Cellulose–polyacrylonitrile blends: 3. Polymer–polymer interactions in dimethylacetamide/LiCl solution determined by viscometry

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Values of intrinsic viscosity $[\eta]$ and Huggins' constant K_H were measured for cellulose, polyacrylonitrile and their mixtures in dimethylacetamide/7% LiCl. The trend of $[\eta]$ is linear with the weight fraction of the two polymers. The Huggins' constant values correspond to the case of ideal mixtures. Observations are made concerning deviations which arise in results obtained at higher concentrations.

(Keywords: cellulose; polyacrylonitrile; blends)

Introduction

A knowledge of the interaction between components of a polymeric mixture is the basis for predicting phase behaviour. Attempts have been made by many authors[1,2] to predict total or partial compatibility in the solid state. Re-examination of literature data[3–8] shows that some simple methods, based on viscosity measurements, have been developed since 1950. The aim has been to present evidence of the existence of attractive or repulsive interactions between the polymeric components. Ideas relating to their compatibility in the solid state can be put forward on this basis. The starting equation[9] is:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c \qquad (1)$$

where η_{sp} and $[\eta]$ are, respectively, the specific and the intrinsic viscosity, and c is the polymer concentration. K_H, the Huggins' constant, is a dimensionless parameter independent of the molecular weight, but dependent on the polymer, the solvent nature and the temperature. It is useful to recall the physical meaning of the terms in equation (1): η_{sp}/c, with the same dimensions as specific volume, is the volume pervaded by 1 g of polymer in the viscous flow of a solution at concentration c. Owing to intermolecular influence, η_{sp}/c is higher than $[\eta]$, which refers to infinite dilution. It follows that the term $K_H[\eta]^2c$ represents the increment of effective hydrodynamic volume due to any interaction present at concentration c.

Equation (1) has been extended to blends of conventional polymers and discussed in terms of attractive and/or repulsive intermolecular interactions[5].

In this paper, we consider the system cellulose (CE)–polyacrylonitrile (PAN)–dimethylacetamide + 7% LiCl (w/w) (DMAc/7% LiCl). The aims are to evaluate extension of the method to blends containing at least one semirigid mesogenic polymer, and to present evidence of the type of interaction between CE and PAN, which are known to demix in solution at relatively high concentration and in the solid state[10,11].

Experimental

The samples of CE (degree of polymerization, $DP = 250$) and PAN ($DP = 1925$) were the same as those used in previous work[11]. The solvent was DMAc/7% LiCl. Polymer stock solutions at $c \simeq 4\%$ (w/w) were prepared according to the method previously described[11]. CE solution was centrifuged for 1 h at 15 000 rev min^{-1} in order to remove any insoluble material, a little of which (<0.1% w/w of the whole solution) has been observed in some cases. The final mass was determined by gravimetry and the concentration deduced therefrom.

Viscosity measurements were performed by using a suspended-level Ubbelohde viscometer at 25 ± 0.01°C. The flow time of the solvent was more than 100 s in order to ensure the independence of viscosity from the shear rate.

A set of about 12 values of η_{sp} at various concentrations was obtained for the pure polymers, according to the following procedure. A solution at $c \simeq 1\%$ (w/v) was prepared by dilution of the respective stock and introduced into the viscometer. After determination of η_{sp}, the solution was diluted three times, measuring the η_{sp} value at each concentration. At this point it was generally impossible to perform further dilution inside the viscometer and the solution had to be replaced, therefore a new solution, with a concentration in the same range as previously explored, was introduced into the viscometer. Following this method, the ranges of concentration of each set of measurements are partially overlapped, assuring the self-consistence of the experiment.

A similar method was applied to the polymeric blends, starting from a suitable mixture of the initial stock solutions. Measurements were performed no more than 24 h after mixing.

Results and discussion

Figure 1 shows the trend of η_{sp}/c *versus* c for CE, PAN and their mixtures in the concentration range $0.1 \leqslant c \leqslant 1\%$ (w/v). The good linearity suggests that equation (1) is

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followed and no additional terms are necessary at a higher concentration. Values of $[\eta]$ and K_H are easily obtained from the intercept and the slope of the straight lines reported in *Figure 1*. *Table 1* contains these results and *Figure 2* shows the trend of $[\eta]$ and K_H with composition.

The linear trend of $[\eta]$ (*Figure 2a*) satisfies the condition that each component contributes to the $[\eta]$ of the mixture proportionally to its weight fraction, w, according to:

$$[\eta]=\sum_i [\eta]_i w_i \tag{2}$$

This trend has been verified experimentally for homopolymers with a wide molecular weight distribution as well as for heterogeneous mixtures[12–14]. Therefore a first conclusion is that our system follows equation (2).

If we now consider K_H values for CE and PAN, it is observed that both are lower than might be expected. In fact, according to Riseman and Ullman[15], K_H should vary from about 0.6 for a coil, to $\simeq 0.73$ for a rod and 1 for a sphere. Therefore, it is noteworthy that the semirigid CE in DMAc/7% LiCl shows $K_H \simeq 0.4$, while PAN, which has a coil conformation, shows a value as low as 0.28.

Table 1 Values of $[\eta]$ and K_H at different weight fractions of cellulose (w_{CE}) in mixed polymer, in the system cellulose–polyacrylonitrile–DMAc/7% LiCl at 25°C

w_{CE}	$[\eta]$ (dl g^{-1})	K_H
1.0	2.25	0.45
0.7	2.03	0.40
0.5	1.94	0.36
0	1.65	0.25

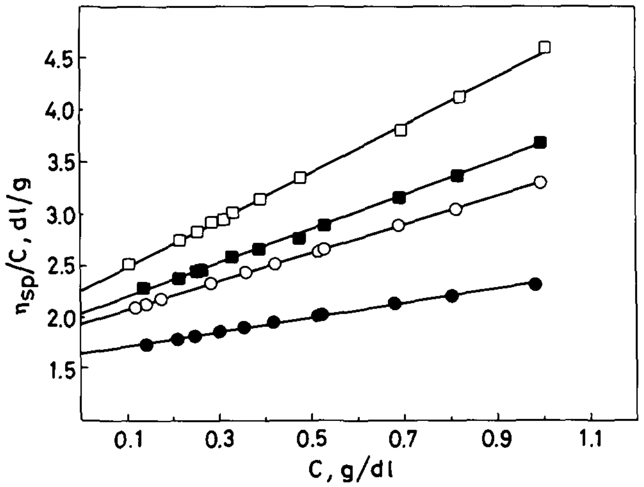

Figure 1 Dependence of reduced specific viscosity on concentration in DMAc/7% LiCl at 25°C: □, pure CE; ■, 0.7 weight fraction of CE; ○, 0.5 weight fraction of CE; ●, pure PAN

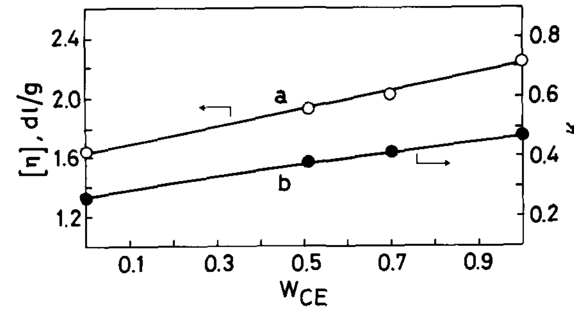

Figure 2 (a) Variation of intrinsic viscosity with weight fraction of cellulose, from equation (2); ○, experimental data. (b) Variation of Huggins' constant with weight fraction of cellulose from equation (3); ●, experimental data

A second point concerns the trend of K_H with the composition (see *Figure 2*). As reported above, the last term of equation (1) represents the effect of all types of interaction on the effective hydrodynamic volume. According to Cragg and Bigelow[5], three types of interaction may contribute to the term $K_H[\eta]^2c$: the long-range hydrodynamic interaction, the short-range intermolecular attraction or repulsion, and the formation of molecular dimers. At a low enough concentration, the last term is generally negligible except for very poor solvents. For binary systems, even the second term can be neglected, and consequently the polymer–polymer interaction is only hydrodynamic in character. This conclusion concerns the pure components, whose representative points fall on the ordinate axes (*Figure 2*).

When we deal with ternary systems, the second condition cannot be neglected, so that a positive (negative) contribution should be added (subtracted) to the hydrodynamic interaction. A simple way of establishing the relevance of this term is to write the theoretical expression of K_H for polymer mixtures, considering that only the long-range hydrodynamic interactions are effective[5]:

$$K_{H\text{-}m}=\frac{K_{H\text{-}1}[\eta]_1^2w_1^2+K_{H\text{-}2}[\eta]_2^2w_2^2+2K_{H\text{-}1}K_{H\text{-}2}[\eta]_1[\eta]_2w_1w_2}{([\eta]_1w_1+[\eta]_2w_2)^2} \tag{3}$$

where the indexes m, 1, 2 indicate the mixture and components 1 and 2, respectively.

When the experimental points fall below (over) the curve $K_{H\text{-}m}$–composition, the occurrence of unfavourable (favourable) intermolecular interaction is demonstrated.

From *Figure 2*, it is evident that there is good agreement between experimental points and the theoretical curve. Therefore, the intermolecular interactions between CE and PAN should be exclusively hydrodynamic in nature. The lack of any other kind of interaction can be interpreted in thermodynamic terms by considering that the mixture is stabilized only by the entropic gain.

In order to better understand this unusual behaviour, we may recall that a strong interaction between CE and the the complex DMAc/7% LiCl[16] was ascertained and subsequently used to explain the solvent power. It is also probable that non-dissimilar interactions occur between PAN and the solvent[17].

As a consequence, we can imagine the two polymeric molecules to be surrounded by a 'shell' of solvent strictly bonded to the chain. This could be one of the main reasons for the lack of short-range interaction between the units of dissimilar chains, i.e. preferential adsorption arises.

If we now look at solutions at higher concentration, the situation may change dramatically. For example, it is well known that even a single polymer can give demixing phenomena in a solvent, when the molecular weight distribution is particularly wide[18]. Moreover, variation of thermodynamic interactions with change in the concentration are quite common[19].

These considerations provide an understanding of why CE–PAN mixtures, notwithstanding the properties exhibited in dilute solution, give liquid–liquid demixing at high concentrations in the same solvent. This point was demonstrated in a recent paper[11]. We will try to extend the viscometric method to the analysis of other blends based on semirigid polymers. However, we suggest that caution be applied in extending the results obtained for these complex systems to higher concentrations.

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