Interaction virial coefficients in some mixed polymer solutions

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The concentration dependence of the osmotic pressure for some aqueous ternary systems (polymer 2/polymer 4/water) has been studied up to relatively high concentrations. The interaction in the ternary systems has been evaluated in terms of mixed virial coefficients up to the third order (A_{24}, A_{224}, A_{244}). Data are also given for the corresponding binary systems. The polymers used were dextran, poly(*N*-vinyl-2-pyrrolidone), Ficoll, hydroxypropylcellulose and ethylhydroxyethylcellulose. An analysis is made of the relative contributions to the total osmotic pressure of various terms as a function of concentration.

(Keywords: ternary systems; osmotic pressure; dextran; poly(*N*-vinyl-2-pyrrolidone); Ficoll; hydroxypropylcellulose; ethylhydroxyethylcellulose)

INTRODUCTION

In an earlier paper[1] an osmotic method was described for determining the thermodynamic interaction in ternary macromolecular systems. The method proved excellent also in relatively concentrated systems and can be used to determine mixed virial coefficients at least up to the third order. In this paper results will be presented for several different aqueous ternary systems.

The immediate need for such data originated in our studies of diffusion-controlled structurized convective flow[2-5]. However, since ternary polymer systems are common in many different applications, data on the interactions in such systems are of general interest.

EXPERIMENTAL

Materials

The dextran samples (T40, T70, T150 and T500) and Ficoll 400 were obtained from AB Pharmacia, Uppsala, Sweden. As regards poly(*N*-vinyl-2-pyrrolidone) (PVP), the sample PVP 360 was obtained from Sigma Chemical Co., St. Louis, USA, and the sample PVP K60 was obtained from Fluka AG, Buchs, Switzerland. Hydroxypropylcellulose (HPC) was obtained from Hercules Inc., Wilmington, USA. Ethylhydroxyethylcellulose (EHEC) was obtained from Berol Kemi AB, Stenungssund, Sweden. The properties of the fractions (producer's data when available) are given in *Table 1*. In all calculations, data obtained in this study are used; however, see *Table 2*. This is necessary since often producer's $\langle M \rangle_n$ data are obtained from g.p.c. measurements.

Preparation of solutions

The polymer fractions were used as received except in the case of HPC and PVP K60. These samples contained relatively large amounts of low-molecular-weight material, which could interfere with the measurements. In order to remove the low-molecular-weight material, the solutions were dialysed for 7 days using a Spectrapore membrane from Spectrum Medical Industries Inc., Los Angeles, USA (molecular weight cutoff 12 000–14 000 daltons). The dialysed solutions were freeze-dried and the moisture content was determined by drying the samples at 105°C until constant weight was obtained.

Stock solutions were prepared by weight, taking into account the water content. For dextran the absolute concentration was determined polarimetrically ($[\alpha]_D^{25} = +200$)[6]. Dilutions were made by weight, and mass per volume concentrations were calculated using partial specific volumes (see *Table 1*). The solvent used was doubly distilled water containing 0.02% sodium azide to reduce bacterial growth.

Solutions of dextran T150 and T500 are known to contain molecular aggregates[7]. To dissolve these aggregates the solutions were treated in a boiling water bath for 30–45 min[8].

Partial specific volumes

The partial specific volume can be calculated from density measurements using the relationship:

$$1/\rho = (v_J - v_1)w_J + v_1 \tag{1}$$

where v = partial specific volume, ρ = density of solution, w = weight fraction, index 1 = solvent and index J = polymer. Densities were determined[9] at 20.0°C in an automatic digital densitometer (Anton Paar, Graz, Austria). The accuracy of the instrument is better than 0.0015 kg m^{-3}. *Figure 1* shows the relationship for the dextrans and for PVP 360. Partial specific volumes are given in *Table 1*.

Osmotic measurements

Osmotic pressure was measured using a membrane colloid osmometer[13] fitted with Diaflo YM-10 membranes (Amicon Corp., Scientific Systems Division,

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Table 1 Properties of the fractions

Sample	Lot no.	$\langle M\rangle_n$ (g mol^{-1})	$\langle M\rangle_w$ (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	v_J (cm^3 g^{-1})
Dextran T40	21945	25400	40500	21	0.604[c]
Dextran T70	23155	39000	75200	28	0.604[c]
Dextran T150	9620	86000	141000	35	
Dextran T500	21917	191500	465000	55	0.604[c]
Ficoll 400	2300	71000[c]		17[e]	0.66[h]
PVP K60[a]	128318	55000[c]			
PVP 360[b]	125B–1500	270000[d]	1190000[d]	155[f]	0.756[c]
HPC		59000[c]			0.77[i]
EHEC (E411G)	92003	110000		522[g]	0.710[j]

[a] Molecular weight 160000; no further information given by the manufacturer
[b] Molecular weight 360000; no further information given by the manufacturer
[c] This study
[d] Ref. 1
[e] Ref. 6
[f] Ref. 5
[g] Estimated from molecular weight relationship in ref. 10
[h] Ref. 11
[i] Ref. 12
[j] Ref. 10

Table 2 Virial coefficients of the two-component systems. Values in parentheses are ($t_{0.975}$ × std error) to give 95% confidence interval

Sample	$1/\langle M\rangle_n$ (10^{-5} mol g^{-1})	A_{JJ} (10^{-4} mol cm^3 g^{-2})	A_{JJJ} (10^{-3} mol cm^6 g^{-3})
Dextran T40[a]	3.37 (±0.16)	5.97 (±0.70)	1.32 (±0.71)
Dextran T70[a]	1.87 (±0.19)	5.71 (±0.85)	1.71 (±0.89)
Dextran T150[b]	1.16 (±0.24)	3.54 (±1.27)	4.99 (±1.58)
Dextran T500[b]	0.54 (±0.12)	3.50 (±0.80)	4.86 (±1.25)
Ficoll[c]	1.40 (±0.08)	1.03 (±0.24)	2.55 (±0.16)
PVP K60[b]	1.83 (±0.15)	7.21 (±0.97)	9.19 (±1.45)
PVP 360[a]	0.373 (±0.068)	6.18 (±0.90)	14.0 (±2.7)
HPC[b]	1.73 (±0.09)	8.59 (±0.22)	
EHEC (E411G)[d]	0.875 (±0.055)	5.82 (±0.68)	

[a] Ref. 1
[b] Concentration interval: $0<c<0.05$ g cm^{-3}
[c] Concentration interval: $0<c<0.07$ g cm^{-3}
[d] Concentration interval: $0<c<0.01$ g cm^{-3}

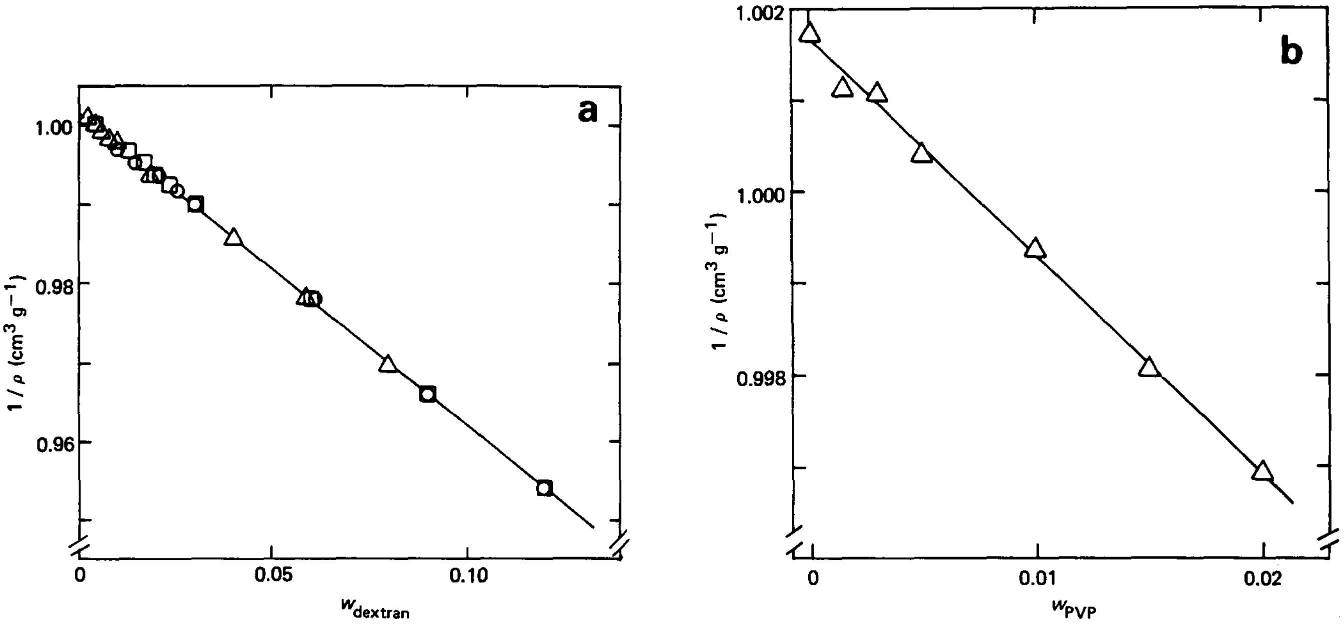

Figure 1 (a) Specific volume of solution *versus* weight fraction of dextran to evaluate the partial specific volume according to (1) for the dextran samples T40 (○), T70 (□) and T500 (△). (b) Corresponding evaluation of the partial specific volume according to (1) for the PVP 360 sample

Danvers, USA). The average temperature was 22.0 ± 0.7°C. The equilibration time was 1–5 min and the sample volume was 250 μl. The measurements were performed against water (containing 0.02% NaN_3) as reference, every third or fourth measurement being a reference measurement with solvent on both sides of the membrane to check the zero pressure. The Diaflo membrane was essentially non-permeable for all samples in this study. The development of the method and a comparison with other methods are made in ref. 1.

Experimental layout

For the two-component systems (polymer J in a solvent) the concentration dependence of the osmotic pressure was determined. Evaluation of the data was made using a polynomial expansion of the form:

$$\pi_J = RT(c_J/\langle M_J\rangle_n + A_{JJ}c_J^2 + A_{JJJ}c_J^3 + \ldots) \qquad (2)$$

where A_{JJ} and A_{JJJ} are the second and third virial coefficients for pure polymer J in a solvent. R and T have their usual meanings. The virial coefficients were calculated from a curve fit of equation (2) to experimental data.

For the three-component systems (polymer 2/polymer 4/solvent) two concentration series were utilized, one with constant concentration of polymer 2 (c_2), varying the concentration of component 4 (c_4), and one series with constant c_4 and varying c_2. From the total osmotic pressure of these solutions, the contributions due to the two separate polymers (π_2 and π_4) were subtracted. This procedure gives the pressure due to the interaction of the two polymers, π_{24}, which is given by:

$$\pi_{24} = RT(2A_{24}c_2c_4 + 3A_{224}c_2^2c_4 + 3A_{244}c_2c_4^2 + \ldots) \qquad (3)$$

A_{24} (the second mixed virial coefficient), A_{224} and A_{244} (the two third mixed virial coefficients) were calculated from a fit of equation (3) to experimental data for the two concentration series.

To make sure that no systematic errors in the virial coefficients arise due to the evaluation procedure, the virial coefficients of both two- and three-component systems were calculated from a fit of the total osmotic pressure. This procedure gave the same results within experimental error, but since this procedure sometimes gives large errors in the virial coefficients of the two-component systems[1], the first procedure is to be preferred. All curve fits were made using the SAS procedure REG[14].

RESULTS AND DISCUSSION

The osmotic pressure of a polymeric solution is related, through the chemical potential of the solvent, to the thermodynamic interaction between the different species in the solution.

In a binary solution the virial coefficients depend on the polymer segment–solvent, segment–segment and solvent–solvent interactions. The magnitude of the interaction depends on the chemical properties of the particular solute–solvent pair, which also includes the conformational statistics of the polymer. In a good solvent, where the polymer segments prefer the solvent environment to the polymer segment environment, the molecules can be considered as non-interpenetrating spheres. Each molecule in a very dilute solution will tend to exclude all other molecules from the volume which it occupies. This excluded volume can be calculated from the interaction between a pair of molecules and it is related to the second virial coefficient, The thermodynamic behaviour of dilute binary polymer solutions depends on the molecular weight, the thermodynamic interactions and the configuration of the molecules in the solution.

In ternary systems the interaction becomes more complex for two reasons. In the first place, new pair interactions are introduced and, secondly, the higher-order interactions will also include mixed interaction.

Two-component systems

For a given polymer–solvent pair the virial coefficients are dependent on a number of factors connected with the polymer sample, such as the molecular weight, the polydispersity (molecular weight distribution) of the sample[15] and the amount of branching in the molecules[16]. In this study, systems differing in these respects have been studied. The results are given in *Table 2*.

The molecular weight dependence of the virial coefficients was studied for a number of dextran fractions with approximately the same polydispersity and branching. The second virial coefficient decreases and the third virial coefficients increase with increasing molecular weight. Virial coefficients from light scattering and osmotic measurements for dextrans have been published for a broad range of molecular weights[15,17–19]. The molecular weight dependence and the magnitude of the coefficients of this study agree well with earlier findings. The results for the PVP samples are also in good agreement with data published earlier[15,19].

Ficoll, which is a relatively compact molecule of crosslinked polysucrose, is characterized by a small second virial coefficient compared to the other polymers. This could be expected since the second virial coefficient is correlated to the excluded volume of the molecule. The cellulose derivatives HPC and EHEC have a more extended structure and hence it is more difficult to perform measurements at high concentrations due to a high solution viscosity. The second virial coefficients are found to be relatively large at room temperature.

Three-component systems

For the three-component systems, the variation with molecular weight was studied using the system dextran/PVP/water (*Table 3*). The mixed virial coefficients vary with molecular weight as in the two-component systems: the second mixed virial coefficient decreases and the third mixed virial coefficients increase with increasing molecular weight. It has been suggested that for mixtures of polymers the second mixed virial coefficient is independent or only slightly dependent on the molecular weight of the sample[20]. For the system dextran/PVP/water the present results show a small but significant decrease in the second mixed virial coefficient with increasing molecular weight.

The variation of the virial coefficient is not very large between the systems in this study. Systems that have

Table 3 Virial coefficients of the three-component systems. Values in parentheses are ($t_{0.975}$ × std error) to give 95% confidence interval

System (component 2/component 4)	A_{24} (10^{-4} mol cm^3 g^{-2})	A_{224} (10^{-3} mol cm^6 g^{-3})	A_{244} (10^{-3} mol cm^6 g^{-3})
Dextran T40/PVP 360[a]	8.65 (±0.60)	2.38 (±0.84)	3.9 (±1.8)
Dextran T70/PVP 360[a]	7.32 (±0.70)	2.9 (±1.0)	6.3 (±1.9)
Dextran T150/PVP 360[b]	6.47 (±0.97)	6.8 (±1.2)	8.4 (±2.9)
Dextran T500/PVP 360[b]	5.63 (±0.86)	7.9 (±1.3)	8.1 (±2.6)
Dextran T70/PVP K60[c]	7.04 (±0.87)	4.23 (±0.96)	7.9 (±1.5)
Dextran T70/Dextran T500[c]	4.99 (±0.22)	1.85 (±0.27)	2.36 (±0.33)
PVP K60/PVP 360[b]	7.92 (±0.42)	5.48 (±0.77)	8.3 (±1.1)
Ficoll/PVP 360[b]	3.26 (±0.39)	3.15 (±0.33)	5.5 (±1.8)
Ficoll/Dextran T70[c]	3.12 (±0.25)	3.02 (±0.19)	3.14 (±0.29)
HPC/PVP 360[b]	8.58 (±0.46)		7.3 (±4.7)
HPC/Dextran T500[d]	9.27 (±0.34)		

[a] Ref. 1

[b] Concentration series: $0<c_2<0.05$, $c_4=0.005$; $c_2=0.010$, $0<c_4<0.025$ g cm^{-3}

[c] Concentration series: $0<c_2<0.05$, $c_4=0.010$; $c_2=0.010$, $0<c_4<0.05$ g cm^{-3}

[d] Concentration series: $0<c_2<0.025$, $c_4=0.005$; $c_2=0.005$, $0<c_4<0.02$ g cm^{-3}. Phase separation occurs at higher concentrations

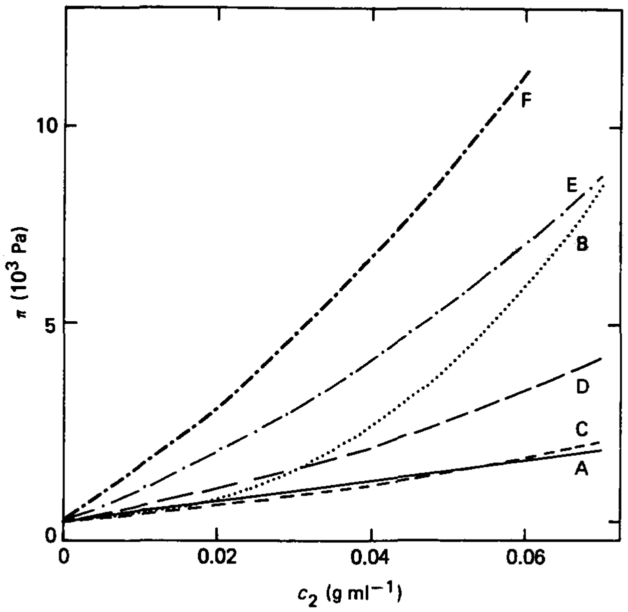

Figure 2 The osmotic pressure *versus* c_2 for an average system with $M_2=M_4=100\,000$ g mol^{-1}, $A_{22}=A_{44}=5.0\times10^{-4}$ mol cm^3 g^{-2}, $A_{222}=A_{444}=3.0\times10^{-3}$ mol cm^6 g^{-3}, $A_{24}=6.0\times10^{-4}$ mol cm^3 g^{-1}, and $A_{224}=A_{244}=5.0\times10^{-3}$ mol cm^6 g^{-1}: curve A, RTc_2/M_2; curve B, $RT(A_{22}c_2^2+A_{222}c_2^3)$; curve C, π_{24} for $c_4=0.005$ g ml^{-1}; curve D, π_{24} for $c_4=0.010$ g ml^{-1}; curve E, π_{24} for $c_4=0.020$ g ml^{-1}; curve F, π_{24} for $c_4=0.030$ g ml^{-1}. Since the system is symmetrical, the pressure due to a variation of component 4 can be evaluated by interchanging index 2 and 4 in this figure

Ficoll as one of the components, however, have relatively low second mixed virial coefficients. This could be anticipated since the second virial coefficient of Ficoll itself is low. HPC is known to 'salt out' in the presence of other macromolecules. This was the case for the system HPC/dextran T500/water for which phase separation occurs at concentrations higher than 0.02 g ml^{-1}. Attempts have been made to relate the mixed virial coefficients to the compatibility of the polymers[19], but it was found that, for pairs of polymers that show phase separation at low concentrations as well as for pairs that mix even at high concentration, the numerical value of the mixed virial coefficient came close to an average between the two individual second virial coefficients.

Since there are no large differences between the systems it could be of some value to construct an average model system. This system has coefficients with values typical for the systems of this study. Such a system serves the purpose of estimating the relative contributions from different types of interactions in a ternary system (*Figure 2*). Depending on the molecular weight of the samples, the part of the osmotic pressure due to mixing (π_{24}) could be larger than the sum of the binary components ($\pi_2+\pi_4$) since the mixed interaction is larger than the interaction in a binary system. For components of low molecular weight the contribution to the total osmotic pressure defined by the molecular weight is usually the dominant contribution.

Different models have been used for explaining and predicting the interaction in three-component systems[21]. From a practical point of view it could be interesting to have a good and simple method to estimate the interaction in a ternary system. Therefore different types of averages ($\langle A\rangle$) of the virial coefficients from the two-component systems were calculated and compared with the virial coefficients of the three-component systems. For the second mixed virial coefficients (*Table 4*) both the arithmetic and geometric means underestimate the actual value. There is a larger variation in the ratio $\langle A_{24}\rangle/A_{24}$ for the arithmetic mean. For the geometric mean the fraction is between 0.7 and 0.9 except for HPC/dextran T500/water. This system gives a larger second mixed virial coefficient compared with the geometric mean than the other systems. This could be due to the phase separation that occurs at relatively low concentrations. Because of the small concentration interval in which the measurements were made, only the second and no higher mixed virial coefficients could be determined. The second mixed virial coefficient could be affected by higher coefficients since they are of importance even at relatively low concentrations[1]. This would give a second mixed virial coefficient that is larger than the true one in the HPC/dextran T500 system.

For the third mixed virial coefficients (*Tables 5* and *6*) the two averages overestimate the coefficients, the geometric mean giving a smaller variation in the ratio $\langle A\rangle/A$. For practical purposes the average of the virial coefficients from the two-component systems gives a relatively good estimate of the virial coefficients in a three-component system.

Table 4 Second virial coefficients of the three-component systems and comparison with averaged values from the two-component systems. Values should be multiplied by 10^{-4} to give A_{24} in mol cm^3 g^{-2}. Values in parentheses are ($t_{0.975} \times$ std error) to give 95% confidence interval

System (component 2/component 4)	A_{24}	$(A_{22}+A_{44})/2$	$\frac{(A_{22}+A_{44})/2}{A_{24}}$	$(A_{22}A_{44})^{1/2}$	$\frac{(A_{22}A_{44})^{1/2}}{A_{24}}$
Dextran T40/PVP 360[a]	8.65 (±0.60)	6.07	0.70	6.07	0.70
Dextran T70/PVP 360[a]	7.32 (±0.70)	5.94	0.81	5.94	0.81
Dextran T150/PVP 360[b]	6.47 (±0.97)	4.86	0.75	4.68	0.72
Dextran T500/PVP 360[b]	5.63 (±0.86)	4.84	0.86	4.65	0.83
Dextran T70/PVP K60[c]	7.04 (±0.87)	6.46	0.92	6.41	0.91
Dextran T70/Dextran T500[c]	4.99 (±0.22)	4.60	0.92	4.47	0.90
PVP K60/PVP 360[b]	7.92 (±0.42)	6.70	0.85	6.68	0.84
Ficoll/PVP 360[b]	3.26 (±0.39)	3.60	1.10	2.52	0.77
Ficoll/Dextran T70[c]	3.12 (±0.25)	3.37	1.08	2.43	0.78
HPC/PVP 360[b]	8.58 (±0.46)	7.38	0.86	7.28	0.85
HPC/Dextran T500[d]	9.27 (±0.34)	6.04	0.65	5.48	0.59

[a] Ref. 1

[b] Concentration series: $0<c_2<0.05$, $c_4=0.005$; $c_2=0.010$, $0<c_4<0.025$ g cm^{-3}

[c] Concentration series: $0<c_2<0.05$, $c_4=0.010$; $c_2=0.010$, $0<c_4<0.05$ g cm^{-3}

[d] Concentration series: $0<c_2<0.025$, $c_4=0.005$; $c_2=0.005$, $0<c_4<0.02$ g cm^{-3}. Phase separation occurs at higher concentrations

Table 5 Third virial coefficients of the three-component systems and averaged values from the two-component systems. Values should be multiplied by 10^{-3} to give A_{224} and A_{244} in mol cm^6 g^{-3}. Values in parentheses are ($t_{0.975} \times$ std error) to give 95% confidence interval

System (component 2/component 4)	A_{224}	$(2A_{222}+A_{444})/3$	$\frac{(2A_{222}+A_{444})/3}{A_{224}}$	A_{244}	$(A_{222}+2A_{444})/3$	$\frac{(A_{222}+2A_{444})/3}{A_{244}}$
Dextran T40/PVP 360[a]	2.38 (±0.84)	5.55	2.33	3.9 (±1.8)	9.77	2.50
Dextran T70/PVP 360[a]	2.9 (±1.0)	5.81	2.00	6.3 (±1.9)	9.90	1.57
Dextran T150/PVP 360[b]	6.8 (±1.2)	7.99	1.17	8.4 (±2.9)	11.0	1.31
Dextran T500/PVP 360[b]	7.9 (±1.3)	7.91	1.00	8.1 (±2.6)	10.9	1.35
Dextran T70/PVP K60[c]	4.23 (±0.96)	4.20	0.99	7.9 (±1.5)	6.70	0.85
Dextran T70/Dextran T500[c]	1.85 (±0.27)	2.76	1.49	2.36 (±0.33)	3.81	1.61
PVP K60/PVP 360[b]	5.48 (±0.77)	10.8	1.97	8.3 (±1.1)	12.4	1.49
Ficoll/PVP 360[b]	3.15 (±0.33)	6.37	2.02	5.5 (±1.8)	10.2	1.85
Ficoll/Dextran T70[c]	3.02 (±0.19)	2.27	0.75	3.14 (±0.29)	1.99	0.63

[a] Ref. 1

[b] Concentration series: $0<c_2<0.05$, $c_4=0.005$; $c_2=0.010$, $0<c_4<0.025$ g cm^{-3}

[c] Concentration series: $0<c_2<0.05$, $c_4=0.010$; $c_2=0.010$, $0<c_4<0.05$ g cm^{-3}

[d] Concentration series: $0<c_2<0.025$, $c_4=0.005$; $c_2=0.005$, $0<c_4<0.02$ g cm^{-3}. Phase separation occurs at higher concentrations

Table 6 Third virial coefficients of the three-component systems and averaged values from the two-component systems. Values should be multiplied by 10^{-3} to give A_{224} and A_{244} in mol cm^6 g^{-3}. Values in parentheses are ($t_{0.975} \times$ std error) to give 95% confidence interval

System (component 2/component 4)	A_{224}	$(A_{222}^2A_{444})^{1/3}$	$\frac{(A_{222}^2A_{444})^{1/3}}{A_{224}}$	A_{244}	$(A_{222}A_{444}^2)^{1/3}$	$\frac{(A_{222}A_{444}^2)^{1/3}}{A_{244}}$
Dextran T40/PVP 360[a]	2.38 (±0.84)	2.90	1.22	3.9 (±1.8)	6.37	1.63
Dextran T70/PVP 360[a]	2.9 (±1.0)	3.45	1.19	6.3 (±1.9)	6.94	1.10
Dextran T150/PVP 360[b]	6.8 (±1.2)	7.04	1.03	8.4 (±2.9)	9.93	1.18
Dextran T500/PVP 360[b]	7.9 (±1.3)	6.91	0.87	8.1 (±2.6)	9.83	1.21
Dextran T70/PVP K60[c]	4.23 (±0.96)	3.00	0.71	7.9 (±1.5)	5.25	0.66
Dextran T70/Dextran T500[c]	1.85 (±0.27)	2.42	1.31	2.36 (±0.33)	3.43	1.45
PVP K60/PVP 360[b]	5.48 (±0.77)	10.57	1.93	8.3 (±1.1)	12.16	1.47
Ficoll/PVP 360[b]	3.15 (±0.33)	4.50	1.43	5.5 (±1.8)	7.93	1.44
Ficoll/Dextran T70[c]	3.02 (±0.19)	2.23	0.74	3.14 (±0.29)	1.95	0.62

[a] Ref. 1

[b] Concentration series: $0<c_2<0.05$, $c_4=0.005$; $c_2=0.010$, $0<c_4<0.025$ g cm^{-3}

[c] Concentration series: $0<c_2<0.05$, $c_4=0.010$; $c_2=0.010$, $0<c_4<0.05$ g cm^{-3}

[d] Concentration series: $0<c_2<0.025$, $c_4=0.005$; $c_2=0.005$, $0<c_4<0.02$ g cm^{-3}. Phase separation occurs at higher concentrations

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