Water activity in aqueous solutions of sucrose: an improved temperature dependence

Maciej STARZAK

School of Chemical Engineering

University of KwaZulu-Natal

Durban, South Africa

Mohamed MATHLOUTHI

Laboratoire de Chimie Physique Industrielle

Université de Reims, Champagne-Ardenne

Reims, France

Outline

1. Introduction
2. Previous studies
3. Experimental database
4. Selection of the water activity model
5. Relationships between experimental variables and activity coefficients
6. Data regression
7. Results
8. Recommended equation for water activity coefficient

Water activity formulae popular amongst food technologists

Norrish, 1966

$$\ln g_A = a\, x_B^2$$

Chen, 1989

$$g_A = \frac{1000 + M_A m}{1000 + M_A m\,(A + B m^n)}$$

Miyawaki, 1997

$$\ln g_A = a\, x_B^2 + b\, x_B^3$$

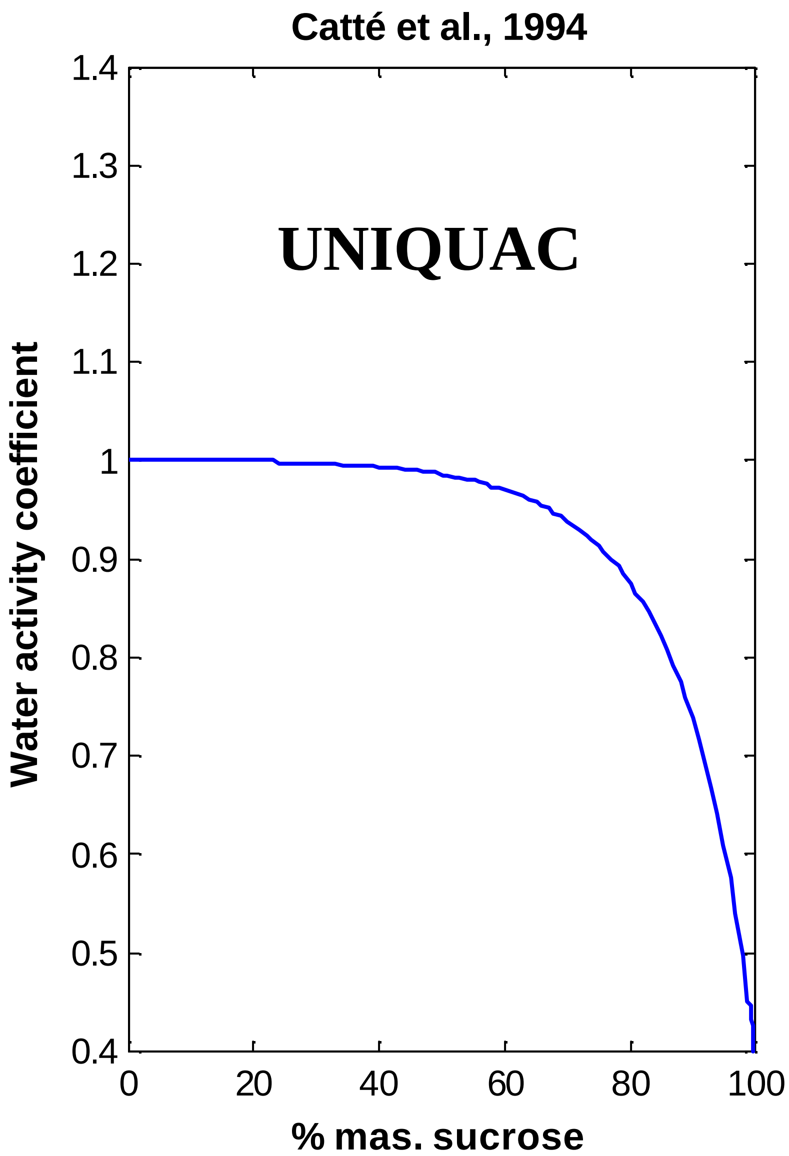
Models used to predict water activity coefficient

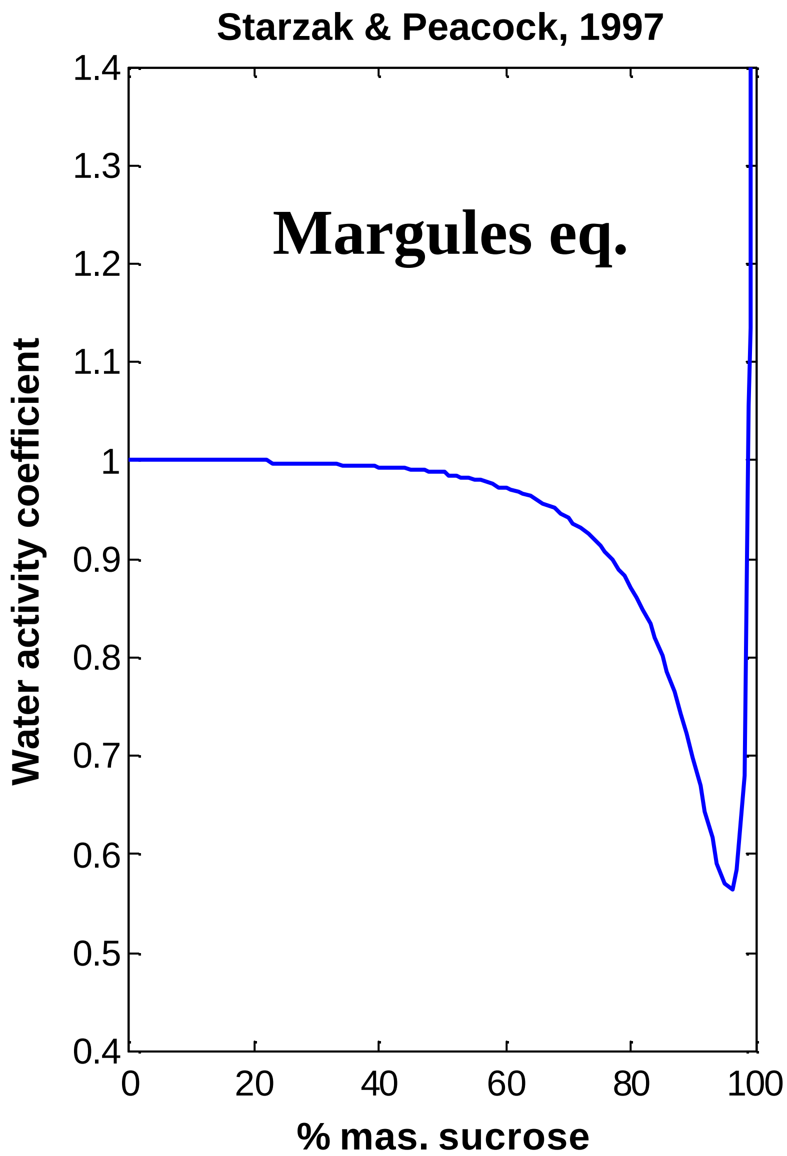
- **Redlich-Kister expansion - empirical (includes Margules equation)**
- **UNIQUAC - phenomenological (two-fluid theory)**
- **group contribution methods (UNIFAC, ASOG)**

Starzak & Peacock, 1997

$$\ln g_A = \frac{Q}{RT} x_B^2 \left(1 + b x_B + c x_B^2\right)$$

Based on 1197 experimental points (56 data sets), mainly VLE data (BPE, vapour pressure, ERH, isopiestic solutions)


Catté et al., 1994
UNIQUAC
Water activity coefficient
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0
20
40
60
80
100
% mas. sucrose


Starzak & Peacock, 1997
Margules eq.
Water activity coefficient
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1.3
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1
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40
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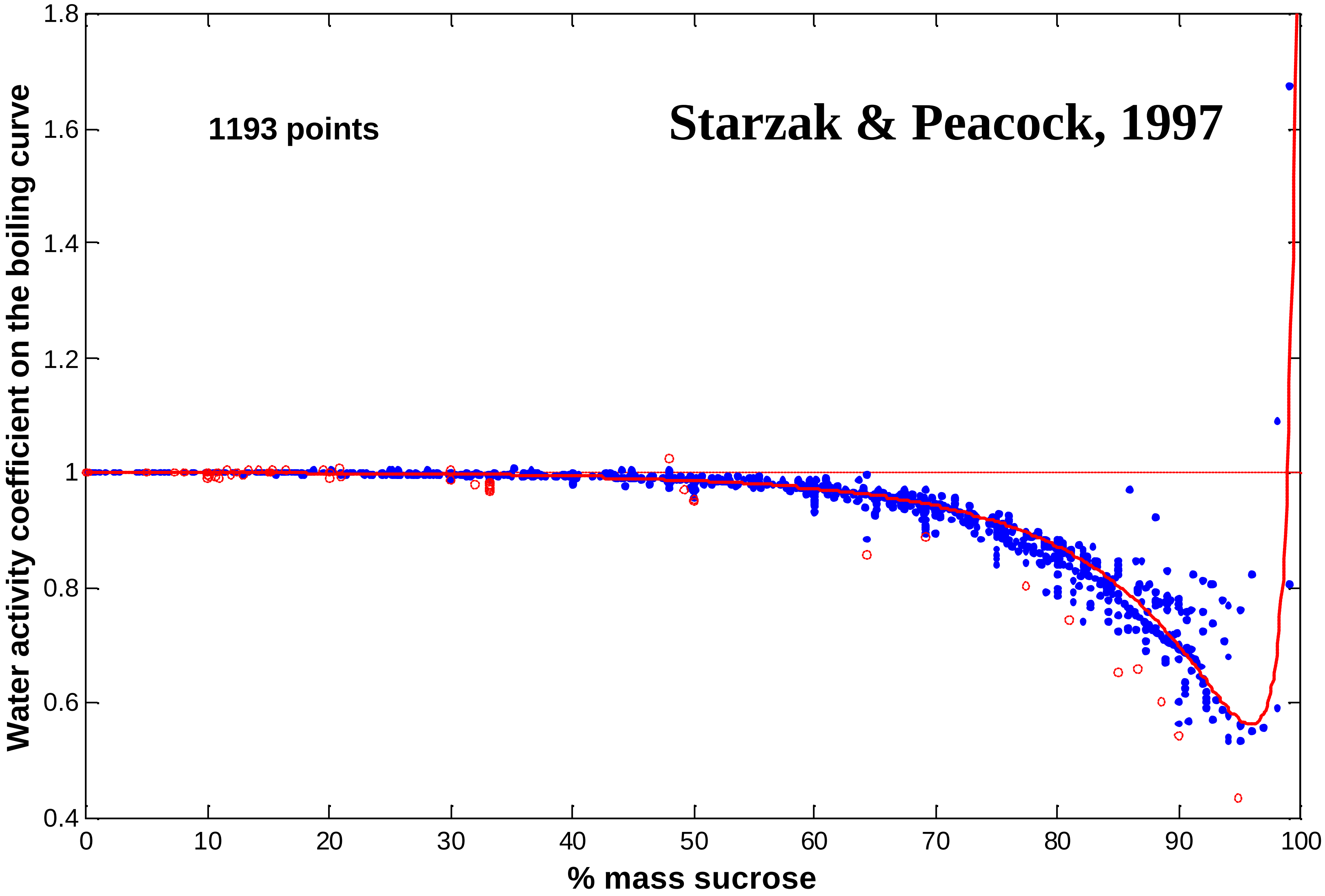
Water activity coefficient (boiling curve)



Theoretical models of activity for highly concentrated sucrose solutions

- **Van Hook, 1987:**
  - sucrose hydration
  - sucrose association (clustering)

- **Starzak & Mathlouthi, 2002:**
  - water association
  - sucrose hydration
  - sucrose association (clustering)

Previous studies (small exptl. databases)

- Le Maguer, 1992 (UNIQUAC)
- Caté et al., 1994 (UNIQUAC)
- Peres & Macedo, 1996 (UNIQUAC)
- Peres & Macedo, 1997 (UNIFAC)
- Spiliotis & Tassios, 2000 (UNIFAC)

Objective of this study:

- an empirical activity equation
- wide range of temp. & concentrations
- large database

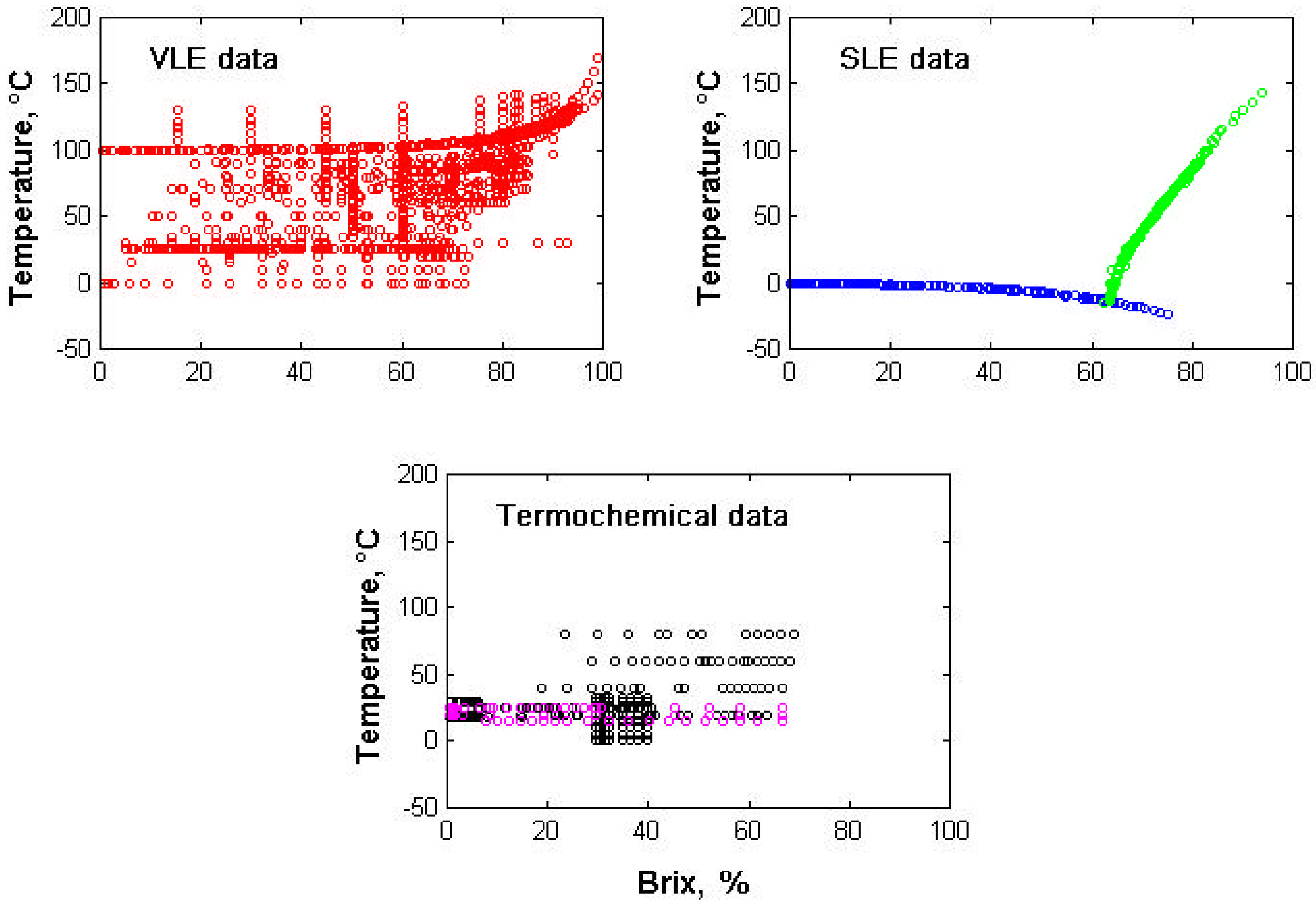
Thermodynamic data typically used to determine the activity coefficient

- **VLE data (BPE, VPL, ERH, osmotic coeff. by isopiestic method)**
- **SLE data (FPD, sucrose solubility)**
- **Termochemical data (heat of dilution, excess heat capacity)**

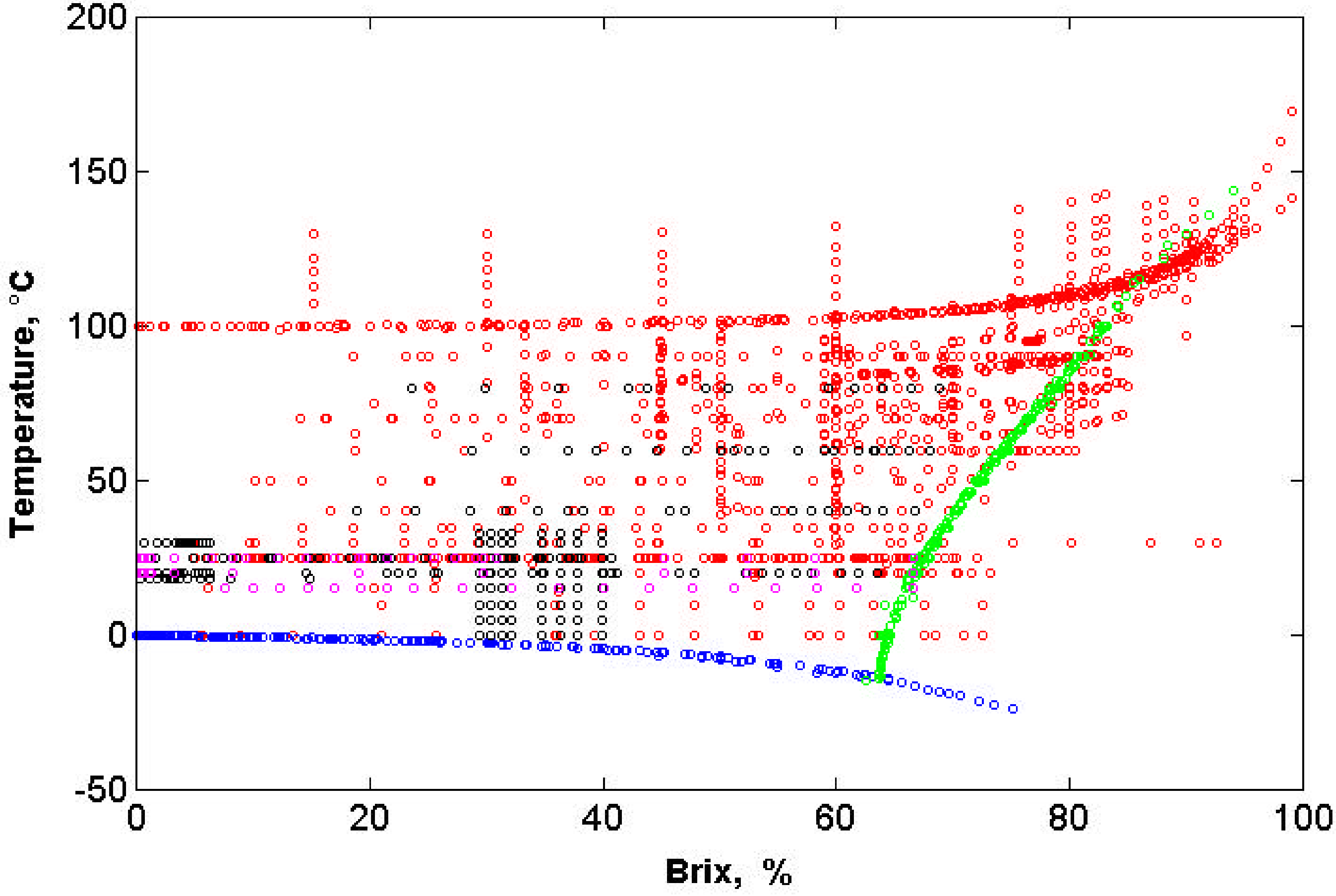
EXPERIMENTAL DATABASE

Data type	Experimental points	Literature sources
VLE	1507	64
FPD	213	13
Solubility	265	34
Heat of dilution	283	10
Heat capacity	70	4
Total	**2338**	**125**

Distribution of experimental data



Distribution of experimental data



Selection of water activity model

***n*-suffix Margules equation**

$$\ln g_{A} = \sum_{k=2}^{n} a_{k} x_{B}^{k}$$

Advantages: **linear with respect to its coefficients**

Drawbacks: **lack of sound theoretical foundation**

General temperature dependence

$$a_k(q) = \frac{a_{k0}}{q} + a_{k1} + a_{k2}\ln q + a_{k3}q + a_{k4}q^2 + a_{k5}q^3$$

$$\text{where} \quad q = T/T_0$$

<u>Disadvantage</u>: large number of parameters

Simplified temperature dependence

$$\ln g_A = a(q)\sum_{k=2}^{n} b_{k-2}\, x_B^k$$

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

Advantage: **reduced number of parameters**

Disadvantage: **temperature effect pattern independent of composition**

Sucrose activity coefficient

$$\ln g_B = \sum_{k=2}^{n} b_k x_A^k$$

Gibbs-Duhem equation

$$x_A \frac{d \ln g_A}{d x_A} = x_B \frac{d \ln g_B}{d x_B}$$

Expansion coefficients of sucrose activity

$$b_k = (-1)^k \sum_{l \geq k}^{n} \binom{l}{k} A_l, \qquad k \geq 2$$

where

$$A_l = a_l - \frac{l+1}{l} a_{l+1}, \quad l = 2,3,\ldots,n-1$$

$$A_n = a_n$$

Expansion coefficients of sucrose activity, $n = 7$

$$b_2 = a_2 + \frac{3}{2}a_3 + 2a_4 + \frac{5}{2}a_5 + 2a_6 + \frac{7}{2}a_7$$

$$b_3 = -a_3 - \frac{8}{3}a_4 - 5a_5 - 8a_6 - \frac{35}{3}a_7$$

$$b_4 = a_4 + \frac{15}{4}a_5 + 9a_6 + \frac{35}{2}a_7$$

$$b_5 = -a_5 - \frac{24}{5}a_6 - 14a_7$$

$$b_6 = a_6 + \frac{35}{6}a_7$$

$$b_7 = -a_7$$

Expansion coefficients of sucrose activity
Matrix representation

$$\mathbf{ß} = \mathbf{M}\,\mathbf{a}$$

$$b_{k+1} = \sum_{l=1}^{n-1} M_{kl}\, a_{l+1}, \qquad k = 1, 2, \ldots, n-1$$

Processing experimental data

VLE data $\Rightarrow \ln g_A$

FPD data $\Rightarrow \ln g_A$

Solubility $\Rightarrow \ln g_B$

Heat of dilution $\Rightarrow H^E_{asym} / RT$

Specific heat $\Rightarrow C^E_{p_{asym}} / R$

VLE data $\Rightarrow \ln g_A$

Modified Raoult's law

BPE, vapour pressure, osmotic coeff. :

$$g_A = \frac{P}{(1-x_B)P_A^0(T)}$$

Equilibrium relative humidity (ERH):

$$g_A = \frac{\mathrm{ERH}/100}{1-x_B}$$

Freezing point data $\Rightarrow \ln g_A$

Solid-liquid equilibrium

$$\ln g_A = -\left[\frac{\Delta H_{fA}(T_m)}{RT_m} - \frac{\Delta C_{pA}(T_m)}{R} + \frac{\Delta B_A T_m}{2}\right]\left[\frac{T_m}{T_f} - 1\right]$$

$$+\left[\frac{\Delta C_{pA}(T_m)}{R} - \Delta B_A T_m\right]\ln\left[\frac{T_f}{T_m}\right] + \frac{\Delta B_A T_m}{2}\left[\frac{T_f}{T_m} - 1\right] - \ln(1 - x_B)$$

Assumed
for pure water:

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

Sucrose solubility data $\Rightarrow \ln \tilde{g}_B$

Solid-liquid equilibrium (asym. convention)

$$\ln\left[\frac{g_B^{\infty}(T_m)}{g_B^{\infty}} g_B\right] = -\left[\frac{\Delta H_{dB}(T_0)}{RT_0} - \frac{\Delta C_{pB}(T_0)}{R} + \frac{\Delta B_B T_0}{2}\right]\left[\frac{T_m}{T} - 1\right]\frac{T_0}{T_m}$$

$$+\left[\frac{\Delta C_{pB}(T_0)}{R} - \Delta B_B T_0\right]\ln\left[\frac{T}{T_m}\right] - \frac{\Delta B_B T_m}{2}\left[1 - \frac{T}{T_m}\right] - \ln(x_B)$$

Assumed for sucrose:

$$\frac{\Delta C_{pB}(T)}{R} = \frac{\Delta C_{pB}(T_0)}{R} + \Delta B_B (T - T_0)$$

Heat of dilution data $\Rightarrow$ H^E_{asym}/RT

Two-step procedure

- **fitting each set of isothermal data to McMillan-Mayer expansion (evaluating coefficients of expansion)**

- **data generated from the expansion used as input data for regression**

Types of experimental heats of dilution

I. **Amount of heat liberated per one mole of sucrose in solution after addition of a known amount of pure water**

$$\frac{\Delta H_{\mathrm{I}}}{n_B} \text{ (J/mol solute)} = \sum_{k=2} h_{k0}\left[m^{k-1}(\mathrm{f}) - m^{k-1}(\mathrm{i})\right]$$

Types of experimental heats of dilution

II. amount of heat liberated per one mole of water in original solution after addition of a known amount of dilute sucrose solution

$$\frac{\Delta H_{\mathrm{II}}}{n_A(\mathrm{i})}\ (\mathrm{J/mol\ solvent}) =$$

$$\sum_{k=2} h_{k0} \frac{\left[n_A(\mathrm{i}) + n_A(\mathrm{a})\right] m^k(\mathrm{f}) - n_A(\mathrm{a})\, m^k(\mathrm{a}) - n_A(\mathrm{i})\, m^k(\mathrm{i})}{n_A(\mathrm{i})}$$

Types of experimental heats of dilution

III. amount of heat liberated per one gram of water added after addition of a small amount of pure water (differential heat of dilution)

$$\frac{\Delta H_{\mathrm{III}}}{w_A}\ (\text{J/g solvent added}) = -\frac{1}{1000}\sum_{k=2} h_{k0} m^k(\mathrm{i})$$

$$m(\mathrm{f}) \cong m(\mathrm{i})$$

Heat of dilution data $\Rightarrow$ H^E_{asym} / RT

Excess enthalpy of solution

from McMillan-Mayer expansion

$$H^E_{asym}\,(\text{J/mol}) = \frac{\sum_{k=2} h_{k0} m^k}{m + 1000/M_A}$$

Specific heat data $\Rightarrow$ $C_{p\,asym}^{E} / R$

Apparent molar heat capacity of sucrose:

$$\Phi_c(m) = \frac{\left[1+\frac{M_B}{1000}m\right]c_p(m) - c_{pA}}{m}$$

Excess heat capacity of solution

$$C_{p\,asym}^{E}\ (\text{J/mol}\cdot\text{K}) = \frac{\left[\Phi_c(m)-\Phi_c(0)\right]m}{m+1000/M_A}$$

Experimental variables
& Margules expansion coefficients

SLE (asym. convention) - solubility

$$\ln\left[\frac{g_B^{\infty}(T_m)}{g_B^{\infty}} g_B\right] =$$

$$a(T)\sum_{k=2}^{n}\sum_{l=1}^{n-1} M_{kl}\, b_{l-1} x_A^k + \left[a(T_m) - a(T)\right]\sum_{k=2}^{n}\frac{b_{k-2}}{k-1}$$

Experimental variables
& Margules expansion coefficients

Excess enthalpy of solution

Derived from free Gibbs energy:

$$G^E = RT\left(x_A \ln g_A + x_B \ln g_B\right)$$

$$\frac{H^E}{RT} = -T\,\frac{\partial(G^E/RT)}{\partial T}$$

$$H^E_{asym} = H^E + RT^2 x_B \frac{\partial \ln g_B^{\infty}}{\partial T}$$

Experimental variables
& Margules expansion coefficients

Excess enthalpy of solution

$$\frac{H^E_{asym}}{RT} = T\,a'(T)\sum_{k=2}^{n}\frac{b_{k-2}}{k-1}\,x_B^k$$

$$T\,a'(T) = -\frac{a_0}{q} + a_2 + a_3 q + 2a_4 q^2 + 3a_5 q^3$$

where $q = T/T_0$

Experimental variables
& Margules expansion coefficients

Excess heat capacity of solution

By definition:

$$\frac{C_{p_{asym}}^{E}}{R} = \frac{\partial\left(H_{asym}^{E}/R\right)}{\partial T}$$

Hence:

$$\frac{C_{p_{asym}}^{E}}{R} = T\left[2a'(T)+Ta''(T)\right]\sum_{k=2}^{n}\frac{b_{k-2}}{k-1}x_B^k$$

$$T\left[2a'(T)+Ta''(T)\right] = a_2+2a_3q+6a_4q^2+12a_5q^3$$

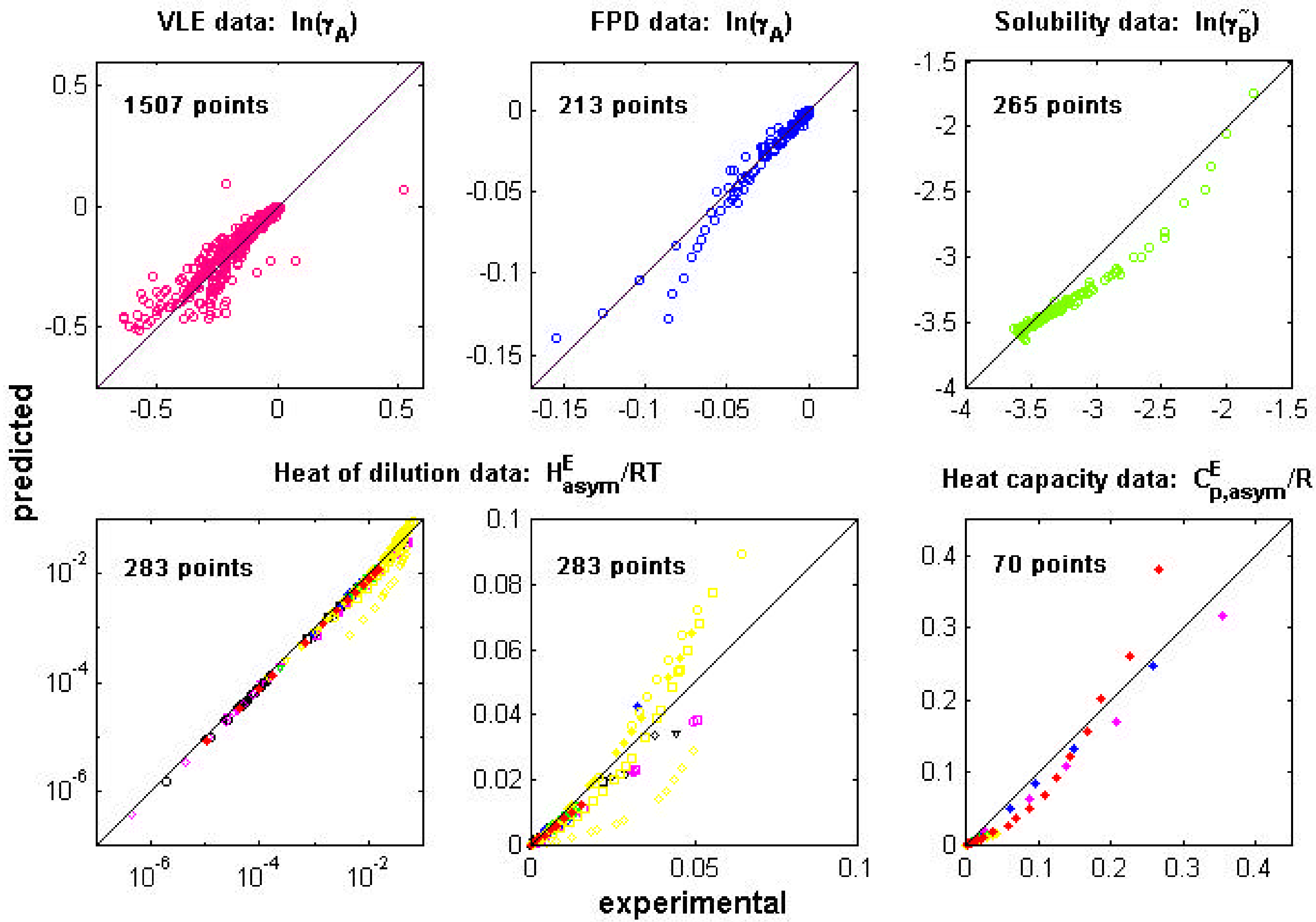
DATA REGRESSION
Performance index

$$I(\mathbf{a},\mathbf{b}) = w_{\mathrm{VLE}}^2 \sum_i w_{\mathrm{VLE},\,i}^2 (\ln g_{A,i} - \ln g_{A,i}^{exp})_{\mathrm{VLE}}^2$$

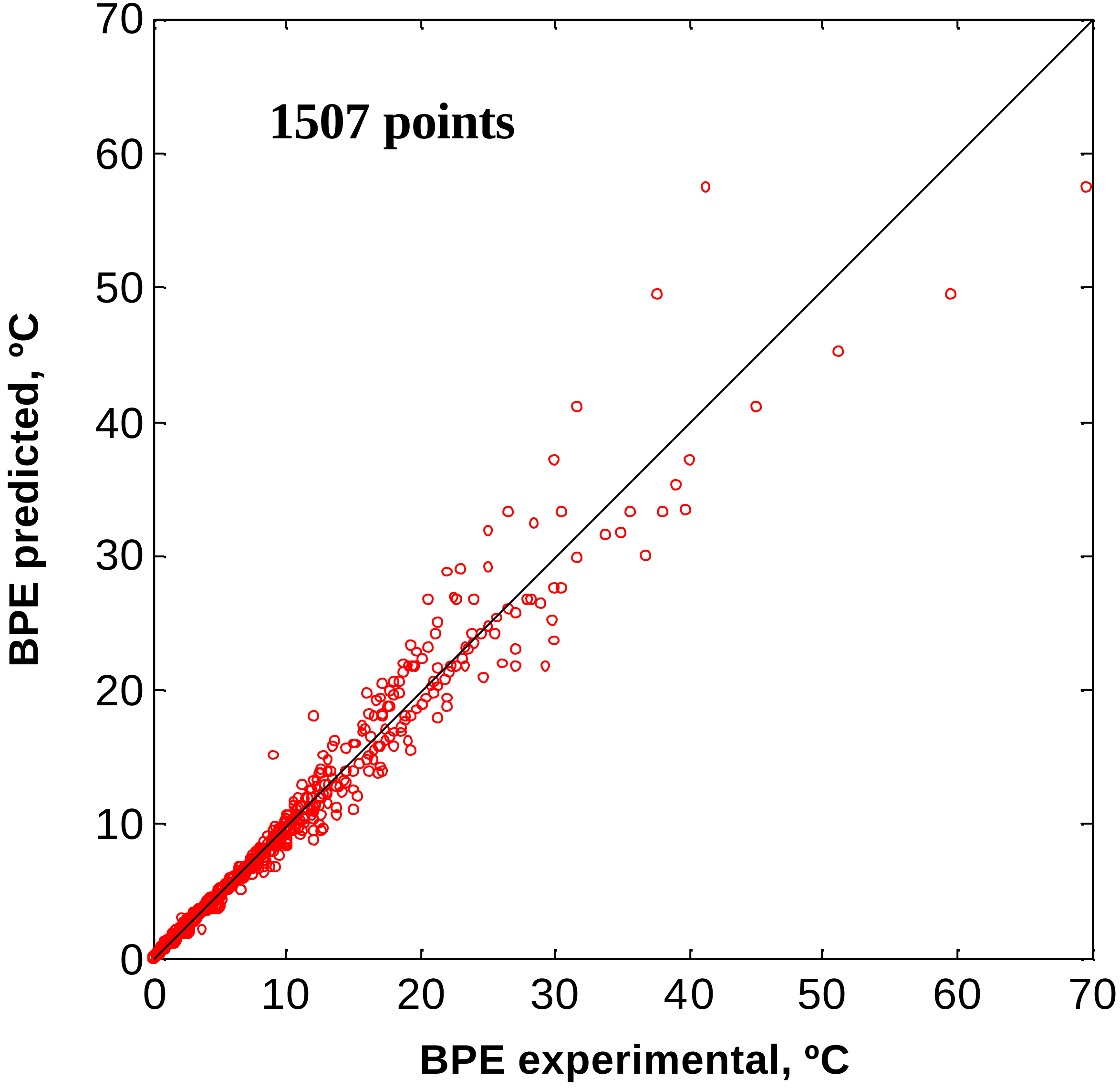
$$+ w_{\mathrm{FPD}}^2 \sum_i (\ln g_{A,i} - \ln g_{A,i}^{exp})_{\mathrm{FPD}}^2 + w_{\mathrm{SOL}}^2 \sum_i (\ln \tilde{g}_{B,i} - \ln \tilde{g}_{B,i}^{exp})_{\mathrm{SOL}}^2$$

$$+ w_{\mathrm{HE}}^2 \sum_i \left[\frac{H_{asym,i}^{E}}{RT_i} - \frac{H_{asym,i}^{E,exp}}{RT_i^{exp}} \right]^2 + w_{\mathrm{CE}}^2 \sum_i \left[\frac{C_{p\,asym,i}^{E}}{R} - \frac{C_{p\,asym,i}^{E,exp}}{R} \right]^2$$

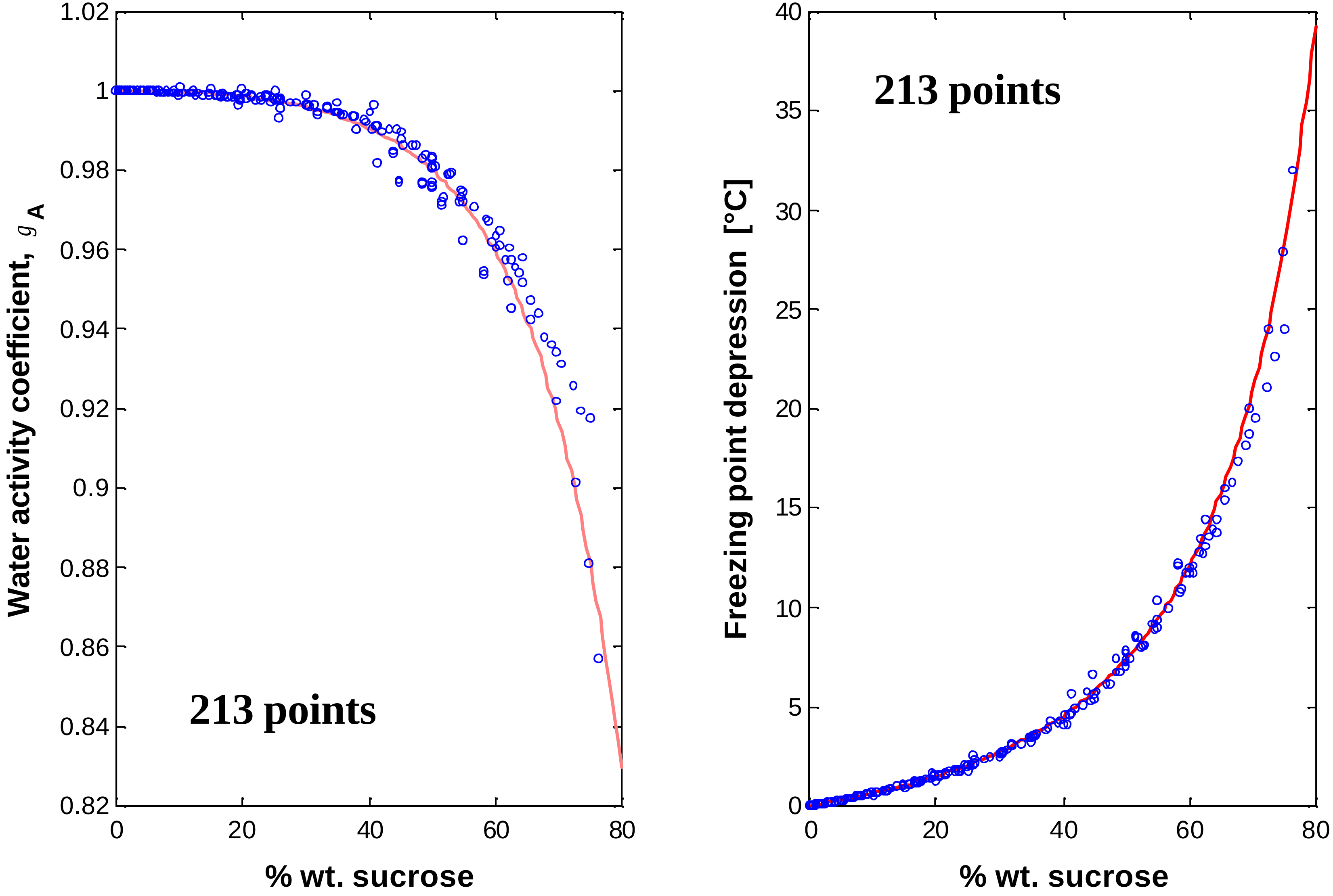
Results of data regression: correlation diagrams



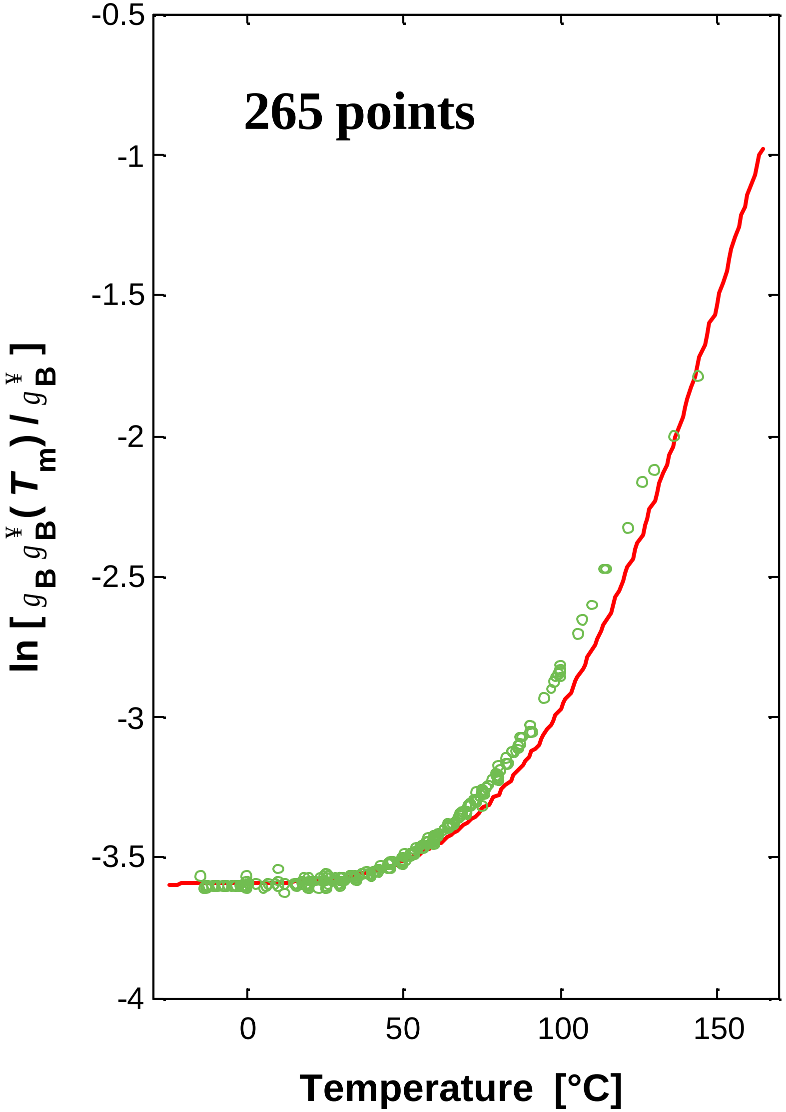
Boiling point elevation – predicted vs experimental

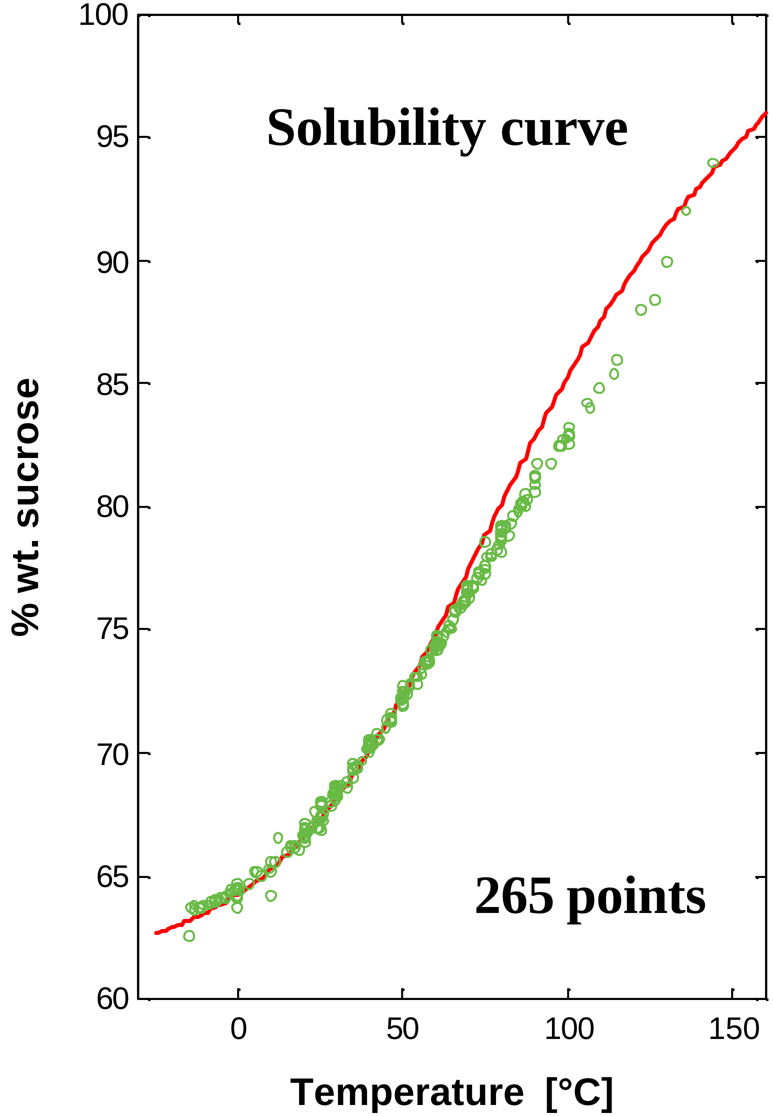


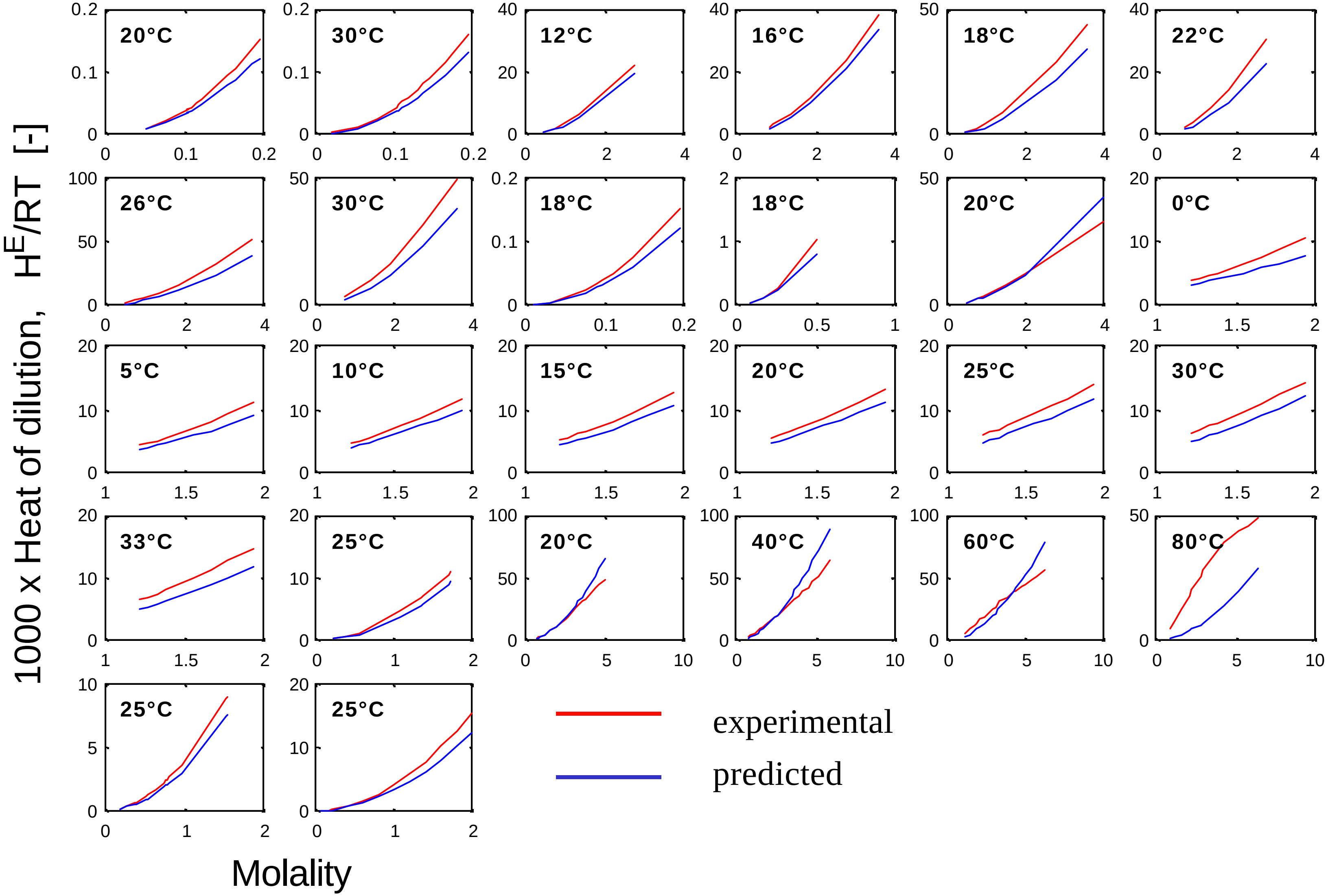
Results of FPD data regression



Results of solubility data regression

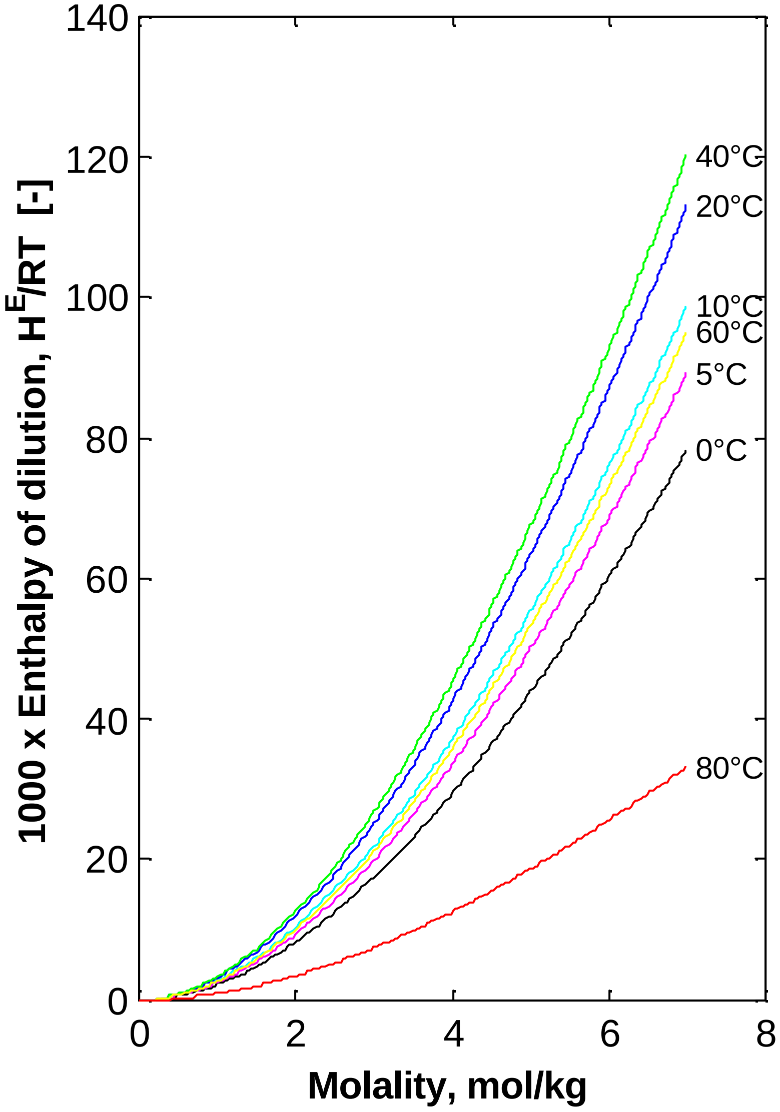


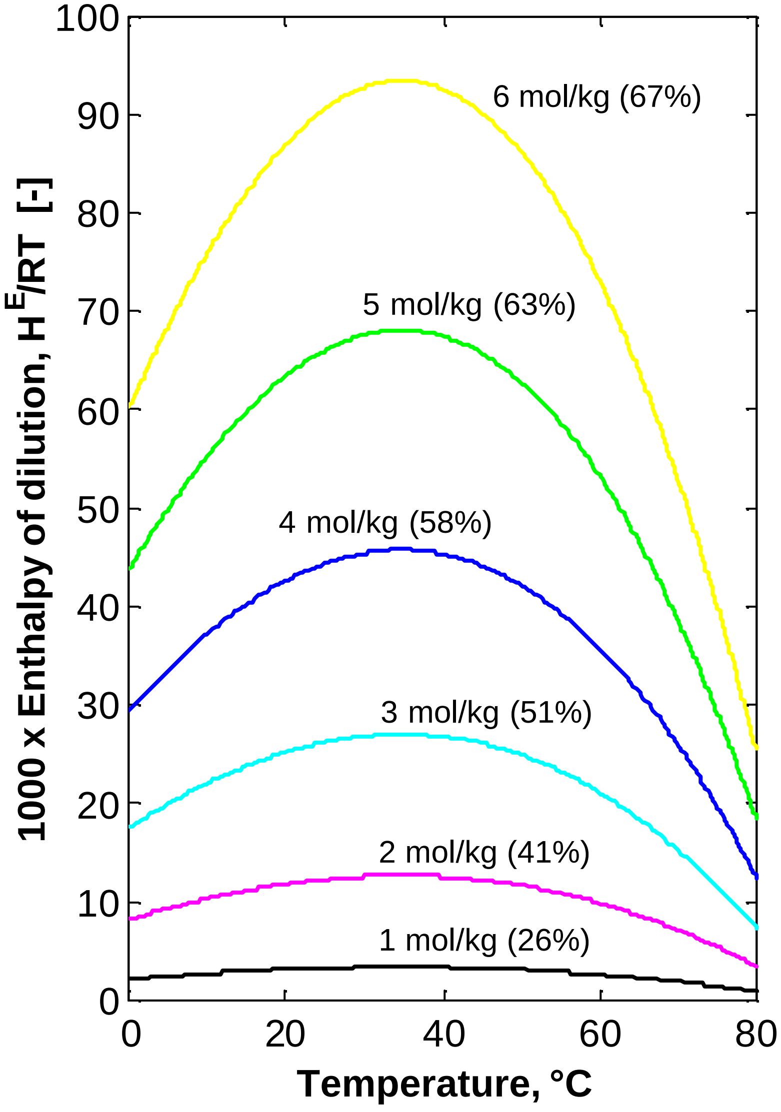




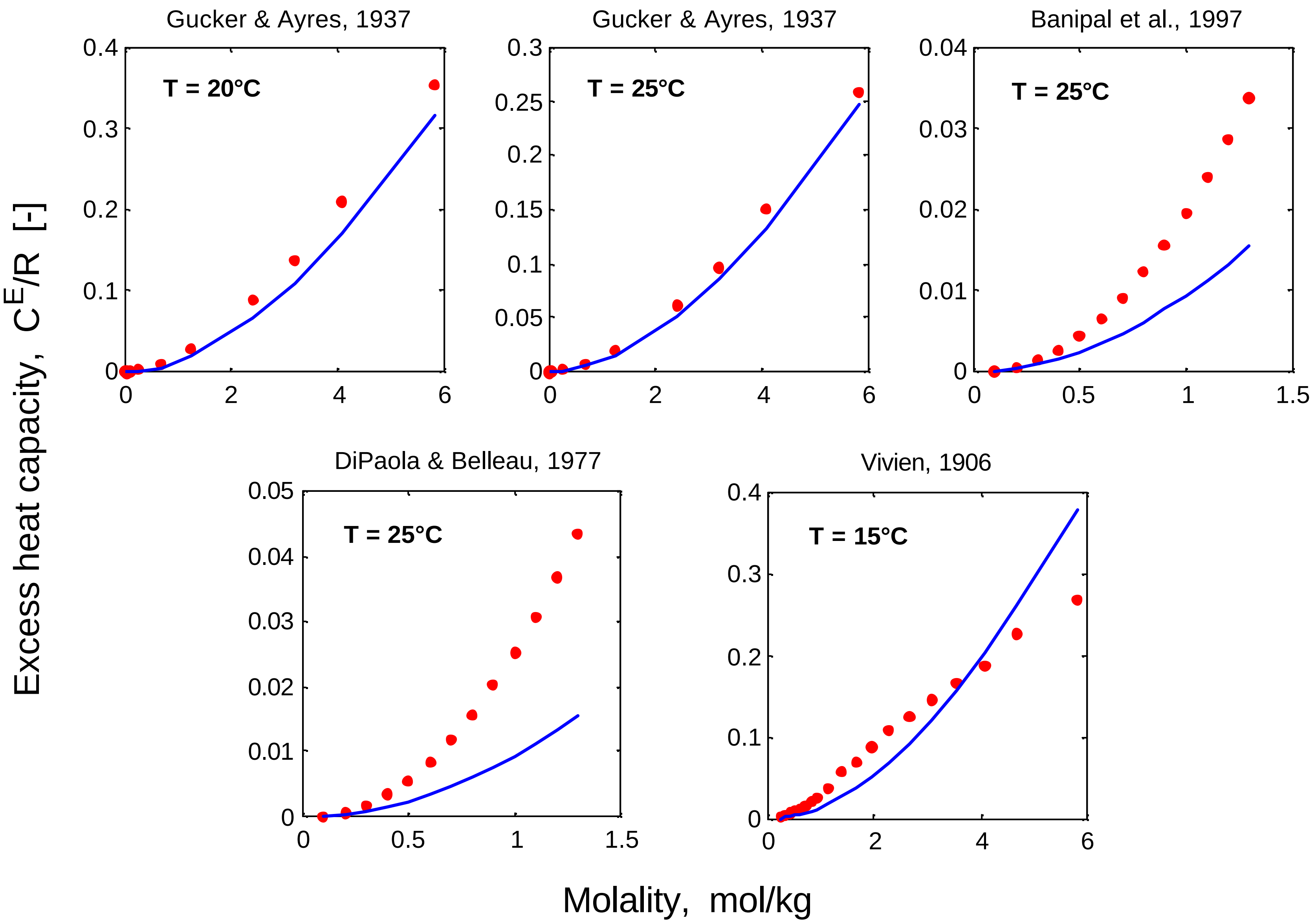
Regression of 26 heat of dilution data sets

Prediction of enthalpy of dilution

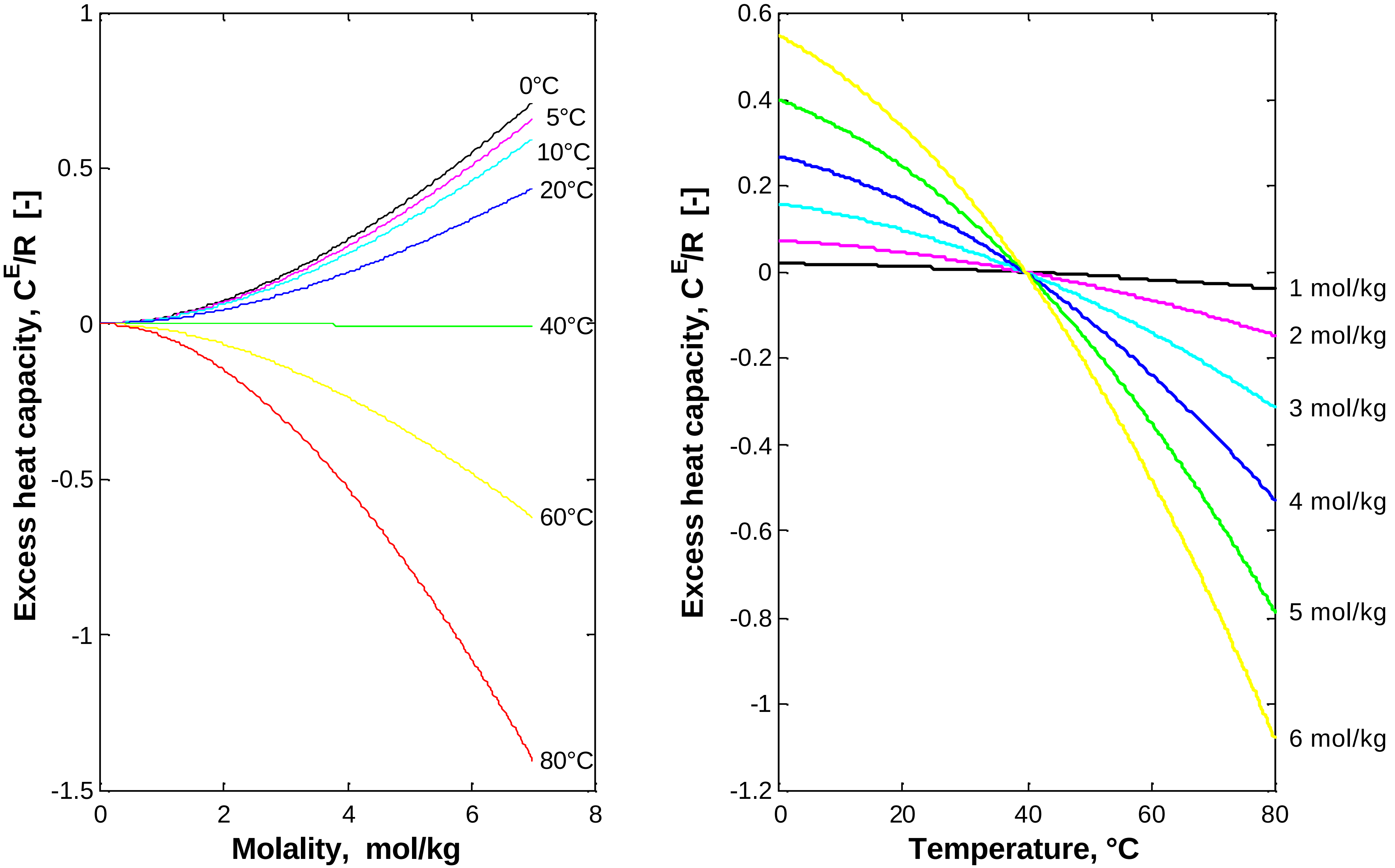




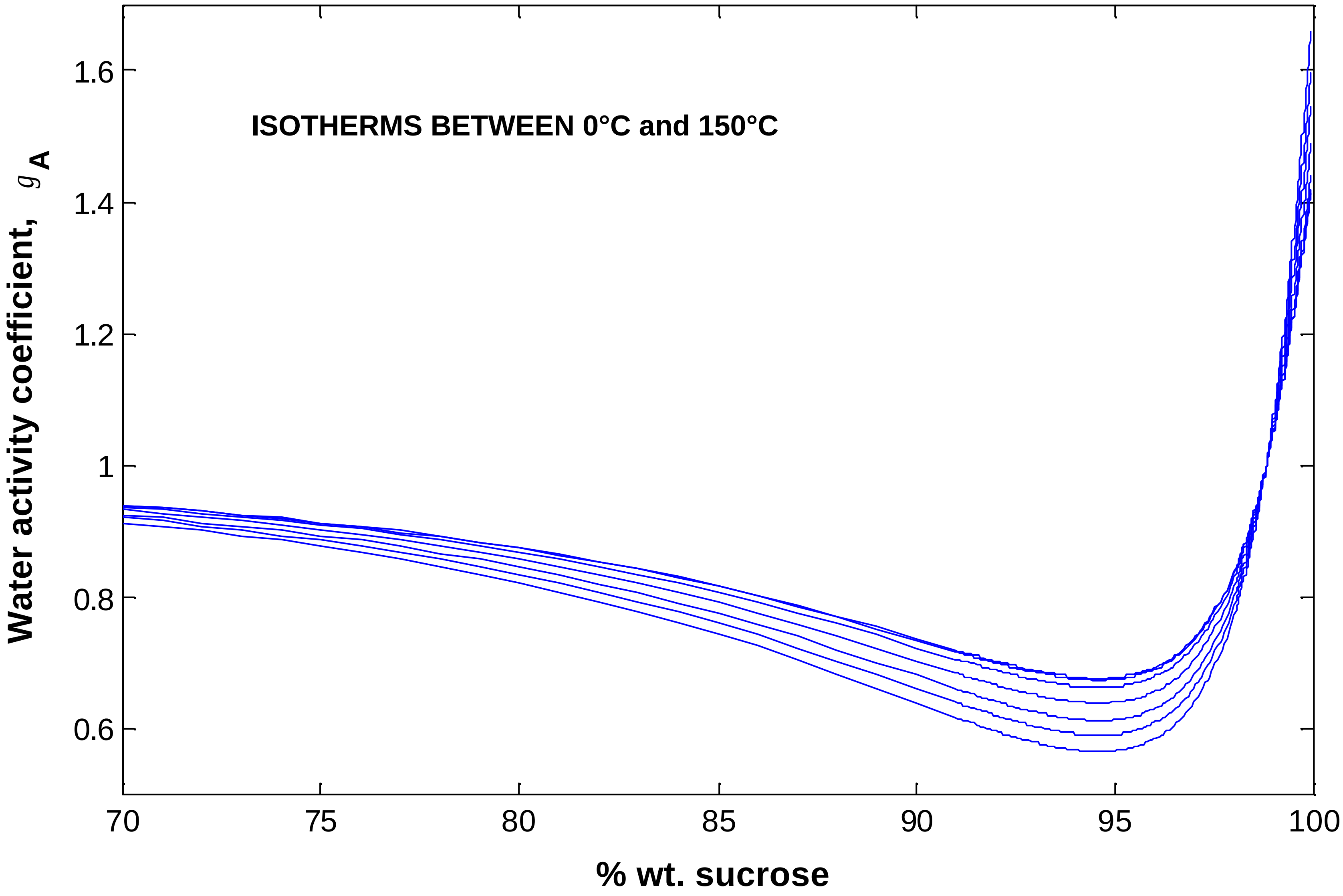
Regression of 5 heat capacity data sets



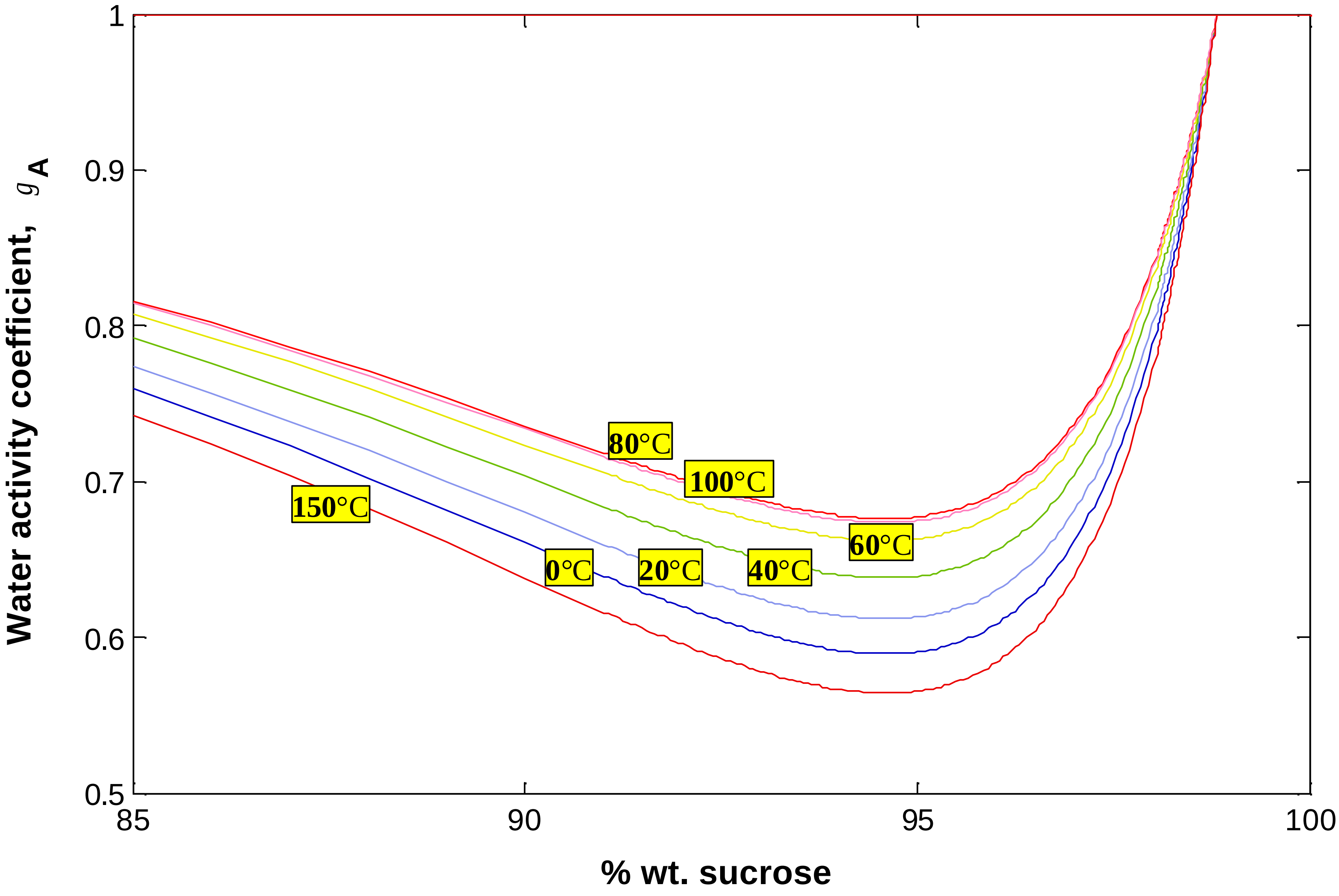
Prediction of excess heat capacity of solution



Prediction of water activity coefficient



Prediction of water activity coefficient



Final water activity coefficient equation

$$\ln g_A = a(q)\,(1 + b_1 x_B + b_2 x_B^2)\,x_B^2$$

$$a(q) = \frac{a_0}{q} + a_1 + a_2 \ln q + a_3 q + a_4 q^2$$

a_0 = -268.59
a_1 = -861.42
a_2 = -1102.3
a_3 = 1399.9
a_4 = -277.88

b_1 = -1.9831
b_2 = 0.92730

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