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Temperature dependence of water activity in aqueous solutions of sucrose

Maciej Starzak [a,*], Mohamed Mathlouthi [b]

[a] School of Chemical Engineering, University of KwaZulu-Natal, 4041 Durban, South Africa
[b] Laboratoire de Chimie Physique Industrielle, Université de Reims Champagne-Ardenne, 51687 Reims Cédex, France

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Abstract

A comprehensive experimental data analysis was performed to evaluate the effect of temperature on the water activity coefficient and selected excess thermodynamic functions for aqueous solutions of sucrose. A four-suffix Margules equation with temperature-dependent parameters was used to fit thermodynamic data such as the vapor pressure, boiling point, osmotic coefficient, freezing point, sucrose solubility, heat of dilution and specific heat of solution. The proposed equation gives an adequate representation of the available literature data on sucrose solutions for temperatures from −15 to +150 °C and sucrose concentrations up to 98% wt. The isotherms of water activity coefficient exhibit a characteristic minimum at about 96% wt. sucrose which is then followed by a dramatic increase to values well exceeding 1, as it was suggested before by some theoretical models [Starzak, M., & Mathlouthi, M. (2002). Water activity in concentrated sucrose solutions and its consequences for the availability of water in the film of syrup surrounding the sugar crystal. *Zuckerindustrie, 127*, 175–185; Van Hook, A. (1987). The thermodynamic activity of concentrated sugar solutions. *Zuckerindustrie, 112*, 597–600]. The effect of temperature on water activity, almost negligible for dilute solutions, was found significant for very concentrated solutions (above 80% wt. sucrose). The new water activity equation should find numerous applications in the food technology and sugar industry.

Keywords: Sucrose–water system; Activity coefficient; Margules equation; Temperature dependence; Data regression

1. Introduction

Aqueous solutions of carbohydrates have been studied for many years due to their both scientific and practical importance (molecular biology and biochemistry, food chemistry and technology, sugar industry, etc.). Due to the common availability of sugar and the ease of its purification, the system sucrose–water was the subject of countless physicochemical studies, especially in the first half of the 20th century. The fact that dilute sucrose solutions could be used as a model system to demonstrate the validity of fundamental laws of physical chemistry and chemical thermodynamics, was an additional factor stimulating the popularity of these studies. However, the system later descended into obscurity being considered thermodynamically almost ideal, and hence no longer challenging from a scientific point of view. New research in the area of physical properties of sugar solutions has been observed over the last two decades with the rapid development of food technology and introduction of non-conventional carbohydrates to industrial processes. Routinely, this research involves also the sucrose–water system, as it is often studied for comparative purposes. Studies on concentrated sucrose solutions, mainly undertaken by renowned industrial laboratories, are rather scarce and in some instances even confidential.

The increasing practical interest in carbohydrate solutions caused a great demand for predictive methods of determining physical properties of both aqueous and

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* Corresponding author. Fax: +27 031 260 1118.
E-mail address: starzak@ukzn.ac.za (M. Starzak).

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Nomenclature

a	function defining the assumed temperature dependence
a_i	constant coefficients in Eq. (4)
A_{ij}	interaction constants in Eq. (41)
b_i	expansion coefficients in Margules equation, Eq. (3)
ΔB	thermochemical parameters in Eqs. (10) and (14)
c_i	expansion coefficients in sucrose activity equation
c_p	specific heat
C_p	molar heat capacity
G^E	excess molar Gibbs energy
h_{i0}	coefficients of McMillan-Mayer expansion, Eq. (19)
H^E	excess molar enthalpy
I	performance index
m	molality of solution
M	molecular mass
$\mathbf{M_0}$, $\mathbf{M_1}$	matrices defined by Eqs. (A5) and (A6), respectively
n	number of terms in Margules equation
n_i	number of moles
P	total pressure
P_i^0	saturated vapor pressure
R	universal gas constant
T	absolute temperature
w	weighting factor
x	mole fraction
α	expansion coefficients in water activity equation
β	expansion coefficients in sucrose activity equation
γ	activity coefficient
θ	dimensionless temperature
λ_i	coefficients defined by Eq. (A3)
τ_{ij}	Boltzmann factors in UNIQUAC model
Φ_c	apparent molar heat capacity of sucrose

Subscripts

asym	asymmetric convention
A	water
B	sucrose
d	dilution property
f	at freezing point
m	at melting point
p	at constant pressure

Superscripts

E	excess property
m	molal property
∞	at infinite dilution

non-aqueous solutions involving various sugars. The last two decades have brought a number of studies in this area. The general trend in recent prediction methods is the development of a comprehensive group contribution model capable of predicting solvent and solute activity coefficients in multicomponent systems containing various types of sugars (mono- and polysaccharides) and sugar-related polyols. The UNIFAC group contribution method is currently the most popular technique used to predict thermodynamic activity for a broad range of chemical compounds, including sugars. Group interaction parameters characterizing sugar molecules have been determined by regressing colligative properties data, such as the boiling point elevation (BPE), vapor pressure lowering, freezing point depression (FPD), osmotic pressure, heat of dilution and solubility, for solutions of various carbohydrates in water and other solvents (Abed, Gabas, Delia, & Bounahmidi, 1992; Achard, Gros, & Dussap, 1992; Catté, Dussap, & Gros, 1995; Ferreira, Brignole, & Macedo, 2003; Peres & Macedo, 1997; Spiliotis & Tassios, 2000). More recently, some of the UNIFAC parameters have even been predicted theoretically with methods of molecular mechanics (Jónsdóttir & Rasmussen, 1999). Data regression studies involving sugars were also performed using other thermodynamic models such as ASOG (Correa, Comesaña, & Sereno, 1994) and UNIQUAC (Catté, Dussap, Achard, & Gros, 1994; LeMaguer, 1992; Peres & Macedo, 1996). However, the selection of experimental data in most of these studies was typically limited to 3–5 literature sources for each data category. Moreover, data for highly concentrated solutions were generally not included while thermochemical data, if used at all, were restricted to room temperatures only. Consequently, the resulting activity equations are valid in a relatively narrow range of conditions, mainly at ambient temperatures and low concentrations. This applies to the sucrose–water system in particular. Despite a vast amount of different experimental data generated for this system over the past decades, there is still no reliable water activity equation covering a sufficiently large temperature-composition domain. Interestingly, ICUMSA – a worldwide organization establishing analytical standards for the sugar industry, which has officially adopted equations for a number of physical properties of pure sucrose solutions (density, viscosity, refractive index and solubility) – gives no recommendation for the water activity coefficient. The two principal sources of information used at present in the sugar industry such as *Sugar Technologists Manual* (Bubnik, Kadlec, Urban, & Bruhns, 1995) and *Sugar*

Technology (Van derPoel, Schwieck, & Schwartz, 1998) recommend polynomial equations for selected colligative properties of sucrose solutions. These were obtained by regressing data from single experimental studies, apparently regarded as being more reliable than other data sources. Bubnik et al. (1995) give a table of water activity data with a reference to the well-known BFMIRA Technical Report by Norrish (1967) which, in turn, is based on an earlier study of the same author (Norrish, 1966). However, a closer inspection of this study shows that the water activity coefficient correlation proposed there rests on 25 experimental measurements taken by several authors at one temperature (25 °C) for sucrose contents never exceeding 60% wt.! More recent correlations of Chen (1989) and Miyawaki et al. (1997), particularly popular amongst food technologists, have been derived from freezing point data and therefore can be used for low temperatures only. In fact, they do not account for the temperature whatsoever, assuming that for relatively dilute solutions the effect of temperature on the water activity coefficient can practically be neglected. In turn, Starzak and Peacock (1997) used the Margules equation with a simple built-in expression for the temperature effect. The equation was developed using a massive amount of literature data and robust statistical analysis. Unfortunately, the experimental database comprised vapor–liquid equilibrium and osmotic coefficient data only (the latter from studies on isopiestic solutions).

The above brief review shows clearly that at present there is no accurate and statistically reliable empirical model of thermodynamic activity for the sucrose–water system which would cover the entire composition range as well as temperatures from the freezing point to the boiling point of highly concentrated solutions. The purpose of this study is, therefore, to develop such a correlation by critically evaluating and regressing various types of experimental data available from the literature.

2. Experimental database

Since activity coefficients have been introduced in thermodynamics to account for non-ideal behavior of mixtures, they can be determined by analysing various pieces of experimental data, especially those in which thermodynamic non-ideality is manifested most. Typically, these are phase equilibrium data as well as thermochemical data on mixing. It was, therefore, decided that the following categories of data would be used in this study:

- vapor–liquid equilibrium data (boiling point elevation, equilibrium vapor pressure above a solution, equilibrium relative humidity, as well as the osmotic coefficient determined from isopiestic vapor pressure measurements);
- solid–liquid equilibrium data (freezing point depression and sucrose solubility);
- thermochemical data (heat of dilution and specific heat of solution).

Osmotic pressure data were not included, since rigorous analysis of these data would require considering the effect of pressure on the activity coefficient, which was beyond the scope of this study.

The vapor–liquid equilibrium (VLE) data used in this study come mainly from the database created by Starzak and Peacock (1997), being the result of an extensive literature search (*Chemical Abstracts* 1902–1995/1996, volumes 2–124; *Sugar Industry Abstracts* 1949–1995, volumes 11–57; and the landmark data collection by Timmermans (1960)). New additions to this database include a few older studies unavailable at the time as well as experimental results published since 1996. Initially, the updated VLE database contained 1603 experimental points from 64 different literature sources. However, after rejection of evident statistical outliers this number was reduced to 1507. The rejection criteria are discussed elsewhere (Starzak & Peacock, 1997). The accepted VLE data consist of various types of measurements such as the boiling temperature of solution at a known total pressure, saturated vapor pressure of solvent at a known temperature, concentrations of isopiestic solutions at a known temperature (leading to osmotic coefficients), and equilibrium relative humidity of air above a solution at a known temperature and total pressure. A brief description of the ultimate VLE data collection is given in Table 1. Because of the natural technological progress, different experimental methods used by different authors, as well as the varying nature and objectives of these studies (scientific/industrial), it is obvious that the data sources listed in Table 1 are characterized by very diverse degrees of precision. In our opinion, however, when considering the quality of data the time factor should not be overestimated. For example, early measurements of Berkeley, Hartley, and Burton (1919), Scatchard, Hamer, and Wood (1938) or Robinson, Smith, and Smith (1942) are far more accurate than some published even quite recently. A system of weighting factors specially developed to account for the quality of individual VLE data sets was discussed in detail by Starzak and Peacock (1997).

The solid–liquid equilibrium (SLE) data include points characterizing two types of phase equilibria possible in the sucrose–water system: equilibrium between ice and sucrose solution, known as the freezing point curve, and equilibrium between sucrose crystals and the solution, known as the sucrose solubility curve. The freezing point data collection consisted of 213 experimental points from 13 different literature sources (freezing point depression and the corresponding su-

Table 1
Collection of experimental VLE data

Original authors	Other sources of information	Type of data[a]	Number of points	Range[b]		Accepted data[c]	
				% wt. Sucrose	Temperature or pressure	Number of points	Weight $w_{\mathrm{VLE},i}$
Wüllner (1858)	Timmermans (1960)	bpe	66	33–60	26–761 mmHg	53	0.1531
Gerlach (1863)	Prinsen Geerligs (1909); Holven (1936)	bpe	14	10–91	760 mmHg	12	0.0885
Flourens and Freutzel (1876)	Wohryzek (1914); Spencer and Meade (1929)	bpe	13	10–90	760 mmHg	11	0.2037
Dupont (1885)	Spengler et al. (1938)	bpe	6	86–94	760 mmHg	6	0.1434
Beckmann (1890a, 1890b)	Timmermans (1960)	bpe	5	5–18	760 mmHg	5	0.2090
Baroni (1893a, 1893b)	Timmermans (1960)	bpe	5	5–17	760 mmHg	5	0.2909
Claassen and Freutzel (1893)	Wohryzek (1914)	bpe	60	10–92	760 mmHg	58	0.2462
Flourens (1897)	Spengler et al. (1938)	bpe	9	67–91	760 mmHg	9	0.2624
Mikhailenko (1901a, 1901b, 1901c)	Timmermans (1960)	vpl	6	11–52	50 °C	6	0.2676
Jüttner (1901)		vpl	17	10–50	100 °C	16	0.2403
Kahlenberg (1901)		bpe	28	17–74	739 mmHg	28	0.2342
Smits (1902)		vpl	12	1–39	0 °C	12	0.4661
Claassen (1904)	Wohryzek (1914); Hugot and Jenkins (1986)	bpe	20	5–94	760 mmHg	17	0.1804
Perman (1905)		vpl	2	12–27	99, 100 °C	2	0.2991
Vivien (1906)	Timmermans (1960)	bpe	13	44–90	760 mmHg	10	0.1626
Tower (1908)		vpl	3	6–26	15 °C	3	0.4080
Krauskopf (1910)		vpl	3	17–38	40 °C	1	0.1663
Perman and Price (1912)		bpe	10	19–64	213–521 mmHg	7	0.2343
Wood (1915)	Timmermans (1960)	bpe	26	48–69	113–527 mmHg	23	0.1930
Berkeley et al. (1919)		vpl	14	25–71	0, 30 °C	14	0.9170
Boswell and Cantelo (1922)	Timmermans (1960)	vpl	2	25–34	23 °C	2	0.2924
Perman and Saunders (1923)		vpl	45	12–77	70, 90 °C	39	0.2108
Świętosławski (1925)		vpl	5	9–33	100 °C	5	0.3758
Mondain-Monval (1925)		vpl	5	60–69	32, 47 °C	5	0.2970
Downes and Perman (1927)		vpl	101	7–76	40–80 °C	91	0.1803
Fricke and Havestadt (1927)		vpl	14	21–73	0, 10 °C	13	0.4118
Jordan (1930)	Holven (1936)	bpe	11	30–90	760 mmHg	9	0.1202
Whittier and Gould (1930)		erh	1	64	25 °C	0	0.0792
Sinclair (1933)		vpl	10	6–32	25 °C	10	0.4363
Bukharov (1934, 1938)		bpe	56	15–90	93–760 mmHg	52	0.2882
Robinson and Sinclair (1934)		iso	31	6–34	25 °C	31	0.5755
Thieme (1934a, 1934b)		erh	6	69–93	30 °C	6	0.2266
Plake (1935)	Bartels et al. (1960)	bpe	7	0–4	760 mmHg	5	0.1514
Holven (1936)		bpe	51	44–94	760 mmHg	48	0.2235
Van Ruyven (1936)	Bartels et al. (1960)	bpe	6	2–18	760 mmHg	6	0.2459
Scatchard et al. (1938)		iso	23	6–68	25 °C	23	0.6285
Spengler et al. (1938)		bpe	95	15–91	176–1988 mmHg	91	0.2680
Pouncy and Summers (1939)		erh	1	64	23 °C	1	0.0980
Tressler et al. (1941)		bpe	21	5–72	760 mmHg	21	0.3170
Robinson et al. (1942)		iso	33	9–67	25 °C	33	0.7103
Grover (1947)		erh	7	60–73	20 °C	7	0.2873
Jackson (1950)	Nicol (1968)	bpe	32	61–80	60, 90 °C	32	1.0000
Money and Born (1951)		erh	9	42–71	20 °C	8	0.3079
Dunning et al. (1951)		vpl	109	45–83	60–96	109	0.4559

(continued on next page)

Table 1 (*continued*)

Original authors	Other sources of information	Type of data[a]	Number of points	Range[b]		Accepted data[c]	
				% wt. Sucrose	Temperature or pressure	Number of points	Weight $w_{\mathrm{VLE},i}$
Hawaiian Sugar Technologists (1955)	Meade and Chen (1977)	bpe	12	30–92	760 mmHg	11	0.2151
Heiss (1955)	Norrish (1966)	erh	7	44–70	25 °C	7	0.3182
Jones (1959)	Norrish (1967)	bpe	20	60–99	760 mmHg	20	0.2802
Rother (1960)		vpl	47	16–72	0–50 °C	40	0.2316
Robinson and Stokes (1961)		iso	28	11–66	25 °C	28	0.6267
Pidoux (1962)		bpe	1	86.5	760 mmHg	1	0.1734
Ingleton (1965)		bpe	9	40–95	760 mmHg	9	0.1834
Hoynak and Bollenback (1966)		bpe	18	10–99	760 mmHg	16	0.2016
Norrish (1966)		erh	5	57–67	25 °C	5	0.3460
Tuzhilkin and Kaganov (1969a, 1969b)		bpe	69	55–95	149–760 mmHg	67	0.4666
Batterham and Norgate (1975)		bpe	20	51–76	54–282 mmHg	20	0.3603
Sarka et al. (1978)		bpe	21	21–81	760 mmHg	21	0.4058
Rüegg and Blanc (1981)		erh	26	24–70	25 °C	25	0.4108
Modell and Reid (1983)		bpe	40	75–95	551–760 mmHg	38	0.1639
Crapiste and Lozano (1988)		bpe	18	23–73	55–525 mmHg	18	0.3207
Abderafi and Bounahmidi (1994)		bpe	11	5–87	760 mmHg	9	0.1127
Lehnberger and Schliephake (1999)		bpe	164	27–80	375–750 mmHg	156	0.3626
Velezmoro et al. (2000)		erh	38	2–45	25–35 °C	32	0.1163
Comesaña et al. (2001)		erh	15	26–67	35 °C	15	0.5913
Cooke et al. (2002)		vpl	9	28–72	25 °C	9	0.3685

[a] bpe – boiling point data, vpl – vapor pressure data, erh – equilibrium relative humidity data, iso – data from the isopiestic method.

[b] Rounded-off values given.

[c] Data finally accepted after the completion of the iterative elimination of outliers.

crose concentration in solution), while the solubility data collection included 265 data points from 34 authors (sucrose concentration in saturated solution and the corresponding temperature). Both the freezing point and solubility data required additional enthalpy data on solvent and solute, respectively, which will be introduced later. The SLE data used in this study were summarized in Tables 2 and 3.

Thermochemical data provide more information on the effect of temperature on activity coefficients than any other type of data. They typically include measurements of the heat of dilution and specific heat of solution. Although dilution of sucrose solutions is an exothermic process, it is associated with a relatively small heat effect. Two groups of experiments for the determination of the heat of dilution are in common use. In the first, a comparatively large amount of sucrose solution is diluted with a small amount of water, whereas in the second, a small amount of solution is diluted with a large amount of water. In both cases, the initial and final concentrations of the solution are recorded and the accompanying heat effect is measured at a constant temperature. The data is then normally reported either as the integral heat of dilution, being the amount of heat released during dilution per mole of sucrose in solution or as the differential heat of dilution, being the amount of heat released per unit mass of water added. While the integral heat can be directly obtained from the experiment, the differential heat is calculated by dividing a relatively small amount of measured heat by also a small (but finite, not infinitesimal) amount of added water. This makes the resulting value of differential heat of dilution approximate. The experimentalist must, therefore, use an optimal amount of diluting water to compromise between the precision of the heat measurement and the accuracy of calculation. The heat of dilution data selected for this study included 283 experimental points taken from 10 different authors (Table 4). A certain lack of consistency was observed across individual data sets regarding the effect of temperature

Table 2
Collection of experimental freezing point depression data

Authors	Number of points	Range[a] % wt. Sucrose
Guthrie (1876)	11	5–51
Pickering (1893a, 1893b)	75	0–64
Abegg and Muller (1894)	4	10–31
Raoult (1897)	6	1–26
Ewan (1899)	5	23–42
Jones and Getman (1904a, 1904b)	10	5–75
Young and Sloan (1904)	12	2–24
Morse et al. (1906)	10	3–26
Kremann and Eitel (1923)	13	9–63
Babinski (1924a, 1924b)	12	21–62
Young and Jones (1949)	29	5–75
Neau et al. (1989)	13	9–63
de Cindio et al. (1995)	13	10–76

[a] Rounded-off values given.

Table 3
Collection of experimental sucrose solubility data

Authors	Number of points	Temperature range (°C)
Courtonne (1877)	2	12, 45
Herzfeld (1892)	6	5–99
Horsin-Deon (1902); after Vavrinecz (1961)	3	0–70
Osaka (1903)	1	25
Scott-Macfie (1906); after Hruby and Kasjanov (1938)	10	10–100
Lebedeff (1908)	3	30–70
Horiba (1917)	7	0–60
Van der Linden (1919)	2	30, 50
Kremann and Eitel (1923)	2	−14, 16
Jackson and Gillis-Silsbee (1924)	3	23–50
Mondain-Monval (1925)	4	1–30
Grube and Nussbaum (1928)	9	0–100
Reinders and Klikenberg (1928)	3	25–45
Nishizawa and Hachihama (1929)	3	25–75
Ahrens (1930)	6	0–100
Grut (1936/1937, 1937/1938)	6	20–80
d'Orazi (1938)	5	40–90
Scatchard et al. (1938)	1	25
Vernon (1939)	14	18–91
Hruby and Kasjanov (1938/1939, 1940)	2	50, 80
Verhaar (1940, 1941)	3	30
Lyle (1941)	9	0–80
Benrath (1942)	6	107–144
Taylor (1947, 1948)	11	64–81
Young and Jones (1949)	5	(−14)–6
Dubourg et al. (1952)	1	87
Wise and Nicholson (1955, 1956)	59	18–90
Kelly (1958)	7	0–100
Charles (1960)	37	1–86
Wagnerowski et al. (1960)	5	40–80
Vavrinecz (1962)	14	(−13)–0
Vasatko et al. (1966)	6	20–70
Smelik et al. (1968)	9	66–126
Abed et al. (1992)	1	70

Table 4
Collection of experimental heat of dilution data

Authors	Number of points	Range[a] % wt. Sucrose	Temperature (°C)
Porter (1917)	7	15–58	20
Pratt (1918)	64	29–40	0–33
Hunter (1926)	34	14–56	12–30
Naudé (1928)	4	3–15	18
Vallender and Perman (1931)[b]	65	19–69	20–80
Gucker et al. (1939)	62	2–6	20, 30
Lange and Markgraf (1950)	9	0–6	18
Savage and Wood (1976)	13	2–41	25
Stroth and Schönert (1977)	9	0–2	25
Wood and Hiltzik (1980)	16	6–35	25

[a] Rounded-off values given.
[b] Data at 0 °C were rejected as unreliable.

on the heat of dilution. This might result from the fact that a considerable portion of data was available in the form of less accurate differential heats of dilution. Analysis of the frequently cited study by Vallender and Perman (1931), involving rare measurements of differential heats of dilution in a broad range of temperatures (0–80 °C), shows that the error made by these authors when calculating mean differential heats of dilution from the measured (integral) amounts of heat was at least 10–15%. Consequently, whenever sufficient information was available to reproduce the actual conditions of the experiment, the reported differential heats of dilution were converted back into the corresponding integral values.

Data on the specific heat of solution were used to determine the excess heat capacity C_p^E, the property which is directly linked to the temperature dependence of chemical potential, and hence to the temperature dependence of activity coefficients. In general, reliable determinations of C_p^E can be obtained only from high precision specific heat data. Unfortunately, many older measurements, especially those popular amongst sugar technologists, are of an industrial nature and not accurate enough to serve this purpose. They typically suggest a linear dependence of specific heat on mass concentration which implies zero excess heat capacity. Moreover, even studies performed with a scientific rigour are often contradictory. For example, the specific heat data reported by Galema, Engberts, Høiland, and Førland (1993) as well as more recent data of Darros-Barbosa, Balaban, and Teixeira (2003) produce negative C_p^E values at 25 °C (Fig. 1), contrary to results obtained by Gucker and Ayres (1937), DiPaola and Belleau (1977) and Banipal et al. (1997) as well as those of Vivien (1906) at 15 °C. A closer inspection of the problem shows that even small inaccuracies in the experimental gradient of the specific heat vs. concentration curve produce large errors in C_p^E, to the extent that even the sign of the excess function is falsified (as was the case in the first two studies mentioned above). It was decided, therefore, to reject at least those data that were evidently inconsistent with the specific heat of pure water when extrapolated to infinite sucrose dilution. As a result, 70 experimental points from four different literature sources were only accepted for the final data regression (Table 5).

Eventually, the entire database contained 2338 experimental points fairly evenly distributed on the concentration-temperature plane, with VLE data being the major contributor (Fig. 2). This allowed, in our opinion, for a statistically significant analysis of the composition and temperature dependence of water and sucrose activity coefficients in a wide range of conditions.

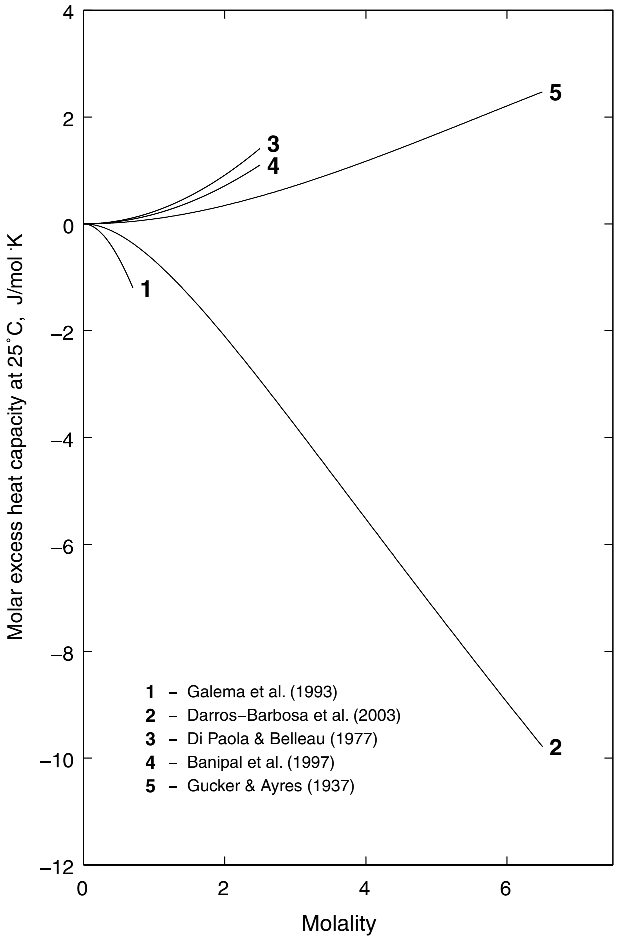

Fig. 1. Molar excess heat capacity of sucrose solutions at 25 °C according to different literature sources (calculated from smoothed heat capacity data).

Table 5
Collection of experimental specific heat data

Authors	Number of points	Range[a]	
		% wt. Sucrose	Temperature (°C)
Vivien (1906)	19	8–67	15
Gucker and Ayres (1937)	25	0–67	20, 25
DiPaola and Belleau (1977)	13	3–31	25
Banipal et al. (1997)	13	3–31	25

[a] Rounded-off values given.

3. Composition and temperature dependence of activity coefficients

The main objective of this study was to establish empirical equations describing the activity coefficients of water and sucrose, γ_A and γ_B, as functions of the sucrose mole fraction x_B and the absolute temperature T. Amongst various possible mathematical forms used in the literature to express the composition dependence in

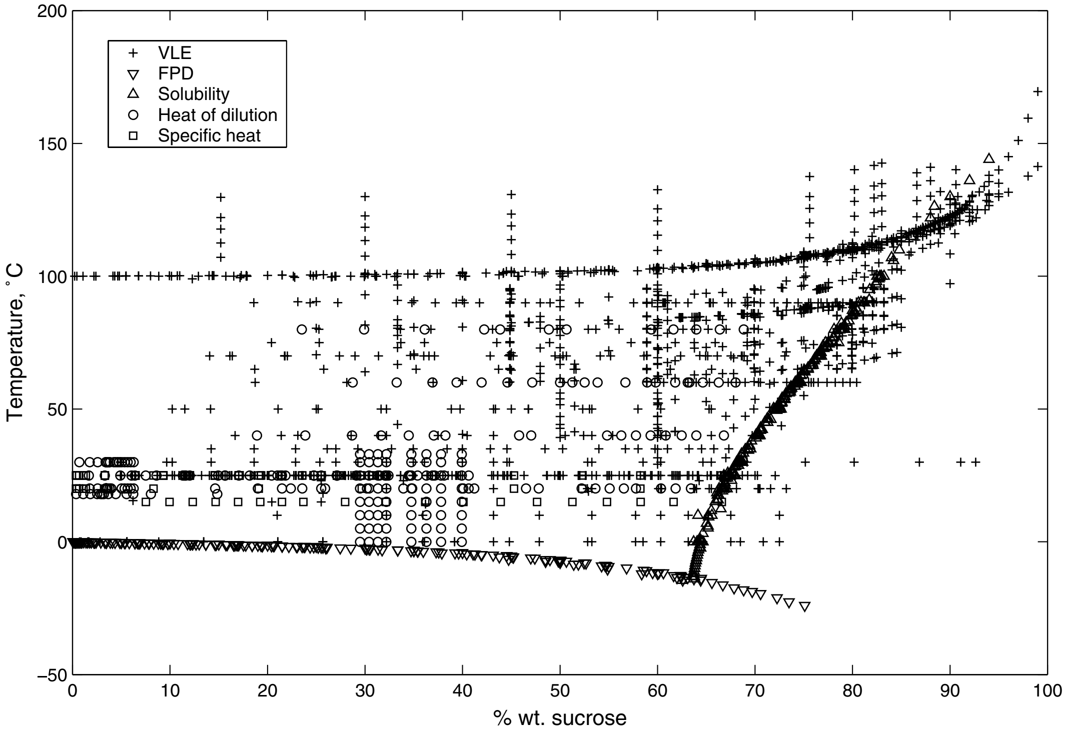

Fig. 2. Distribution of all experimental points on the concentration-temperature plane.

binary systems, the conventional Margules equation was found to be particularly suitable for the data regression approach used in this study. The single-constant Margules equation (also known as the two-suffix Margules equation) provides a satisfactory representation for the activity coefficient behavior only for binary liquid mixtures containing constituents of similar size, shape, and chemical nature. However, for mixtures of dissimilar molecules, such as the sucrose–water system, a higher-order expansion (an n-suffix Margules equation) is required. In particular, the water activity coefficient γ_A is given by

$$\ln \gamma_A = \sum_{k=2}^{n} \alpha_k x_B^k, \tag{1}$$

where the expansion coefficients α_k are, in general, temperature dependent. The following mathematical form of the temperature dependence, commonly applied in thermochemistry, was assumed:

$$\alpha_k(\theta) = \frac{\alpha_{k0}}{\theta} + \alpha_{k1} + \alpha_{k2} \ln \theta + \alpha_{k3}\theta + \alpha_{k4}\theta^2 + \alpha_{k5}\theta^3, \quad \text{with} \quad \theta = T/T_0, \tag{2}$$

where $T_0 = 298.15$ K is a reference temperature chosen merely for numerical convenience. Since the adoption of Eq. (2) would result in an excessive number of parameters to be estimated, for the sake of simplicity, it was assumed that all expansion coefficients $\alpha_k(\theta)$ depend on temperature in the same way, i.e., $\alpha_k(\theta) = a(\theta)b_{k-2}$. Consequently, the proposed Margules equation could be written as:

$$\ln \gamma_A = a(\theta) \sum_{k=2}^{n} b_{k-2} x_B^k, \tag{3}$$

where

$$a(\theta) = \frac{a_0}{\theta} + a_1 + a_2 \ln \theta + a_3\theta + a_4\theta^2 + a_5\theta^3 \tag{4}$$

and the resulting new expansion coefficients b_k are temperature independent (with $b_0 = 1$ by definition). Obviously, by producing an identical temperature trend irrespective of composition, Eq. (3) offers much less flexibility in terms of data fitting than the more general Eq. (2). There is no convincing experimental evidence, however, indicating a dramatic change of the temperature trend with the increasing sucrose concentration. The only exception is a portion of the heat of dilution data by Vallender and Perman (1931) in the region of concentrated solutions and elevated temperatures, where some heat of dilution isotherms (for 40, 60 and 80 °C) intersect at about 62–63% wt. sucrose, as shown in Fig. 3, and then exhibit a reverse temperature behavior (i.e., for a given composition heat of dilution decreases with increasing temperature). However, the validity of these results is disputable, as the authors of this study reported serious problems with strict temperature control during experimentation due to high viscosity of the investigated media. Since the other two isotherms (0 and 20 °C) did not follow the same pattern, we found Vallender's results inconclusive in this regard.

The sucrose activity coefficient γ_B can also be expressed in a polynomial form:

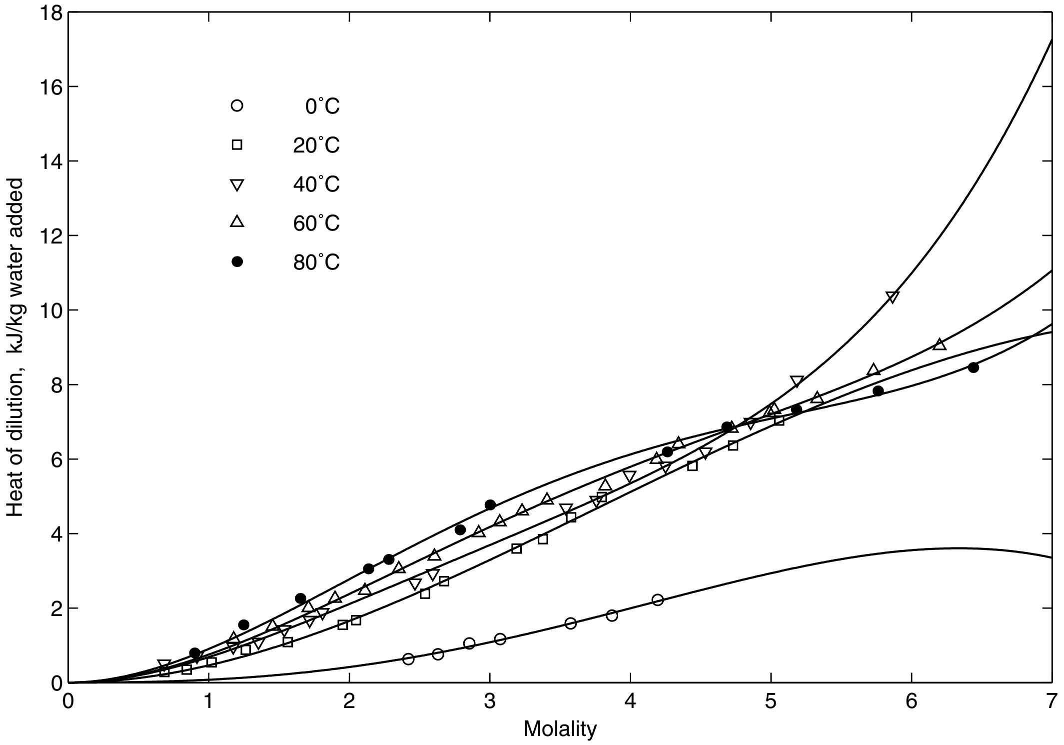

Fig. 3. Heat of dilution data from Vallender and Perman (1931).

$$\ln \gamma_B = \sum_{k=2}^{n} \beta_k x_A^k. \tag{5}$$

The expansion coefficients β_k are not independent, however (see Appendix). For example, the following set of relations between β_k and α_k holds for the seven-suffix Margules equation ($n = 7$):

$$\beta_2 = \alpha_2 + \frac{3}{2}\alpha_3 + 2\alpha_4 + \frac{5}{2}\alpha_5 + 2\alpha_6 + \frac{7}{2}\alpha_7, \tag{6a}$$

$$\beta_3 = -\alpha_3 - \frac{8}{3}\alpha_4 - 5\alpha_5 - 8\alpha_6 - \frac{35}{3}\alpha_7, \tag{6b}$$

$$\beta_4 = \alpha_4 + \frac{15}{4}\alpha_5 + 9\alpha_6 + \frac{35}{2}\alpha_7, \tag{6c}$$

$$\beta_5 = -\alpha_5 - \frac{24}{5}\alpha_6 - 14\alpha_7, \tag{6d}$$

$$\beta_6 = \alpha_6 + \frac{35}{6}\alpha_7, \tag{6e}$$

$$\beta_7 = -\alpha_7. \tag{6f}$$

4. Relations between activity coefficients and measured data

The entire study is based on the assumption that in neutral sucrose solutions (pH 7), the effect of sucrose inversion on the measured variables is negligible (Peacock & Starzak, 1995) and, consequently, the solution can be treated in modeling as a binary system involving sucrose and water only. In order to avoid heavy non-linear and multi-parameter regression calculations, the original data were transformed to new experimental variables that could theoretically be expressed as linear functions of the expansion coefficients α_k (or β_k).

4.1. Vapor–liquid equilibrium

All kinds of available VLE data were converted to corresponding water activity coefficients by using the generalized Raoult's law:

$$\gamma_A = \frac{P}{(1 - x_B)P_A^0(T)}, \tag{7}$$

where P is the measured pressure of water vapor above the solution and $P_A^0(T)$ is the saturated vapor pressure of pure water at temperature T, calculated from the Wagner equation as described by Starzak and Peacock (1997). The pressure P is identical with the total pressure, except the measurements of equilibrium relative humidity (% ERH) when it represents the partial pressure of water vapor in air, in which case Eq. (7) simplifies to:

$$\gamma_A = \frac{\mathrm{ERH}/100}{1 - x_B}. \tag{8}$$

Eq. (7) is valid under the assumption that the vapor phase is thermodynamically ideal, the pressure P is moderate (the Poynting factor equal to 1), and the solute (sucrose) is non-volatile. All these assumptions were met in the investigated range of *x*–*P*–*T* conditions. The estimated saturated vapor pressure of sucrose was found negligible even at temperatures approaching the melting point of sucrose.

4.2. Solid–liquid equilibrium – freezing point depression

Experimental values of the water activity coefficient were also determined from the freezing point data. It is well known that a small amount of solute added to a liquid solvent affects the temperature T_f at which the pure solvent starts to separate out as a solid during the freezing process. This temperature is lower than T_m, the freezing (or melting) point of the pure solvent. The freezing point depression phenomenon can be described mathematically using a rigorous thermodynamic approach. From the condition of thermodynamic equilibrium between the crystal of pure solvent and the solution, after computing the Gibbs free energy of fusion, one can easily arrive at the following formula linking the freezing point depression, $\Delta T = T_m - T_f$, to the activity coefficient of solvent, γ_A (symmetric convention):

$$\ln(\gamma_A x_A) = -\frac{\Delta H_{fA}(T_m)}{RT_m}\frac{T_m - T_f}{T_f} + \frac{1}{RT_f} \times \int_{T_f}^{T_m} \Delta C_{pA}\,dT - \frac{1}{R}\int_{T_f}^{T_m} \frac{\Delta C_{pA}}{T}\,dT, \tag{9}$$

where $\Delta H_{fA}(T_m)$ is the enthalpy of fusion of solid solvent at its normal melting point temperature (according to Dickinson & Osborne (1915), for ice $T_m = 273.16$ K and $\Delta H_{fA}(T_m) =$ 6008 J/mol), and ΔC_{pA} is the difference between molar heat capacities of solvent in the liquid and solid state. For small temperature changes, ΔC_{pA} can be assumed constant (temperature independent). However, in the case of concentrated sucrose solutions, reported ΔT values exceed 20 °C and some correction is needed. From heat capacity data for supercooled water and ice (Dickinson & Osborne, 1915; Osborne, Stimson, & Ginnings, 1939), one can obtain a linear representation of $\Delta C_{pA}(T)$ valid approximately from −30 to 0 °C:

$$\frac{\Delta C_{pA}(T)}{R} = \frac{\Delta C_{pA}(T_m)}{R} + \Delta B_A(T - T_m) \tag{10}$$

with $\Delta C_{pA}(T_m)/R = 4.555$ and $\Delta B_A = 0.045\ \mathrm{K}^{-1}$. Then, Eqs. (9) and (10) yield:

$$\begin{aligned}\ln\gamma_A = &-\left[\frac{\Delta H_{fA}(T_m)}{RT_m} - \frac{\Delta C_{pA}(T_m)}{R} + \frac{\Delta B_A T_m}{2}\right]\left[\frac{T_m}{T_f} - 1\right] \\ &+ \left[\frac{\Delta C_{pA}(T_m)}{R} - \Delta B_A T_m\right]\ln\left[\frac{T_f}{T_m}\right] \\ &+ \frac{\Delta B_A T_m}{2}\left[\frac{T_f}{T_m} - 1\right] - \ln(1 - x_B)\end{aligned} \tag{11}$$

Eq. (11) was used to determine experimental values of the water activity coefficient γ_A from the freezing point temperature at different sucrose concentrations.

4.3. Solid–liquid equilibrium – sucrose solubility

The sucrose solubility data allow for the calculation of experimental values of the sucrose activity coefficient γ_B. Thermodynamics of solubility is usually described by applying the same theoretical concepts as those used for the freezing point depression. Unfortunately, because of the thermal decomposition of sucrose above 185 °C, experimental values of its melting point temperature and, more importantly, fusion enthalpy are uncertain. As a result, the condition of solid–liquid equilibrium written in a form analogous to Eq. (9) becomes impractical in this case. A more effective solution to this problem can be obtained by adopting the asymmetric convention for activity coefficients, i.e., by choosing the state of infinite dilution for the solute and pure liquid for the solvent, at the equilibrium *T* and *P*, as a new reference system (Catté et al., 1994). Then, the solubility curve is defined by

$$\ln(\gamma_B^* x_B) = -\frac{\Delta H_{dB}(T_m)}{RT}\left[1 - \frac{T}{T_m}\right] + \frac{1}{RT} \times \int_{T}^{T_m} \Delta C_{pB}\,dT - \frac{1}{R}\int_{T}^{T_m} \frac{\Delta C_{pB}}{T}\,dT - \ln\gamma_B^{\infty}(T_m), \tag{12}$$

where $\gamma_B^* = \gamma_B/\gamma_B^{\infty}$, and $\Delta H_{dB} = H_B^{\infty} - H_B^{0S}$ is the enthalpy of sucrose dissolution, i.e., the difference between the enthalpy of sucrose at infinite dilution in water and the enthalpy in its pure solid state. Similarly, for the heat capacity we have $\Delta C_{pB} = C_{pB}^{\infty} - C_{pB}^{0S}$. Since experimental values of H_B^{∞} and C_{pB}^{∞} are usually available at ambient temperatures (typically at $T_0 = 298.15$ K) rather than at the melting point of sucrose, it is more convenient to write Eq. (12) in the following equivalent form:

$$\begin{aligned}\ln\left[\frac{\gamma_B x_B}{\gamma_B^{\infty}}\right] = &-\frac{\Delta H_{dB}(T_0)}{RT}\left[1 - \frac{T}{T_m}\right] - \frac{1}{RT} \\ &\times \int_{T_0}^{T} \Delta C_{pB}\,dT + \frac{1}{RT_m}\int_{T_0}^{T_m} \Delta C_{pB}\,dT \\ &- \frac{1}{R}\int_{T}^{T_m} \frac{\Delta C_{pB}}{T}\,dT - \ln\gamma_B^{\infty}(T_m).\end{aligned} \tag{13}$$

The required thermochemical data at $T_0 = 298.15$ K were taken from Jasra and Ahluwalia (1984):

$$\Delta H_{\mathrm{dB}}(T_0) = 5760 \text{ J/mol},$$
$$C^{\infty}_{\mathrm{pB}}(T_0) = 647 \text{ J/(mol K)},$$
$$C^{0\mathrm{S}}_{\mathrm{pB}}(T_0) = 427.8 \text{ J/(mol K)}.$$

The heat capacity difference ΔC_{pB} was assumed to be a linear function of temperature:

$$\frac{\Delta C_{\mathrm{pB}}(T)}{R} = \frac{\Delta C_{\mathrm{pB}}(T_0)}{R} + \Delta B_{\mathrm{B}}(T - T_0), \tag{14}$$

where ΔB_{B} is a constant. Under this assumption, Eq. (13) leads to

$$\begin{aligned}\ln \tilde{\gamma}_{\mathrm{B}} = &-\left[\frac{\Delta H_{\mathrm{dB}}(T_0)}{RT_0} - \frac{\Delta C_{\mathrm{pB}}(T_0)}{R} + \frac{\Delta B_{\mathrm{B}} T_0}{2}\right]\left[\frac{T_{\mathrm{m}}}{T} - 1\right]\frac{T_0}{T_{\mathrm{m}}} \\ &+ \left[\frac{\Delta C_{\mathrm{pB}}(T_0)}{R} - \Delta B_{\mathrm{B}} T_0\right] \ln\left[\frac{T}{T_{\mathrm{m}}}\right] \\ &- \frac{\Delta B_{\mathrm{B}} T_{\mathrm{m}}}{2}\left[1 - \frac{T}{T_{\mathrm{m}}}\right] - \ln(x_{\mathrm{B}}),\end{aligned} \tag{15}$$

where

$$\tilde{\gamma}_{\mathrm{B}} = \frac{\gamma^{\infty}_{\mathrm{B}}(T_{\mathrm{m}})}{\gamma^{\infty}_{\mathrm{B}}} \gamma_{\mathrm{B}}. \tag{16}$$

The unknown constant ΔB_{B} was optimized together with the other parameters of the activity model. Eq. (15) was used eventually to determine experimental values of the sucrose activity coefficient $\tilde{\gamma}_{\mathrm{B}}$ at different temperatures from the sucrose solubility data. The corresponding theoretical values of $\tilde{\gamma}_{\mathrm{B}}$ were calculated from Eqs. (5) and (6). The same equations were used to evaluate the required values of γ_{B} at infinite dilution, i.e., $\gamma^{\infty}_{\mathrm{B}}(T)$ and $\gamma^{\infty}_{\mathrm{B}}(T_{\mathrm{m}})$. By finding the limit $x_{\mathrm{A}} \to 1$, one can easily show that

$$\ln \gamma^{\infty}_{\mathrm{B}}(T) = \sum_{k=2}^{n} \frac{\alpha_k}{k-1} = a(T) \sum_{k=2}^{n} \frac{b_{k-2}}{k-1}. \tag{17}$$

Hence, the proposed activity model produces the following expression for the left-hand side of Eq. (15):

$$\begin{aligned}\ln \tilde{\gamma}_{\mathrm{B}} &= \ln\left[\frac{\gamma^{\infty}_{\mathrm{B}}(T_{\mathrm{m}})}{\gamma^{\infty}_{\mathrm{B}}} \gamma_{\mathrm{B}}\right] \\ &= a(T) \sum_{k=2}^{n} (\mathbf{M}_1 \mathbf{M}_0 \mathbf{b})_{k-1} x_{\mathrm{A}}^k + [a(T_{\mathrm{m}}) - a(T)] \sum_{k=2}^{n} \frac{b_{k-2}}{k-1}.\end{aligned} \tag{18}$$

4.4. Thermochemical data – enthalpy of dilution

The enthalpy of dilution data selected for this study represent various types of heat effect measurements. They have originally been reported as:

(i) the amount of heat, $(-\Delta H_{\mathrm{I}})$, liberated per one mole of sucrose in solution after the addition of a known amount of pure water to the system,
(ii) the amount of heat, $(-\Delta H_{\mathrm{II}})$, liberated per one mole of water in the original solution after the addition of a known amount of a dilute sucrose solution to the system,
(iii) the amount of heat, $(-\Delta H_{\mathrm{III}})$, liberated per one gram of water added after the addition of a small known amount of pure water to the system.

Although it was theoretically possible to express each of these observables in terms of the coefficients of the proposed activity model and fit the data accordingly, a more uniform two-step data handling procedure was implemented instead. First, the McMillan–Mayer expansion – a formula widely used in solution chemistry to relate the excess enthalpy to the molality of solution (Barone, Cacace, Castronuovo, & Elia, 1981) – was fitted by multi-linear regression for each set of isothermal heat of dilution data, in order to obtain the corresponding coefficients of expansion. In the next step, an equivalent number of smoothed molal excess enthalpy values was generated from the resulting McMillan–Mayer expansion, converted to molar values, and then used as experimental input data in further analysis. According to the McMillan–Mayer theory, in the asymmetric convention, the molal excess enthalpy is given by

$$H^{\mathrm{Em}}_{\mathrm{asym}} \text{ (J/kg solvent)} = \sum_{k=2} h_{k0} m^k, \tag{19}$$

where m is the molality of solution and h_{k0} are temperature dependent expansion coefficients. Then, the molar excess enthalpy $H^{\mathrm{E}}_{\mathrm{asym}}$ is

$$H^{\mathrm{E}}_{\mathrm{asym}} \text{(J/mol)} = \frac{H^{\mathrm{Em}}_{\mathrm{asym}}}{m + 1000/M_{\mathrm{A}}}. \tag{20}$$

The following working formulae associate the three types of measured heats of dilution with the McMillan–Mayer expansion coefficients h_{k0}:

(i) $$\frac{\Delta H_{\mathrm{I}}}{n_{\mathrm{B}}} \text{ (J/mol solute)} = \sum_{k=2} h_{k0}[m^{k-1}(\mathrm{f}) - m^{k-1}(\mathrm{i})], \tag{21a}$$

where m(f) and m(i) are the molality of the final and initial solution, respectively;

$$\text{(ii)}\quad \frac{\Delta H_{\mathrm{II}}}{n_{\mathrm{A}}(\mathrm{i})}(\mathrm{J/mol\ solvent}) = \sum_{k=2} h_{k0}\frac{[n_{\mathrm{A}}(\mathrm{i})+n_{\mathrm{A}}(\mathrm{a})]m^k(\mathrm{f})-n_{\mathrm{A}}(\mathrm{a})m^k(\mathrm{a})-n_{\mathrm{A}}(\mathrm{i})m^k(\mathrm{i})}{n_{\mathrm{A}}(\mathrm{i})}, \tag{21b}$$

where $m(\mathrm{f})$, $m(\mathrm{i})$, and $m(\mathrm{a})$ are the molality of the final, initial and added solution, respectively, $n(\mathrm{i})$ and $n(\mathrm{a})$ are the number of moles of solvent in the initial and added solution, respectively;

$$\text{(iii)}\quad \frac{\Delta H_{\mathrm{III}}}{w_{\mathrm{A}}}\ (\mathrm{J/g\ solvent\ added}) = -\frac{1}{1000}\sum_{k=2} h_{k0}m^k(\mathrm{i}),\quad m(\mathrm{f})\cong m(\mathrm{i}) \tag{21c}$$

where w_{A} is the mass of water added to dilute the solution.

Eqs. (21a–c) were used to determine coefficients h_{k0} from heat of dilution data. Then, Eqs. (19) and (20) were applied to generate the corresponding $H^{\mathrm{E}}_{\mathrm{asym}}$ values. The latter were finally used to estimate parameters of the proposed activity model, as demonstrated below. By combining the well-known expression for the molar excess Gibbs energy,

$$G^{\mathrm{E}} = RT(x_{\mathrm{A}}\ln\gamma_{\mathrm{A}} + x_{\mathrm{B}}\ln\gamma_{\mathrm{B}}) \tag{22}$$

with Eqs. (3), (5) and (6), one can arrive at:

$$\frac{G^{\mathrm{E}}}{RT} = \left(\sum_{k=2}^{n}\frac{\alpha_k}{k-1}\right)x_{\mathrm{B}} - \sum_{k=2}^{n}\frac{\alpha_k}{k-1}x_{\mathrm{B}}^k. \tag{23}$$

In the symmetric convention, the molar excess enthalpy, H^{E}, can be obtained as follows:

$$\frac{H^{\mathrm{E}}}{RT} = -T\frac{\partial(G^{\mathrm{E}}/RT)}{\partial T} = -T\left[\left(\sum_{k=2}^{n}\frac{\alpha_k'(T)}{k-1}\right)x_{\mathrm{B}} - \sum_{k=2}^{n}\frac{\alpha_k'(T)}{k-1}x_{\mathrm{B}}^k\right], \tag{24}$$

where $\alpha_k'(T)$ is the first derivative of $\alpha_k(T)$ with respect to temperature. In turn, the molar excess enthalpy in the asymmetric convention is (Catté et al., 1994):

$$H^{\mathrm{E}}_{\mathrm{asym}} = H^{\mathrm{E}} + RT^2x_{\mathrm{B}}\frac{\partial\ln\gamma_{\mathrm{B}}^{\infty}}{\partial T} \tag{25}$$

or after applying Eqs. (17) and (24):

$$H^{\mathrm{E}}_{\mathrm{asym}} = RT^2\sum_{k=2}^{n}\frac{\alpha_k'(T)}{k-1}x_{\mathrm{B}}^k. \tag{26}$$

For the temperature dependence given by Eq. (4), this yields finally

$$\frac{H^{\mathrm{E}}_{\mathrm{asym}}}{RT} = Ta'(T)\sum_{k=2}^{n}\frac{b_{k-2}}{k-1}x_{\mathrm{B}}^k, \tag{27}$$

where

$$Ta'(T) = -\frac{a_0}{\theta} + a_2 + a_3\theta + 2a_4\theta^2 + 3a_5\theta^3,\quad \text{with}\quad \theta = T/T_0. \tag{28}$$

Eqs. (27) and (28) were used to predict molar excess enthalpies at different temperatures and sucrose concentrations from the activity model.

4.5. Thermochemical data – excess heat capacity

The excess molar heat capacity $C_{\mathrm{p}}^{\mathrm{E}}$ can be determined from experimental specific heat data. The heat capacity of 1 kg of water and m moles of sucrose dissolved in it (note that m is also the molality of solution) is

$$\bar{C}_{\mathrm{p}} = m\Phi_{\mathrm{c}} + c_{\mathrm{pA}}, \tag{29}$$

where Φ_{c} is the apparent molar heat capacity of sucrose in solution (J/mol sucrose K), and c_{pA} is the specific heat of pure water (J/kg water K). On the other hand, $\bar{C}_{\mathrm{p}}$ can also be calculated from the specific heat of solution, c_{p} (J/kg solution K), as follows:

$$\bar{C}_{\mathrm{p}} = \left[1 + \frac{M_{\mathrm{B}}}{1000}m\right]c_{\mathrm{p}}(m). \tag{30}$$

Combining these two equations results in the apparent molar heat capacity of sucrose, $\Phi_{\mathrm{c}}(m)$, in terms of the experimental specific heat of solution, $c_{\mathrm{p}}(m)$:

$$\Phi_{\mathrm{c}}(m) = \frac{\left[1+\frac{M_{\mathrm{B}}}{1000}m\right]c_{\mathrm{p}}(m) - c_{\mathrm{pA}}}{m} \tag{31}$$

In turn, $\Phi_{\mathrm{c}}(m)$ can be used to calculate the molal excess heat capacity, since in the asymmetric convention, the latter is defined as:

$$C^{\mathrm{Em}}_{\mathrm{p\,asym}}(\mathrm{J/kg\ water\ K}) = [\Phi_{\mathrm{c}}(m) - \Phi_{\mathrm{c}}(0)]m. \tag{32}$$

Similarly to the molar excess enthalpy, the molar excess heat capacity is then:

$$C^{\mathrm{E}}_{\mathrm{p\,asym}}(\mathrm{J/mol\ K}) = \frac{C^{\mathrm{Em}}_{\mathrm{p\,asym}}}{m + 1000/M_{\mathrm{A}}}. \tag{33}$$

The major problem with the accurate determination of $C^{\mathrm{E}}_{\mathrm{P\,asym}}$ from experimental data is the evaluation of $\Phi_{\mathrm{c}}(0)$, the apparent molar heat capacity of sucrose at infinite dilution. Since Eq. (31) becomes indeterminate at $m = 0$, $\Phi_{\mathrm{c}}(0)$ can be evaluated only as a mathematical limit:

$$\Phi_{\mathrm{c}}(0) = \lim_{m\to 0}\Phi_{\mathrm{c}}(m) = \frac{M_{\mathrm{B}}}{1000}c_{\mathrm{pA}} + \left(\frac{\mathrm{d}c_{\mathrm{p}}}{\mathrm{d}m}\right)_{m=0}. \tag{34}$$

Clearly, even small errors in experimental values of $c_{\mathrm{p}}(m)$, inevitable in practice, and subsequent large inaccuracies in the slope determination have a tremendous impact on $C^{\mathrm{E}}_{\mathrm{P\,asym}}$ values. Even with the aid of refined data smoothing techniques, the estimates of $\Phi_{\mathrm{c}}(0)$ are still subject to significant errors. Fig. 4 illustrates this

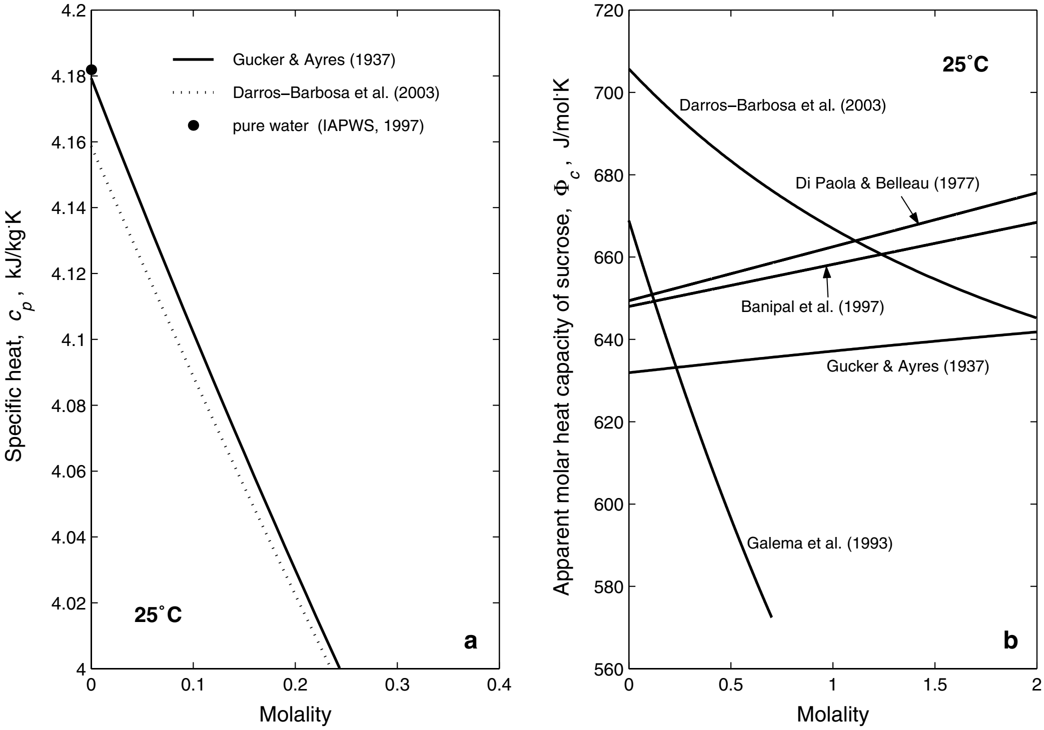

Fig. 4. Errors in specific heat measurements (a) and their effect on Φ_c, the apparent molar heat capacity of sucrose in solution (b). See above-mentioned references for further information.

problem on a series of literature data which show relatively small differences in terms of observed c_{p} values, but surprisingly large discrepancies in terms of the corresponding values of $\Phi_{\mathrm{c}}(m)$, and $\Phi_{\mathrm{c}}(0)$ in particular.

Theoretical values of the excess heat capacity $C^{\mathrm{E}}_{\mathrm{P\,asym}}$ can be obtained by direct differentiation of the excess enthalpy (Eq. (27)) with respect to temperature:

$$\frac{C^{\mathrm{E}}_{\mathrm{P\,asym}}}{R} = \frac{\partial(H^{\mathrm{E}}_{\mathrm{asym}}/R)}{\partial T} = T\sum_{k=2}^{n}\frac{2\alpha'_k + T\alpha''_k}{k-1}x_{\mathrm{B}}^{k}, \qquad (35)$$

where $\alpha''_k(T)$ is the second derivative of $\alpha_k(T)$. For the assumed temperature dependence of activity coefficients this results in

$$\frac{C^{\mathrm{E}}_{\mathrm{P\,asym}}}{R} = T[2a'(T) + Ta''(T)]\sum_{k=2}^{n}\frac{b_{k-2}}{k-1}x_{\mathrm{B}}^{k}, \qquad (36)$$

where the temperature dependent term is

$$T[2a'(T) + Ta''(T)] = a_2 + 2a_3\theta + 6a_4\theta^2 + 12a_5\theta^3, \quad \text{with} \quad \theta = T/T_0. \qquad (37)$$

Eqs. (36) and (37) were used to calculate from the activity model the molar excess heat capacity at required temperatures and sucrose concentrations.

5. Data regression technique

The proposed model of thermodynamic activity in the sucrose–water system was identified using the experimental data discussed in detail in previous sections. The following least-squares performance index, composed of five different types of deviations, was used in data regression:

$$\begin{aligned} I = {} & w^2_{\mathrm{VLE}}\sum_i w^2_{\mathrm{VLE},i}(\ln\gamma_{\mathrm{A},i} - \ln\gamma^{\mathrm{exp}}_{\mathrm{A},i})^2_{\mathrm{VLE}} + w^2_{\mathrm{FPD}} \\ & \times \sum_i(\ln\gamma_{\mathrm{A},i} - \ln\gamma^{\mathrm{exp}}_{\mathrm{A},i})^2_{\mathrm{FPD}} + w^2_{\mathrm{SOL}}\sum_i(\ln\tilde{\gamma}_{\mathrm{B},i} \\ & - \ln\tilde{\gamma}^{\mathrm{exp}}_{\mathrm{B},i})^2_{\mathrm{SOL}} + w^2_{\mathrm{HE}}\sum_i\left[\frac{H^{\mathrm{E}}_{\mathrm{asym},i}}{RT_i} - \frac{H^{\mathrm{E,exp}}_{\mathrm{asym},i}}{RT^{\mathrm{exp}}_i}\right]^2 \\ & + w^2_{\mathrm{CE}}\sum_i\left[\frac{C^{\mathrm{E}}_{\mathrm{P\,asym},i}}{R} - \frac{C^{\mathrm{E,exp}}_{\mathrm{P\,asym},i}}{R}\right]^2. \end{aligned} \qquad (38)$$

The weighting factors w_{VLE}, w_{FPD}, w_{SOL}, w_{HE} and w_{CE} were taken as inverted mean values of the corresponding experimental variables and only $w_{\mathrm{VLE},i}$ were specific to the given set of VLE data. The latter were estimated beforehand by considering the VLE data only and applying the technique of iteratively reweighted least squares (IRLS) with the elimination of outliers and rigorous statistical analysis. They were intended to reflect the performance of individual data sets as compared to the performance of the entire VLE database. More details on this technique can be found in Starzak and Peacock (1997). Values of the normalized weighting factors $w_{\mathrm{VLE},i}$ are given in the last column of Table 1.

The expansion coefficients of the water activity coefficient equation, representing both the temperature and composition dependence, $\mathbf{a} = [a_0, a_1, \ldots, a_5]^T$ and $\mathbf{b} = [b_0, b_1, \ldots, b_{n-2}]^T$, respectively, were the estimated parameters of the model. In addition, the parameter ΔB_B of the solubility model was also optimized. As a polynomial, the Margules equation is linear with respect to its expansion coefficients. However, for temperature dependent coefficients, the equation becomes parametrically non-linear because of the crossover of parameters describing the temperature dependence and those associated with the concentration dependence. Consequently, in general, the problem of data regression is highly non-linear and numerically complex. The type of temperature dependence assumed in this study allowed for the total separation of these two groups of parameters, so the resulting regression problem was at least partly linear. For example, for fixed values of the composition dependence parameters b_k, the water activity coefficient can be considered a linear function of the temperature dependence parameters a_i (see Eq. (3)). The same conclusion can be drawn after inspecting other relationships derived in previous sections which express experimental variables in terms of activity coefficients, such as those given by Eq. (5) with (6), Eq. (27) with (28), and finally Eq. (36) with (37). All these regression equations are of the following general form:

$$Y = \sum_{i=0}^{5} f_i(\mathbf{X}, \mathbf{b}) a_i, \tag{39}$$

where Y is the selected experimental output variable and f_i are known functions of the vector of experimental input variables $\mathbf{X}$ and the vector of non-linear parameters $\mathbf{b}$. This type of structure allows for a parameter optimization technique in which the full data regression problem is decomposed into two problems of a smaller size. The computational algorithm consists then of an inner and outer regression loop. The outer loop optimizes the performance index for the group of non-linear parameters (b_k), using the simplex method of optimization, while the inner loop performs multi-linear regression on the group of linear parameters (a_i). The solubility parameter ΔB_B was optimized in the third outermost loop using a one-dimensional direct search technique.

Table 6
Estimated parameters of the proposed activity coefficient model

Estimated parameters (water activity coefficient)		Parameters calculated as: $\mathbf{c} = \mathbf{M_1 M_0 b}$ (sucrose activity coefficient)	
a_0	−268.59	c_0	−0.12001
a_1	−861.42	c_1	−0.48972
a_2	−1102.3	c_2	0.92730
a_3	1399.9		
a_4	−277.88		
a_5 (assumed)	0		
b_0 (by definition)	1		
b_1	−1.9831		
b_2	0.92730		

6. Results of data regression

Expansions of different lengths have been tested for both the temperature and composition dependence to find the most suitable mathematical representation of the activity model. Finally, in order to avoid over-parametrization of the model, it was decided to drop the cubic term in the temperature dependence (by assuming $a_5 = 0$ in Eq. (4)) and consider only three non-zero terms ($n = 4$) in the composition dependent part of Eq. (3). This resulted finally in a four-suffix Margules equation with temperature dependent parameters. The optimized parameters of the model minimizing the weighted sum of all experimental deviations are given in Table 6. The optimal value of the solubility parameter ΔB_B was 0.698 K^{-1}.

Contributions from different data categories to the global performance index were shown in Fig. 5 in the form of correlation diagrams. The largest discrepancies between predicted and measured values occur for highly concentrated sucrose solutions, regardless of the type of data considered. This was expected, as the experimental results in this region are not highly reliable (mainly due to strict temperature control problems when working with very viscous media) and show sometimes serious inconsistencies when compared amongst different literature sources. Also in this region, the system exhibits particularly strong non-ideal behavior that cannot be fully described using a relatively simple non-mechanistic model of thermodynamic activity.

For the purpose of illustration, the original VLE data were expressed in terms of the corresponding values of boiling point elevation (BPE) and presented as a correlation graph in Fig. 6. It is clear from this graph that the new activity equation represents a statistical compromise for scarce and rather inconsistent measurements from the region of high sucrose concentrations. A much better data fit was obtained for the water activity coefficient along the curve representing SLE between ice and sucrose solution (Fig. 7(a)) which also resulted in an excellent match of the freezing point depression (FPD) data (Fig. 7(b)). For the sucrose activity coefficient at the conditions of SLE between sucrose crystals and the solution, the data fit is excellent only up to about 70–75% wt. sucrose and deteriorates slightly at higher concentrations (Fig. 8(a)). A similar pattern exhibits the solubility curve (Fig. 8(b)). The results of data regression for

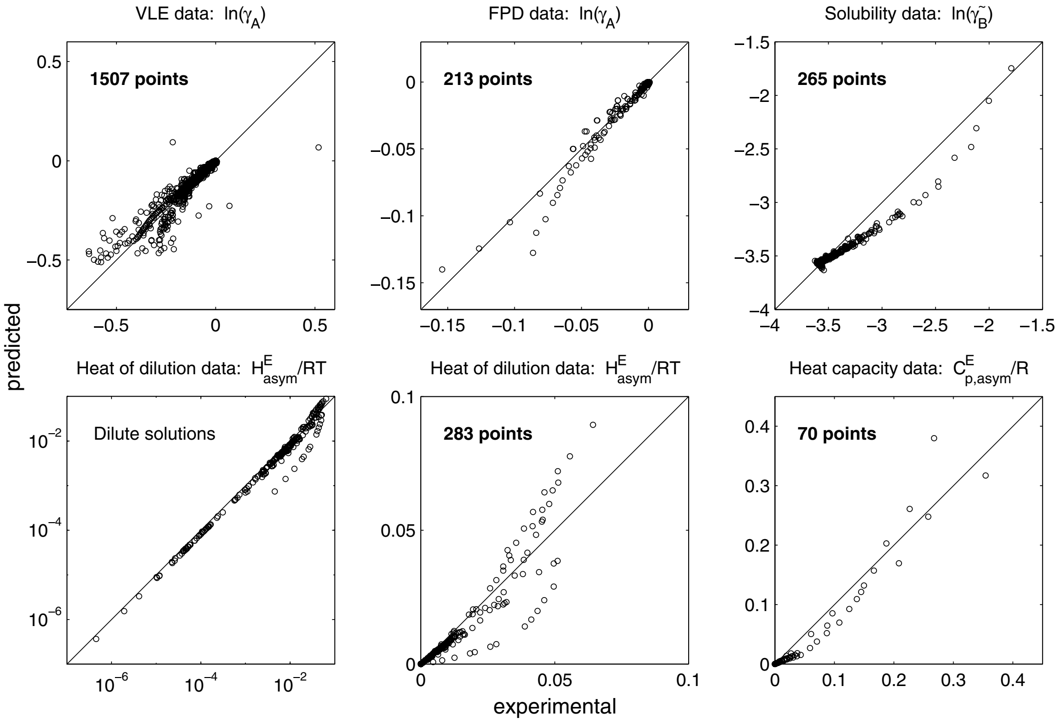

Fig. 5. Correlation diagrams for different categories of experimental data.

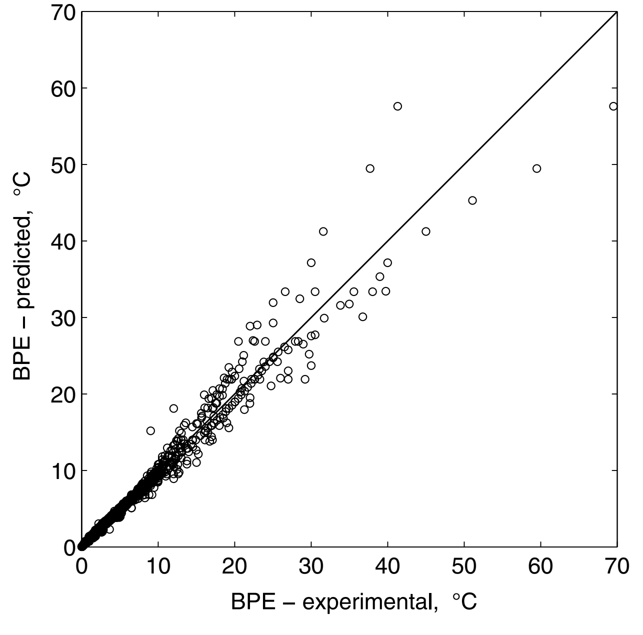

Fig. 6. Correlation of VLE data presented in terms of BPE (boiling point elevation).

the heat of dilution can be considered satisfactory as well, except in the case of the highest studied temperature (80 °C) at which the model underpredicts the enthalpy. Fig. 9 presents these calculations for selected data sets at different temperatures. Figs. 10(a) and (b) show predicted values of the dimensionless excess enthalpy plotted against sucrose concentration and temperature, respectively. Interestingly, for each solution composition the excess enthalpy shows a maximum with respect to temperature. In fact, because of the simplified temperature/concentration relationship assumed in this activity model, all predicted maxima occur at the same temperature of about 35 °C (Fig. 10(b)). The fit for heat capacity data is generally acceptable, although for dilute solutions (below 1 mol/kg water), when the excess heat capacities are relatively small, the predicted values are well below some of the observed data (Fig. 11). This was mainly due to the evident discrepancy between the heat capacity data published by Gucker and Ayres (1937) and those reported more recently (Banipal, Banipal, Ahluwalia, & Lark, 1997; DiPaola & Belleau, 1977). Following the temperature trend already observed for excess enthalpy, the excess heat capacity assumes positive values at temperatures below 40 °C and negative values above this temperature (Fig. 12). A zero excess heat capacity at 40 °C, regardless of the sucrose concentration, is again a result of the specific mathematical form of the activity model assumed. Due to the lack of direct experimental data, the results of heat capacity calculations for non-ambient temperatures are rather uncertain. They should be seen as predictions deduced indirectly from the temperature effect on heat of dilution rather than derived directly from the specific heat data.

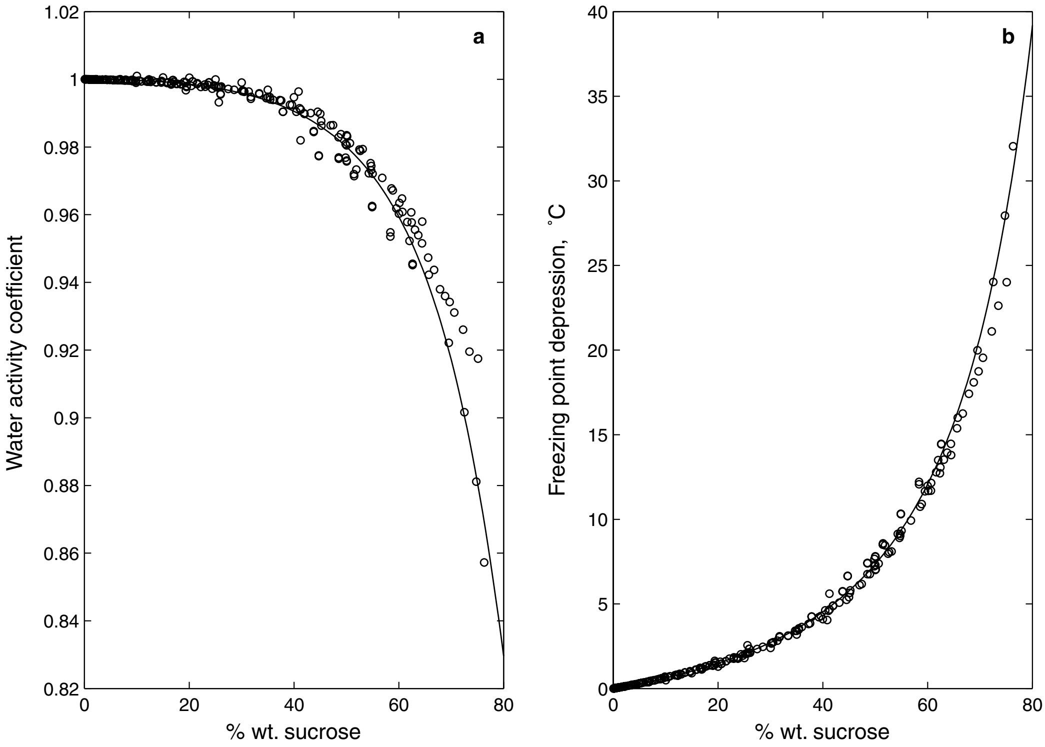

Fig. 7. SLE between ice and aqueous solution of sucrose – predicted (solid line) and experimental data (circles): (a) water activity coefficient; (b) freezing point depression.

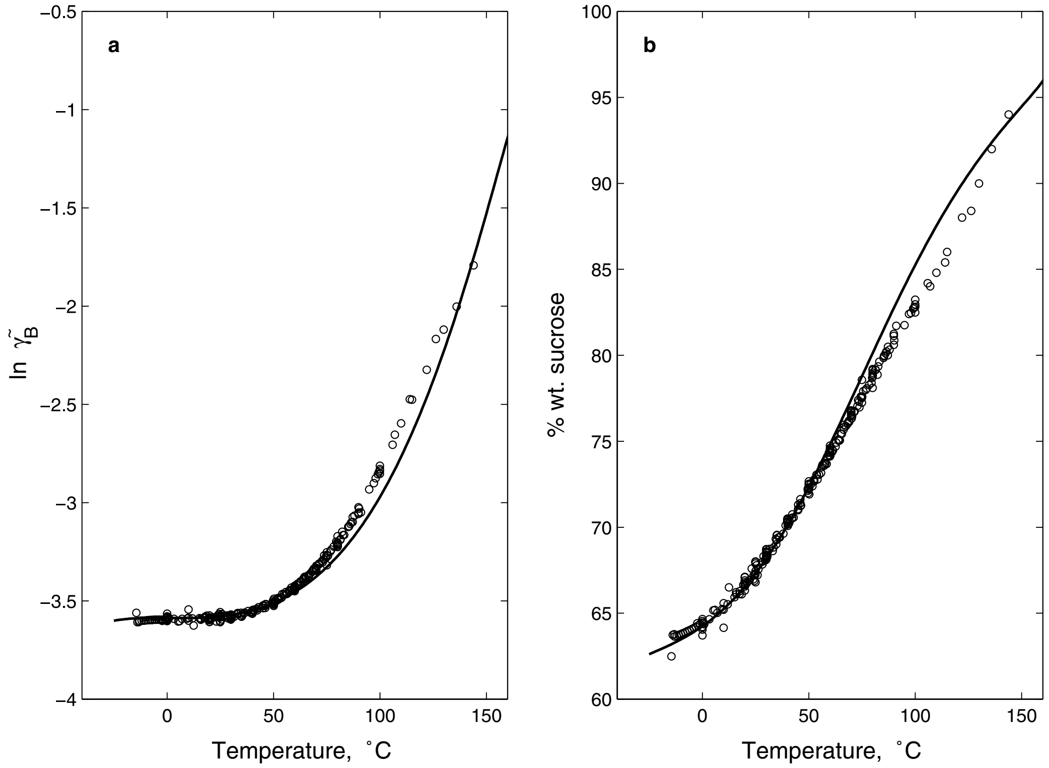

Fig. 8. SLE between sucrose crystals and aqueous solution of sucrose – predicted (solid line) and experimental data (circles): (a) logarithm of the sucrose activity coefficient $\tilde{\gamma}_B$; (b) sucrose solubility.

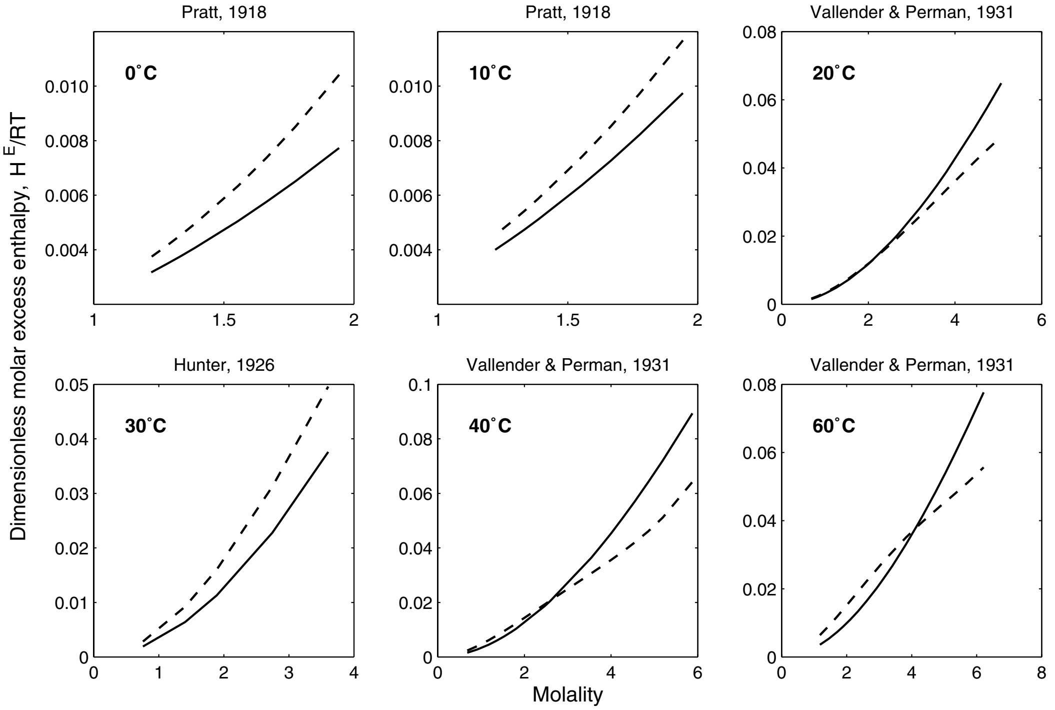

Fig. 9. Predicted (solid lines) and experimental (broken lines) dimensionless molar excess enthalpy at selected temperatures.

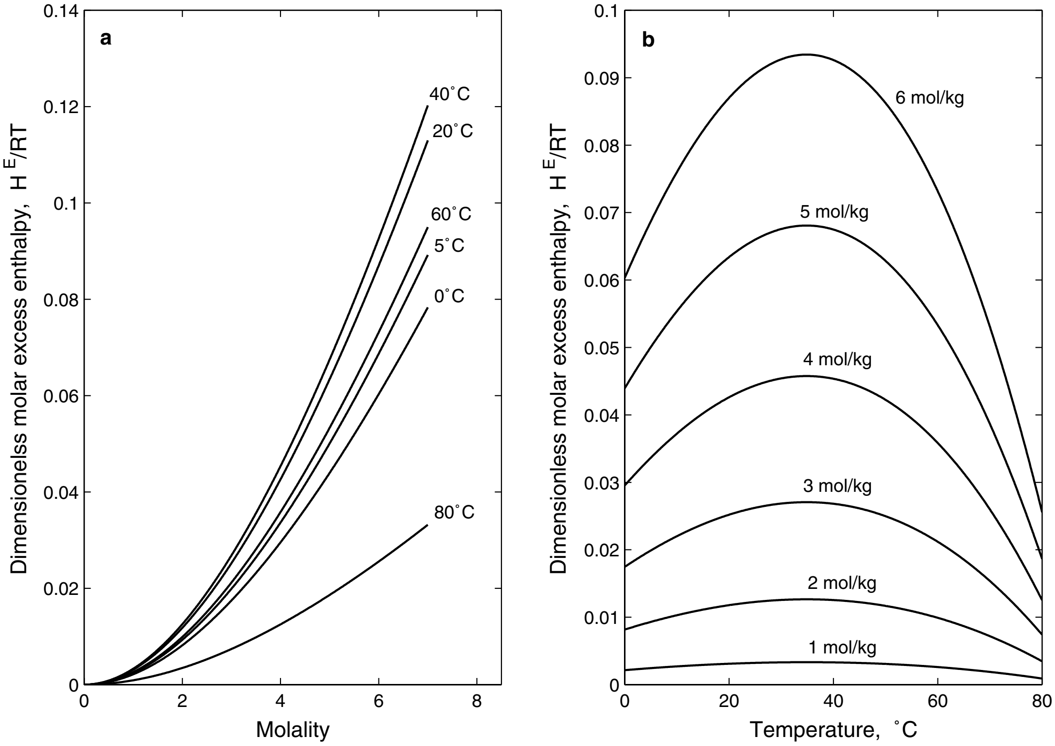

Fig. 10. Model predictions of dimensionless molar excess enthalpy as a function of: (a) molality; (b) temperature.

The water activity coefficient γ_A predicted by the proposed activity model exhibits a characteristic minimum with regard to the sucrose content in the region of very high concentrations (Fig. 13(a)). According to the model, the minimum occurs at about 96% wt. sucrose and its location does not depend on tempera-

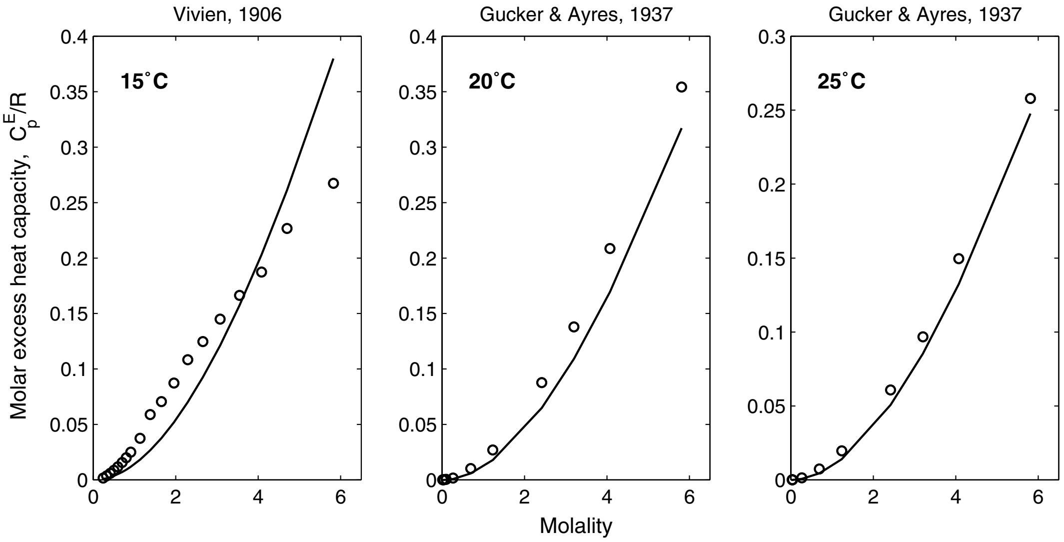

Fig. 11. Predicted (solid lines) and experimental (circles) dimensionless molar excess heat capacity at selected temperatures.

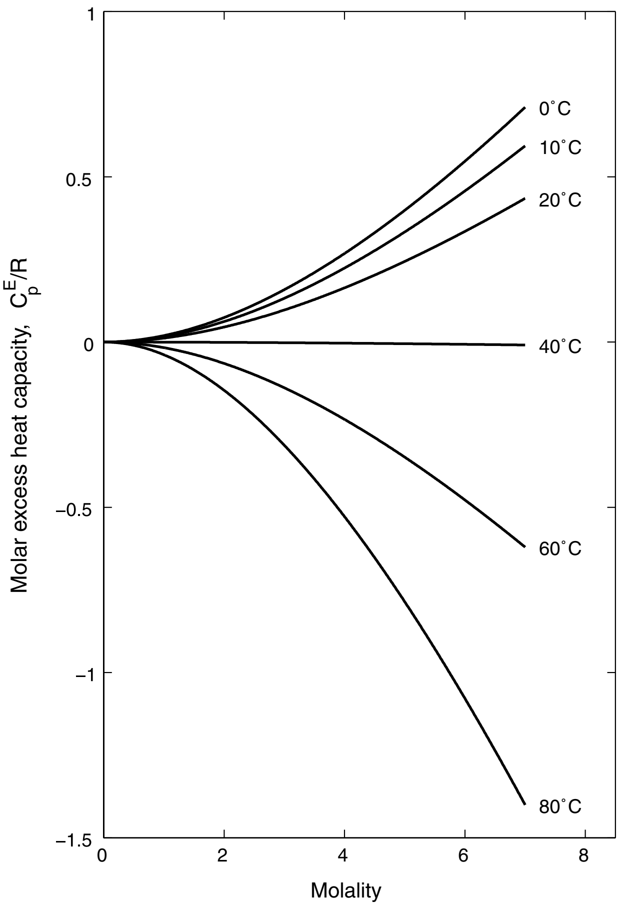

Fig. 12. Dimensionless molar excess heat capacity as a function of molality and temperature – model predictions.

ture. The latter is, however, the result of a specific mathematical form of the temperature dependence adopted in this study for the activity coefficient. Consequently, the water activity coefficient evaluated for the conditions of isobaric VLE (when the boiling point temperature of solution varies together with the composition) also show a minimum at the same location (Fig. 13(b)).

7. Comparison with the UNIQUAC and UNIFAC models

Since in a number of previous works on activity coefficients in the sucrose–water system the UNIQUAC model was used to correlate experimental data (Catté et al., 1994; LeMaguer, 1992; Peres & Macedo, 1996), it is worth comparing this model with the activity model developed in our study. Equations describing the molar excess Gibbs energy as well as other thermodynamic functions according to the modified UNIQUAC model (Larsen, Rasmussen, & Fredenslund, 1987) are not presented here as they can be all found elsewhere (Catté et al., 1994). The temperature dependence of this model is represented by the Boltzmann factors:

$$\tau_{ij} = \exp[-A_{ij}(T)], \quad i,j = 1,2; \; i \neq j \tag{40}$$

where the interaction parameters $A_{ij}(T)$ have the mathematical form similar to Eq. (4):

$$A_{ij}(T) = \frac{A_{ij,0}}{T} + A_{ij,1} + A_{ij,2}\ln T + A_{ij,3}T. \tag{41}$$

The required Van der Waals molecular volume and surface area parameters for sucrose and water were taken from Catté et al. (1994), while the constants $A_{ij,k}$ ($k = 1, 2, 3$) were estimated by regressing the experimental

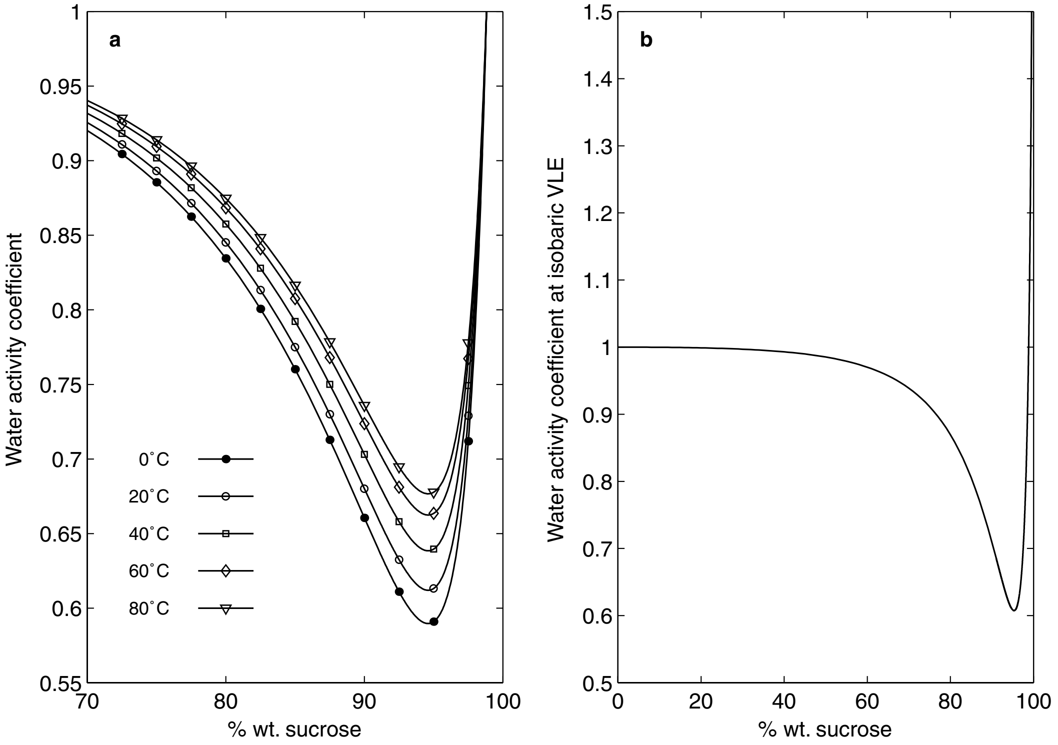

Fig. 13. Model predictions of water activity coefficient as a function of sucrose concentration and temperature: (a) selected isotherms; (b) for VLE at 760 mmHg.

data used in the main part of this study. The Van der Waals parameters as well as optimized values of $A_{ij,k}$ are listed in Table 7.

Calculations show that the UNIQUAC model gives an adequate description of the sucrose–water system only for concentrations not exceeding 90% wt. sucrose. In some instances, such as the solubility curve and heat of dilution, it even results in a slightly better data fit than the Margules model, which might imply that the temperature dependence built-in to the UNIQUAC model is more versatile than the restrictive expression employed in this study. On the other hand, the UNIQUAC model predicts a monotonic decline of the water activity coefficient γ_A with increasing sucrose concentration for all investigated temperatures. A similar monotonic behavior was also reported in the previous studies involving this model. In fact, the inability of the UNIQUAC model to reproduce a strongly pronounced minimum of $\gamma_A(x_B)$ in the region of highly concentrated solutions has been demonstrated numerically in one of our earlier studies (Starzak & Peacock, 1998).

Table 7
Parameters of the UNIQUAC model

Van der Waals molecular parameters (Catté et al., 1994)		Estimated interaction constants	
r_A	0.9200	$A_{12,0}$	227.30
q_A	1.4000	$A_{12,1}$	−8.3359
r_B	14.550	$A_{12,2}$	1.2520
q_B	14.310	$A_{12,3}$	-5.0513×10^{-4}
		$A_{21,0}$	−224.72
		$A_{21,1}$	12.554
		$A_{21,2}$	−1.8257
		$A_{21,3}$	-4.4100×10^{-4}

In a few earlier studies (Starzak & Mathlouthi, 2002; Starzak, Peacock, & Mathlouthi, 2000; Van Hook, 1987), it was demonstrated that the intriguing minimum of the water activity coefficient could be predicted theoretically from relatively simple chemical models of thermodynamic activity by considering competitive water–sucrose (sucrose hydration) and sucrose-sucrose (sucrose clustering) interactions in the solution. Therefore, for comparative purposes, we also investigated the behavior of a more recent A-UNIFAC model developed by Ferreira et al. (2003) for aqueous solutions of sugars. This model is particularly interesting since it attempts to incorporate the effect of hydrogen-bonded molecular association caused by the presence of numerous hydroxyl groups in the system. The results of simulation showed, however, no minimum of the water activity coefficient in the concentration region of interest (90–98% wt. sucrose). Interestingly, a very sharp minimum was found numerically at a non-realistic sucrose content

(>99.5% wt.). This shows that the A-UNIFAC model has the theoretical capacity to reproduce the minimum provided its parameters are determined using a larger number of experimental points from the region of very high sucrose concentrations.

8. Conclusions

The empirical four-suffix Margules equation with an extended temperature dependence developed in this study gives a satisfactory representation of all experimental measurements currently available for this system including VLE, SLE, as well as thermochemical data. The new equation predicts the existence of a sharp minimum of the water activity coefficient occurring at about 96% wt. sucrose, confirming some trends observed earlier in the relatively scarce experimental data for highly concentrated solutions. This prediction is also in line with theoretical results derived from the analysis of specific hydrogen-bonded interactions involving molecules of sucrose and water in solution. The proposed model is based on the simplifying assumption that the temperature dependence of the activity coefficient can be separated from its composition dependence. This was done in order to reduce the number of estimated parameters of the model as well as to simplify the data regression procedure. Consequently, some model predictions, especially those regarding the temperature effect on the excess enthalpy and excess heat capacity, are perhaps less reliable than others. However, since some discrepancies are also observed amongst various pieces of the original thermochemical data, adopting a more elaborate activity equation (by releasing the restrictive assumption mentioned above and hence increasing the number of estimated parameters) was not considered an option for further model refinement.

Well-established methods of predicting activity coefficients in liquid phase such as UNIQUAC, UNIFAC or ASOG can produce models which are flexible enough to describe thermodynamic properties of the sucrose–water system for dilute and relatively high concentrated solutions (up to 90% wt. sucrose). At extreme sucrose concentrations, predictions of these models and the proposed empirical correlation are substantially different. The experimental data presently available in this region are insufficient to prove beyond any doubt the occurrence of a minimum of the water activity coefficient at about 96% wt. sucrose and also to convincingly demonstrate that the UNIQUAC/UNIFAC models are inadequate. Nevertheless, these data do show a statistically significant trend which indicates the existence of such an intriguing feature. Moreover, some mechanistic models of water activity in the sucrose–water system can explain this hypothetical phenomenon. We agree, however, that the issue can be resolved only by direct experimentation which is unfortunately not easy bearing in mind extreme conditions such as temperatures close to the melting point of sucrose, high viscosity causing poor mixing and heat transfer, the risk of sucrose crystallization, etc.

The empirical activity equation developed in this study represents the most reasonable compromise between the model complexity and the quality of the experimental data available at present for the sucrose–water system. It should find applications in various areas of the sugar and food industries whenever the knowledge of water as well as sucrose activities in aqueous sugar solutions is required in a wide range of operating conditions. The proposed equation can also be used as a predictive tool for high temperatures and large sucrose concentrations not yet explored experimentally, these being of particular interest to the sugar confectionery technologist.

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Appendix

The partial molar excess Gibbs energies (chemical potentials) of the components in a mixture are related to one another through the Gibbs–Duhem equation which represents a differential relation between the activity coefficients of all the components in the solution. In binary systems, this leads to unique relations between the expansion coefficients β_k and α_k. For this special case, the Gibbs–Duhem equation may be written as:

$$x_A \frac{d \ln \gamma_A}{dx_A} = x_B \frac{d \ln \gamma_B}{dx_B}. \tag{A1}$$

On substituting Eqs. (1) and (5) to Eq. (A1), one can arrive at:

$$\beta_k = (-1)^k \sum_{l \geqslant k}^{n} \binom{l}{k} \lambda_l, \quad k \geqslant 2, \tag{A2}$$

where

$$\lambda_l = \alpha_l - \frac{l+1}{l}\alpha_{l+1}, \quad l = 2, 3, \ldots, n-1;$$
$$\lambda_n = \alpha_n. \tag{A3}$$

In the more transparent matrix form:

$$\boldsymbol{\beta} = \mathbf{M_1 M_0} \boldsymbol{\alpha} = a(\theta)\mathbf{M_1 M_0 b} \tag{A4}$$

where $\boldsymbol{\alpha} = [\alpha_2, \alpha_3, \ldots, \alpha_n]^{\mathrm{T}}$, $\boldsymbol{\beta} = [\beta_2, \beta_3, \ldots, \beta_n]^{\mathrm{T}}$, $\mathbf{b} = [b_0, b_1, \ldots, b_{n-2}]^{\mathrm{T}}$, and the matrices $\mathbf{M_0}$ and $\mathbf{M_1}$ are defined as follows:

$$\mathbf{M}_0 = \begin{bmatrix} 1 & -\frac{3}{2} & 0 & 0 & 0 & \cdots & 0 & 0 \\ 0 & 1 & -\frac{4}{3} & 0 & 0 & \cdots & 0 & 0 \\ 0 & 0 & 1 & -\frac{5}{4} & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \ldots & 1 & -\frac{n}{n-1} \\ 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 1 \end{bmatrix} \tag{A5}$$

$$\mathbf{M}_1 = \begin{bmatrix} \binom{2}{2} & \binom{3}{2} & \binom{4}{2} & \cdots & \binom{n-1}{2} & \binom{n}{2} \\ 0 & -\binom{3}{3} & -\binom{4}{3} & \cdots & -\binom{n-1}{3} & -\binom{n}{3} \\ 0 & 0 & \binom{4}{4} & \cdots & \binom{n-1}{4} & \binom{n}{4} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & (-1)^{n-1}\binom{n-1}{n-1} & (-1)^{n-1}\binom{n}{n-1} \\ 0 & 0 & 0 & \cdots & 0 & (-1)^{n}\binom{n}{n} \end{bmatrix} \tag{A6}$$

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