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# Thermodynamic properties of aqueous solutions of maltodextrins from laser-light scattering, calorimetry and isopiestic investigations

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## Abstract

The thermodynamic properties of maltodextrins in aqueous solutions were studied by the isopiestic method, laser-light scattering and calorimetry. Three different maltodextrin samples with molar masses between 1000 and 3000 were investigated. The second and third osmotic virial coefficients of oligomers were determined. It was found that an influence of the molar mass on the second and third osmotic virial coefficients has to be considered only for the low molecular oligomers (up to maltotriose), whereas it can be neglected for oligomers with higher molecular mass. Furthermore, the Virial Equation with Relative Surface Fractions (VERS) model was used to correlate the experimental data for the activity of water and the heat of dilution. The results of that investigation were used to predict the activity of water and some other thermodynamic properties of some other low molecular saccharides for which experimental results are available in the literature.

*Keywords:* Maltodextrins; Saccharides; Polydisperse water-soluble polymers; Isopiestic method; Calorimetry; Multiangle laser-light scattering; Osmotic virial coefficients; VERS model

## 1. Introduction

Water-soluble polymers are found in a wide range of industrial products in particular in the food and pharmaceutical areas. This group of compounds comprises molecules from natural (renewable resource raw material) to synthetic (from petrochemical base feed stocks) origin. Due to environmental protection aspects, natural and biodegradable polymers, such as polysaccharides, are of great and still increasing interest for industrial purposes (Swift, 1998). Maltodextrins are one of the most important groups of industrial important polysaccharides (Glicksman, 1986; Marchal, Beeftink, & Tramper, 1999). They are also discussed for application in new areas, e.g. aqueous two-phase systems (Silva & Meirelles, 2000, 2001). Maltodextrins are starch hydrolysates consisting of α-D-glucose units bounded by (1→4) glycosidic linkages (primarily) as well as by (1→6) linkages (Fig. 1). The starch hydrolysis is achieved by enzymes and/or acids at elevated temperatures. The resulting maltodextrins typically exhibit a broad molecular mass distribution (with number-average molar masses varying between $10^3$ and $10^5$). The molecular mass distribution is commonly expressed by the degree of polydispersity which is the ratio of the weight average ($M_w$) to the number-average ($M_n$) molecular mass. α-Amylase is commonly employed in starch hydrolysis. While it predominantly hydrolyses α-1→4 linkages, it has nearly no effect on α-1→6 linkages. Moreover, α-amylase does not readily hydrolyse α-1→4 linkages in maltose and maltotriose. Thus, maltose, maltotriose and other low molar mass saccharides can be found in the final hydrolysates. These different components confer maltodextrins a wide range of properties such as water solubility, viscosity, and chemical stability (Kasapis, Morris, Norton, & Clark, 1993a–d).

The thermodynamic properties of aqueous solutions of polymers have to be known for many applications.

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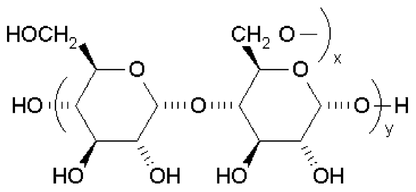

Fig. 1. Structure of maltodextrins ($x=1\rightarrow6$ linkages; $y=1\rightarrow4$ linkages).

Such data have been reported for a variety of polymer solutions (Gaube, Pfennig, & Stumpf, 1993; Großmann, Tintinger, Zhu, & Maurer, 1995; Hasse, Kany, Tintinger, & Maurer, 1995; Kany, Hasse, & Maurer, 1999, 2003; Silva & Loh, 2000), but the data base for aqueous solutions of maltodextrins is still rather scarce. For example, Cesàro, Cuppo, Fabri, and Sussich (1999) reported the results of calorimetric investigations on aqueous solutions of maltodextrin and gelatin. The experimental results for the heat of dilution of the single polymers and of the mixed polymer solutions were correlated by Flory's equation (Flory, 1953) for the Gibbs excess energy of polymer solutions. Some publications describe results of experimental investigations of gel-forming maltodextrins. Radosta and Schierbaum (1990), Radosta, Schierbaum, and Yuriev (1989), and Radosta, Schierbaum, Yuriev, Reuther, and Anger (1989) presented a comprehensive study on the physico-chemical properties of maltodextrins in aqueous solutions. In that work a gel-forming maltodextrin sample was separated in six fractions of different average molecular masses. The amount of non-freezable water in the different fractions was determined and the sorption/desorption of water was studied. The gelation of low dextrose equivalent maltodextrins and the phase equilibrium in gelatin/maltodextrin systems were investigated by Kasapis et al. (1993a–d). Schierbaum et al. (1992) presented a study on the gelation process of maltodextrin–water systems using low resolution H-NMR. They observed the time required for the beginning of gelation as a function of temperature and concentration, and the influence of amylose on the gelation process.

The present paper reports results from experimental investigations of several aqueous solutions of maltodextrins by three different techniques: isopiestic, laser-light scattering and calorimetric methods. The experimental results from the isopiestic and laser-light scattering measurements are used to determine the second and third osmotic virial coefficients of maltodextrin components: glucose, maltose, maltotriose, oligo and polysaccharides—following published procedures described for example by Hasse et al. (1995) for poly(ethylene glycol), and by Kany et al. (1999, 2003) for dextran and poly(vinyl pyrrolidone). Furthermore, the VERS equation—a semi-empirical group contribution model for the Gibbs excess energy—is tested for correlating and predicting some thermodynamic properties (the activity of water and the heat of dilution) of aqueous maltodextrin and saccharide systems.

## 2. Materials

### 2.1. Materials

Aqueous solutions of three different corn maltodextrins purchased from Aldrich Chemical and designated here according to their dextrose equivalent range as MD 4–7, MD 13–17 and MD 16–19 were studied in the present work. The polymers were used as received. The water concentration of each sample was determined by Karl Fischer titration: MD 4–7: 3.3±0.2 mass%, MD 13–17: 4.4±0.2 mass% and MD 16–19: 3.3±0.2 mass%. HPLC water (Merck, Darmstadt, Germany; impurities below 5 mg kg$^{-1}$) was used for the preparation of all aqueous solutions.

### 2.2. Characterization of polymers: molecular mass distributions

The maltodextrins were characterized by gel permeation chromatography (GPC) using a column MCX 1000 Å from PSS Polymer Systems, Mainz, Germany for separation. A 0.05 M aqueous solution of sodium nitrate was used as eluent. The flow rate was 1 cm$^3$ min$^{-1}$. The eluent was degassed on-line (ERMA, type ERC-3512). About 100 μl of an aqueous maltodextrin solution with polymer concentration of about 0.01 g cm$^{-3}$ was injected in the eluent using a Reodyne valve. A combination of a multiangle laser-light scattering detector (MALLS, Wyatt Technology, type DAWN DSP) and a interferometric refractometer (RI, Wyatt Technology, type Optilab 903) was used for analysis. The RI detector is used to determine the concentration of the polymer in the eluent after separation in the GPC column. The MALLS detector is used to determine the molecular mass of a polymer sample in the eluent. During the calibration procedure the difference in retention times between the RI and MALLS detectors—which is required to assign the concentration to the molecular mass of a sample—was determined. The calibration of the detectors was performed as described by Hasse et al. (1995). For the evaluation of the light scattering data the differential refractive index increment d$n$/d$c$ of the aqueous polymer solution is required. $n$ is the refractive index and $c$ is the polymer concentration (amount of mass per volume). It was determined in the present work: d$n$/d$c$=0.1486, 0.1510, and 0.1522 cm$^3$ g$^{-1}$, for MD 4–7, MD 13–17 and MD 16–19, respectively. The differences in these numbers are smaller than the estimated experimental uncertainty of d$n$/d$c$ which is ±2%.

Samples were prepared by dissolving maltodextrin in water at ambient temperature. However, some experiments were repeated with samples which had been heated to 70 °C for about 1 h. The experimental results did not reveal an influence of that pre-treatment on the molecular weight and molecular weight distribution. Each maltodextrin sample was analyzed by GPC at least three times. Fig. 2 shows the gel permeation profiles of the maltodextrins determined by

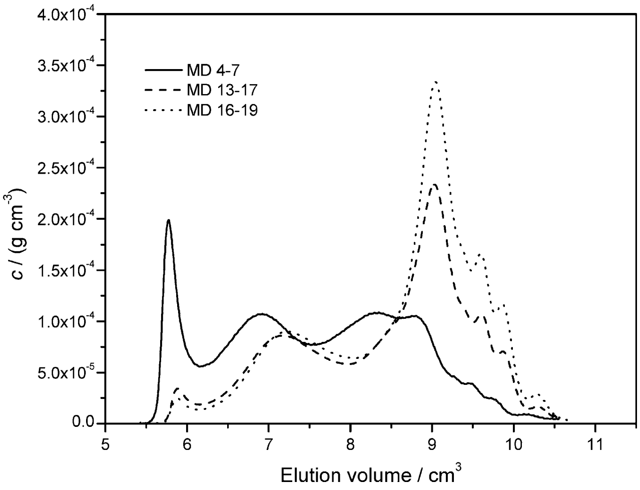

Fig. 2. Gel permeation profiles of maltodextrins.

the RI detector. MD 4–7 comprises higher concentrations of high molecular mass saccharides than both other MD samples. Maltodextrins MD 13–17 and 16–19 reveal significant differences in the gel permeation profiles only at higher retention volumes, i.e. in the concentrations of low molecular mass saccharides. The gel permeation profile reveals that the hydrolysis process that resulted in the MD 4–7 sample converted less starch to low saccharides, than the hydrolysis process that yielded both other MD samples. The presence of more high molecular mass components allows to form thermally reversible gels from MD 4–7 in aqueous solutions.

In the MALLS detector the light scattering from each eluted fraction is detected simultaneously at 16 angles between 28.7 and 143.8°. The detector's response is the excess Raleigh ratio $R_\theta^{\mathrm{E}}$ at angle $\theta$. $R_\theta^{\mathrm{E}}$ is used to determine the molar mass of each polymer sample from the light scattering equation (Huglin, 1972):

$$\frac{K_0 c}{R_\theta^{\mathrm{E}}} = \frac{1}{M_{\mathrm{w}} P_\theta} + 2A_2^{\mathrm{LS}} c + 3A_3^{\mathrm{LS}} c^2 + \cdots \tag{1}$$

$R_\theta^{\mathrm{E}}$ accounts primarily for the difference between the intensity of light scattered from the polymer solution to that scattered from the pure solvent. $K_0$ is an optical constant (Wyatt, 1993):

$$K_0 = \frac{4\pi^2 (\mathrm{d}n/\mathrm{d}c)^2 n^2}{N_{\mathrm{A}} \lambda^4} \tag{2}$$

$\lambda$ is the laser wave length (633 nm), $N_{\mathrm{A}}$ is Avogado's number, $M_{\mathrm{w}}$ is the weight-average molar mass of the light scattering sample. $P_\theta$ is a form factor describing the angular and size dependence of the scattered light intensity.

$$\frac{1}{P_\theta} = 1 + \left(\frac{16\pi^2 n^2 \sin^2(\theta/2)}{3\lambda^2}\right)\langle R_{\mathrm{g}}^2\rangle \tag{3}$$

where $\langle R_{\mathrm{g}}^2\rangle$ is the mean-square radius of gyration. $A_2^{\mathrm{LS}}$ and $A_3^{\mathrm{LS}}$ are the second and third osmotic light scattering virial coefficients of the polymer sample.

Extrapolating the light scattering data to zero polymer concentration and zero scattering angle allows for the determination of the weight-averaged molecular mass of the light scattering polymer sample:

$$\lim_{c\to 0;\theta\to 0} \frac{K_0 c}{R_\theta^{\mathrm{E}}} = \frac{1}{M_{\mathrm{w}}} \tag{4}$$

The evaluation of the light scattering data was performed using the commercial software package ASTRA (Wyatt, 1999). The final results are shown in Fig. 3, where the molar mass is plotted versus the elution volume $V$. Fig. 3 reveals the typical linear dependency of $\log M$ on $V$. Fig. 3 also shows that the scattering of the data increases considerably at elution volumes above 9 cm$^3$, which corresponds to low molecular carbohydrates ($M < 10^3$). The scattering is due to the uncertainty of the laser-light scattering data for low molecular substances. However, the correct slope of $\log M$ versus $V$ is important for a reliable evaluation of the experimental data, i.e. for reliable results for the molecular mass distributions of the polymers (as shown below). It is assumed that the molecular mass distribution of each maltodextrin is the sum of contributions of some high molecular polydisperse fractions and some low molecular monodisperse components, e.g. glucose, maltose and maltotriose. It was also assumed that the straight lines in the $\log M$ versus $V$ diagram shown in Fig. 3 give a good representation of the molecular mass distribution also for the low molecular part of the molecular mass distributions (i.e. at retention volumes above 9 cm$^3$) where the experimental light scattering data is not reliable. In order to verify these assumptions, the GPC results for the molar mass distribution of each maltodextrin were approximated by the sum of Gauss–Lorentz functions to separate the whole distribution in fractions and to evaluate if the peaks that elute later in the chromatographic runs correspond to the lower molar mass compounds (glucose, maltose and maltotriose). The Gauss–Lorentz (G–L) function is given by:

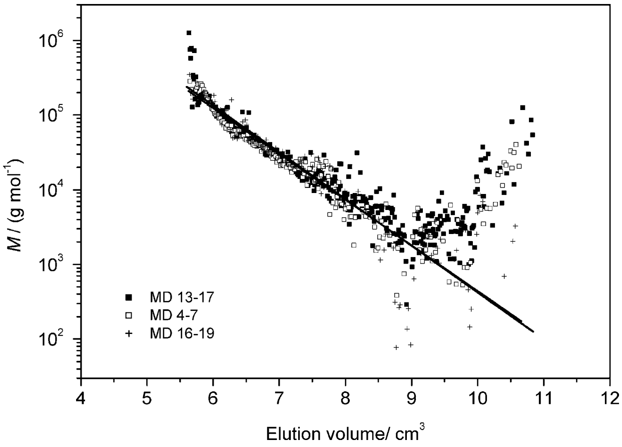

Fig. 3. Results of the experimental investigations of aqueous solutions of maltodextrins by GPC/MALLS.

Table 1
Parameters of the Gauss–Lorentz functions representing the studied maltodextrin samples

| $G–L_i$ function | $a_i$ ($10^5$) | $b_i$ | $c_i$ | $d_i$ | $w_i$ (g $g^{-1}$)[a] |
|---|---|---|---|---|---|
| *MD 16–19* | | | | | |
| 1 | 1.9027 | 0.4673 | 5.8823 | 10.2767 | 0.0075 |
| 2 | 0.9351 | 3.3712 | 6.0810 | 3.5067 | 0.0083 |
| 3 | 5.9795 | 0.1373 | 7.1685 | 1.6977 | 0.1423 |
| 4 | 4.2400 | 0.4672 | 7.8393 | 0.8144 | 0.1863 |
| 5 | 5.7008 | −0.1097 | 8.6973 | 1.7178 | 0.1342 |
| 6 | 7.1745 | 3.4969 | 8.9746 | 1.5825 | 0.0944 |
| 7 | 21.5030 | 3.6488 | 9.0677 | 2.8541 | 0.2096 |
| 8 | 8.5406 | 4.6575 | 9.4010 | 4.9981 | 0.0538 |
| Malto-triose | 11.9950 | 4.0937 | 9.6130 | 6.5596 | 0.0643 |
| Maltose | 10.7921 | 5.7395 | 9.8723 | 3.6056 | 0.0750 |
| Glucose | 2.6817 | 6.9100 | 10.2984 | −0.8883 | 0.0242 |
| *MD 13–17* | | | | | |
| 1 | 2.5941 | 0.4673 | 5.8863 | 10.2768 | 0.0125 |
| 2 | 1.1700 | 3.3709 | 6.0793 | 3.5061 | 0.0127 |
| 3 | 5.7714 | 0.1354 | 7.1051 | 1.6750 | 0.1699 |
| 4 | 3.9267 | 0.4499 | 7.8119 | 0.76005 | 0.2242 |
| 5 | 5.9855 | −0.1093 | 8.7012 | 1.7121 | 0.1726 |
| 6 | 7.2161 | 3.5040 | 8.9795 | 1.5913 | 0.1156 |
| 7 | 11.1130 | 3.6215 | 9.0736 | 2.8325 | 0.1333 |
| 8 | 5.2759 | 3.2499 | 9.4225 | 5.4745 | 0.0418 |
| Malto-triose | 6.9437 | 0.3631 | 9.6322 | 7.8073 | 0.0440 |
| Maltose | 6.5277 | 7.0092 | 9.8831 | 2.0761 | 0.0602 |
| Glucose | 1.2573 | 6.7220 | 10.3297 | −1.3566 | 0.0132 |
| *MD 4–7* | | | | | |
| 1 | 14.0581 | 0.3545 | 5.7554 | 12.2160 | 0.0571 |
| 2 | 8.3251 | −0.0502 | 5.8544 | 8.3973 | 0.04924 |
| 3 | 3.1601 | 4.0280 | 6.0430 | 3.1899 | 0.0340 |
| 4 | 10.5772 | −0.0755 | 6.8973 | −1.4304 | 0.3667 |
| 5 | 2.9055 | 0.0124 | 7.7594 | 2.5091 | 0.0575 |
| 6 | 8.7807 | −0.0161 | 8.2930 | 1.9725 | 0.2211 |
| 7 | 7.7245 | 2.9674 | 8.8799 | 1.0913 | 0.1582 |
| 8 | 1.4024 | 3.1358 | 9.3156 | 5.1048 | 0.0119 |
| Malto-triose | 2.0218 | 4.2452 | 9.5195 | 5.7705 | 0.0145 |
| Maltose | 1.4656 | 4.7626 | 9.7593 | 6.1395 | 0.0097 |
| Glucose | 0.7696 | 2.1232 | 10.1260 | −1.0209 | 0.0200 |

[a] Mass fraction of polymer sample covered by this Gauss–Lorenz function.

$$G - L_i = \frac{a_i}{1 + b_i^2 (V - c_i)^2} \exp(d_i^2 (V - c_i)^2) \quad (5)$$

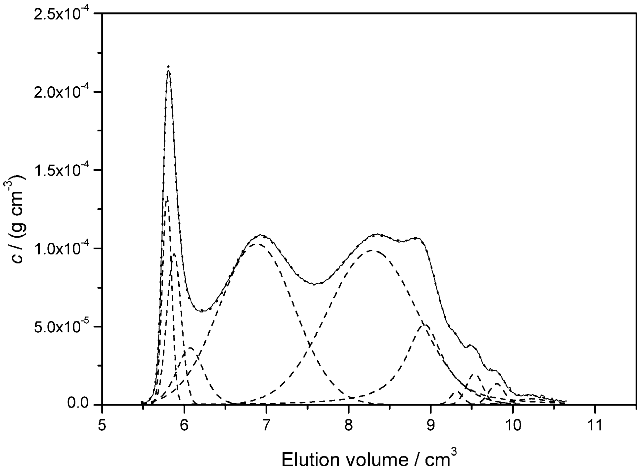

Fig. 4. Gauss–Lorentz functions for the molecular mass distribution of MD 4–7.

For each maltodextrin, the parameters $a_i$, $b_i$, $c_i$ and $d_i$ ($i = 1, 2, \ldots, N$; $N$ is the number of $G–L_i$ functions) were fitted to the molar mass distribution. The results are given in Table 1. An example (for MD 4–7) is shown in Fig. 4. For each fraction represented by a $G–L_i$ function, the corresponding elution volumes are known. Plotting $\log M$ versus the elution volume $V$ with data points obtained by laser-light scattering experiments up to a elution volume of about 8 $cm^3$ and assuming that the first three adjusted $G–L_i$ functions correspond to glucose, maltose and maltotriose, respectively, gives a diagram where one should expect that the extrapolation of the straight line through the light scattering data hits the results from the adjusted $G–L_i$ functions for glucose ($M = 180$ g $mol^{-1}$), maltose ($M = 342$ g $mol^{-1}$) and maltotriose ($M = 504$ g $mol^{-1}$), respectively. As can be seen from Fig. 5, that assumption is fulfilled. Therefore, the concentrations of the lower molar mass fractions were estimated by the Gauss–Lorentz method and those fractions were assumed to consist of glucose, maltose and maltotriose, respectively. The results can also be compared to some literature data for other maltodextrins. For example, Defloor, Vandenreyken, Grobet, and Delcour (1998) reported concentrations of 1.8, 4.3 and 8.1 mass% for glucose, maltose and maltotriose, respectively, for a maltodextrin with a average molecular mass of approximately 1300 g $mol^{-1}$ (In the present work, the corresponding concentrations—as determined by the method described above—are 2.4, 7.5 and 6.4 mass% for MD 16–19, which has a molar mass of 1140 g $mol^{-1}$). Therefore, it can be considered that the results from GPC/MALLS analysis are

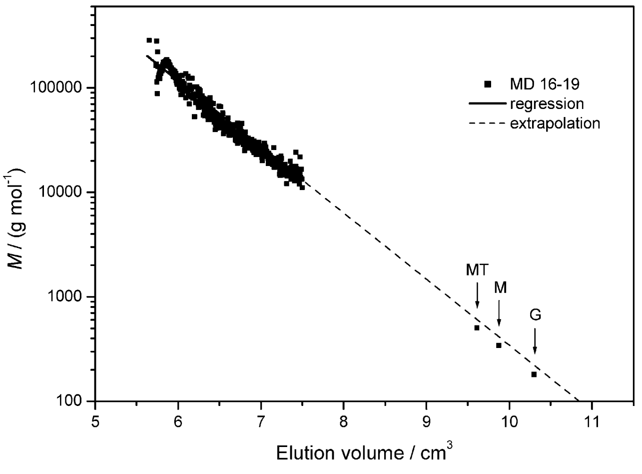

Fig. 5. Molecular mass as a function of elution volume (from MALLS data) and elution volumes of glucose (G), maltose (M) and maltotriose (MT) from the Gauss–Lorentz functions.

Table 2
Experimental results for the number- and mass-average molecular masses of the maltodextrins samples

| | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| MD 4–7 | 2683 | 38,360 | 14.31 |
| MD 13–17 | 1475 | 13,710 | 8.38 |
| MD 16–19 | 1140 | 8283 | 7.31 |

reliable, i.e. they give sufficiently accurate approximations for the molar mass distribution of the maltodextrins.

The results of these evaluations are given as number-averaged molecular mass ($M_n$) and weight-averaged molecular mass ($M_w$) and polydispersity ratio ($M_w/M_n$) in Table 2. The relative deviation between those data from different experiments are between 3 and 13%. The polydispersity is about 7–15, i.e. each maltodextrin studied reveals a rather wide molecular mass distribution—as is also shown in Figs. 2–4.

## 3. Thermodynamic properties of aqueous solutions of maltodextrins

### 3.1. From isopiestic investigations

The activity of water in aqueous solutions of maltodextrins was determined in isopiestic investigations at 25 °C for all three maltodextrins, as well as at 45 °C for MD 13–17 and 16–19. The experimental arrangement consisted of a glass multilegged manifold with nine standard taper female ground-glass joints for the attachment of solution flasks and a high vacuum stopcock for isolation of the system after evacuation. In order to increase the mass transfer and enhance sample mixing during the equilibration period, the glass was allowed to rotate around an axis inclined at 45°. The equipment was immersed in a constant temperature water bath. The temperature fluctuations were below ± 0.1 K. In experiment, the flasks were filled with about one gram of an aqueous solution of a non-volatile substance—either a maltodextrin or sodium chloride which was used as a reference. The nine flasks of the experimental arrangement were used as follows: three flasks were filled with aqueous NaCl solutions (NaCl concentration: NaCl(1)), three flasks also with aqueous NaCl solutions but with a different concentration (NaCl(2)), and three flasks with aqueous solutions of a single maltodextrin. The two NaCl concentrations (NaCl(1) and NaCl(2)) were chosen in such a way that it was to be expected that the final sodium chloride concentration was above (NaCl(1)) and below (NaCl(2)). All solutions were prepared with bidistilled water. During the equilibration period (typically for about 12 days), water is transferred between the flasks through the vapor phase until the activity of water reaches the same values in all flasks. After equilibration the amount of mass in each flask was determined using a high precision microbalance. As the amount of substance of the non-volatile component was known from sample preparation, that gravimetric analysis provided the composition of the aqueous solution in each flask. The activity of water in an aqueous solution of sodium chloride was calculated using the correlation of Pitzer and Peiper (1984). The experimental results for the activity of water in aqueous solutions of all three maltodextrins at 25 °C are given in Table 3. The maximum uncertainty of that data is ±0.1 K in temperature, $\pm 0.002\ \mathrm{g\,g^{-1}}$ in polymer concentration, and ±0.001 in water activity (this number also includes a possible bias of the correlation of Archer, 1992; Archer & Carter, 2000; Clarke & Glew, 1985; Pitzer & Peiper, 1984).

The experimental results for 45 °C are given in Table 4. For that somewhat higher temperature, different experimental isopiestic equipment was applied. It consists of a thermostated tank made of stainless steel. The tank holds up to 30 glass cells in a copper block. In an experiment, each glass cell is filled with about 1 ml of an aqueous solution. After placing the cells into the tank, the tank is sealed, evacuated and thermostated. The process of mass transfer and the evaluation of water activities are the same as those described above.

The apparatuses and experimental procedures used for the isopiestic experiments in this work were described before by Großmann et al. (1995), Kany (1998) and Lammertz and Maurer (2002).

### 3.2. From calorimetric investigations

Aqueous solutions of single maltodextrins were mixed with pure water at 40 °C in a batch calorimeter (model MS 80, Setaram, Lyon, France). Specially designed cells were used to enable isothermal and isobaric mixing. Experimental details have been given before (Großmann et al., 1995;

Table 3
Experimental results for the activity of water ($a_1$) in aqueous solutions of maltodextrins at 25 °C

| MD 13–17 | | MD 16–19 | | MD 4–7 | |
|---|---|---|---|---|---|
| Polymer mass fraction $w_{MD}$ ($\mathrm{g\,g^{-1}}$) | $a_1$ | Polymer mass fraction $w_{MD}$ ($\mathrm{g\,g^{-1}}$) | $a_1$ | Polymer mass fraction $w_{MD}$ ($\mathrm{g\,g^{-1}}$) | $a_1$ |
| 0.1750 | 0.9962 | 0.2598 | 0.9928 | 0.2859 | 0.9967 |
| 0.2234 | 0.9948 | 0.2743 | 0.9922 | 0.2644 | 0.9970 |
| 0.2419 | 0.9942 | 0.3434 | 0.9886 | 0.2914 | 0.9966 |
| 0.3029 | 0.9917 | 0.3887 | 0.9854 | 0.3167 | 0.9960 |
| 0.3408 | 0.9898 | 0.3844 | 0.9860 | 0.3365 | 0.9953 |
| 0.3796 | 0.9875 | 0.4197 | 0.9831 | 0.3399 | 0.9957 |
| 0.4286 | 0.9838 | 0.4492 | 0.9802 | 0.3379 | 0.9957 |
| 0.4408 | 0.9829 | 0.4559 | 0.9797 | 0.3488 | 0.9956 |
| 0.4872 | 0.9779 | 0.4824 | 0.9763 | 0.3802 | 0.9945 |
| 0.4867 | 0.9781 | 0.5357 | 0.9689 | 0.4099 | 0.9939 |
| 0.5307 | 0.9724 | 0.5850 | 0.9594 | 0.4590 | 0.9919 |
| 0.5671 | 0.9664 | | | 0.4615 | 0.9922 |
| 0.5898 | 0.9622 | | | | |

Table 4
Experimental results for the activity of water ($a_1$) in aqueous solutions of MD 13–17 and MD 16–19 at 45 °C

| Solute | Polymer mass fraction $w_{MD}$ (g g$^{-1}$) | $a_1$ |
|---|---|---|
| MD 13–17 | 0.2767 | 0.9927 |
| | 0.3284 | 0.9903 |
| | 0.4452 | 0.9821 |
| | 0.4968 | 0.9767 |
| MD 16–19 | 0.2683 | 0.9927 |
| | 0.3156 | 0.9903 |
| | 0.4327 | 0.9821 |
| | 0.4852 | 0.9767 |

Rumpf, Weyrich, & Maurer, 1997), therefore, only the main features of the calorimetric cell are repeated here. The cell consists of two compartments separated by a teflon foil. A small cylinder with a piston is mounted in the upper compartment. The piston separates the solution in the upper compartment of the cell from compressed air and thus allows for a pressurization to 0.2 MPa. The cells were filled with liquids from syringes in such a way that no gas bubbles remained. The upper compartment contained the polymer solution, the lower compartment contained pure water. To start the dilution process, the teflon foil was cut off and the heat upon dilution was determined from the integrated signal of the thermocouples of the calorimeter. To enhance mixing the calorimeter was rotated around a horizontal axis and some small metal spheres were charged to the cell. The calorimeter was calibrated using an electrical heater. The calibration results could be reproduced with relative deviations well below 1%. The experimental results were corrected for the energy required to cut the teflon foil. That energy amounts to about 1 J. It was determined in ‘blind’ experiments.

The experimental results of the calorimetric investigations are given in Tables 5 and 6 for aqueous solutions of MD 13–17 and MD 16–19, respectively. Superscripts ‘bottom’ and ‘top’ designate the solutions placed in the lower and upper compartment of the cells. Note that the measured heats of dilution are negative, corresponding to an exothermic behavior upon dilution and that the heat involved in the mixing process is small. Dextran, another polysaccharide, reveals a similar exothermic behavior (Großmann et al., 1995; Silva & Loh, 2000).

Table 5
Experimental results for the heat of dilution $Q$ when aqueous solutions of maltodextrin MD 13–17 are diluted with pure water at 40 °C

| Solution in upper chamber $m^{top}$ (g) | Water in lower chamber $m^{bottom}$ (g) | Mass fraction of solute in upper chamber $w_{MD}^{top}$ (g g$^{-1}$) | $Q$ (J) |
|---|---|---|---|
| 28.850 | 15.938 | 0.290 | −1.19 |
| 27.346 | 15.857 | 0.290 | −1.23 |
| 28.801 | 15.902 | 0.300 | −1.22 |
| 29.752 | 15.916 | 0.398 | −1.68 |
| 30.587 | 15.855 | 0.404 | −2.05 |
| 29.850 | 15.905 | 0.398 | −1.82 |
| 39.874 | 14.805 | 0.508 | −3.16 |
| 39.484 | 14.976 | 0.481 | −2.80 |
| 40.436 | 14.783 | 0.548 | −3.64 |
| 40.564 | 14.822 | 0.548 | −3.66 |
| 41.342 | 14.979 | 0.579 | −4.49 |
| 41.518 | 15.000 | 0.579 | −4.49 |
| 40.569 | 14.866 | 0.638 | −5.89 |
| 40.309 | 14.772 | 0.638 | −5.46 |
| 42.170 | 14.854 | 0.694 | −6.69 |
| 43.049 | 14.855 | 0.694 | −6.77 |

The experimental results for the heat of dilution of aqueous solutions of MD 4–7 are of the same order of magnitude as the energy required to cut the teflon foil. Two different effects were observed upon the dilution of aqueous solutions of maltodextrin MD 4–7. In the beginning of an experiment, the signal corresponded to an endothermic process, later to an exothermic process. It is supposed that the endothermic effect is caused by the fast ‘physical’ dilution of the polymer solution (which is a mixture of hydrogel and solution) in pure water, whereas the exothermic process results from a slow rearrangement of the molecules to a new network. Schierbaum et al. (1984, 1992) studied the formation of thermally reversible potato starch maltodextrin gels by H-NMR, viscometry and electron microscopy. They found—in agreement with the explanation given above—that the gelling of these maltodextrins in aqueous solutions is a rather slow process in particular when the transition from a homogeneous structureless solution to a two-phase system is involved. That two-phase system consists of a network (hydrogel) and a coexisting liquid solution of non-structured low molar mass maltodextrin components. The gelling process is in particular important at high polymer concentrations and low temperatures. According to Schierbaum et al. (1984), products with dextrose equivalent (DE) up to 5–8 are able to form thermally reversible gels when the polymer concentration is above 10 mass%. The small

Table 6
Experimental results for the heat of dilution $Q$ when aqueous solutions of maltodextrin MD 16–19 are diluted with pure water at 40 °C

| Solution in upper chamber $m^{top}$ (g) | Water in lower chamber $m^{bottom}$ (g) | Mass fraction of solute in upper chamber $w_{MD}^{top}$ (g g$^{-1}$) | $Q$ (J) |
|---|---|---|---|
| 38.488 | 15.014 | 0.404 | −3.50 |
| 37.672 | 14.953 | 0.393 | −2.62 |
| 39.794 | 14.779 | 0.501 | −4.49 |
| 38.575 | 15.472 | 0.511 | −3.90 |
| 40.396 | 15.057 | 0.548 | −6.43 |
| 40.276 | 15.030 | 0.543 | −6.03 |
| 41.918 | 15.038 | 0.608 | −8.94 |
| 41.314 | 15.039 | 0.608 | −8.48 |
| 42.519 | 14.871 | 0.649 | −10.34 |
| 42.182 | 14.953 | 0.637 | −9.61 |
| 41.810 | 14.801 | 0.700 | −12.21 |
| 42.727 | 15.021 | 0.700 | −12.19 |

values of the heat of dilution that seems to be a combination of endothermical and exothermical effects, certainly request more detailed investigations, which are beyond the scope of the present work. Therefore, no results of the calorimetric investigations for aqueous solutions of MD 4–7 are reported here.

### *3.3. From laser-light scattering experiments*

The multiangle laser-light scattering device used for the characterization of the polymers by GPC analysis was also used to determine some thermodynamic properties of aqueous solutions of maltodextrins. The only difference was that the light scattering cell was charged with aqueous solutions of the non-fractionated maltodextrins and the light scattering signals were recorded as a function of the polymer concentration. A flow rate of 0.5 cm$^3$ min$^{-1}$ was maintained using a syringe pump (Infors, type Predicor). In-line filters (Sartorius, pore size: 0.20 μm) were used between the syringe and the flow cell to remove particles from the aqueous solutions which otherwise would have caused an unfavorable signal to noise ratio. The experiments were performed at 25 °C with at least six different polymer concentrations per maltodextrin. The results of the laser-light scattering experiments are given as excess Raleigh ratios in Tables 7 and 8 for the maltodextrins MD 13–17 and 16–19, respectively.

Table 7
Excess Rayleigh ratios of aqueous solutions of MD 13–17 at 25 °C

| Scattering angle $\theta$ (°) | Run | 100 $c$ (g cm$^{-3}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0.720 | 1.438 | 2.183 | 3.001 | 3.617 | 4.341 | 5.076 | 5.805 |
| | | $10^5 K_0 c/R_\theta^{\mathrm{E}}$ (mol g$^{-1}$) | | | | | | | |
| 28.71 | 1 | 8.117 | 8.444 | 8.847 | 9.268 | 9.605 | 10.030 | 10.340 | 10.700 |
| | 2 | 7.909 | 8.227 | 8.882 | 9.177 | 9.547 | 9.951 | 10.160 | 10.530 |
| 36.2 | 1 | 8.155 | 8.387 | 8.860 | 9.212 | 9.600 | 9.959 | 10.320 | 10.690 |
| | 2 | 7.903 | 8.252 | 8.878 | 9.093 | 9.503 | 9.918 | 10.250 | 10.670 |
| 44.5 | 1 | 8.088 | 8.375 | 8.846 | 9.234 | 9.597 | 10.010 | 10.340 | 10.710 |
| | 2 | 7.99 | 8.294 | 8.858 | 9.153 | 9.529 | 9.926 | 10.240 | 10.590 |
| 54.0 | 1 | 8.038 | 8.313 | 8.759 | 9.141 | 9.506 | 9.863 | 10.230 | 10.590 |
| | 2 | 7.976 | 8.296 | 8.777 | 9.055 | 9.430 | 9.835 | 10.180 | 10.550 |
| 64.9 | 1 | 8.135 | 8.436 | 8.890 | 9.278 | 9.632 | 10.020 | 10.380 | 10.750 |
| | 2 | 8.137 | 8.429 | 8.909 | 9.230 | 9.578 | 9.983 | 10.330 | 10.680 |
| 77.1 | 1 | 8.077 | 8.354 | 8.785 | 9.158 | 9.511 | 9.869 | 10.240 | 10.610 |
| | 2 | 8.092 | 8.396 | 8.817 | 9.108 | 9.464 | 9.865 | 10.220 | 10.610 |
| 90.0 | 1 | 8.313 | 8.591 | 9.021 | 9.416 | 9.742 | 10.130 | 10.500 | 10.870 |
| | 2 | 8.355 | 8.629 | 9.048 | 9.381 | 9.725 | 10.120 | 10.480 | 10.840 |
| 115.1 | 1 | 8.242 | 8.520 | 8.922 | 9.294 | 9.618 | 9.991 | 10.360 | 10.740 |
| | 2 | 8.304 | 8.577 | 8.951 | 9.289 | 9.615 | 10.000 | 10.360 | 10.730 |
| 125.4 | 1 | 8.170 | 8.445 | 8.842 | 9.208 | 9.535 | 9.883 | 10.270 | 10.640 |
| | 2 | 8.234 | 8.534 | 8.890 | 9.209 | 9.537 | 9.924 | 10.290 | 10.680 |
| 135.5 | 1 | 8.220 | 8.509 | 8.909 | 9.281 | 9.593 | 9.968 | 10.330 | 10.720 |
| | 2 | 8.336 | 8.611 | 8.969 | 9.298 | 9.626 | 10.020 | 10.360 | 10.740 |
| 143.8 | 1 | 8.068 | 8.388 | 8.793 | 9.150 | 9.467 | 9.826 | 10.210 | 10.600 |
| | 2 | 8.202 | 8.512 | 8.896 | 9.199 | 9.544 | 9.939 | 10.250 | 10.670 |

### *3.4. Densimetric data*

In order to convert polymer mass fractions into concentrations (i.e. mass densities), the specific density $\rho^*$ (g cm$^{-3}$) of aqueous solutions of maltodextrin was determined at 25 °C. Density measurements were performed in triplicate using a digital vibrating tube densimeter (model DMA 58, Anton Paar, Austria) which was calibrated with water and air at 25 °C. The accuracy of the density measurements is estimated to $\pm 3\times 10^{-5}$ g cm$^{-3}$. The experimental results for the density of aqueous solutions of MD 13–17 and MD 16–19 are given in Table 9. The difference between the specific densities of both solutions (at the same polymer mass fraction) is very small.

## 4. Modeling

### *4.1. Osmotic virial equation*

The thermodynamic data of aqueous maltodextrin and mono-, di- and tri-saccharides were correlated by the osmotic virial equation:

$$\ln a_1 = -\frac{c}{\rho_1}\left(\frac{1}{M_{\mathrm{n}}} + A_2^{\mathrm{osm}} c + A_3^{\mathrm{osm}} c^2 + \cdots\right) \qquad (6)$$

where $a_1$ is the activity of water, $\rho_1$ is the molar density of pure water, $M_{\mathrm{n}}$ is the (number-averaged) molecular mass of

Table 8
Excess Rayleigh ratios of aqueous solutions of MD 16–19 at 25 °C

| Scattering angle $\theta$ (°) | Run | 100 $c$/(g cm$^{-3}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1.408 | 2.111 | 2.823 | 3.530 | 4.230 | 4.919 | 5.644 |
| | | $10^5 K_0 c/R_\theta^E$ (mol g$^{-1}$) | | | | | | |
| 36.2 | 1 | 1.051 | 1.073 | 1.124 | 1.188 | 1.243 | 1.295 | 1.379 |
| | 2 | 1.043 | 1.107 | 1.199 | 1.214 | 1.285 | 1.344 | 1.382 |
| 44.5 | 1 | 1.061 | 1.087 | 1.133 | 1.191 | 1.245 | 1.312 | 1.359 |
| | 2 | 1.068 | 1.102 | 1.196 | 1.222 | 1.279 | 1.329 | 1.354 |
| 54.0 | 1 | 1.058 | 1.083 | 1.128 | 1.198 | 1.244 | 1.298 | 1.374 |
| | 2 | 1.079 | 1.116 | 1.200 | 1.224 | 1.283 | 1.342 | 1.375 |
| 64.9 | 1 | 1.083 | 1.111 | 1.153 | 1.217 | 1.265 | 1.332 | 1.382 |
| | 2 | 1.116 | 1.124 | 1.210 | 1.244 | 1.295 | 1.345 | 1.375 |
| 77.1 | 1 | 1.079 | 1.107 | 1.151 | 1.217 | 1.262 | 1.319 | 1.387 |
| | 2 | 1.115 | 1.135 | 1.214 | 1.244 | 1.297 | 1.352 | 1.388 |
| 90.0 | 1 | 1.118 | 1.149 | 1.189 | 1.253 | 1.298 | 1.361 | 1.413 |
| | 2 | 1.159 | 1.162 | 1.243 | 1.280 | 1.329 | 1.379 | 1.411 |
| 102.9 | 1 | 1.087 | 1.117 | 1.158 | 1.223 | 1.265 | 1.321 | 1.387 |
| | 2 | 1.131 | 1.138 | 1.216 | 1.251 | 1.298 | 1.352 | 1.389 |
| 115.1 | 1 | 1.118 | 1.148 | 1.185 | 1.249 | 1.292 | 1.354 | 1.403 |
| | 2 | 1.156 | 1.155 | 1.233 | 1.274 | 1.317 | 1.367 | 1.400 |
| 125.4 | 1 | 1.112 | 1.14 | 1.179 | 1.246 | 1.288 | 1.341 | 1.405 |
| | 2 | 1.151 | 1.158 | 1.233 | 1.269 | 1.316 | 1.368 | 1.407 |
| 135.5 | 1 | 1.121 | 1.152 | 1.188 | 1.250 | 1.294 | 1.354 | 1.400 |
| | 2 | 1.160 | 1.152 | 1.234 | 1.273 | 1.318 | 1.366 | 1.400 |
| 143.8 | 1 | 1.108 | 1.138 | 1.176 | 1.242 | 1.285 | 1.337 | 1.401 |
| | 2 | 1.149 | 1.148 | 1.230 | 1.264 | 1.315 | 1.366 | 1.409 |

the solute and $A_2^{\mathrm{osm}}$ and $A_3^{\mathrm{osm}}$ are the second and third osmotic virial coefficients of the solute in the solvent, respectively. A plot of $(-\rho_1 \ln a_1/c)$ versus $c$, allows the determination of the number-averaged molecular mass $M_\mathrm{n}$ and the second and third osmotic virial coefficients by an extrapolation to zero polymer concentration. The second and third osmotic virial coefficients and the density of a polydisperse polymer can be expressed as (Kurata, 1982)

$$A_2^{\mathrm{osm}} = \sum_{i=2}^{N}\sum_{j=2}^{N} w_i w_j A_{ij} \tag{7}$$

$$A_3^{\mathrm{osm}} = \sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2}^{N} w_i w_j w_k A_{ijk} \tag{8}$$

and

$$c = \sum_{i=2}^{N} c_i \tag{9}$$

where $N$ is the number of components in a polydisperse sample, $c_i$ and $w_i$ are the concentration (mass/volume) and mass fraction of component $i$, respectively. $A_{ij}$ and $A_{ijk}$ are the second and third (mixed) osmotic virial coefficients for interactions between monodisperse polymers $i$, $j$ and $k$.

$A_{ij}$ and $A_{ijk}$ might depend on the molecular masses of the monodisperse polymers $i$, $j$ and $k$. If that is the case, the osmotic virial coefficients of a polydisperse polymer depend on its molecular mass distribution. Then, the evaluation of experimental data requires the polydispersity of the sample to be considered. The polydispersity can be taken into account either by introducing the molecular mass distribution function or by splitting the polymer sample in some monodisperse components (called pseudocomponents). The pseudocomponent procedure was used, for example, to investigate the influence of polydispersity on the thermodynamic properties of aqueous solutions of dextran (DEX) (Kany et al., 1999) and poly(vinyl pyrrolidone) (PVP) (Kany et al., 2003). Kany et al. approximated the molar mass distributions of their DEX- and PVP-samples by eight

Table 9
Specific density $\rho^*$ of aqueous solutions of MD 13–17 and MD 16–19 at 25 °C

| MD 13–17 | | MD 16–19 | |
|---|---|---|---|
| Polymer mass fraction $w_{\mathrm{MD}}$ (g g$^{-1}$) | $\rho^*$ (g cm$^{-3}$) | Polymer mass fraction $w_{\mathrm{MD}}$ (g g$^{-1}$) | $\rho^*$ (g cm$^{-3}$) |
| 0.0499 | 1.01573 | 0.0500 | 1.01591 |
| 0.0999 | 1.03516 | 0.0995 | 1.03525 |
| 0.1487 | 1.05472 | 0.1416 | 1.05224 |
| 0.2004 | 1.07628 | 0.1988 | 1.07614 |
| 0.2497 | 1.09761 | 0.2506 | 1.09869 |
| 0.2996 | 1.11995 | 0.2878 | 1.11537 |
| 0.3512 | 1.14387 | 0.3489 | 1.14380 |
| 0.4025 | 1.16867 | 0.3980 | 1.16776 |
| 0.4992 | 1.21786 | 0.4507 | 1.19390 |
| 0.5491 | 1.24457 | 0.4938 | 1.21650 |
| | | 0.5392 | 1.24056 |
| | | 0.5941 | 1.27196 |

Table 10
Components of the maltodextrin samples

| Component | Mass fraction $w_i$ (g g$^{-1}$) | $M_n$ (g mol$^{-1}$) (from GPC) | $M_w$ (g mol$^{-1}$) (from GPC) |
|---|---|---|---|
| *MD 13–17* | | | |
| Glucose | 0.0184 | 180.1 | 180.1 |
| Maltose | 0.0606 | 342.2 | 342.2 |
| Maltotriose | 0.0449 | 504.4 | 504.4 |
| Polydisperse fraction | 0.8760 | 2552.0 | $1.4098\times10^4$ |
| *MD 16–19* | | | |
| Glucose | 0.0266 | 180.1 | 180.1 |
| Maltose | 0.0594 | 342.2 | 342.2 |
| Maltotriose | 0.0792 | 504.4 | 504.4 |
| Polydisperse fraction | 0.8348 | 1909.2 | $9.161\times10^3$ |

pseudocomponents. The results of their evaluations showed that for both polymers the influence of the molecular mass on the osmotic virial coefficients can be neglected. In those investigations the number-averaged molar mass of the polymers varied from (3000 to 150,000) g mol$^{-1}$. They confirmed a similar observation by Hasse et al. (1995), who investigated the thermodynamic properties of aqueous solutions of (nearly monodisperse) poly(ethylene glycol)s.

As was shown above, the maltodextrins studied in the present work are strongly polydisperse polymers as they contain low molecular components (mono-, di- and trisaccharides such as glucose, maltose and maltotriose) as well as oligo and polysaccharides. Therefore, the polydispersity of the maltodextrins was taken into account by splitting a polymer into glucose (G), maltose (M), maltotriose (MT) and a polydisperse fraction (PF) which was again described by eight pseudocomponents (cf. Fig. 4). For the maltodextrins investigated in the present work, the number- and weight-averaged molecular masses of these components as well as their mass fractions are given in Table 10.

The evaluation and interpretation of the laser-light scattering data is based on the following equation (Hasse et al., 1995):

$$\frac{K_0 c}{R_\theta^{\mathrm{E}}} = -\frac{\rho_1}{RT}\frac{\partial \mu_1}{\partial c} \tag{10}$$

The experimental results for the term on the left hand side of Eq. (10) are given in Tables 7 and 8. The right hand side is calculated from

$$\frac{\mu_1}{RT} = \frac{\mu_{1,\mathrm{pure}}}{RT} + \ln a_1 \tag{11}$$

where the activity of the solvent is calculated from Eq. (6)—resulting in Eq. (1).

The second and third light scattering virial coefficients $A_2^{\mathrm{LS}}$ and $A_3^{\mathrm{LS}}$ are related to the osmotic virial coefficients for interactions between monodisperse polymers by (Kurata, 1982):

$$A_2^{\mathrm{LS}} = \frac{1}{2M_\mathrm{w}^2}\sum_{i=2}^{N}\sum_{j=2}^{N} w_i w_j M_i M_j A_{ij} \tag{12}$$

$$\begin{aligned} A_3^{\mathrm{LS}} = {} & \frac{1}{3M_\mathrm{w}^2}\sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2} w_i w_j w_k M_i M_j A_{ijk} - \frac{1}{3M_\mathrm{w}^3} \\ & \times \sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2}^{N}\sum_{l=2}^{N} w_i w_j w_k w_l M_i M_j M_k M_l \\ & \times (A_{ik}A_{jk} - A_{ik}A_{jl}) \end{aligned} \tag{13}$$

It can be seen from Eqs. (7), (8), (12) and (13) that, there is no difference between osmotic and light scattering virial coefficients (i.e. $A_2^{\mathrm{osm}} = A_2^{\mathrm{LS}}$ and $A_3^{\mathrm{osm}} = A_3^{\mathrm{LS}}$) as long as a polymer is monodisperse or the osmotic virial coefficients for interactions between monomers $A_{ij}$ and $A_{ijk}$ do not depend on the molecular mass.

There are by far more unknown osmotic virial coefficients (for interactions between monomers) in these equations then can be determined from the experimental data. Therefore, as is normally the case, the mixed virial coefficients $A_{ij}$ and $A_{ijk}$ were estimated using geometric mixing rules:

$$A_{ij} = (A_{ii}A_{jj})^{1/2} \tag{14}$$

$$A_{ijk} = (A_{iii}A_{jjj}A_{kkk})^{1/3} \tag{15}$$

The new experimental results from the isopiestic and the laser-light scattering experiments and literature data for the activity of water in aqueous solutions of glucose, maltose and maltotriose at 25 °C (Cooke, Jónsdóttir, & Westh, 2002; Miyajima, Sawada, & Nakagaki, 1983a,b; Taylor & Rowlinson, 1955; Uedaira, Uedaira, Miyajima, Sawada, & Nakagaki, 1969) were simultaneously evaluated to determine the osmotic virial coefficients. At first it was assumed that the pure component second and third osmotic virial coefficients $A_{ii}$ and $A_{iii}$ of all maltodextrin species (including glucose, maltose and maltotriose) do not depend on the molecular mass. However, this resulted in an unsatisfactory representation of the experimental data. Therefore, the assumption was modified. It was assumed that the second osmotic virial coefficients were different for glucose ($A_{\mathrm{G\ G}}$), maltose ($A_{M\ M}$), and maltotriose ($A_{\mathrm{MT\ MT}}$), and that for all other monomers of the polydisperse maltodextrins, a single number for the osmotic virial coefficient ($A_{\mathrm{PF\ PF}}$) is appropriate. The assumption on the third osmotic virial coefficient was kept unchanged: $A_{\mathrm{G\,G\,G}} = A_{M\,M\,M} = A_{\mathrm{MT\,MT\,MT}} = A_{\mathrm{PF\ PF\ PF}}$. The results from that assumption are given in Fig. 6, where for 25 °C the reduced water activity ($-\rho_1 \ln a_1/c$) is plotted versus the polymer concentration $c$. The deviation between the experimental data and the correlation is small at low polymer concentrations, but it increases with polymer content, resulting in systematic

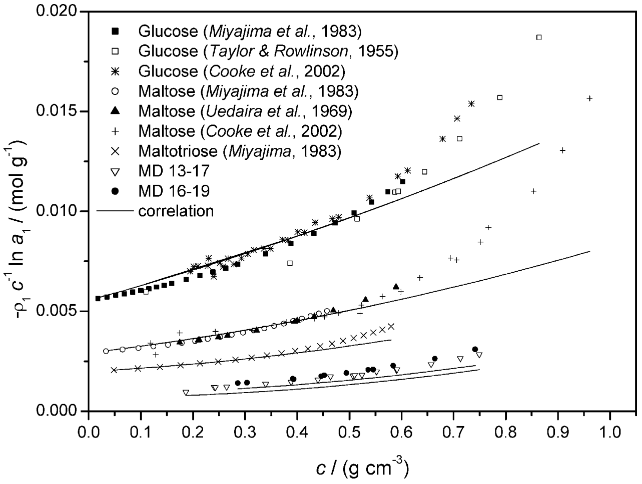

Fig. 6. Reduced activity of water in aqueous solutions of saccharides at 25 °C: experimental data and correlation results from the osmotic virial equation.

deviations from the experimental data. An essential improvement was achieved by adapting the above mentioned assumption for the second osmotic virial coefficients ($A_{\mathrm{G\,G}} \neq A_{M\,M} \neq A_{\mathrm{MT\,MT}} \neq A_{\mathrm{PF\,PF}}$) to the third osmotic virial coefficients: $A_{\mathrm{G\,G\,G}} \neq A_{M\,M\,M} \neq A_{\mathrm{MT\,MT\,MT}} \neq A_{\mathrm{PF\,PF\,PF}}$). The resulting numbers for the osmotic virial coefficients are given in Table 11 and shown in Fig. 7. Fig. 8 shows the improvement achieved in representing the activity of water. The experimental data for the activity of water are described within experimental uncertainty up to polymer concentrations of around 0.7 g cm$^{-3}$. Deviations which might surmount the experimental uncertainty are only observed for the high concentration data reported by Cooke et al. (2002) for aqueous solutions of maltose.

In the process of determining the osmotic virial coefficients the experimental results from the light scattering investigations of aqueous solutions of maltodextrin systems were neglected in regions where the signals were caused by the low molecular mass fractions (corresponding to glucose, maltose and maltotriose), i.e. it is assumed that the experimental results for $K_0c/R_\theta^{\mathrm{E}}$ are caused only by the light scattering of the high molecular mass molecules. In these evaluations, the weight-averaged molar masses ($M_\mathrm{w}$) of the maltodextrins were also adjusted. However, the resulting numbers for $M_\mathrm{w}$ agree within the experimental error with the results from the GPC experiments (cf. chapter 2.2). A comparison between the experimental light scattering results and the correlation is shown in Fig. 9. The agreement is satisfactory.

Table 11
Second ($A_{ii}$) and third ($A_{iii}$) osmotic virial coefficients of glucose (G), maltose (M), maltotriose (MT) and polydisperse fractions (PF) at 25 °C

| $i$ | $A_{\mathrm{ii}}$ (mol cm$^3$ g$^{-2}$) | $A_{\mathrm{iii}}$ (mol cm$^6$ g$^{-3}$) |
|---|---|---|
| G | 0.003353 | 0.011556 |
| M | 0.001315 | 0.007468 |
| MT | 0.000572 | 0.005230 |
| PF | 0.000213 | 0.003075 |

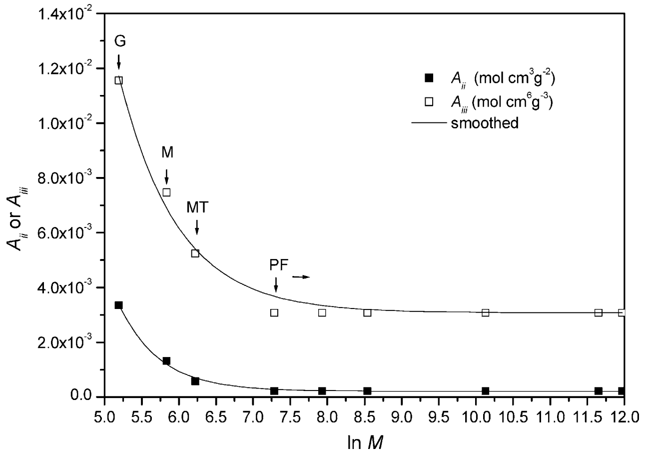

Fig. 7. Influence of the molecular mass on the second and third osmotic virial coefficients.

## 4.2. VERS model

There are some other methods known in the literature for modeling the thermodynamic properties of aqueous solutions of neutral polymers. Here, one of those methods, the VERS model of Großmann et al. (1995), is used as an alternative to describe the experimental data for the activity of water and the enthalpies of dilution of the aqueous solutions of maltodextrins. The VERS model (Virial Equation with Relative Surface Fractions) was successfully applied to correlate and predict some thermodynamic properties of aqueous solutions of PEG and DEX. It is a modification of the osmotic virial equation of state and uses a group contribution approach for the excess Gibbs energy in a structure similar to Pitzer's Gibbs excess energy equation for electrolyte solutions (Pitzer, 1991).

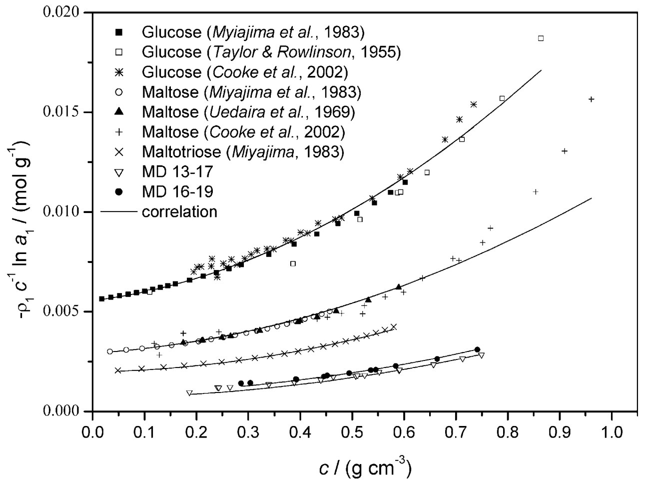

Fig. 8. Reduced activity of water in aqueous solutions of saccharides at 25 °C: experimental data and correlation results from the osmotic virial equation.

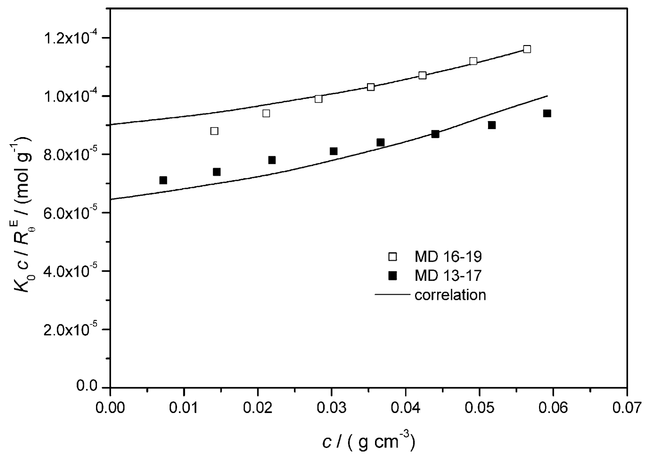

Fig. 9. Laser-light scattering data of aqueous maltodextrin solutions: experimental data and correlation results from the osmotic virial equation.

The activity coefficients are normalized according to the asymmetric convention: the reference state for water is pure liquid water at systems temperature and pressure, whereas for a solute component the reference state is a hypothetical solution of the solute in pure water at unit concentration and systems temperature and pressure. A normalized surface fraction (solute's surface fraction $\varphi_i$ is normalized by the surface fraction of water $\varphi_1$) is used to describe the solute concentration. The equations for the activities of water ($a_1$) and solute ($a^*_{i,m}$) are:

$$\ln a_1 = -\frac{M_1}{1000}\sum_i m_i - \frac{1000}{M_1}\sum_{i\neq 1}\sum_{j\neq 1}\frac{\varphi_i}{\varphi_1}\frac{\varphi_j}{\varphi_1}A_{ij} \tag{16}$$

$$\ln a^*_{i,m} = \ln m_i + 2\left(\frac{1000}{M_1}\right)\frac{q_i}{q_1}\sum_{j\neq 1}\frac{\varphi_j}{\varphi_1}A_{ij} \tag{17}$$

$$\varphi_i = \frac{m_i q_i}{\sum_{\text{all components } i} m_j q_j} \tag{18}$$

$$q_i = \sum_{\text{all components } i} \nu_l^{(i)} Q_l \tag{19}$$

where $m_i$ is the molality of component $i$, $Q_l$ the surface parameter of group $l$, $\nu_l^{(i)}$ the number of groups $l$ in component $i$, and $q_i$ the surface parameter of component $i$. The interaction parameter $A_{ij}$ is given by

$$A_{ij} = \sum_{\text{all groups } l}\sum_{\text{all groups } m}\varphi_l^{(i)}\varphi_m^{(j)}a_{lm} \tag{20}$$

where $a_{lm}$ is a binary parameter for interactions between solute groups $l$ and $m$. The influence of temperature on $a_{lm}$ is expressed by

$$a_{lm} = \beta_{l,m}^{(0)} + \beta_{l,m}^{(1)}[(T/T_0) - 1] + \beta_{l,m}^{(2)}\ln(T/T_0) \tag{21}$$

where $T_0 = 298.15$ K.$\varphi_l^{(i)}$ is the surface fraction of groups $l$ in species $i$:

$$\varphi_l^{(i)} = \nu_l^{(i)}\frac{Q_l}{q_i} \tag{22}$$

The partial molar excess enthalpies of water ($h_1^E$) and solute $i$ ($h_i^E$) are calculated from the equation for the excess Gibbs energy $g^E$

$$h_1^E = -T^2\left(\frac{\partial(\mu_i^E/T)}{\partial T}\right)_{p,n_j} \tag{23}$$

resulting in

$$\frac{h_1^E}{RT} = T\left(\frac{1000}{M_1}\right)\sum_{i\neq 1}\sum_{j\neq 1}\frac{\varphi_i}{\varphi_1}\frac{\varphi_j}{\varphi_1}\frac{\partial A_{ij}}{\partial T} \tag{24}$$

$$\frac{h_{i\neq 1}^E}{RT} = -2T\left(\frac{1000}{M_1}\right)\frac{q_i}{q_1}\sum_{j\neq 1}\frac{\varphi_j}{\varphi_1}\frac{\partial A_{ij}}{\partial T} \tag{25}$$

where

$$\frac{\partial A_{ij}}{\partial T} = \sum_{\text{all groups } l}\sum_{\text{all groups } m}\varphi_l^{(i)}\varphi_m^{(j)}\left(\frac{\beta_{l,m}^{(1)}}{T_0} + \frac{\beta_{l,m}^{(2)}}{T}\right) \tag{26}$$

All parameters are assumed to be symmetric, i.e. $\beta_{l,m}^{(j)} = \beta_{m,l}^{(j)}$.

Water is treated as a single group. The maltodextrins are split into four structural groups as proposed by Catté, Dussap, and Gros (1995): $n$ pyranose rings, $(n-1)$ osidic bonds (–O–), $n$ alkane ($CH_2$) and $(3n+2)$ hydroxyl groups.

$$n = \frac{M_n - M_1}{M_G - M_1} \tag{27}$$

$M_n$ is the number-averaged molecular mass of the solute. $M_1$ ($=18.015$ g mol$^{-1}$) and $M_G$ ($=180.16$ g mol$^{-1}$) are the molecular mass of water and glucose, respectively. The group surface parameters of the structural groups are estimated from the method of Bondi (1964):

$q_{\text{pyranose ring}} = 1.5620$,
$q_{\text{osidic bond}} = 0.442$,
$q_{CH_2} = 0.540$ and
$q_{OH} = 1.200$.

The maltodextrins were treated as a single component, i.e. the polydispersity is neglected. The number-averaged

Table 12
Interaction parameters of the VERS model for aqueous solutions of maltodextrins

| | |
|---|---|
| $\beta^{(0)}_{\text{pyr-pyr}}$ | 0.653 |
| $\beta^{(0)}_{\text{pyr-O}}$ | −0.885 |
| $\beta^{(0)}_{\text{pyr-CH}_2}$ | 0.864 |
| $\beta^{(0)}_{\text{pyr-OH}}$ | −0.160 |
| $\beta^{(1)}_{\text{pyr-pyr}}$ | $7.26\times10^{-4}$ |
| $\beta^{(1)}_{\text{pyr-O}}$ | $-1.18\times10^{-3}$ |
| $\beta^{(1)}_{\text{pyr-CH}_2}$ | $3.59\times10^{-3}$ |
| $\beta^{(1)}_{\text{pyr-OH}}$ | $-5.34\times10^{-4}$ |
| $\beta^{(2)}_{\text{pyr-pyr}}$ | $9.80\times10^{-3}$ |

Table 13
Survey of the representation of the experimental data for aqueous solutions of maltodextrins by the VERS model

| Solute s | Solute mass fraction $w_s$ (g $g^{-1}$) | Temperature $T$ (K) | %AAD[a] | Reference |
|---|---|---|---|---|
| *Activity of water* | | | | |
| Glucose | 0.0177–0.7478 | 298.15–317.99 | 0.65 | –[b,c,d,e] |
| Maltose | 0.0331–0.8372 | 298.15–317.99 | 0.63 | –[b,d,f] |
| Maltotriose | 0.0218–0.6567 | 298.15–317.99 | 0.14 | –[b,d] |
| Maltotetraose | 0.0904–0.7952 | 317.99 | 0.44 | –[d] |
| Maltopentaose | 0.1382–0.7750 | 317.99 | 1.55 | –[d] |
| MD 16–19 | 0.2598–0.5850 | 298.15–318.15 | 0.04 | This work |
| MD 13–17 | 0.1750–0.5898 | 298.15–318.15 | 0.13 | This work |
| MD 4–7 | 0.2859–0.4615 | 298.15 | 0.19 | This work |
| *Freezing point depression* | | | | |
| Glucose | 0.005–0.7 | | 0.38 | –[g] |
| Maltose | 0.005–0.44 | | 0.02 | –[h] |
| *Boiling point elevation* | | | | |
| Glucose | | | 0.23 | –[i] |

[a] $\mathrm{AAD}\% = \left[\sum_{i=1}^{N} \left|\frac{Y_{\mathrm{exp},i}-Y_{\mathrm{calc},i}}{Y_{\mathrm{exp},i}}\right|\right] \times \frac{100}{N}$ where $Y_{\mathrm{exp},i}$ and $Y_{\mathrm{calc},i}$, are the experimental and calculated thermodynamic property, respectively, and $N$ is the number of experimental points.

[b] Miyajima et al. (1983).

[c] Taylor and Rowlinson (1955).

[d] Cooke et al. (2002).

[e] Velezmoro, Oliveira, Cabral, and Meirelles (2000).

[f] Uedaira et al. (1969).

[g] Young (1957).

[h] Weast (1973).

[i] Abderafi and Bounahmidi (1994).

molecular masses used are those given in Table 2. As shown elsewhere (Ninni, 2003), a modification of that method which accounts for the polydispersity of the maltodextrins does not give better results.

Model parameters were fitted as follows: parameters $\beta^{(0)}_{\mathrm{pyr,\,pyr}}$, $\beta^{(0)}_{\mathrm{pyr,\,O}}$, $\beta^{(0)}_{\mathrm{pyr,\,CH_2}}$ and $\beta^{(0)}_{\mathrm{pyr,\,OH}}$ were fitted to the experimental results for the activity of water in aqueous solutions of saccharides and maltodextrins at 25 °C; parameters $\beta^{(1)}_{l,m}$ and $\beta^{(2)}_{l,m}$ for ($l$ or $m$) = (pyranose ring, osidic bond, $CH_2$ and OH) were fitted to the experimental results for the heat $\Delta H$ observed when aqueous maltodextrin solutions were diluted with water at 40 °C. These parameters were estimated by minimizing the sum of squares:

$$\mathrm{SSQ} = \sum_N (a_1^{\mathrm{exp}} - a_1^{\mathrm{calc}})^2 \tag{28}$$

$$\mathrm{SSQ} = \sum_N (\Delta H^{\mathrm{exp}} - \Delta H^{\mathrm{calc}})^2 \tag{29}$$

where $N$ is the number of experimental data points.

The numerical values of the parameters are given in Table 12 and the average deviation of the correlated numbers from the experimental ones are given in Table 13.

Fig. 10 shows the results of the correlation for the activity of water in aqueous solutions of maltodextrins as well as prediction results for the activity of water in aqueous solutions of mono-, di-, and tri-saccharides, where the experimental data were taken from the literature. The studied maltodextrins reduce the activity of water by only about 4% at 60% mass fraction, whereas glucose (at the same concentration) reduces the activity of water by 16%. As is shown in Fig. 10, the calculated values are in close agreement with the experimental data even at high polymer concentrations. The VERS model's capability for predictions was also tested by comparing predictions for the freezing point depression and the boiling point elevation of aqueous solutions of glucose and maltose. The deviations are also small (see Figs. 11 and 12), except at very high solute concentrations, where the predictions fail.

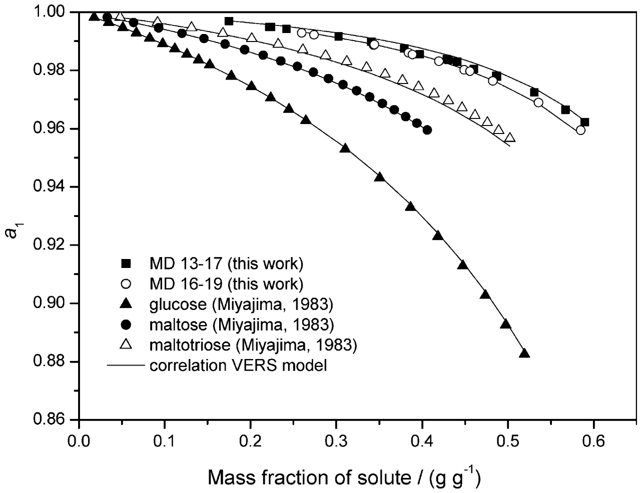

Fig. 10. The activity of water in aqueous solutions of maltodextrin, glucose, maltose, and maltotriose at 25 °C: experimental data and correlation results from the VERS model.

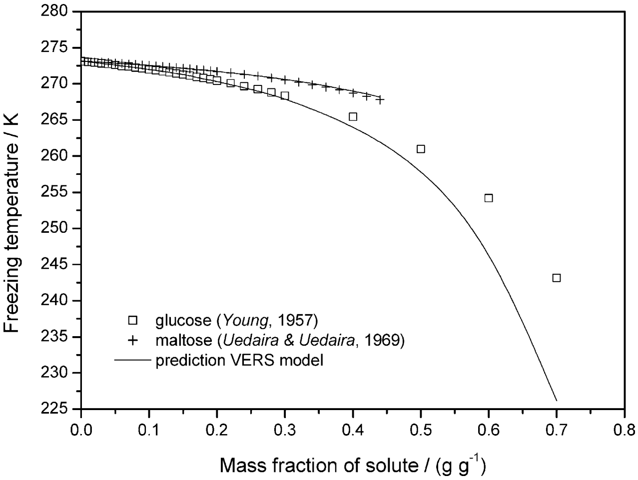

Fig. 11. Freezing point temperatures of aqueous solutions of glucose and maltose: experimental data and predictions from the VERS model.

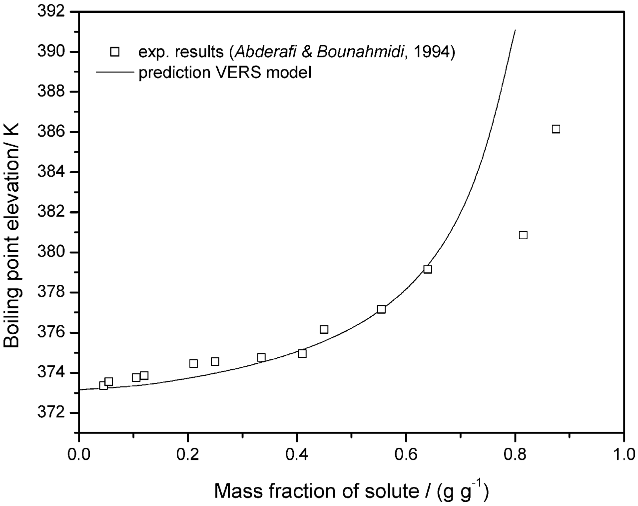

Fig. 12. Boiling point temperatures of aqueous solutions of glucose experimental data and predictions from VERS model.

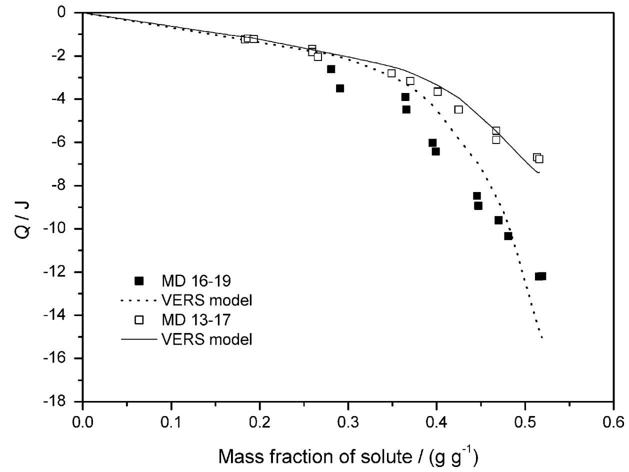

Fig. 13. Heat of dilution of aqueous solutions of MD 13–17 and MD 16–19 at 40 °C: experimental data and calculation results from the VERS model.

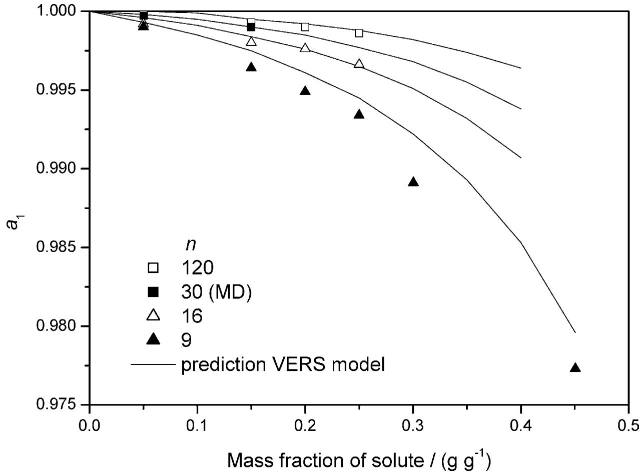

Fig. 14. Activity of water in aqueous solutions of maltodextrin fractions: experimental data (Radosta, Schierbaum, & Yuriev, 1989; Radosta, Schierbaum, Yuriev, Reuther, et al., 1989) and prediction results from the VERS model (*n* is the polymerisation number).

In the VERS model, a ternary parameter for interactions between solute species needs to be take into account at high solute concentration (Großmann et al., 1995).

The influence of temperature on the activity of water is almost negligible in the temperature range from 25 to 45 °C. This is confirmed by the calorimetric measurements which revealed that the heat of dilution is very small. Similarly small values for the heat of dilution were also observed in experiments with dextran solutions (Großmann et al., 1995). Fig. 13 shows a comparison between calculated and experimentally determined heats of dilution for MD 13–17 and 16–19. As can be seen from this figure, the experimental results for both maltodextrins slightly depend on the molar mass. The model gives the correct behavior.

In order to test the applicability of the adjusted parameters the activity of water in aqueous solutions of some high as well as low molecular mass compounds was calculated and compared to the experimental data from Radosta, Schierbaum, and Yuriev (1989) and Radosta, Schierbaum, Yuriev, Reuther, et al. (1989). As shown in Fig. 14, these comparisons prove that the model is able to describe properly the influence of molecular mass on the activity of water even for rather high molecular polymers (e.g. $n=120$ indicates a molar mass of approximately 19,500).

## 5. Conclusions

The thermodynamic properties of aqueous solutions of three maltodextrins were studied experimentally (by isopiestic investigations, laser-light scattering and calorimetry) at around ambient temperature and correlated by two methods (the osmotic virial equation and the VERS model, a semi-empirical group contribution model). The experimental results cover diluted as well as concentrated solutions. Therefore, it was possible to evaluate the second and third osmotic virial coefficients of saccharides and polysaccharides. It was found that the second and third osmotic virial coefficients of the low molecular components (up to maltotriose) depend on the molecular mass, whereas that influence becomes negligibly small for compounds with higher molecular mass. Such a behavior was expected from previous investigations on poly(ethylene glycol), dextran and poly(vinyl pyrrolidone). Good agreement between experimental data and correlation results was also obtained with the VERS model. The model was also able to predict other thermodynamic properties for glucose and maltose such as freezing point depression and boiling point elevation. The new results may be in particular valuable for predicting the properties aqueous solutions of other maltodextrins.

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## References

Abderafi, S., & Bounahmidi, T. (1994). Measurement and modeling of atmospheric pressure vapor–liquid equilibrium data for binary, ternary and quaternary mixtures of sucrose, glucose, fructose and water components. *Fluid Phase Equilibria*, *93*, 337–351.

Archer, D. G. (1992). Thermodynamic properties of the NaCl+$H_2O$ system. II. Thermodynamic properties of NaCl (aq), NaCl·2$H_2O$ (cr), and phase equilibria. *Journal of Physical Chemistry Reference Data*, *21*, 793–829.

Archer, D. G., & Carter, R. W. (2000). Thermodynamic properties of the NaCl+$H_2O$ system. 4. Heat capacities of $H_2O$ and NaCl (aq) in cold-stable and supercooled states. *Journal of Physical Chemistry B*, *104*, 8563–8584.

Bondi, A. (1964). Van der Waals volumes and radii. *Journal of Physical Chemistry*, *68*, 441–451.

Catté, M., Dussap, C.-G., & Gros, J.-B. (1995). A physical chemical UNIFAC model for aqueous solutions of sugars. *Fluid Phase Equilibria*, *105*, 1–25.

Cesàro, A., Cuppo, F., Fabri, D., & Sussich, F. (1999). Thermodynamic behavior of mixed biopolymers in solution and in gel phase. *Thermochimica Acta*, *328*, 143–153.

Clarke, R. C. W., & Glew, D. W. (1985). Evaluation of the thermodynamic functions for aqueous sodium chloride from equilibrium and calorimetric measurements below 154 °C. *Journal of Physical Chemistry Reference Data*, *14*, 489–610.

Cooke, S. A., Jónsdóttir, S.Ó., & Westh, P. A. (2002). Thermodynamic study of glucose and related oligomers in aqueous solution: vapor pressures and enthalpies of mixing. *Journal of Chemical Engineering Data*, *47*, 1185–1192.

Defloor, I., Vandenreyken, V., Grobet, P. J., & Delcour, J. A. (1998). Fractionation of maltodextrins by ethanol. *Journal of Chromatography*, *803*, 103–109.

Flory, P. J. (1953). *Principles of polymer chemistry*. Ithaca: Cornell University Press.

Gaube, J., Pfennig, A., & Stumpf, M. (1993). Vapor–liquid equilibrium in binary and ternary aqueous solutions of poly(ethylene glycol) and dextran. *Journal of Chemical Engineering Data*, *38*, 163–166.

Glicksman, M. (1986). *Food hydrocolloids*. New York: CRC Press.

Großmann, C., Tintinger, R., Zhu, J., & Maurer, G. (1995). Aqueous two-phase systems of poly(ethylene glycol) and dextran—experimental results and modeling of thermodynamics. *Fluid Phase Equilibria*, *106*, 111–138.

Hasse, H., Kany, H.-P., Tintinger, R., & Maurer, G. (1995). Osmotic virial coefficients of aqueous poly(ethylene glycol) from laser-light scattering and isopiestic measurements. *Macromolecules*, *28*, 3540–3552.

Huglin, M. B. (1972). *Light scattering from polymer solutions*. London: Academic Press.

Kany, H. -P. (1998). *Thermodynamische Eigenschaften wässriger Polymer-Lösungen*. PhD Thesis. University of Kaiserslautern, Germany.

Kany, H.-P., Hasse, H., & Maurer, G. (1999). Thermodynamic properties of aqueous dextran solutions from laser-light scattering, membrane osmometry, and isopiestic measurements. *Journal of Chemical Engineering Data*, *44*, 230–242.

Kany, H.-P., Hasse, H., & Maurer, G. (2003). Thermodynamic properties of aqueous poly(vinylpyrrolidone) solutions from laser-light-scattering, membrane osmometry, and isopiestic measurements. *Journal of Chemical Engineering Data*, *48*, 689–698.

Kasapis, S., Morris, E. R., Norton, I. T., & Clark, A. H. (1993a). Phase equilibria and gelation in gelatin/maltodextrin systems—Part I: Gelation of individual components. *Carbohydrate Polymers*, *21*, 243–248.

Kasapis, S., Morris, E. R., Norton, I. T., & Clark, A. H. (1993b). Phase equilibria and gelation in gelatin/maltodextrin systems—Part II: Polymer incompatibility in solution. *Carbohydrate Polymers*, *21*, 249–259.

Kasapis, S., Morris, E. R., Norton, I. T., & Clark, A. H. (1993c). Phase equilibria and gelation in gelatin/maltodextrin systems—Part III: Phase separation in mixed gels. *Carbohydrate Polymers*, *21*, 261–268.

Kasapis, S., Morris, E. R., Norton, I. T., & Clark, A. H. (1993d). Phase equilibria and gelation in gelatin/maltodextrin systems—Part IV: Composition-dependence of mixed-gel moduli. *Carbohydrate Polymers*, *21*, 269–276.

Kurata, M. (1982). *Thermodynamics of polymer solutions*. Chrur: Harwood Academic Publishers.

Lammertz S., & Maurer G. (2002). Thermodynamic properties of aqueous solutions of polyelectrolytes and an inorganic salt. *Proceedings of the 19th ESAT*. Santorini, Greece (pp. 102–105).

Marchal, L. M., Beeftink, H. H., & Tramper, J. (1999). Towards a rational design of commercial maltodextrins. *Trends in Food Science and Technology*, *10*, 345–355.

Miyajima, K., Sawada, M., & Nakagaki, M. (1983a). Studies on aqueous solutions of saccharides. I. Activity coefficients of monosaccharides in aqueous solutions at 25 °C. *Bulletin of the Chemical Society of Japan*, *56*, 1620–1623.

Miyajima, K., Sawada, M., & Nakagaki, M. (1983b). Studies on aqueous solutions of saccharides. II. Viscosity B-coefficients, apparent molar volumes, and activity coefficients of D-glucose, maltose, and maltotriose in aqueous solutions. *Bulletin of the Chemical Society of Japan*, *56*, 1954–1957.

Ninni, L. (2003). *Emprego de métodos de contribuição de grupos no cálculo e predição de propriedades físico-químicas*. PhD Thesis, University of Campinas, Brazil.

Pitzer, K. S. (1991). *Activity coefficients in electrolyte solutions*. Boca Raton: CRC Press.

Pitzer, K. S., & Peiper, C. (1984). Thermodynamic properties of aqueous sodium chloride solutions. *Journal of Physical Chemistry Reference Data*, *13*, 1–102.

Radosta, S., Schierbaum, F., Reuther, F., & Anger, H. (1989). Polymer–water interaction of maltodextrins. Part I: Water vapour sorption and desorption of maltodextrin powders. *Starch*, *41*, 395–401.

Radosta, S., Schierbaum, F., & Yuriev, W. P. (1989). Polymer–water interaction of maltodextrins. Part II: NMR study of bound water in liquid maltodextrin–water systems. *Starch*, *41*, 428–430.

Radosta, S., & Schierbaum, F. H. (1990). Polymer–water interaction of maltodextrins. Part III: Non-freezable water in maltodextrin solutions and gels. *Starch*, *41*, 142–147.

Rumpf, B., Weyrich, F., & Maurer, G. (1997). Enthalpy of dilution in aqueous systems of single solutes ammonia, sodium sulfate and ammonium sulfate: Experimental results and modeling. *Thermochimica Acta*, *303*, 77–91.

Schierbaum, F., Kettlitz, B., Radosta, S., Reuther, F., Richter, M., & Vorweg, W. (1984). Zum Stand der Kenntnisse über Struktur-Eigenschaftsbeziehungen von Maltodextrinen. *Acta Alimentaria Polonica*, *10*, 69–99.

Schierbaum, F., Radosta, S., Vorweg, W., Ynriev, V. P., Brando, E. E., & German, M. L. (1992). Formation of thermally reversible maltodextrin gels as revealed by low resolution H-NMR. *Carbohydrate Polymers*, *18*, 155–163.

Silva, L. H. M., & Loh, W. (2000). Calorimetric investigation of the formation of aqueous two-phase systems in ternary mixtures of water, poly(ethylene oxide) and electrolytes (or dextran). *Journal of Physical Chemistry B*, *104*, 10069–10073.

Silva, L. H. M., & Meirelles, A. J. A. (2000). Phase equilibrium in polyethylene glycol/maltodextrin aqueous two-phase systems. *Carbohydrate Polymers*, *42*, 273–278.

Silva, L. H. M., & Meirelles, A. J. A. (2001). Phase equilibrium and protein partitioning in aqueous mixtures of maltodextrin with polypropylene glycol. *Carbohydrate Polymers*, *46*, 267–274.

Swift, G. (1998). Requirements for biodegradable water-soluble polymers. *Polymer Degradation and Stability*, *59*, 19–24.

Taylor, J. B., & Rowlinson, J. S. (1955). The thermodynamic properties of aqueous solutions of glucose. *Transactions of the Faraday Society*, *51*, 1183–1192.

Uedaira, H., Uedaira, H., Miyajima, K., Sawada, M., & Nakagaki, M. (1969). Activity coefficients of aqueous xylose and maltose solutions. *Bulletin of the Chemical Society of Japan*, *42*, 2137–2140.

Velezmoro, C. E., Oliveira, A. L., Cabral, F. A., & Meirelles, A. J. A. (2000). Prediction of water activity in sugar solutions using models of group contribution and equation of state. *Journal of Chemical Engineering of Japan*, *33*, 645–653.

Weast, R. C. (1973). *CRC Handbook of chemistry and physics* (53rd ed). Cleveland: The Chemical Rubber.

Wyatt, P. J. (1993). Light scattering and the absolute characterization of macromolecules. *Analytica chimica Acta*, *272*, 1–40.

Wyatt Technology Corporation (1999). *Software ASTRA version 4.73.04*. Santa Barbara, CA.

Young, F. E. (1957). D-Glucose–water diagram. *Journal of Physical Chemistry*, *61*, 616–619.