Polymer mixing in aqueous solution

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The phase separation behaviour of two polymers (1 and 2) in organic solvents is relatively well understood and is usually due to repulsive interactions between 1 and 2 chain segments. In aqueous solutions, however, where the interaction of the polymer with the solvent is expected to be large, the behaviour is less well understood. In this paper the phase separation of polymers in aqueous solution has been studied and some of the factors which could control the phase separation have been investigated. The volumes of the separated phases were found to be related to the sizes of the polymer/solvent interactions. The polymer with the most positive second virial coefficent was found to occupy the phase with the largest volume. For both miscible and immiscible pairs the mixed second virial coefficients (A_{12}) was assessed from osmotic pressure measurements and was found to be an average of the individual second virial coeffients $(A_{11}$ and $A_{22})$. A few polymer pairs were found to mix and this was thought to be caused by hydrogen bonding between 1 and 2 chain segments. Mixtures of rod-like and coiled polymers were expected to phase separate to give a concentrated, ordered phase containing nearly all of the rod-like polymer and a larger phase containing the coiled polymer. However this behaviour was not found when a cellulose derivative (rod-like) was mixed with dextran (flexible).

(Keywords: polymer mixing; second virial coefficient; miscibility; immiscibility; aqueous solution; phase separation)

INTRODUCTION

The phase separation of two polymers (1 and 2) in organic solvents in relatively well understood and is usually due to repulsive interactions between 1 and 2 chain segments, giving an endothermic heat of mixing. Polymer/polymer phase behaviour in aqueous solution is less well understood, although phase separated polymer solutions have been widely used to separate biological materials[1]. The mixing of polymers in aqueous solution can lead to phase separation (immiscibility), the formation of insoluble complexes of homogeneous solutions (miscibility). Knowing the factors which control polymer mixing in aqueous solution is important for several reasons, e.g. when colloidal particles bearing different absorbed layers are mixed, whether the polymers are miscible or immiscible can determine the colloidal properties of the suspension[2]. In this work the phase separation of polymers in aqueous solution is studied by the determination of phase diagrams and by osmotic pressure measurements in dilute solutions. Some of the factors which could control the mixing behaviour have been investigated.

EXPERIMENTAL

Details of the polymers used in this work are given in *Table 1*. A nominally nonionic PAaM sample, Versicol W13, was shown to be partially ionic in character by viscometry and osmotic pressure measurements. Water contents were determined by the Karl-Fischer method and by drying to constant weight in a heated vacuum oven. Polymers used for osmotic pressure measurements were dialysed in Visking tubing against water, freeze dried and the water content determined. Osmotic pressures were measured using a Knauer membrane osmometer with Duplex membranes, at 303 K. Number average

molecular weights and second virial coefficients were determined as usual, using a least mean squares method (95% confidence limits were calculated, see *Table 4*). Mixed second virial coefficients (A_{23}) were obtained using the following equation:

$$\pi = RT\frac{C_2}{M_2} + \frac{C_3}{M_3} + A_{22}C_2^2 + A_{33}C_3^2 + 2A_{23}C_2C_3$$

where A_{22} and A_{33} are the second virial coefficients of polymers 2 and 3 respectively.

Phase diagrams were determined at ~ 298 K and the approximate concentration region where phase separation occurred was found by mixing solutions of increasing concentration. Binodals were determined either by measurement of polymer concentrations or by dilution of a phase separated solution until the one phase region was reached. Sometimes clear, but phase separated solutions were obtained, when both phases had the same refractive index. The mixtures were therefore allowed to stand or were gently centrifuged to allow two distinct phases to form.

It is difficult to demonstrate compatibility of a polymer/polymer mixture conclusively. In this work two criteria were used, no visual sign of phase separation in concentrated aqueous mixtures of high molecular weight materials and, secondly, no phase separation in films cast from these mixtures. The aqueous solutions were left to stand for long periods to allow any separation to occur. Therefore, in this work the term compatibability implies, at least, that the polymers mix at high polymer concentrations.

Dextran concentrations were determined polarimetrically $([\alpha]_D^{25} = +200°)$. HPMC was removed from dextran solutions by addition of concentrated

Table 1 Details of polymers

Polymer	Trade name	Supplier	Manufacturers M_W	Determined M_W	Comments
Dextran	—	Sigma	80 000	37500 $(\bar{M}_W)$	$(\bar{M}_W/\bar{M}_n) = 1.48$ [a]
Dextran	—	Sigma	10 000	25500 $(\bar{M}_n)$	
Dextran	T70	Pharmacia	70 000	41000 $(\bar{M}_W)$	$(\bar{M}_W/\bar{M}_n) = 1.25$ [a]
				33000 $(\bar{M}_n)$	
				49000 $(\bar{M}_n)$ [d]	
Hydroxypropyl methyl	Methocel E15	Dow	22 000		Methoxy DS = 1.86–1.90
cellulose (HPMC)	Methocel E400	Dow	92 000		Hydroxypropyl MS =
					0.22–0.25
Poly(acrylamide) (PAaM)	Versicol W13	Allied Colloids	109 000	57000 $(\bar{M}_n)$ [b]	Contains ionic character
Poly(acrylamide) (PAaM)	—	Synthesized at URPSL		14000 [c]	
Poly(acrylamide) (PAaM)	Crosfloc CFN10	Crosfields	High		Meant to be nonionic
Poly(acrylamide-co-acrylate)	Crosfloc CFA20	Crosfields	High		—5% acrylate)
	Crosfloc CFA80	Crosfields	High		—35% acrylate) sodium
Poly(acrylic acid) (PAA)		Aldrich	90 000	73000 $(\bar{M}_n)$ [b]	
Poly(ethylene glycol) (PEG)	—	Hoechst	10 000		
Poly(ethylene glycol) (PEG)	HM100	Hoechst	35 000		
Poly(ethylene glycol) (PEG)	—	Aldrich	100 000	30000 $(\bar{M}_n)$ [d]	
Poly(vinyl methyl ether)	Gantrez M-154	GAF		230900 $(\bar{M}_W)$	$(\bar{M}_W/\bar{M}_n) = 7.60$ [e]
(PVME)				30300 $(\bar{M}_n)$	
Poly(vinyl alcohol-co-acetate)	Gohsenol GH-17	Vinyl Products	98 000		88% alcohol
(PVA)	Gohsenol KH-17	Vinyl Products	111 000		80% alcohol
	Gohsenol N-300	Vinyl Products	80 000		99% alcohol
Poly(vinyl pyrrolidone)	—	Sigma	10 000		
(PVP)					
Poly(vinyl pyrrolidone)	PVPK30	GAF	40 000	56400 $(\bar{M}_W)$	$(\bar{M}_W/\bar{M}_n) = 1.70$ [f]
(PVP)				33200 $(\bar{M}_n)$	
Poly(vinyl pyrrolidone)	—	BDH	44 000		
(PVP)					
Poly(vinyl pyrrolidone)	PVPK60	GAF	160 000	82000 $(\bar{M}_n)$ [d]	
(PVP)					
				193000 $(\bar{M}_W)$	$(\bar{M}_W/\bar{M}_n) = 2.1$ [f]
				91000 $(\bar{M}_n)$	

[a] These molecular weights were determined by g.p.c., using water as the solvent and with one based on a sodium poly(styrene sulphonate) standard.
[b] Determined by osmometry in a 0.2 M acetate buffer at pH = 3.4 with 0.5 M ammonium sulphate.
[c] Determined by viscometry.
[d] Determined by osmometry in water.
[e] Determined by g.p.c., using chloroform as the solvent and based on a poly(styrene) standard.
[f] Determined by g.p.c., using DMF as the solvent and based on a sodium poly(styrene) standard.

Table 2 Polymer pairs which are known to form insoluble complexes when added together in aqueous solution

(1) Poly(acrylic acid)	)	
(2) Poly(methacrylic acid) (PMMA)	)	
(3) Poly(vinyl methyl ether/maleic anhydride copolymer)	)	Poly(ethylene glycol) [39]
(4) Carboxymethyl cellulose	)	
(5) Carboxymethyl dextran	)	
PAA, PMAA, PVME/MA		/Poly(vinyl pyrrolidone) [39]
PMAA		/Poly(vinyl methyl ether) [19]
PMAA		/Poly(vinyl alcohol) [19]

To form insoluble complexes polymers (1) to (5) must be in the acid form. It was shown in this work that if the pH in the PAA/PEG system was raised, the complex dissolved and a two phase, immiscible system was obtained

Table 3 Polymer pairs which were shown in this work to be miscible

Polymers		Comments
Poly(vinyl alcohol (88%) — co-acetate (12%)	)) Poly(vinyl	In water.
Poly(vinyl alcohol (99%) — co-acetate (1%)	) pyrrolidone))	80% alcohol sample immiscible with PVP.
Poly(acrylamide) [Versicol W13 or Crosfloc CFN10]	Dextran	In water, acid solution or sodium chloride solution.
Poly(acrylic acid)	Dextran	In water. If the pH is raised above ~6, a two phase, immiscible system results.
Poly(acrylic acid)	Poly(acrylamide) (Versicol W13)	As above.

ammonium sulphate solution, followed by centrifugation. Ratios of PEG to PVA concentrations were determined by high resolution 'H n.m.r. Viscosities were determined using an Ubbelodhe type viscometer ($t_0 \sim 100$ s) at 298 K.
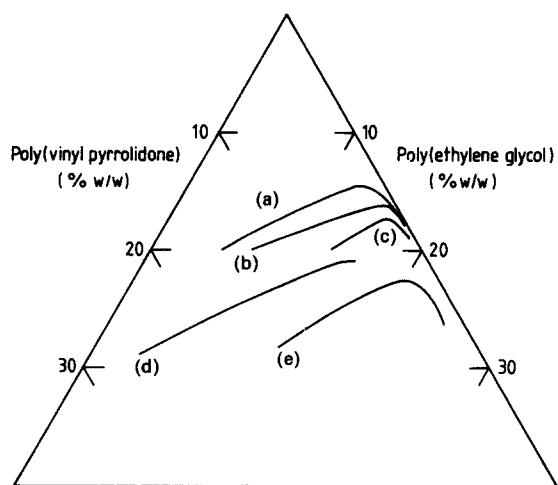
RESULTS AND DISCUSSION

The majority of polymer pairs studied in this work were found to be immiscible and their phase behaviour is represented on ternary phase diagrams (see *Figures 1–7*). The Flory–Huggins theory[4–6] suggests that immiscibility is due to an unfavourable interation between the

polymers, which outweighs the small favourable combinatorial entropy of mixing. As the entropy of mixing is related to the number of molecules in the system, the binodal should move to lower concentrations as the molecular weight of the polymers increases. If one polymer is of higher molecular weight than the other, the binodal is expected to be displaced towards the side of the phase diagram rich in the lower molecular weight polymer[5,6]. In this work the former prediction always occurs, whereas
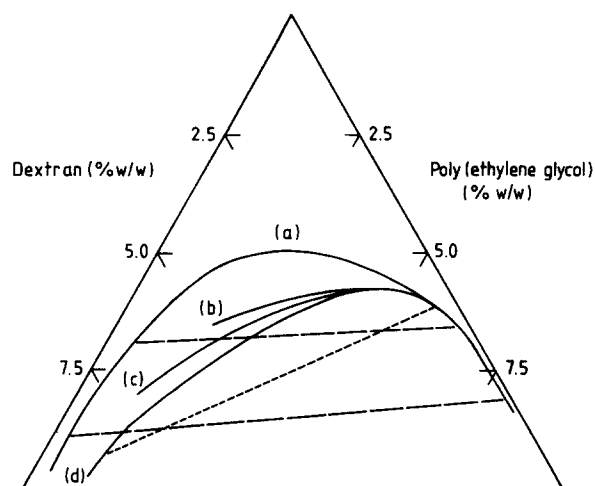
the latter is not always true. When PEG is present the binodal is nearly always displaced to the side of the diagram rich in PEG (see *Figures 1–3*). The tie lines on these diagrams indicate that the volume of the PEG-rich phase is usually much greater than that of the other phase (see *Table 6*). This behaviour is consistent with the large value of the second virial coefficient (A_2) for PEG in water. Although the Flory–Huggins theory does predict a displacement of the binodal if the polymer/solvent interaction parameters are unequal[7], the effect is much smaller than observed in this work. Addition of sodium sulphate to the PEG/dextran/water system changes a skewed binodal to one that is nearly symmetrical, whereas sodium chloride or potassium iodide have little effect. Sulphate is a strong salting out ion[8], reducing A_2 for PEG, whilst not altering the A_2 value of dextran. In mixtures where both polymers can be saltered out by sulphate e.g. PEG and PVP, the binodal is unaffected by the addition of sulphate (see *Figure 2*). The binodals of PEG and sodium PAA or partially hydrolysed PAaM (at pH ~7 in water) are displaced to the side of the phase diagram which is rich in the polyelectrolyte (see *Figure 4*). This is consistent with a relatively larger A_2 value for the polyelectrolyte in these

Figure 3 Effect of some electrolytes on the poly(ethylene glycol) (HM100)/Dextran (8.0×10^4)/water system. (a) 0.4 M Na_2SO_4 (b) 1.0 M NaCl (c) 0.4 M KI (d) water
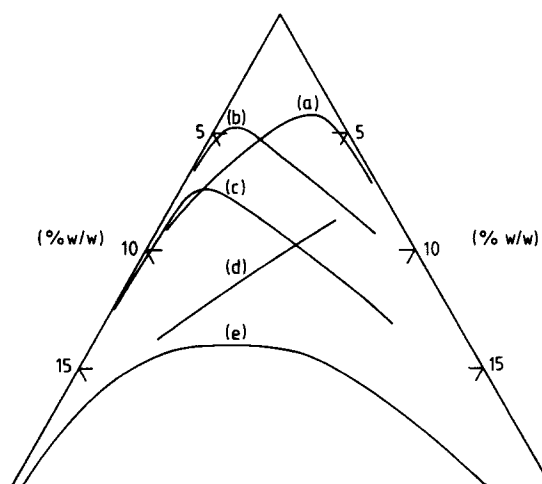

Figure 1 Effect of molecular weight on the binodal of poly(ethylene glycol) (HM100)/poly(vinyl pyrrolidone)/water. Molecular weights $(\times 10^{-4})$ are (a) 3.5/4.4 (b) 3.5/4.0 (c) 1.0/4.4 (d) 3.5/1.0 (e) 1.0/1.0

Figure 4 Phase behaviour of Versicol W13 with some nonionic polymers in water and showing the effect of electrolyte. (a) PEG (HM100) in 0.2 M Na_2SO_4, 1.0 NaCl, 0.1 M NaCl, 0.1 M HNO_3 (b) PVME (c) PVA (GH-17) (d) PAaM (0.14×10^4)/PEG (1.0×10^4) (e) PEG (HM 100)

Figure 2 Phase behaviour of poly(ethylene glycol) (HM100) with some nonionic polymers in water. (a) PVA (GH-17) or PVME (b) Dextran (8.0×10^4) (c) Dextran (0.9×10^4) (d) PVP (K30) (similar in 0.2 M sodium sulphate)

systems (see *Table 5*). However, if the A_2 value is lowered by the addition of electrolyte the binodal moves to lower concentrations and is displaced to the PEG-rich side of the diagram. The increase in immiscibility of the system with addition of electrolyte is probably due to the reluctance of the polyelectrolyte to separate into a polymer-rich phase if large electrostatic repulsions are present.

Although the Flory–Huggins theory is capable of predicting the qualitative aspects of the phase behaviour of polymer mixtures in aqueous media, it was not intended for use with strongly associated systems and it has yet to be made entirely quantitative even for the simplest polymer mixtures[9-12]. The importance of free volume differences in aqueous ternary systems has not been investigated, although in blends and non-aqueous systems at room temperatures, its importance is thought to be low[17]. At room temperatures it is only in polymer/polymer systems where all the other effects are evenly balanced, that free volume effects are important in determining phase behaviour[18].

A few polymer pairs were found to give homogeneous solutions and clear films and are, therefore, considered to

Table 4 Mixed second virial coefficient values (A_{23}) for some polymer/polymer systems in aqueous media

Polymers		Solvent	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$ (cm³ g⁻² mole)	$A_{23} \times 10^4$ (cm³ g⁻² mole)
Dextran T70	)	Water	4.9 (±0.2)	6.5 (±1.2)	
Poly(vinyl pyrrolidone) PVPK60	)		8.2 (±0.3)	6.5 (±1.3)	6.5 (±1.3)
Dextran T70	)	Water		6.5 (±1.2)	
Poly(ethylene glycol) HM100	)		3.0 (±0.1)	21.4 (±0.7)	15.4 (±1.7)
Poly(vinyl pyrrolidone) PVPK60	)	Water		7.6 (±0.4)	
Poly(ethylene glycol) HM100	)			21.4 (±0.7)	14.5 (±2.1)
Versicol W13	)	0.1 NaCl	6.4 (±0.7)	11.9 (±1.2)	
Dextran T70	)			6.5 (±1.2)	4.5 (±1.7)
Versicol W13	)	0.5 M NaCl	6.3 (±1.3)	9.9 (±2.4)	
Dextran T70	)			6.5 (±1.2)	8.5 (±3.2)
Versicol W13	)	acetate buffer*	5.7 (±0.1)	7.2 (±0.2)	
Dextran T70	)			6.5 (±1.2)	5.6 (±1.6)
Poly(acrylic acid)	)	acetate buffer*	7.3 (±0.6)	3.4 (±0.7)	
Dextran T70	)			6.5 (±1.2)	6.6 (±1.5)

Attempts were made to perform this measurement on the poly(vinyl pyrrolidone)/poly(vinyl alcohol (88%)-co-acetate (12%)) system. However it proved difficult to obtain reproducible results for the PVA sample, particularly for the A_2 value.
* 0.2 M acetate buffer pH = 3.4, with 0.5 M ammonium sulphate added

Table 5 Second virial coefficient values for some nonionic polymers in water

Polymer	T (K)	$\bar{M}_n$ (×10⁻⁴)	$A_2 \times 10^4$ (cm³ g⁻² mole)	Ref.
Dextran	298	2.9	5.5	40
	298	37.4	4.2	40
	303	4.9	6.5	40
PAaM	298	10.7	1.4	41
PEG	298	4.4	19.3	40
	301	1.9	25.9	42
	303	3.0	21.4	
PVA	303	18–19.6	3.9–5.2	43
PVP	298	2.8	7.0	40
	303	8.2	7.6	
Hydroxyethyl ethyl cellulose	298	7.7–17.6	9.8–5.5	40
Sodium PAA	298ᵃ	6.4	32.6	45
	298ᵇ	3.0–64.4	~2.8	
	298ᶜ	5.8	0.3	

ᵃ 0.01 M NaCl
ᵇ 0.05M NaCl
ᶜ 1.0M NaCl

Table 6 The initial and final concentrations* and phase volumes for two immiscible mixtures of PEG HM100 (A_2 = 21.4 × 10⁻⁴ cm³ g⁻² mole) and dextran 80 000 ($A_2 \simeq 6.5 \times 10^{-4}$ cm³ g⁻² mole) in water

	Concentration (% w/w)		
	Initial	Final	Phase volume (cm³)
Sample 1			
PEG	10.3	18.5	11.4 (Top phase)
Dextran	13.0	29.5	7.9 (Bottom phase)
Sample 2			
PEG	15.3	19.5	7.4 (Top phase)
Dextran	7.0	31.7	1.9 (Bottom phase)

* This relates to the major component in each phase (PEG in the top phase and dextran in the bottom phase). The concentration of the minor component was low

be miscible (see *Table 3*). These are probably a result of an unlike polymer attraction occurring through hydrogen bonding. Such an interaction is known to exist between polymer pairs which form insoluble complexes (see *Table 2*). In these pairs, one of the polymers always contains carboxylic acid groups, which are good proton donors and form hydrogen bonds with oxygen acceptors. This can also occur internally e.g. dimer formation in acetic acid. If the pH of these systems is increased the interaction is destroyed and phase separation occurs. A ladder structure of co-operative hydrogen bonds in a linear sequence is thought to exist in these complexes[19] and the composition and properties of the complexes are dependent on the chain stereo-regularity e.g. PEG with isotactic or atactic PAA[20]. Steric factors are particularly important in the interaction of naturally occurring polymers. An example of this[21] is the gel formation of locust bean gum which interacts in solution through unsubstituted 'smooth' regions, while substituted 'hairy' regions remain hydrated and prevent the structure from collapsing.

In the PVP/PVA system a weak hydrogen bonding interaction between the hydroxyl of PVA and the carboxyl of PVP may exist. This is sufficient to cause mixing of PVP in solution with 88% and 98% hydrolysed PVA but not with 80% hydrolysed PVA (see *Table 3*).

PAA forms homogeneous solutions with both dextran and PAaM. This behaviour is in contrast to the previously discussed ability of polymers containing carboxylic acid to form insoluble complexes with polymers containing oxygen. It is interesting to note that PAA forms insoluble complexes with polymers that exhibit LCST (e.g. PEG, PVP) and homogeneous solutions with polymers that exhibit a UCST (e.g. PAaM[46] and dextran). The value of the θ temperature in water for both these polymers is less than 0°C, however, critical behaviour can be observed if large concentrations of sulphate are added[3].

The mixing behaviour of polymers in solution is clearly determined by a delicate balance of forces. A strong polymer/solvent interaction has already been shown to

affect the phase behaviour of immiscible polymer pairs in aqueous solution. An extreme example of this behaviour occurs in some non-aqueous systems e.g. polystyrene and PVME[22-25] are compatible in the blend and in solvents such as benzene, but they are immiscible in chloroform which interacts strongly with PVME. In this work attempts were made to discover polymer pairs which were miscible in the absence of solvent, but incompatible in aqueous media, by slowly drying out immiscible systems. However, such behaviour was not observed.

Information about the strength of polymer/polymer interactions in aqueous media can be obtained from dilute solution techniques such as osmometry, light scattering, calorimetry or viscometry. The interpretation of calorimetric data is complicated by heat of dilution effects. Viscometry data is difficult to interpret correctly[26,27] as the presence of attractive polymer/polymer interactions can increase[28,29] or decrease[30] the solution viscosity. In this work osmometry was used to measure the mixed second virial coefficient (A_{23}; see experimental section). If contacts between the polymer segments were random, A_{23} might be expected to be a weighted average of A_{22} and A_{33}. However, if the two polymers are immiscible due to an additional repulsion between them, the value of A_{23} might be larger than expected. Conversely if the polymers are miscible due to an attraction between the unlike molecules, a smaller or negative value for A_{23} might be obtained. Some experimentally determined values for A_{23} are given in *Table 4*, and these results show that an overall repulsive interaction exists between the unlike polymers in dilute solutions containing two different polymers. However, none of the A_{23} values differ significantly from weighted averages of the A_{22} and A_{33} values, either for miscible or immiscible polymer pairs.

Flory[31-34] and others[35] have shown that the rod-like nature of a molecule can lead to phase separation from solution and from ternary mixtures. Such behaviour has been demonstrated in a non-aqueous ternary system[36], but not in aqueous solutions, although xanthan[37] and some cellulose derivatives[38] form anisotropic phases at high concentrations in water. The phase behaviour of HPMC (rod-like)/dextran (flexible)/water is shown in *Figure 5*. Flory's theory suggests that a concentrated phase containing the rod-like species and little (if any) flexible species should be formed. However, with HPMC
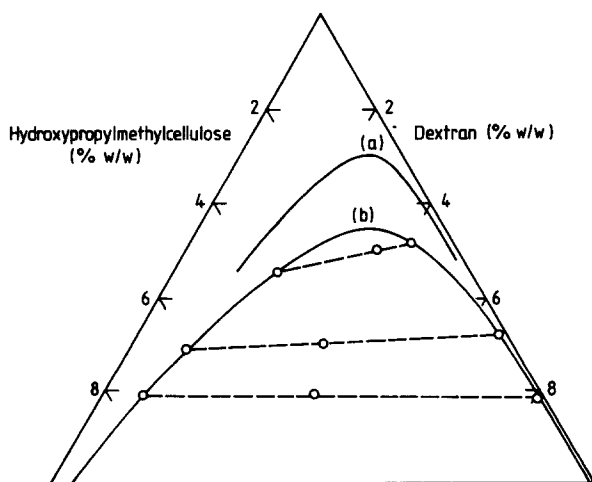
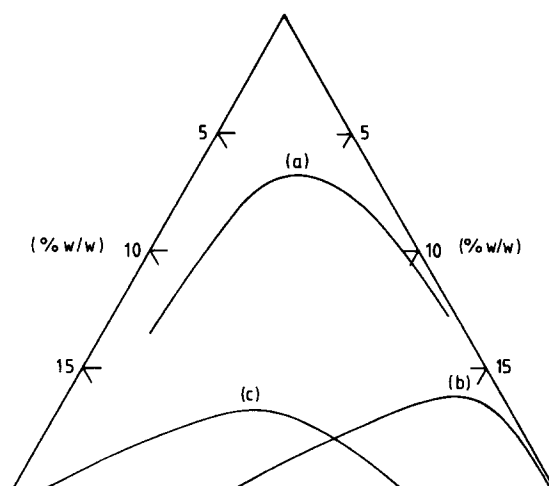**Figure 6** Phase behaviour of some immiscible polymer pairs in water (a) PVP (4.4×10⁴)/PVME (b) PVP (K30)/PEG (HM 100) (c) (K30)/Dextran (8.0×10⁴)
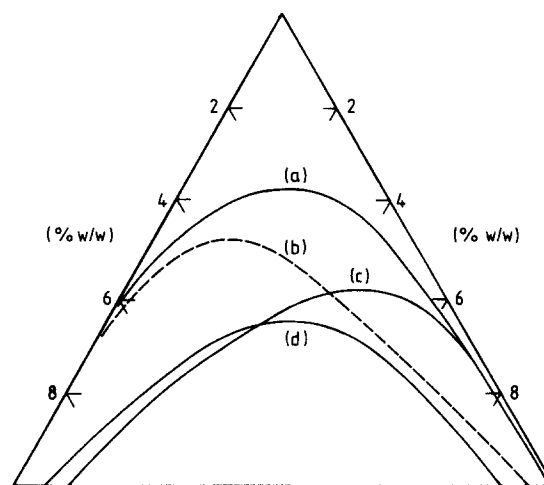
Figure 7 Phase behaviour of some immiscible polymer pairs in water (a) Dextran (8.0×10⁴)/PVME (b) Dextran (8.0×10⁴)/HPMC (E15) (c) Dextran (8.0×10⁴)/PEG (HM100) (d) Dextran (T70)/PVP (K60)

and dextran, this does not occur and no evidence of anisotropic phase formation was found by cross-polarized light microscopy. Water soluble cellulose derivatives may be insufficiently rigid to give ordered solutions at these relatively low polymer concentrations. However, the rigidity may partly explain the relatively low concentrations at which phase separation occurs.

The phase behaviour of some other polymer pairs is given in *Figures 6* and *7*. The polyethers are in general more immiscible than other polymers and PVP is one of the least immiscible polymers.

Polymers in aqueous solution are probably surrounded by a hydration layer of water molecules which differs in structure from the structure of bulk water. In immiscible systems any interaction between the unlike polymers is likely to occur through the hydration layers. The interaction of some unlike hydration layers may be more repulsive than the interaction of like hydration layers. Such an effect has not been demonstrated clearly in this work, although an effect due to strong polymer/solvent interactions on polymer/polymer phase behaviour (phase volumes, displacement of binodal) has been shown.

Figure 5 Phase behaviour of Dextran (8.0×10⁴)/HPMC/water. (a) HPMC E15 and (b) E400

CONCLUSIONS

The volumes of separated phases were found to be related to the magnitudes of the polymer/solvent interactions. The polymer with the most positive second virial coefficient was found to occupy the phase with the largest volume. For both miscible and immiscible pairs the mixed second virial coefficient was found to be an average of the values of the individual second virial coefficients. A few polymer pairs were found to mix and this was thought to be caused by hydrogen bonding between the different polymers. This attraction was probably weaker than that found in systems which give insoluble polymer complexes. Mixtures of rod-like and coiled polymers were expected to separate to give a concentrated, ordered phase containing nearly all of the rod-like polymer, however, this behaviour was not found when a cellulose derivative (rod-like) was mixed with dextran (flexible).

ACKNOWLEDGEMENTS

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