occurs within the area B of the phase diagram when C_p is increased between 46% and 48%:

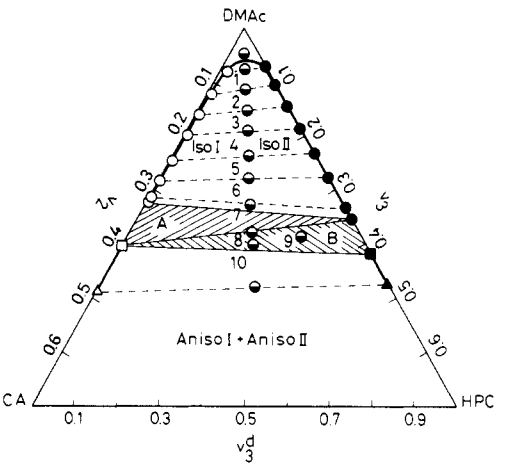

Figure 2. Same data of Figure 1 with compositions given as volume fraction.

$$\text{isotropic II} \rightarrow \text{anisotropic II} \quad \text{anisotropic I unchanged} \tag{1}$$

When all iso II has been transformed to aniso II (overall $C_p > 48\%$), the system is biphasic again and consists of aniso I and aniso II. The data in Table IV for mixture 11 show that now the compositions of the two anisotropic phases increase with the overall C_p.

In no case did we observe a single anisotropic phase or crystallization. In order to verify the occurrence of equilibrium conditions within the B region, three-phase mixtures were heated to ~100 °C until a clear, apparently homogeneous solution was formed. Upon cooling again to room temperature, the three phases reappeared. Determination of the corresponding Φ gave results coinciding with those obtained without the heating cycle.

Table IV
Composition of Conjugated Anisotropic Phases

	anisotropic I				anisotropic II			
	CA		HPC		CA		HPC	
mixt	C_p, %	v_2	C_p, %	v_3	C_p, %	v_2	C_p, %	v_3
8	50.8	0.4138					nd[a]	nd[a]
9	50.1	0.4070					48.2	0.4171
10	51.5	0.4206					49.0	0.4249
11	58.5	0.4908					54.4	0.4785

[a] Insufficient amount to perform determination.

As stated above, centrifugation in the area A of the diagram gave a clear plus a turbid phase. We believe that failure to observe a three-phase system and the equilibrium

$$\begin{matrix}\text{isotropic I} \rightarrow \text{anisotropic I} \\ \text{isotropic II unchanged}\end{matrix} \quad (2)$$

in area A is due to the difficulty in separating the isotropic and anisotropic phases of CA, which was mentioned above for binary systems. It is, however, reassuring that the composition of aniso I isolated in the area B yields a C_p''/C_p' ratio for CA of ~1.2, which, as discussed above, is the expected value for both CA and HPC.

In spite of the difficulty in proving the occurrence of transformation 2, we believe that ample evidence has been offered to indicate the occurrence of equilibrium conditions. Under prevailing nonequilibrium conditions, one could have expected the simultaneous occurrence of four phases (iso I transforming to aniso I, and iso II transforming to aniso II). Such a possibility is not allowed by the phase rule. The systems appears to prefer, upon increasing C_p, the sequence represented by equilibrium 2 followed, when all iso I disappears, by equilibrium 1. Only the relative volumes of phases change, but the compositions stay constant within the area of three-phase equilibria.

Concluding Remarks

Incompatibility is exhibited already in the isotropic phase. It is useful to verify if the occurrence of demixing is in line with the conventional evaluation of enthalpy parameters in isotropic solutions.[2] Proceeding in a similar manner to that described in part 1,[1] we have calculated the Hildebrand solubility parameter[2] δ at room temperature for HPC and derived the experimental value of δ for CA from the data in the ref 15. From these data, the interaction parameter χ_{23} for the CA/HPC pair and the critical χ_{23}^c were calculated. Data thus obtained are as follows:

pair	χ_{23}	χ_{23}^c
CA/HPC	0.24	0.02

Since $\chi_{23}^c < \chi_{23}$, the two polymers are expected to demix at some percentage composition in the undiluted state. In solution, assuming $\chi_{12} \cong \chi_{13}$, the maximum polymer volume fraction at which the two polymers should be compatible is evaluated[2] to be $v_2 \sim 0.08$. Therefore, this crude evaluation is in line with the experimental observation of demixing in isotropic phases at $C_p \gtrsim 7\%$. Note, however, that these evaluations are affected by a considerable indetermination, and the excellent agreement with our experimental data may be somewhat fortuitous.

The lack of compatibility in the anisotropic phase may be attributed to the unfavorable interaction of the two polymers discussed above and, also, to deviation from the rodlike conformation. The persistence length, q, of HPC in DMAc at 25 °C is 70 Å.[8,14] Considering the molecular weight of our present sample, it turns out that an average of about $24q$, or 12 Kuhn segments, compose the HPC chain. Preliminary results[16] indicate that for CA in DMAc, q is also ~70 Å (a value of q = 60 Å was reported by Saito[17]). This corresponds to ~14 Kuhn segments for the sample we have used. Thus, the two polymers have very similar sizes and semirigid conformations. This similarity of conformation should correspond to a similarity in the details of the cholesteric structure for the binary HPC/DMAc and CA/DMAc systems. In turn, the latter similarity should not disfavor mixing, leaving the unfavorable enthalpy parameters as the prevailing cause of the observed incompatibility. The above conclusion, however, is not entirely rigorous. We feel that a complete analysis of these equilibria requires the extension of the theory of ternary systems to various types of semirigid chains and the determination of ternary equilibria for rigid and semirigid chains showing compatibility in the isotropic phase.

We should, however, point out that all our attempts to identify compatible systems based on two rigid polymers, two semirigid polymers, or one rigid and one semirigid polymer had, so far, been unsuccessful. Incompatibility in the isotropic state was observed for systems such as poly(hexyl isocyanate)/poly(γ-benzyl L-glutamate) (PγBLG)/dichloromethane, PγBLG/poly(L-glutamic acid)/dimethylformamide, and HPC/CA with DS $\cong$ 1/DMAc. Crystallization prevented the study of systems such as cellulose/HPC, cellulose/CA, cellulose/poly(*p*-benzamide) (PBA), and PγBLG/PBA, all in the presence of DMAc + LiCl. The fundamental cause of the poor compatibility of high molecular weight compounds in the isotropic phase was discussed several years ago by Flory.[18]

It thus appears that the compatibility rule, which is used for mesophase identification in the case of low molecular weight liquid crystals (cf. introductory section), might be seldom applied to polymeric mesogens. Similarly, it might be difficult to prepare molecularly dispersed composites based on rigid polymers, unless favorable interactions occur. On the other hand, mesophase formation by rigid polymers having different chain lengths but the same chemical constitution is well documented by theoretical[4] and experimental results.[19]

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