MODELING OF THE THERMO-PHYSICAL PROPERTIES OF AQUEOUS SUCROSE SOLUTIONS II. BOILING POINT, SPECIFIC HEAT CAPACITY AND THERMAL CONDUCTIVITY

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Received 10 September 2011, accepted 25 October 2011

Abstract: *The aim of this study was to establish mathematical relations between temperature or pressure and sucrose concentration with boiling point, specific heat capacity and thermal conductivity of aqueous sucrose solutions. In order to assess and select a suitable mathematical model the known data were fitted in different equations. Two equations were generated for each thermo-physical properties, taking in consideration the level of precision and simplicity of formulation.*
For boiling point of aqueous sucrose solutions two equations with an average of relative errors of 0.22% and regression coefficients greater than 0.999 were generated, for ranges of 5 – 90% in sucrose concentration and pressure of $0.123 \cdot 10^5 - 1 \cdot 10^5$ *Pa. For specific heat capacity two equations were formulated with average relative errors of 0.002% and* $R^2 = 0.9994$ *for intervals of temperature of 0 to 100 °C and sucrose concentration of 0 to 90% and for thermal conductivity were generated two equation with average relative errors of 0.004% and* $R^2 = 0.9992$ *for a range of temperature of 0 to 80 °C and sucrose concentration between 0 and 60%.*
The obtained equations can be loaded in computer software available both for industrial and academic users and so facilitating the sizing and optimization calculations of various technological equipment and processes.

Keywords: *sucrose, aqueous solutions, mathematical models*

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 sucrose and the ease of its purification, the system sucrose - water was the subject of many physicochemical studies. 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 additionally stimulated the popularity of these studies [1].
The increasing practical interest in sucrose solutions caused a great demand for predictive methods of determining its physical properties such as boiling point, heat capacity and thermal conductivity.
The boiling point can be directly correlated to the chemical structure of the molecule and reflects the strength of the intermolecular forces (among other forces

present) that hold the sucrose molecules together. The stronger the intermolecular forces, the more tightly the atoms will be held together and, therefore, the boiling point is higher [2].

Heat capacity and thermal conductivity are two of the most fundamental thermodynamic properties of liquid substances and they are closely related to their other physical and chemical properties. They are intimately related to the temperature dependence of fundamental thermodynamic functions [3].

These properties may be relatively easily determined in the laboratory with great accuracy; and they are of key importance for linking thermodynamics with microscopic fluid structure and dynamics but having predictive models can be a useful adjunct.

The accumulated data have led to the development of both empirical and phenomenological correlations, and many such correlations have been incorporated into design and analysis methods [4]. Most correlations, however, are applicable to only a relatively narrow range of conditions.

The purpose of this study is, therefore, to develop correlations by critically evaluating and regressing various types of experimental data available from the literature.

2. Experimental

Tabular data (Table 1, 2 and 3) concerning the variation of aqueous sucrose solutions boiling point, thermal conductivity and specific heat capacity with sucrose concentration and temperature were used as primary data for the regression analysis.

Microsoft Excel™ 2007 spreadsheets, CurveExpert® and TableCurve 3D® v.4 software were used to establish the equations.

The tabular data were plotted in *Temperature – Thermo-physical property, sucrose content – Thermo-physical property* coordinates and different regression techniques, involving the method of least squares were used to reveal the best-fit equation.

Table 1

Boiling point B_p [°C] of aqueous sucrose solutions as a function of the mass fraction X [%] pressure p [Pa]

	Boiling point, B_p [°C]					
Sucrose concentration, X	Pressure $p \cdot 10^5$, Pa					
w [%]	0.123	0.199	0.311	0.473	0.7	1
5	50.05	60.05	70.05	80.06	90.06	100.06
10	50.12	60.10	70.11	80.11	90.12	100.12
15	50.17	60.18	70.18	80.19	90.19	100.20
20	50.26	60.27	70.28	80.28	90.29	100.30
25	50.39	60.40	70.42	80.43	90.44	100.45
30	50.52	60.54	70.55	80.57	90.58	100.60
35	50.69	60.71	70.73	80.76	90.78	100.80
40	50.80	60.85	70.90	80.95	91.00	101.05
45	51.01	61.10	71.18	81.25	91.32	101.40
50	51.32	61.40	71.52	81.61	91.72	101.80
55	51.70	61.82	71.94	82.06	92.18	102.30
60	52.30	62.45	72.60	82.75	92.90	103.05
65	52.80	63.00	73.20	83.40	93.60	103.80
70	53.65	63.90	74.18	84.46	94.75	105.05
75	55.05	65.40	75.80	86.20	96.60	107.00
80	56.80	67.30	77.85	88.35	98.90	109.40
85	-	70.00	80.75	91.50	102.25	113.00
90	-	-	86.00	97.20	108.40	119.60

Table 2
Thermal conductivity λ [W/(m · K)] of aqueous sucrose solutions as a function of the mass fraction *X* [%] and temperature *t*, [°C][5, 6]

Sucrose concentration, X w [%]	Thermal conductivity λ, [W/(m · K)] at temperatures t, [°C]								
	0	10	20	30	40	50	60	70	80
0	0.565	0.583	0.599	0.614	0.628	0.641	0.652	0.663	0.672
10	0.544	0.551	0.566	0.581	0.594	0.607	0.617	0.628	0.636
20	0.505	0.52	0.535	0.548	0.56	0.572	0.588	0.592	0.6
30	0.473	0.488	0.501	0.514	0.526	0.536	0.547	0.555	0.563
40	0.443	0.457	0.47	0.48	0.492	0.502	0.512	0.519	0.526
50	0.413	0.391	0.437	0.449	0.458	0.467	0.477	0.484	0.491
60	0.383	0.384	0.405	0.415	0.419	0.432	0.441	0.449	0.455

Table 3
Specific heat capacity C_p [J/(kg · K)] of aqueous sucrose solutions as a function of the mass fraction *X* [%] and temperature *t*, [°C][7]

Temperature, t [°C]	Specific heat capacity C_p [J/(kg · K)] at sucrose concentration, X [%]									
	0	10	20	30	40	50	60	70	80	90
0	3936	3684	3433	3182	2931	2680	2428	2177	1926	3936
10	3936	3684	3475	3224	2973	2721	2470	2219	2010	3936
20	3936	3726	3475	3224	3014	2763	2554	2303	2052	3936
30	3977	3726	3517	3266	3056	2805	2596	2345	2135	3977
40	3977	3726	3517	3308	3098	2847	2638	2428	2219	3977
50	3977	3726	3559	3349	3140	2889	2680	2470	2261	3977
60	3977	3726	3559	3349	3140	2973	2763	2554	2345	3977
70	3977	3810	3601	3391	3182	3014	2805	2596	2386	3977
80	3977	3810	3601	3433	3224	3056	2847	2680	2470	3977
90	4019	3810	3643	3475	3266	3098	2889	2721	2554	4019
100	4016	3852	3643	3475	3308	3140	2973	2763	2596	4016

3. Results and Discussion

3.1 Boiling point

Using Microsoft Excel™ 2007 spreadsheets and CurveExpert® software, a Modified Hoerl Model correlation between pressure *p* and boiling point, at constant aqueous sucrose concentration *X*, [%] has been established:

$$B_p = A + B^{(1/p)} p^C \qquad (1)$$

For ranges of sucrose concentration between 5 and 85%, the coefficients of the Modified Hoerl Model equations *A, B* and *C* are presented in Table 4. The regression coefficients R^2 are greater than 0.99, thus indicating a good correlation of variables.

Table 4
Coefficients for equation (1)

Sucrose conc., X [%]	A	B	C	R^2
5	101.596	0.98196	0.26788	0.999
10	101.644	0.98211	0.26803	0.999
15	101.728	0.98204	0.26762	0.999
20	101.973	0.98214	0.26712	0.999
25	101.973	0.98214	0.26712	0.999
30	102.308	0.98236	0.26670	0.999
35	102.112	0.98226	0.26697	0.999
40	102.562	0.98234	0.26675	0.999
45	102.917	0.98231	0.26629	0.999
50	103.313	0.98251	0.26609	0.999
55	103.791	0.98273	0.26558	0.999
60	104.521	0.98304	0.26462	0.999
65	105.264	0.98320	0.26411	0.999
70	106.475	0.98373	0.26404	0.999
75	108.405	0.98422	0.26228	0.999
80	110.793	0.98466	0.25944	0.999
85	114.586	0.98295	0.25192	0.999
90	121.375	0.98210	0.24535	0.999

In order to correlate *A*, *B* and C coefficients with sucrose mass concentration, more models were used in CurveExpert® software (1st, 2nd and 3rd degree polynomial equations, "vapor pressure" model, "heat capacity" model etc.). The best fit model is a 3rd degree polynomial equation for the *A* coefficient and quadratic equations for the *B* and *C* coefficients (Table 5).

$$Coefficient_A = a + bT + cT^2 + dT^3$$
$$Coefficients_{B,C} = a + bT + cT^2 \quad (2)$$

Table 5
Coefficients for equation (2)

Coeff.	*A*	*B*	*C*
a	101	0.9823	0.2672
b	0.1128961704	-3.00E-05	6.00E-05
c	-3.820845E-03	7.004E-07	-2.00E-06
d	4.88158E-05	-	-
R^2	0.994	0.970	0.932

Combining the equations (1) and (2) and replacing the coefficients with numeric values, the final form of proposed equation model (Eq. 3) is:

$$B_p = (4.88158E-05X^3 - 3.8208452E-03X^2 + 0.1128961704X + 101) + (7E-07X^2 - 3E-05X + 0.9823)^{(1/p)} \cdot p^{(-2E-06X^2+6E-05+0.2672)} \quad (3)$$

To quantify the deviation of calculated densities from tabular data, the relative error equation was use and its values are presented in Table 6:

$$\varepsilon = \left| \frac{\rho_{tabular} - \rho_{calculated}}{\rho_{tabular}} \right| \cdot 100 \quad [\%] \quad (4)$$

The average of the induced relative errors for the proposed models is 0.22% for the proposed mathematical model.

By plotting the tabular data for aqueous sucrose solutions boiling point in TableCurve 3D® v.4 software (Fig. 1) an equation for the response function was generated, chosen due to the relative simplicity of formulation and regression coefficient (Eq. 5).

The coefficients of the fitted polynomial equation are presented in Table 7.

Table 6
The induced relative errors for the proposed model (3) for boiling point of aqueous sucrose solutions

	Relative errors, ε [%]					
Sucrose concentration, *X*	Pressure $p \cdot 10^5$, Pa					
w [%]	0.123	0.199	0.311	0.473	0.7	1
5	0.00422	0.24345	0.03757	0.12326	0.17590	0.02649
10	0.06781	0.40210	0.21822	0.09753	0.05329	0.21966
15	0.10495	0.42817	0.29134	0.17967	0.16393	0.33292
20	0.03253	0.39174	0.26487	0.18448	0.17006	0.34955
25	0.11270	0.27933	0.16100	0.08590	0.08578	0.27582
30	0.21509	0.17721	0.08711	0.00734	0.01369	0.19789
35	0.31780	0.08829	0.00604	0.08982	0.08762	0.10193
40	0.18847	0.14724	0.00229	0.10788	0.13819	0.0239
45	0.10589	0.15940	0.02143	0.14693	0.19018	0.04984
50	0.03310	0.25959	0.02919	0.10964	0.18603	0.03455
55	0.12519	0.36936	0.16137	0.00217	0.06926	0.05520
60	0.11667	0.38017	0.18842	0.04117	0.02193	0.10741
65	0.59176	0.79412	0.55981	0.38047	0.29154	0.39870
70	0.72748	0.95659	0.70410	0.51124	0.40029	0.47823
75	0.21195	0.52791	0.31942	0.16027	0.08526	0.19893
80	0.50231	0.10705	0.24715	0.29716	0.33774	0.15364
85	-	1.44869	1.45175	1.45218	1.40415	1.19791
90	-	-	4.84629	4.71030	4.55567	4.26999

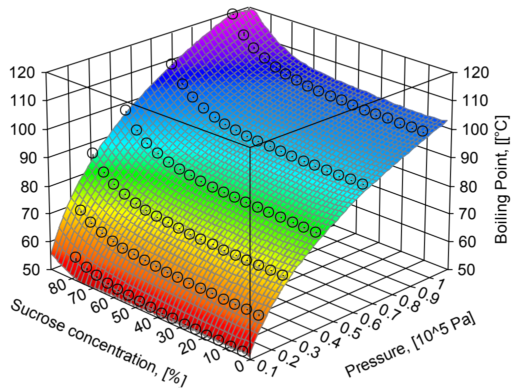

Figure 1. Aqueous sucrose solutions boiling point values plotted in TableCurve 3D and fitted polynomial equation (5) with residuals.

$$\ln B_p = a + b\ln p + c/p^{0.5} + dX^2 + eX^2\ln X + fX^{2.5} + gX^3 \quad (5)$$

Table 7
Coefficients for equation (5)

Coeff.	*Value*	*Coeff.*	*Value*
a	4.7356452	*e*	0.00044369357
b	0.20791255	*f*	-0.00026010431
c	-0.1303382	*g*	9.6176697E-06
d	-0.0003725448		

The equation (5) is a polynomial equation, Rank 31, Eqn. 157010504 in TableCurve 3D® v.4 library with R^2 = 0.99958643, R^2adj = 0.9995565, FitSdErr = 0.0003725 and Fstat. = 39477.482.

3.2 Specific Heat Capacity

Using Microsoft Excel™ 2007 spreadsheets linear correlation between temperature *T*, [K] and specific heat capacity, at constant aqueous sucrose concentration *X*, [%] has been established:

$$C_p = a + bT \quad (6)$$

For ranges of temperature between 273 and 373 K, the values of the *A* and *B* coefficients and regression coefficients, R^2 of each linear equation are presented in Table 8.

In order to correlate *A* and B coefficients with sucrose concentration, more models were used in Microsoft Excel™ 2007. The best fit model is also a linear equation.

$$Coefficients_{A,B} = a + bX \quad (7)$$

Table 8
Coefficients for equation (6)

Sucrose conc., *X* [%]	*A*	*B*	R^2
10	3722.12	0.777273	0.813
20	3234.75	1.603636	0.864
30	2869.25	2.100000	0.975
40	2339.64	3.079091	0.985
50	1952.12	3.619091	0.991
60	1371.81	4.755455	0.995
70	984.973	5.293636	0.994
80	511.335	6.088182	0.996
90	93.2872	6.734545	0.997

Table 9
Coefficients for equation (7)

Coeff.	*a*	*b*
A	4182.8620454545	-45.7032772727
B	0.0045707071	0.0755772727

Combining the equations (6) and (7) and replacing the coefficients with numeric values, the final form of proposed equation model (Eq. 8) is:

$$C_p = (4182.86 - 45.70327X) + (0.00457070 + 0.075577 \cdot X)T \quad (8)$$

To quantify the deviation of calculated densities from tabular data, the relative error equation was use and its values are presented in Table 10. The average of the induced relative errors for the proposed models is 0.002% for the proposed mathematical model.
By plotting the tabular data for aqueous sucrose solutions specific heat capacity in TableCurve 3D® v.4 software (Fig. 2) an equation for the response function was generated (Eq. 9).

Table 10
The induced relative errors for the proposed model (8) for specific heat capacity of aqueous sucrose solutions

Temperature, *T* [K]	Relative errors, *ε* [%]									
	Sucrose concentration, *X* [%]									
	0	10	20	30	40	50	60	70	80	90
273	0.066	0.035	0.029	0.023	0.014	0.005	0.048	0.067	0.091	0.066
283	0.127	0.376	0.584	0.386	0.154	0.157	0.490	0.900	0.706	0.127
293	0.320	0.348	0.070	0.553	0.257	0.277	0.742	0.153	0.579	0.320
303	0.523	0.058	0.479	0.187	0.390	0.394	0.308	0.639	0.143	0.523
313	0.331	0.465	0.167	0.170	0.519	0.507	0.112	0.309	0.856	0.331
323	0.140	0.872	0.377	0.488	0.645	0.617	0.519	0.445	0.313	0.140
333	0.051	1.279	0.261	0.416	0.560	0.699	0.584	0.489	0.378	0.051
343	0.242	0.556	0.277	0.065	0.422	0.544	0.185	0.231	0.763	0.242
353	0.433	0.158	0.354	0.277	0.287	0.425	0.202	0.652	0.092	0.433
363	0.427	0.240	0.180	0.611	0.156	0.310	0.578	0.074	0.535	0.427
373	0.163	0.459	0.444	0.260	0.028	0.198	0.482	0.743	0.478	0.163

The equation (9) is a polynomial equation, Rank 50, Eqn. 302 in TableCurve 3D® v.4 library with R^2 = 0.99944977, R^2adj = 0.9994138, FitSdErr = 13.701972, Fstat. = 33785.237.

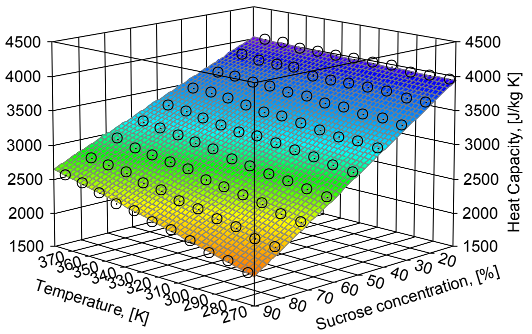

Figure 2. Aqueous sucrose solutions specific heat capacity values plotted in TableCurve 3D and fitted polynomial equation (9) with residuals.

$$C_p = a + b\ln T + cX + d(\ln T)^2 + eX^2 + \\ + fX\ln T \qquad (9)$$

The coefficients of the fitted polynomial equation are presented in Table 11.

Table 11
Coefficients for equation (5)

Coeff.	*Value*	*Coeff.*	*Value*
a	25132.56	*d*	630.05763
b	-7267.3551	*e*	-0.0010015742
c	-161.21331	*f*	24.255336

3.3 Thermal Conductivity

Using Microsoft Excel™ 2007 spreadsheets linear correlation between aqueous sucrose concentration *X*, [%] and specific heat capacity, at constant temperature *T*, [K] has been established:

$$C_p = A + BX \qquad (10)$$

The *A* and *B* values for the fitted linear equation are presented in Table 12.

$$Coefficients_{A,B} = a + bT \qquad (11)$$

Table 12
Coefficients for equation (10)

Temperature, *T* [K]	*A*	*B*	R^2
273	0.568357	0.00311	0.997
283	0.584857	0.00330	0.998
293	0.598821	0.00323	0.999
303	0.613964	0.00332	0.999
313	0.628893	0.00345	0.999
323	0.641393	0.00349	1.000
333	0.653679	0.00353	0.999
343	0.663179	0.00358	0.999
353	0.672036	0.00363	1.000

In order to correlate *A* and B coefficients with temperature, more models were used in Microsoft Excel™ 2007. The best fit model is also a linear equation (Table 13).

Table 13
Coefficients for equation (11)

Coeff.	*a*	*b*
A	0.2145613296	0.0013113690
B	-0.0014797877	-0.0000061488

Combining the equations (10) and (11) and replacing the coefficients with numeric values, the final form of proposed equation model (Eq. 12) is:

$$\lambda = (0.2145613296 + 0.0013113690T - \\ -(0.001479787 + 6.1488\text{E}-06\text{T})X \quad (12)$$

To quantify the deviation of calculated densities from tabular data, the relative error equation was use and its values are presented in Table 15. The average of the induced relative errors for the proposed models is 0.004% for the proposed mathematical model.

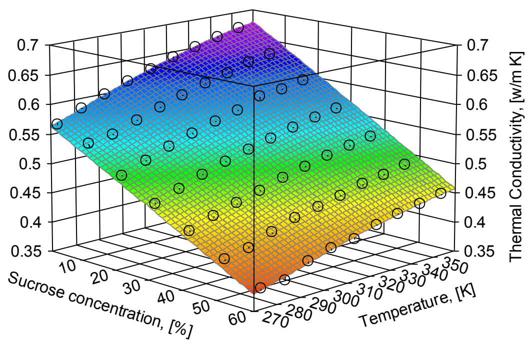

Figure 3. Aqueous sucrose solutions thermal conductivity values plotted in TableCurve 3D and fitted polynomial equation (13) with residuals.

By plotting the tabular data for aqueous sucrose solutions thermal conductivity in TableCurve 3D® v.4 software (Fig. 3) an equation for the response function was generated chosen due to the best regression coefficient (Eq. 13).

$$\lambda = a + bX + c/T + dX^2 + e/T^2 + \\ + fX/T + h/T^3 + iX/T^2 + jX^2/T \quad (13)$$

The coefficients of the fitted polynomial equation are presented in Table 14.

Table 14
Coefficients for equation (13)

Coeff.	*Value*	*Coeff.*	*Value*
a	-0.84385948	*f*	0.45271455
b	-0.0051670655	*g*	3.7037037E-08
c	1602.2814	*h*	53598501
d	2.3609905E-06	*i*	42.375474
e	-528571.74	*j*	-0.0020785223

The equation (13) is a polynomial equation, Rank 17, Eqn. 316 in TableCurve 3D® v.4 library with R^2 = 0.999440883, R2adj = 0.999295, FitSdErr = 0.00196514, Fstat. = 9955.553.

4. Conclusions

Two equations were generated for each thermo-physical properties, taking in consideration the level of precision and simplicity of formulation.

Table 15
The induced relative errors for the proposed model (12) for thermal conductivity of aqueous sucrose solutions

Temperature, *T* [K]	Relative errors, *ε* [%]						
	Sucrose concentration, *X* [%]						
	0	10	20	30	40	50	60
273	1.339	0.555	0.871	1.017	0.729	0.398	0.016
283	0.459	0.450	0.246	0.222	0.026	0.875	2.210
293	0.035	0.004	0.343	0.130	0.524	0.521	0.763
303	0.341	0.434	0.539	0.463	0.377	0.944	0.883
313	0.475	0.509	0.548	0.591	0.641	0.698	0.420
323	0.447	0.581	0.557	0.344	0.498	0.462	0.421
333	0.115	0.166	1.241	0.288	0.361	0.444	0.316
343	0.205	0.075	0.099	0.306	0.348	0.190	0.007
353	0.815	0.782	0.745	0.882	1.038	0.806	0.760

For boiling point of aqueous sucrose solutions two equations with an average of relative errors of 0.22% and regression coefficients greater than 0.999 were generated, for ranges of 5 – 90% in sucrose concentration and pressure of $0.123 \cdot 10^5$ – $1 \cdot 10^5$ Pa. For specific heat capacity two equations were formulated with average relative errors of 0.002% and $R^2 = 0.9994$ for intervals of temperature of 0 to 100 °C and sucrose concentration of 0 to 90% and for thermal conductivity were generated two equation with average relative errors of 0.004% and $R^2 = 0.9992$ for a range of temperature of 0 to 80 °C and sucrose concentration between 0 and 60%.

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