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# Polymer conformation in mixed aqueous-polar organic solvents

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ABSTRACT

The conformation of the common polysaccharide dextran has been investigated in mixed solvents at two different temperatures using viscosity measurements. In particular we considered binary mixtures of water with the polar organic solvents glycerol, formamide, dimethylsulfoxide, or ethanol. The intrinsic viscosity of dextran T500 in the different systems has been determined, and the solvent effects, as manifested in variations of the dextran intrinsic viscosity and coil radius, have been correlated to the surface tension and the fractional solubility parameters of the solvent mixture. The coil dimension changes observed in the different solvent mixtures are consistent with expectations from water–cosolvent–dextran interactions, especially as they pertain to hydrogen bonding.



## 1. Introduction

Solvents can have a great impact on the conformation of polymers [1–4]. Depending on the interactions between the polymer and the solvent molecules, a polymer may dissolve fully or phase separate. In a good solvent, polymer coils swell and expand, whereas in marginal solvent conditions they contract to their unperturbed dimensions. Addition of another solvent in a polymer solution can greatly enhance or reduce the polymer miscibility. This is especially the case when the main solvent is water. Polymers dissolved in mixtures of water with polar organic solvents are widely used in applications such as coatings, paints and inks, pharmaceutics, personal care products, and protein processing [5,6]. In many such multi-component products, e.g., pharmaceutics, the mixed solvents serve to enhance the solubility of substances that have too low solubility in neat solvents [7–9]. At the same time, these solvents affect the solubility, conformation and function of the polymers which are typically incorporated in the formulations for reasons such as viscosity control, colloidal stability, or delivery of actives.

Motivated by the fundamental and practical considerations outlined above, our research group has been active in the study of solution properties of water-soluble polymers in single and mixed organic solvents [4,10–12]. The polysaccharide dextran is a water-soluble polymer that offers the advantages of being biocompatible and biodegradable [13]. Mainly used as plasma volume expander in clinical applications, dextran also serves as a rheology modifier in food, drink, cosmetics, pharmaceutical, coating, paint, photographic, and agricultural products. Several studies of dextran in pure solvents have been reported [14–18], but there is a dearth of information on dextran in mixed solvents. Only Mahapatra et al. [19] has published data of dextran fractions in mixtures of water and polar solutes (NaOH, KOH, urea, glycine, and glucose).

In this work we investigate solution properties of dextran in binary mixtures of water and polar organic solvents such as formamide, glycerol, dimethylsulfoxide (DMSO), and ethanol. We are interested in the conformation of dextran as affected by the addition of a good or a bad solvent, or the variation of temperature. We use viscosity measurements to obtain the polymer intrinsic viscosity, coil radius, and coil volume, and we discuss these properties in terms of the quality of the mixed solvent. In order to interpret our results in mixed solvents we sought literature information concerning water–cosolvent interactions.

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The solvents examined in this work have been identified utilizing the polymer–solvent interaction parameter $\chi_{12}$ and the free energy of interfacial interaction $\Delta G_{121}$. Dextran is a hydrophilic, monopolar, neutral polymer. As an electron donor, dextran manifests a strong, Lewis acid–base (AB) repulsion ($\Delta G^{AB} > 0$) in water, also an electron donor [20]. The $\chi_{12}$ interaction parameters (Table 1) were determined following procedures in Hansen [21]. A polymer dissolves in a solvent when the $\chi_{12}$ value is lower than 0.5. On the basis of $\chi_{12}$ parameters close or lower than 0.5, dextran is expected to dissolve in glycerol, formamide, and DMSO. The value of the dextran–ethanol $\chi_{12}$ parameter was significantly higher than 0.5, which indicates that ethanol is a bad solvent for dextran. The free energy of interfacial interaction, $\Delta G_{121}$, when positive, suggests that molecules of type (1) will repel each other in solvent (2) and will spontaneously dissolve in it [20]. If $\Delta G_{121}$ is negative, then molecules (1) will attract each other in solution, and will thus tend to precipitate from the solvent (2). According to the $\Delta G_{121}$ values resulting from the van Oss method [20] (Table 1), dextran is expected to dissolve in formamide, DMSO or water (where the $\Delta G_{121}$ values are positive), but not in ethanol or glycerol (negative $\Delta G_{121}$ values). These two different approaches (by Hansen [21] and van Oss [20]) concur that formamide, DMSO and water are good solvents for dextran, while ethanol is a bad solvent. Glycerol appears to be a good solvent for dextran if we use the $\chi_{12}$ data and a bad solvent if we use the $\Delta G_{121}$ values. However, the $\chi_{12}$ value of glycerol 0.491 is very close to the limit of 0.5, and the $\Delta G_{121} = -2.11$ is relatively close to 0 in comparison to the $-9.66$ $\Delta G_{121}$ value for ethanol. Clearly, glycerol is expected a better solvent for dextran than ethanol.

To our best knowledge, this is the first time that the conformation of dextran is being reported in mixed solvents. Moreover, we have successfully correlated here the dextran coil dimensions to properties (surface tension and fractional solubility parameters) of the solvent mixtures. A few studies have attempted to correlate dextran solution behavior to solvent properties in single solvents [22], but none in mixed solvents.

## 2. Materials and methods

### 2.1. Materials

Dextran, a polysaccharide biopolymer consisting of glucose units, is the subject of this investigation. We consider the T500 dextran fraction, with weight average ($M_w$) and number average ($M_n$) molecular weights 500,000 and 191,500 respectively, purchased from Amersham Biosciences AB (now part of GE Healthcare, Uppsala, Sweden) and Pharmcosmos A/S (Holbaek, Denmark). Dimethylsulfoxide (DMSO) and glycerol (purified grade, 99% min) were obtained from Fisher Scientific (Fair Lawn, NJ). Formamide (molecular biology grade) was purchased from VWR International (West Chester, PA) and ethanol from Decon Labs, Inc. (King of Prussia, PA). The water used was purified with a Milli-Q system.

Two solvents were mixed to create a binary solvent mixture of desired vol.% composition. Samples were prepared individually for every dextran concentration by dissolving appropriate amount of polymer in a given binary solvent mixture. The samples remained under stirring for at least one day at room temperature and then equilibrated at 20° or 40 °C for at least an hour before the measurements were conducted at the same temperature.

### 2.2. Methods

We performed viscosity measurements at both 20° and 40 °C for dextran T500 in mixtures of water with one of the following polar organic solvents: glycerol, formamide, DMSO and ethanol. The viscosity of dilute dextran solutions was determined using Cannon Fenske Routine type viscometers [23] for transparent Newtonian fluids (aqueous solutions of up to 30 wt.% dextran exhibit Newtonian flow characteristics according to [17]). Different sizes of viscometers were used depending on the viscosity range of the samples. The viscometer was placed inside a constant temperature bath to ensure that the measurements were taken under constant temperature (controlled to within ±0.1 °C). The efflux times were reproducible to ±0.1% (each measurement was repeated three times) and were measured with an accuracy of ±0.1 s. The kinematic viscosity $\eta$ is calculated by multiplying the efflux time with the viscometer calibration constant (supplied by the manufacturer, Cannon Instrument Co., State College, PA). The viscosity data analysis procedure has been presented elsewhere [24]. Briefly, focusing on data in the dilute regime, we obtain the intrinsic viscosity for dextran and extract the coil dimensions using the Einstein viscosity relation (see below).

### 2.3. Intrinsic viscosity

The intrinsic viscosity values of dextran in different solvents and at different temperatures are determined using

**Table 1**
Surface tension, $\gamma$, surface tension apolar component, $\gamma^{LW}$, surface tension polar component, $\gamma^{AB}$, electron-acceptor parameter of the surface tension, $\gamma^+$, electron-donor parameter of the surface tension $\gamma^-$, according to van Oss [20], free energy of interfacial interaction, $\Delta G_{121}$, estimated with the van Oss [20] procedure for the single solvents used in this study, and Flory–Huggins parameter, $\chi_{12}$, estimated using the Hansen [21] procedure and data.

| Solvent | $\gamma$ | $\gamma^{LW}$ | $\gamma^{AB}$ | $\gamma^+$ | $\gamma^-$ | $\Delta G_{121}$ | $\chi_{12}$ |
|---|---|---|---|---|---|---|---|
| Dimethylsulfoxide | 44.0 | 36.0 | 8.0 | 0.50 | 32.0 | 4.51 | 0.500 |
| Formamide | 58.0 | 39.0 | 19.0 | 2.28 | 39.6 | 6.67 | 0.419 |
| Glycerol | 64.0 | 34.0 | 30.0 | 3.92 | 57.4 | −2.11 | 0.491 |
| Ethanol | 22.4 | 18.8 | 2.6 | 0.02 | 68.0 | −9.66 | 0.696 |
| Water | 72.8 | 21.8 | 51.0 | 25.50 | 25.5 | 41.24 | |
| Dextran T70 | 55.5 | 41.8 | 13.7 | 1.00 | 47.2 | | |
| Dextran T150 | 42.0 | 42.0 | 0.0 | 0.00 | 55.0 | | |