

# Solution Thermodynamics of the Dextran/Methoxy Ethylene Glycol System

ALI GÜNER,<sup>1</sup> EFKAN ÇATIKER<sup>2</sup>

<sup>1</sup> Hacettepe University, Faculty of Science, Department of Chemistry, Beytepe, TR-06532, Ankara, Turkey

<sup>2</sup> Abant İzzet Baysal University, Department of Chemistry, TR-14280, Bolu, Turkey

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**ABSTRACT:** The main thermodynamic parameters were evaluated for the dextran/methoxy ethylene glycol (MEG) system by viscosity measurements at 25, 30, 35, 40, and 45°C. The long-range and short-range interaction parameters were determined by extrapolation methods, i.e, Kurata-Stockmayer-Fixman, Berry, and Inagaki-Suzuki-Kurata equations. Calculated values, as well as the unperturbed root-mean-square end-to-end distance and hydrodynamic expansion factor, were interpreted mainly on the basis of hydrogen-bond formation between polymer segments and dextran/MEG molecules in solution. The thermodynamic interaction parameter was also evaluated for the same system. The theta temperatures were obtained from the temperature dependence of the interaction parameter, dependence of  $(1/2-\chi)$  and the second virial coefficient in the temperature interval of 25 and 45°C for the system and quite a good accordance was indicated with the calculated values evaluated via extrapolation and interpolation methods. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 948–953, 2001

**Key words:** dextran; methoxy ethylene glycol; solution thermodynamics

## INTRODUCTION

Dextran, a polysaccharide, is soluble in water and some conventional polar solvents, and has great importance/applications in different technologies. Polymer has a ring oxygen and bridge oxygen atoms in each repeating unit besides the hydroxyl groups in the ring structure.

Dextran forms complexes of the therapeutic use with certain transition metal cations,<sup>1–5</sup> rare earth,<sup>6</sup> and light lanthanoid elements<sup>7</sup> in aqueous solutions. These complexations were investigated by different methods; viscosity,<sup>4,6,7</sup> spectrophotometry,<sup>4</sup> conductometry,<sup>7</sup> fluorescence measurements,<sup>6</sup> optical rotatory dispersion,<sup>3,5,6</sup> dialysis equilibrium,<sup>4</sup> etc.

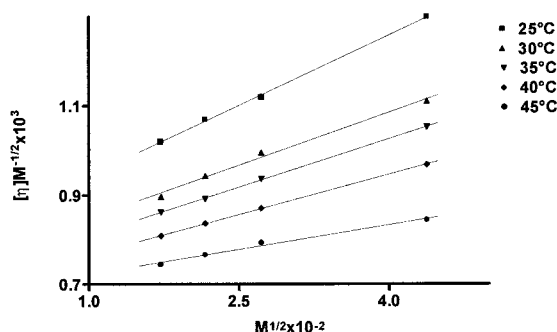
The solubility of polymer in aqueous medium can be explained by the strong hydrogen bonding between polymer segments and water molecules. In previous studies it has been reported that denaturing agents<sup>8,9</sup> have been effective compounds for destroying the molecular association in the aqueous solutions of dextran.

Our ongoing studies are mainly focused on thermodynamic aspects of hydrogen bond formation in dextran/water,<sup>10</sup> dextran/DMSO,<sup>11</sup> and dextran/ethylene glycol<sup>12</sup> systems mainly considered with regard to long- and short-range interactions.

This article describes the thermodynamic aspects of dextran/MEG system to determine the unperturbed dimensions, thermodynamic expansion, long-range interaction behavior, thermodynamic interaction parameter (including enthalpic and entropic terms), and finally the theta temperature of the polymer found by different ways in the employed solvent.

Correspondence to: A. Güner (agun@hacettepe.edu.tr).

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**Figure 1** Kurata-Stockmayer-Fixman plot for the dextran/MEG system.

## EXPERIMENTAL

Dextran samples used in this study were obtained from Pharmacia Fine Chemicals AB, Uppsala, Sweden. The molecular weight characteristics of polymer samples were determined by Pharmacia, and the number-average molecular weights of T40, T110, and T500 are given as 29,500, 74,000, and 191,500  $\text{gmol}^{-1}$ , respectively. The number-average molecular weight of the T70 sample was determined as 46,800  $\text{gmol}^{-1}$  by a Knauer Membrane Osmometer in aqueous solution at room temperature. The solvent, methoxy ethylene glycol, was of analytical grade and obtained from Merck, Darmstadt.

The viscometric measurements were carried out at 25, 30, 35, 40, and 45°C, using an Ubbelohde type of capillary viscometer. The temperature of the thermostat was controlled within a range of  $\pm 0.1^\circ\text{C}$ , and the flow times were measured with a digital accuracy of  $\pm 0.1$  s. The concentration dependence of the viscosity results of dilute polymer solutions (in a 0.4–0.2  $\text{gdL}^{-1}$  concentration range) was followed by the well-known Huggins equation.

Densities of the polymer samples were determined as, 1.37( $\pm 0.02$ ) (T40), 1.55( $\pm 0.01$ ) (T70), 1.61( $\pm 0.02$ ) (T110), and 1.93( $\pm 0.03$ ) (T500)  $\text{gmL}^{-1}$  in water and dimethylsulfoxide using a pycnometer at room temperature.

## RESULTS AND DISCUSSION

The unperturbed dimension parameter,  $K_o$ , is independent of temperature, molecular weight of the polymer, and solvent. It measures only the short-range interactions of the polymer segments, and can be determined by various techniques.

One of the basic techniques to receive information on unperturbed dimensions has been found from extrapolation methods starting from viscosity measurements, namely, the Kurata-Stockmayer-Fixman equation<sup>13</sup> employed in the present study,

$$[\eta]M^{-1/2} = K_o + 0.51B\Phi_o M^{1/2} \quad (1)$$

and the relationship between  $K_o$  and  $\langle r^2 \rangle_o$  is given by

$$K_o = [\eta]_o M^{-1/2} = \Phi_o (\langle r^2 \rangle_o / M)^{3/2} \quad (2)$$

where,  $[\eta]$  is the intrinsic viscosity,  $M$  is the molecular weight of the polymer (number-average molecular weight),  $B$  is the parameter for long-range (polymer-solvent) interactions,  $\Phi_o$  is Flory's constant ( $2.1 \times 10^{23} \text{mol}^{-1}$ ),  $[\eta]_o$  is the intrinsic viscosity at theta temperature, and finally,  $\langle r^2 \rangle_o^{1/2}$  represents the root-mean-square end-to-end distance of unperturbed polymer chain.

The Berry equation<sup>14</sup>

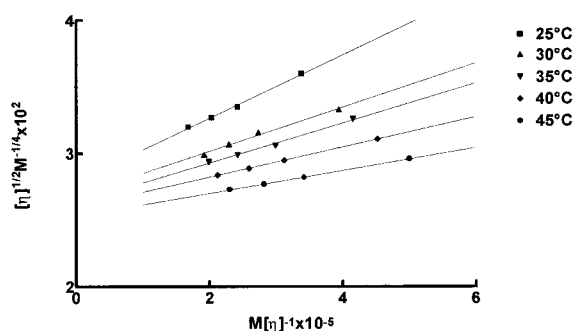
$$[\eta]^{1/2} M^{-1/4} = K_o^{1/2} + 0.42K_o^{1/2} B \Phi_o M [\eta]^{-1} \quad (3)$$

and the Inagaki-Suzuki-Kurata equation<sup>15</sup>

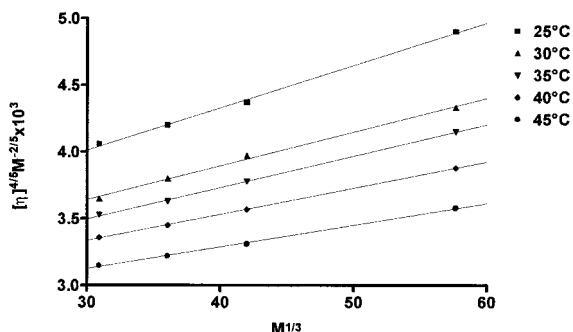
$$[\eta]^{4/5} M^{-2/5} = 0.786K_o^{4/5} + K_o^{2/5} B^{2/3} \Phi_o^{2/3} M^{1/3} \quad (4)$$

have been used for the determination of short- and long-range interaction parameters for the dextran/methoxy ethylene glycol system.

By the use of these equations, the plots of  $[\eta]M_n^{-1/2}$  against  $M_n^{1/2}$ ,  $[\eta]^{1/2}M_n^{-1/4}$  against  $M_n[\eta]^{-1}$ , and  $[\eta]^{4/5}M_n^{-2/5}$  against  $M_n^{1/3}$  yielded straight lines with high correlation, the intercept being  $K_o$  and the slope characterizing the polymer-solvent interactions was determined by lin-



**Figure 2** Berry plot for the dextran/MEG system.



**Figure 3** Inagaki-Suzuki-Kurata plot for the dextran/MEG system.

ear regression analysis as shown in Figures 1–3, respectively. Calculated short and long-range interaction parameters are given in Table I.

The unperturbed dimension parameters evaluated from Kurata-Stockmayer-Fixman and Berry are in high accordance with each other, and a decrease in  $K_o$  values at increasing temperatures is quite obvious with all these extrapolation techniques as well as the observation for the long-range interaction parameter–temperature behavior. At this point, it would be better to discuss the interactions between the polymer segments and polymer–solvent molecules. Corresponding the structure of dextran, it is strongly expected that molecular association/interaction will form between the polymer segments and solvent molecules through hydrogen bonding. Of course, this decrement in terms of temperature increment results in the break of polymer–solvent associations, i.e., hydrogen bonds between polymer and methoxy ethylene glycol molecules as well as in the rupture of the interactions between the polymer segments.

It is also possible to follow the effect of temperature on different hydrodynamic magnitudes, such as root-mean-square end-to-end distance of

the polymer at unperturbed state according to eq. (2) by determination of the intrinsic viscosity at the theta temperature, and the hydrodynamic expansion factor,  $\alpha_\eta$ , of the polymer is simply given below,

$$\alpha_\eta^3 = [\eta]_T / [\eta]_\Theta \quad (5)$$

where  $[\eta]_T$  is the intrinsic viscosity of the solution at different temperatures.

The magnitudes,  $[\eta]$ ,  $\alpha_\eta$  and  $\langle r^2 \rangle_o$  (Table II) are the measures of the hydrodynamic volume, intensity of the thermodynamic interactions and the hydrodynamic expansion/contraction of the polymer in solution, respectively. It is clearly seen that in the hydrodynamic volume, intensity of the thermodynamic interactions and the hydrodynamic expansion of the coil are in a decrement trend by temperature increment. Of course, this significant change mainly shows the effect of temperature on the interactions between the polymer and solvent molecules in solution.

The temperature dependence of long-range interaction parameters is given by<sup>16</sup>

$$B = B_o(1 - \Theta/T) \quad (6)$$

where  $B_o$  is a constant (independent of temperature) and  $\Theta$  is the theta temperature of the polymer–solvent pair.

The plots of  $B$  obtained from extrapolation methods vs. the reciprocal of the temperature, according to eq. (6), resulted in straight lines (Figs. 4 and 5), where the slope yielded the theta temperature of the studied system. The theta temperatures were determined as:  $\Theta = 340.01$  K [according to  $B$  values obtained from eq. (1)],  $\Theta = 333.16$  K [according to  $B$  values obtained from eq. (3)], and  $\Theta = 334.07$  K [according to  $B$  values

**Table I** Calculated Thermodynamic Parameters for Dextran/MEG Solutions

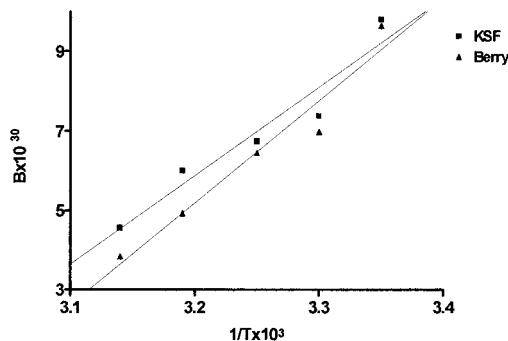
T (K)	KSF		Berry		ISK	
	$K_o \times 10^4$ (dL g <sup>-1</sup> )	$B \times 10^{30}$ (cm <sup>3</sup> )	$K_o \times 10^4$ (dL g <sup>-1</sup> )	$B \times 10^{30}$ (cm <sup>3</sup> )	$K_o \times 10^4$ (dL g <sup>-1</sup> )	$B \times 10^{30}$ (cm <sup>3</sup> )
298	8.40	9.80	7.79	9.64	9.74	178
303	7.70	7.37	7.23	6.97	9.05	132
308	7.38	6.73	6.92	6.44	8.69	121
313	7.06	6.00	6.75	4.93	8.51	93.7
318	6.61	4.56	6.40	3.84	8.05	73.1

**Table II** Calculated Data for Dextran/MEG Solutions from Intrinsic Viscosity Measurements in the Temperature Range of 25–45°C

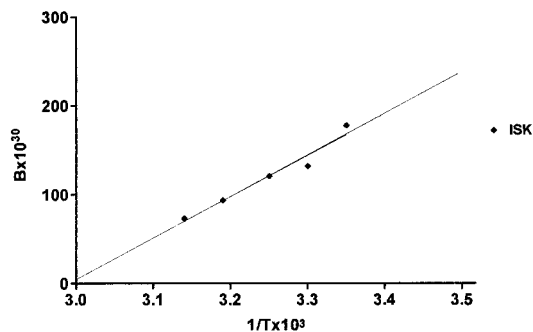
Dextran	$[\eta]\theta$ (dL g <sup>-1</sup> )	$\alpha_\eta$	$\langle r^2 \rangle_o^{1/2} \times 10^7$ (cm)
[ $\eta$ ] 25°C			
T40	0.176	0.144	1.069
T70	0.231	0.182	1.083
T110	0.306	0.229	1.101
T500	0.567	0.368	1.155
[ $\eta$ ] 30°C			
T40	0.154	0.132	1.053
T70	0.204	0.167	1.069
T110	0.271	0.209	1.090
T500	0.486	0.337	1.130
[ $\eta$ ] 35°C			
T40	0.148	0.127	1.052
T70	0.193	0.160	1.065
T110	0.255	0.201	1.083
T500	0.461	0.323	1.126
[ $\eta$ ] 40°C			
T40	0.139	0.121	1.047
T70	0.181	0.153	1.058
T110	0.237	0.192	1.073
T500	0.424	0.309	1.111
[ $\eta$ ] 45°C			
T40	0.128	0.114	1.042
T70	0.166	0.143	1.051
T110	0.216	0.180	1.053
T500	0.383	0.289	1.098

obtained from eq. (4)] for dextran in methoxy ethylene glycol solutions.

Determination of the reliable theta temperature of a studied polymer/solvent system has a



**Figure 4** Plot of the interaction parameter obtained from KSF and Berry equations as a function of the reciprocal of the temperature for the dextran/MEG system.



**Figure 5** Plot of the interaction parameter obtained from the ISK equation as a function of the reciprocal of the temperature for the dextran/MEG system.

great physicochemical importance for polymer solution thermodynamically. To obtain more accurate/reliable values of theta temperatures, Flory interaction parameter–temperature and second virial coefficient–temperature relationships were also determined individually for dextran/methoxy ethylene glycol system.

The relation between hydrodynamic linear expansion factor,  $\alpha$ , and  $\alpha_\eta$  is given by Kurata and Yamakawa<sup>17</sup>

$$\alpha_\eta^3 = \alpha^{2.43} \quad (7)$$

The thermodynamic linear expansion factor has been related to Flory interaction parameter,  $\chi$ , through the Flory Fox<sup>18</sup> equation,

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)M^{1/2} \quad (8)$$

and

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi_S)(1 - \Theta/T)M^{1/2} \quad (9)$$

The coefficient  $C_M$  presented below is given by,

$$C_M = 27v_2^2M^{3/2}/[2NV_1(2\pi\langle r^2 \rangle_o)^{3/2}] \quad (10)$$

where  $v_2$  is the specific volume of the polymer,  $N$  is the Avogadro's number, and  $V_1$  is the molar volume of the solvent. The interaction parameter is the sum of  $\chi_H$  and  $\chi_S$ , which are the excess enthalpy and excess entropy of dilution parameters.

Calculated Flory interaction parameters are given in Table III, and it must be equal to 0.5 at the theta temperature. This stipulation is formed as,  $(1/2 - \chi) < 1.0 \times 10^{-4}$  for the dextran/methoxy ethylene glycol system.

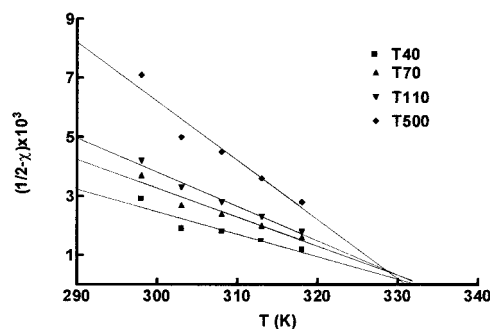
**Table III** Thermodynamic Parameters for the Dextran/MEG System

Dextran	$\alpha$	$C_M$	$\chi_S$	$\chi_H$	$\chi$
$T = 298$ K					
T40	1.086	2.313	0.502	$-2.344 \cdot 10^{-3}$	0.499
T70	1.103	1.823	0.503	$-3.011 \cdot 10^{-3}$	0.499
T110	1.126	1.685	0.503	$-3.394 \cdot 10^{-3}$	0.499
T500	1.079	1.166	0.505	$-5.799 \cdot 10^{-3}$	0.499
$T = 303$ K					
T40	1.065	2.529	0.502	$-1.749 \cdot 10^{-3}$	0.499
T70	1.086	1.974	0.502	$-2.476 \cdot 10^{-3}$	0.499
T110	1.112	1.846	0.502	$-2.996 \cdot 10^{-3}$	0.499
T500	1.163	1.273	0.504	$-4.591 \cdot 10^{-3}$	0.499
$T = 308$ K					
T40	1.065	2.647	0.502	$-1.888 \cdot 10^{-3}$	0.499
T70	1.086	2.065	0.502	$-2.537 \cdot 10^{-3}$	0.499
T110	1.103	1.928	0.503	$-2.975 \cdot 10^{-3}$	0.499
T500	1.158	1.331	0.504	$-4.839 \cdot 10^{-3}$	0.499
$T = 313$ K					
T40	1.058	2.773	0.502	$-1.891 \cdot 10^{-3}$	0.499
T70	1.072	2.162	0.502	$-2.489 \cdot 10^{-3}$	0.499
T110	1.091	1.999	0.503	$-2.869 \cdot 10^{-3}$	0.499
T500	1.139	1.387	0.504	$-4.570 \cdot 10^{-3}$	0.499
$T = 318$ K					
T40	1.052	2.941	0.502	$-1.917 \cdot 10^{-3}$	0.499
T70	1.063	2.309	0.502	$-2.446 \cdot 10^{-3}$	0.499
T110	1.078	2.138	0.503	$-2.729 \cdot 10^{-3}$	0.499
T500	1.122	1.487	0.504	$-4.389 \cdot 10^{-3}$	0.499

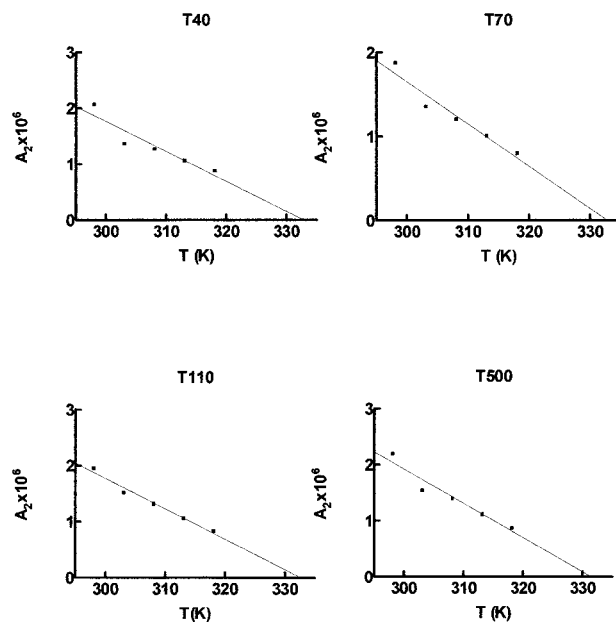
Calculated excess enthalpy and excess entropy of dilution parameters for the dextran/MEG system are also presented in Table III. Enthalpically, solubility/solvation of polymer in the MEG solution is preferred; however, entropically it is not, due to surrounding of the polymer chain with regular solvent molecules, which is not preferred at all. Solvation/association between polymer segments and MEG molecules are disturbed with an increment of temperature for polymer/polar solvent systems. According to determined dynamic and thermodynamic magnitudes it is observed that the strong interactions between polymer and solvent molecules through hydrogen binding will occur for the dextran/MEG system. It is obvious that  $\chi_H$  must be negative. Calculated  $\chi$  values seem to be higher than 0.5, as shown in Table III, and  $\chi_S$  is the only indicated force in setting  $\chi$  numerically to 0.5, which is believed to be the ideal condition of polymer solutions.

The dependence of  $(1/2 - \chi)$  on the temperature is seen in Figure 6. The theta temperatures for T40, T70, T110, and T500 samples are determined as 332.94, 332.82, 332.63, and 331.21 K for the dextran/methoxy ethylene glycol system as the interpolated values at  $(1/2 - \chi) = 0$ , respectively.

It is well known that the second virial coefficient can be determined from light scattering and osmometry measurements, which consequently exhibits a temperature dependence, finally yielding the theta temperature for the system under study. However, the determination of the second virial coefficient from the Zimm plot is really a time-consuming and difficult task, although quite reliable. This coefficient can be evaluated from Flory interaction parameter, as suggested by Wakker,<sup>19</sup> and is given by,



**Figure 6** Dependence of  $(1/2 - \chi)$  on the temperature for the dextran samples in the MEG solutions.



**Figure 7** Dependence of  $A_2$  on the temperature for the dextran samples in the MEG solutions.

$$A_2 = (1/2 - \chi)(\rho_p^2 V_1)^{-1} \quad (11)$$

where  $\rho_p$  is density of the polymer.

The plot of the second virial coefficient against temperature (Fig. 7) also yielded straight lines, from which interpolated values were determined as 332.93, 332.89, 332.71, and 331.14 K for T40, T70, T110, and T500 samples, respectively.

As can be clearly noticed, the theta temperatures obtained from Flory interaction parameter–temperature and second virial coefficient–temperature behavior of the dextran samples are in quite good agreement with each other.

## CONCLUSION

Despite keen interest in the solution properties of dextran, few investigations have been reported involving the thermodynamic aspects of polymer solution as far as is known. In this respect, this study reports unperturbed dimensions, hydrodynamic expansions, the short-range interactions, and the thermodynamic aspects of the dextran/methoxy ethylene glycol system in dilute solution between 25 and 45°C, extensively.

Referring to hydrodynamic magnitudes, it has been pointed out that interaction between both polymer segments and polymer–solvent mole-

cules are in competition with each other, and with increasing temperature, it is most probable that both types of interaction may be suppressed.

The important role of Flory interaction parameter in the determination of theta temperature of polymer/solvent systems were also pointed out in the present study. Three theta temperature sets obtained from different methods, namely extrapolation and interpolation methods, have all resulted in almost similar values, which are in quite good agreement with each other (except in the theta temperature, the  $B$  values obtained from Kurata-Stockmayer-Fixman equation). In our published<sup>10–12</sup> and ongoing work investigation of the effect of solvent in theta temperature is being studied in detail for water soluble polymers/polar solvent systems.

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