MODELLING OF THE THERMOPHYSICAL PROPERTIES OF CITRIC ACID AQUEOUS SOLUTIONS. DENSITY AND VISCOSITY

Andrei Ionuţ **Simion**[1], Cristina-Gabriela **Grigoraş**, Lucian Gheorghe **Gavrilă**

[1]"Vasile Alecsandri" University of Bacău, Department of Chemical and Food Engineering, 157 Calea Mărăşeşti, 600115 Bacău, Romania
E-mail: asimion@ub.ro

Abstract
Citric acid is an organic acid produced by carbohydrates fermentation process under microorganisms' action. Its uses in a large variety of fields going from food products to cosmetics and medicines require a good knowledge of its industrial behavior. From this point of view, thermo-physical properties (density, viscosity, thermal heat capacity, thermal conductivity and so on) present a major interest. As consequence, in this paper, different mathematical relations between temperature and concentration and density and dynamic viscosity of aqueous solutions made of anhydrous citric acid were established. The known data were fitted in different equations in order to assess and select suitable mathematical models. Their accuracy was studied using several statistical analysis tools such as correlation coefficient, ANOVA test, relative error etc. Taking into consideration the level of precision and the simplicity of formulation, several equations were generated for each of the studied thermo-physical property. For density proposed model the correlation coefficient R^2 is 0.999 and the average relative errors is 0.03% (absolute value). The dynamic viscosity equation was based on the Arrhenius model with average relative errors of 0.59% (absolute value). All the obtained equations can be uploaded in computer software available both for industrial and academic users and successfully used to facilitate the sizing and the optimization calculations of various technological processes and equipment.

Keywords: citric acid, thermo-physical properties, mathematical modeling.

Submitted: 13.01.2014 Reviewed: 19.03.2014 Accepted: 10.04.2014

1. INTRODUCTION

Citric acid is a common metabolite of plants and animals (Angumeenal A.R. and Venkappayya D, 2013). It dominates the category of organic acids, with a global production estimated in 2007 at more than 1.6 million of tons (Berovic M. and Legisa M., 2007). Many different studies were realized in order to assess the appropriate conditions for citric acid production. The world's existing demand is almost entirely (over 99%) met by fermentative technologies (Dhillon, G.S. et al, 2011). The microbial process for production of a high volumes of the aforementioned metabolite is based especially on the use of filamentous fungus *Aspergillus niger* (Sauer M. et al, 2008, El-Abyad M.S. et al, 1992, Saha M.L. and Takahashi F., 1997) in submerged (Paul G.C., et al, 1999, Papagianni M. and Mattey M., 2004) or static (Berovic M. and Legisa M., 2007) liquid cultures but other microorganisms such *Yarrowia lipolytica* (Papanikolaou S., 2008) can also conduct to remarkable quantities of this acid. However, its production requires high energy consumption and expensive raw materials. These aspects leaded to the search of alternative law cost substrates. In recent years, considerable interest has been focused on agro-industrial wastes knowing that this direction serves also to solve waste management problem faced by agro-industries. Moreover, industries will be benefitted by extra revenue from the value addition of wastes. Thus, different types of substrates were successfully employed for microorganisms' development. Dhillon et al, 2011, shown that the apple pomace ultrafiltration sludge presents a promising potential for the production of citric acid by *Aspergillus niger*. Imandi et al, 2008, study involved the use of statistical experimental designs to optimize medium constituents of the fermentation process for the production of citric acid from pineapple waste. The use of lignocellulosic materials available in agricultural wastes as a source of raw material for citric acid production (Khosravi-Darani K. and Zoghi A, 2008, Kumar D. et al, 2003) is also of considerable interest because of their renewable nature and abundance. Various other materials such as wastes from fruits processing industry (Kumar D. et al, 2003, Sassi G. et al, 1991) or molasses (El-Abyad M.S. et al, 1992, Jianlong, W. et al, 2000) have been also subjected to specific treatments able to conduct to citric acid.

Once obtained, the citric acid has a broad range of versatile applications, e.g. in food (as acidifying and flavor-enhancing agent, for the extraction of pectin from citrus peel (Kurita O. et al, 2008), or from cacao pod husks (Vriesmann L.C. et al, 2012), in combination with high-intensity pulsed electric fields for non-thermal pasteurization of fruit juices (Mosqueda-Melgar J. et al, 2008), in combination with CO_2 for the development of new packaging methods for fish storage (Schirmer B.C. et al, 2009)), in pharmaceuticals and cosmetics (for the production of inhalers for smoking cessation (Behm F.M. et al, 1993), to prolong the in vivo gastro-retention of a floating dosage form in the fasted state (Stops F. et al, 2006), as a release-modifying agent in melt extruded matrix tablets (Schilling S.U. et al, 2008), in combination with chitosan for the development of calcium phosphate cement for bone substitute materials (Yokoyama A. et al, 2002)). It is involved also in many advanced domains such as: biomedicine (for the production of biopolymers for culturing a variety of human cell lines (Vieira M.G.A. et al, 2011), nanotechnology (for the production of nanocomposites (Chung E.J. et al, 2011)), agriculture (for processes of bioremediation of heavy metals due to its powerful sequestering action with various transitional metals (Chen Y.X. et al, 2003)) or chemical industry (for the production or improvement of catalysts (Ibeh B. et al, 2009, Rinaldi N. et al, 2010, Li H. et al, 2011)). Small quantities of citric acid are employed in silvering and engraving and in dying and calico printing (Angumeenal A.R. and Venkappayya D, 2013).

In order to commercially produce this valuable microbial product and to use it in an effective and economically way in so many different areas of interest it is necessary to know how its thermophysical properties evolve. As we have shown in other of our researches ([a]Simion A. I. et al, 2011, [b]Simion A. I. et al, 2011, [c]Simion A. I. et al, 2011) previously published this type of properties can be illustrated by various relations. Thus, this paper focuses on the study of citric acid aqueous solutions density and viscosity. Their evolution when influenced by parameters such as temperature and concentration was analyzed.

Table 1. Variation of citric acid aquos solutions density with temperature and citric acid content (Kharat S. J., 2008)

Citric acid concentration, *C* [% w/w]	**Density, *ρ* [kg·m^{-3}]**			
	Temperature, *T* [K]			
	298.15	**303.15**	**308.15**	**313.15**
0	997.00	995.60	994.00	992.20
6.43	1022.5	1020.9	1019.1	1017.1
9.94	1035.3	1033.6	1031.7	1029.7
16.99	1059.4	1057.6	1055.5	1053.4
19.82	1068.5	1066.6	1064.5	1062.3
25.18	1085.0	1083.0	1080.7	1078.5
30.00	1099.0	1096.8	1094.5	1092.2
34.00	1110.1	1107.8	1105.3	1103.1
39.94	1125.7	1123.3	1120.7	1118.5
44.99	1138.3	1135.8	1133.1	1130.9

Table 2. Variation of citric acid aquos solutions dynamic viscosity with temperature and citric acid content (Kharat S. J., 2008)

Citric acid concentration, *C* [% w/w]	Dynamic viscosity, $\mu \cdot 10^3$ [Pa·s]			
	Temperature, *T* [K]			
	298.15	303.15	308.15	313.15
0	0.894	0.800	0.722	0.658
6.43	1.045	0.920	0.813	0.725
9.94	1.118	0.985	0.869	0.772
16.99	1.280	1.131	1.002	0.885
19.82	1.365	1.205	1.068	0.943
25.18	1.532	1.345	1.193	1.059
30.00	1.693	1.482	1.331	1.179
34.00	1.843	1.631	1.445	1.275
39.94	2.122	1.857	1.632	1.454
44.99	2.432	2.120	1.825	1.613

Our work was aimed to develop mathematical models able to describe the above mentioned thermophysical properties of citric acid and to compare them with the experimental data presented in literature. The developed models were verified using the relative error, ANOVA analysis and correlation coefficient. The obtained results showed good level of agreement for the proposed equations.

2. EXPERIMENTAL

Tabular data provided by the technical and scientific publications (Tables 1 and 2) concerning the variation of aqueous citric acid solutions density and dynamic viscosity with concentration and temperature were used as primary data for the regression analysis. For simple data integration, plotting and ANOVA analysis the Microsoft Excel™ 2007 spreadsheets was used. ANOVA analysis tool is able to offer more precise information between existing data and the predicted values obtained by the proposed mathematical models. For more complex and atypical data plotting in 2D ("vapor pressure" model, "heat capacity" model etc.) the CurveExpert® software was employed. The representation of tabular data in 3D as a surface response was fitted and analyzed in TableCurve 3D® v.4 software. The experimental data were plotted in *Temperature – Thermo-physical property, Citric acid concentration in aqueous solutions – Thermo-physical property* coordinates and different types of regression techniques, involving the method of least squares, relative error ε (Equation 1) and ANOVA were used to reveal the best-fit equation.

$$\varepsilon = \left| \frac{Data_{tabular} - Data_{calculated}}{Data_{calculated}} \right| \cdot 100[\%] \qquad (1)$$

3. RESULTS AND DISCUSSIONS

Density

Using Microsoft Excel™ 2007 spreadsheets and CurveExpert® software, 10 linear correlations (taking in consideration the best fit and simplicity in formulation) between temperature *T*, [K] and density ρ [kg·m^{-3}], at constant citric acid concentrations *C* [% w/w] have been established:

$$\rho = a_1 + a_2 T \qquad (2)$$

The a_1 and a_2 values are presented in Table 3. The regression coefficients R^2 are greater than 0.99, thus indicating a good correlation of variables. In order to correlate a_1 and a_2 coefficients with concentration *C*, [%, w/w], different models were used in CurveExpert® software (1st, 2nd and 3rd degree polynomial equations, "vapor pressure" model, "heat capacity" model, etc.).

Table 3. Coefficients for equation no. 2

Citric acid concentration, *C* [% w/w]	Equation 2 coefficients		
	a_1	a_2	R^2
0	1092.5	-0.320	0.9985
6.43	1129.9	-0.360	0.9990
9.94	1146.9	-0.374	0.9995
16.99	1179.3	-0.402	0.9999
19.82	1192.0	-0.414	0.9992
25.18	1215.1	-0.436	0.9989
30.00	1234.4	-0.454	0.9987
34.00	1250.2	-0.470	0.9987
39.94	1270.0	-0.484	0.9975
44.99	1286.7	-0.498	0.9969

The best fit model is the quadratic equation with good regression coefficients (Table 4).

$$Coefficient = b_1 + b_2 T + b_3 T^2 \tag{3}$$

Combining the equations 2 and 3 and replacing the coefficients with numeric values, the final form of proposed equation model becomes (Equation 4):

$$\begin{aligned}\rho = {} & (1093.8 + 5.53238 \cdot C - 0.02784 \cdot C^2) + \\ & + (-0.3226 - 0.005345 \cdot C + \\ & + 0.0000328 \cdot C^2) \cdot T\end{aligned} \tag{4}$$

Using the relative error equation, the calculated data given by the density mathematical model and the existing tabular data were compared (Table 5) obtaining a final average of 0.03% (absolute value). The ANOVA analysis (Table 6) was used to compare the values of density tabular and calculated data at 10 different concentrations in 4 temperatures variation.
The results presented in Table 6 showed that the sample *P*-value is 0.975118 greater than the targeted alpha 0.05 and the *F crit* value is larger than the *F*-test one. The null hypothesis is not rejected indicating that is not a statistical difference between tabular and calculated data.

By plotting tabular data for aqueous citric acid solutions in TableCurve 3D® v.4 software (Figure 1) an equation for the response function was generated, chosen due to the accuracy and simplicity of formulation.
The Equation 5 is a simple equation, Rank 1, Eqn. 151232557 in TableCurve 3D® v.4 library, with a precision of R^2 = 0.999982817, FitSdErr = 0.38247068, Fstat. = 257528.25. The coefficients values are presented in Table 7.

$$\ln \rho = a_1 + a_2 \cdot C^{(0.5)} \ln C + a_3 \cdot T^3 \tag{5}$$

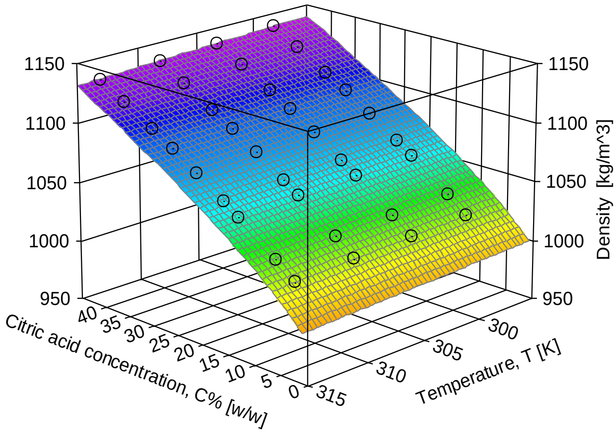

Figure 1. Citric acid aqueous solutions density values plotted in TableCurve 3D and fitted with simple equation type (Equation 5) with residuals

Table 4. Coefficients for equation no. 3

Equation 2 coefficients	Equation 3 coefficients			
	b_1	b_2	b_3	R^2
a_1	1093.8	5.53238	-0.02784	0.9998
a_2	-0.3226	-0.005345	0.0000328	0.9985

Table 5. For densities of citric acid aqueous solutions the absolute value of relative errors for calculated data versus tabular data

Citric acid concentration, C [% w/w]	Density, ρ [kg·m^{-3}]											
	Temperature, T [K]											
	298.15		ε, %	303.15		ε, %	308.15		ε, %	313.15		ε, %
	TD*	CD*		TD	CD		TD	CD		TD	CD	
0	997.00	997.80	0.08	995.60	996.20	0.05	994.00	994.60	0.05	992.20	993.00	0.07
6.43	1022.5	1022.4	0.01	1020.9	1020.6	0.02	1019.1	1018.8	0.02	1017.1	1017.1	0.00
9.94	1035.3	1035.2	0.01	1033.6	1033.3	0.02	1031.7	1031.4	0.02	1029.7	1029.6	0.01
16.99	1059.4	1059.5	0.01	1057.6	1057.5	0.01	1055.5	1055.5	0.00	1053.4	1053.5	0.00
19.82	1068.5	1068.8	0.02	1066.6	1066.7	0.00	1064.5	1064.6	0.01	1062.3	1062.5	0.02
25.18	1085.0	1085.5	0.04	1083.0	1083.3	0.03	1080.7	1081.2	0.04	1078.5	1079.0	0.04
30.00	1099.0	1099.7	0.06	1096.8	1097.4	0.05	1094.5	1095.2	0.06	1092.2	1092.9	0.06
34.00	1110.1	1110.8	0.06	1107.8	1108.5	0.06	1105.3	1106.2	0.07	1103.1	1103.8	0.06
39.94	1125.7	1126.3	0.05	1123.3	1123.9	0.05	1120.7	1121.5	0.06	1118.5	1119.1	0.04
44.99	1138.3	1138.4	0.01	1135.8	1136.0	0.01	1133.1	1133.5	0.03	1130.9	1131.0	0.00
	Average ε, %		0.03	Average ε, %		0.03	Average ε, %		0.03	Average ε, %		0.03

* TD – tabular data, CD – calculated data

Table 6. The ANOVA test summary

SUMMARY	Temperature, T [K]					Total
	298.15	303.15	308.15	313.15		
Tabular data						
Count	10	10	10	10		40
Sum	10740.8	10721	10699.1	10677.9		42838.8
Average	1074.08	1072.1	1069.91	1067.79		1070.97
Variance	2130.986	2097.662	2065.228	2053.679		1932.047
Calculated data						
Count	10	10	10	10		40
Sum	10744.41	10723.4	10702.4	10681.39		42851.61
Average	1074.441	1072.34	1070.24	1068.139		1071.29
Variance	2139.427	2112.978	2086.694	2060.575		1944.043
ANOVA						
Source of Variation	*SS**	*df**	*MS**	*F*	*P-value**	*F crit*
Sample	2.050654	1	2.050654	0.00098	0.975118	3.973897
Columns	442.4069	3	147.469	0.070445	0.97555	2.731807
Interaction	0.044861	3	0.014954	7.14E-06	1	2.731807
Within	150725.1	72	2093.404			

* *SS* – sum of squares, *df* – degrees of freedom, *MS* – mean square, *P-value* – level of significance

Table 7. Coefficients for equation no. 5

	Equation 5 coefficients			
Coefficient	a_1	a_2	a_3	R^2
Value	6.9429198	0.0051584066	-1.40881576e-0.9	0.9999

Dynamic viscosity

The most common mathematical model, in literature, for calculating the viscosity is based on the equation of Arrhenius because it creates a good correlation between experimental data and calculated values.

$$\mu = \mu_0 \cdot e^{-\frac{E_a}{R \cdot T}} \quad (6)$$

where: μ – dynamic viscosity [Pa·s,], μ_0 – water dynamic viscosity [Pa·s,], *Ea* – activation energy [kcal·mol^{-1}], *R* – universal gas constant [$1.987 \cdot 10^{-3}$ kcal·mol^{-1}·K^{-1}], *T* – absolute temperature [K].
Taking logs of equation (6), it gets (7):

$$\log \mu = \log \mu_0 - \frac{E_a}{2.303 \cdot R} \cdot \frac{1}{T} \quad (7)$$

and:

$$\frac{E_a}{R} = 2.303(\log \mu_0 - \log \mu) \cdot T \quad (8)$$

By plotting the results obtained from Equation 8 in TableCurve 3D® v.4 software (Figure 2) an equation for the response surface was generated (Equation 9). It correlates tabular data from Table 1 and water viscosity.
The Equation 9 is a polynomial equation, Rank 17, Eqn. 301 in TableCurve 3D® v.4 library with a precision of R^2 = 0.99939759, FitSdErr = 2.4040784, Fstat. = 11281.2.

$$\frac{E_a}{R} = a_1 + a_2 \cdot C + a_3 \cdot T + a_4 \cdot C^2 + + a_5 \cdot T^2 + a_6 \cdot C \cdot T \quad (9)$$

Combining the equations 6 and 9 and replacing the coefficients with numeric values, the final form of the proposed equation model is (Equation 10):

$$\mu = \mu_0 \cdot e^{-\frac{(2803.9225 - 7.3756887 \cdot C\% - 19.001965 \cdot T - 0.014509371 \cdot C\%^2 + 0.032140717 \cdot T^2 + 0.0052423574 \cdot T \cdot C\%)}{T}} \quad (10)$$

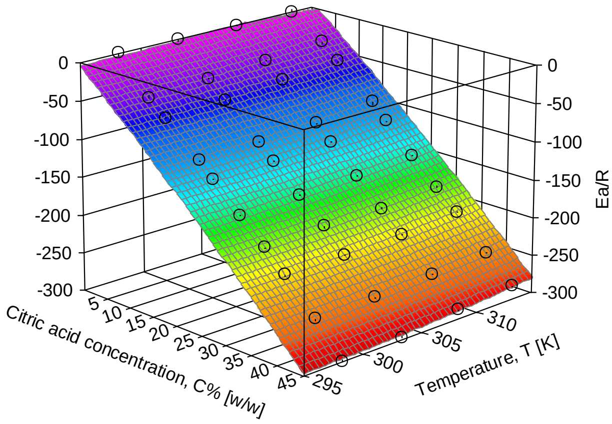

Figure 2. Ea/R values plotted in TableCurve 3D and fitted with polynomial equation type (Equation 9) with residuals

The relative error calculus was used as tool for the comparison between the calculated data generated with the dynamic viscosity final equation and the existing tabular data (Table 9). The obtained results revealed a final average of 0.59% (absolute value) indicating a neglectable difference for the analyzed data.
The ANOVA analysis (Table 10) was used to compare the values of dynamic viscosity tabular and calculated data at 10 different concentrations in 4 temperatures variation. The results presented in Table 10 showed that the sample *P*-value is 0.9997 greater than the targeted alpha 0.05 and the *F crit* value is larger than the *F*-test value. As presented in the case of citric acid density data the null hypothesis is not rejected indicating that is not a statistical difference between tabular and calculated data.

Table 8. Coefficients for equation no. 9

Coefficient	Value	Coefficient	Value
a_1	2803.9225	a_4	-0.014509371
a_2	-7.3756887	a_5	0.032140717
a_3	-19.001965	a_6	0.0052423574

Table 9. For dynamic viscosities of citric acid aqueous solutions the absolute value of relative errors for calculated data versus tabular data

Citric acid concentration, *C* [% w/w]	Dynamic viscosity, $\mu\cdot10^3$ [Pa·s]											
	Temperature, *T* [K]											
	298.15		ε, %	303.15		ε, %	308.15		ε, %	313.15		ε, %
	TD*	CD*		TD	CD		TD	CD		TD	CD	
0	0.894	0.907	1.49	0.800	0.807	0.92	0.722	0.721	0.14	0.658	0.647	1.66
6.43	1.045	1.030	1.36	0.920	0.914	0.56	0.813	0.814	0.21	0.725	0.729	0.60
9.94	1.118	1.106	1.01	0.985	0.980	0.43	0.869	0.872	0.37	0.772	0.779	1.00
16.99	1.280	1.281	0.13	1.131	1.132	0.12	1.002	1.004	0.21	0.885	0.895	1.14
19.82	1.365	1.361	0.27	1.205	1.201	0.31	1.068	1.063	0.38	0.943	0.947	0.45
25.18	1.532	1.528	0.20	1.345	1.345	0.06	1.193	1.189	0.30	1.059	1.056	0.22
30.00	1.693	1.701	0.48	1.482	1.494	0.83	1.331	1.317	0.99	1.179	1.168	0.90
34.00	1.843	1.862	1.04	1.631	1.632	0.10	1.445	1.437	0.53	1.275	1.272	0.23
39.94	2.122	2.136	0.66	1.857	1.867	0.57	1.632	1.639	0.46	1.454	1.447	0.45
44.99	2.432	2.407	1.02	2.120	2.099	0.96	1.825	1.839	0.76	1.613	1.619	0.41
	Average ε, %		0.76	Average ε, %		0.48	Average ε, %		0.43	Average ε, %		0.70

* TD – tabular data, CD – calculated data

Table 10. The ANOVA test summary

SUMMARY	Temperature, *T* [K]				Total	
	298.15	303.15	308.15	313.15		
Tabular data						
Count	10	10	10	10	40	
Sum	15.324	13.476	11.9	10.563	51.263	
Average	1.5324	1.3476	1.19	1.0563	1.281575	
Variance	0.243082	0.181768	0.133103	0.102487	0.184821	
Calculated data						
Count	10	10	10	10	40	
Sum	15.32305	13.47675	11.89911	10.56272	51.26163	
Average	1.532305	1.347675	1.189911	1.056272	1.281541	
Variance	0.2425	0.180038	0.134774	0.102028	0.184565	
ANOVA						
Source of Variation	*SS**	*df**	*MS**	*F*	*P-value**	*F crit*
Sample	2.34E-08	1	2.34E-08	1.42E-07	0.9997	3.973897
Columns	2.528057	3	0.842686	5.108037	0.002922	2.731807
Interaction	9.3E-08	3	3.1E-08	1.88E-07	1	2.731807
Within	11.87802	72	0.164973			

* *SS* – sum of squares, *df* – degrees of freedom, *MS* – mean square, *P-value* – level of significance

Table 11. Coefficients for equation no. 11

Coefficient	Value	Coefficient	Value
b_1	-0.85692331	b_4	0.0004995215
b_2	-0.00043388783	b_5	-0.18401808
b_3	0.14271232		

By plotting directly the tabular data for the dynamic viscosity in TableCurve 3D® v.4 software an equation for the response surface was generated. The Equation 11 is a linear equation, Rank 5, Eqn. 1025 in TableCurve 3D® v.4 library with a precision of R^2 = 0.99950889, FitSdErr = 0.01056894, Fstat. = 17808.03. Its coefficients are presented in Table 11.

$$\mu = \frac{b_1 + b_2 \cdot C + b_3 \cdot \ln T}{1 + b_4 \cdot C + b_5 \cdot \ln T} \qquad (11)$$

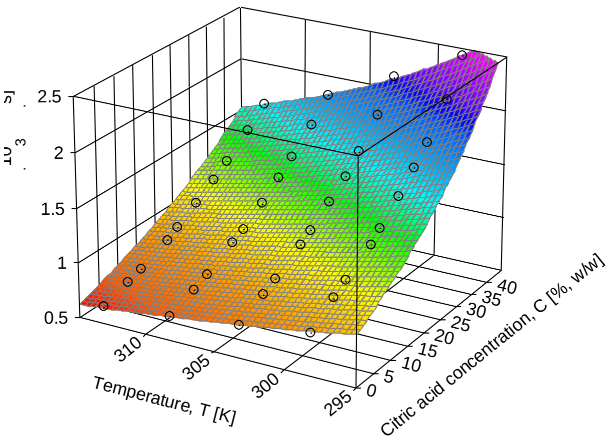

Figure 3. Citric acid aqueous solutions dynamic viscosity values plotted in TableCurve 3D and fitted with linear equation type (Equation 11) with residuals

Combining the models developed for the calculation of dynamic viscosity and density of citric acid aqueous solutions, the kinematic viscosity (ν) can be calculated using equation 12:

$$\nu = \frac{\mu}{\rho} \, [\mathrm{m^2 \cdot s^{-1}}] \qquad (12)$$

4. CONCLUSIONS

The approach of the realized work leaded to mathematical relations with good adjustments to tabular existing data. For density two equations were formulated with average relative errors (absolute value) of 0.03% (Equation 4) and respectively R^2 = 0.9999 and average relative errors (absolute value) of 0.01% (Equation 5) for intervals of temperature of 298.15 to 313.15 K and dry matter concentration range between 6 to 45%. Dynamic viscosity variation is well described by an equation based on Arrhenius mathematical model with average relative errors of 0.59% (Equation 10) generated in the same range of temperature and citric acid concentration.

The proposed mathematical models can be loaded in the common or dedicated PC software and for targeted concentrations and temperatures the values of the studied thermophysical properties can be found easier and with a higher precision than using the existing experimental data in tabular form or graphic form. More if considering that for the tabular experimental data when values are not founded an inter- or extrapolation calculus is needed and for graphic form a software digital extraction of represented values is necessary.

REFERENCES

[1] Angumeenal, A.R., Venkappayya, D.: An overview of citric acid production, *LWT - Food Science and Technology*, 2013, 50 (2), 367-370;

[2] Berovic, M., Legisa, M.: Citric acid production, in Biotechnology Annual Review (El-Gewely, M.R.s: El-Gewely, M.R.), Elsevier, 2007, 303-343;

[3] Dhillon, G.S., Brar, S.K., Verma, M., Tyagi, R.D.: Apple pomace ultrafiltration sludge – A novel substrate for fungal bioproduction of citric acid: Optimisation studies, Food Chemistry, 2011, 128 (4), 864-871;

[4] Sauer, M., Porro, D., Mattanovich, D., Branduardi, P.: Microbial production of organic acids: expanding the markets, Trends in Biotechnology, 2008, 26 (2), 100-108;

[5] El-Abyad, M.S., Hamissa, F.A., Gad, A.S.: Treatment of beet molasses for citric acid production by a potent strain of Aspergillus niger van Tieghem, Bioresource Technology, 1992, 39 (2), 191-197;

[6] Saha, M.L., Takahashi, F.: Continuous citric acid fermentation by magnetic rotating biological contactors using Aspergillus niger AJ 117173, Journal of Fermentation and Bioengineering, 1997, 84 (3), 244-248;

[7] Paul, G.C., Priede, M.A., Thomas, C.R.: Relationship between morphology and citric acid production in submerged Aspergillus niger fermentations, Biochemical Engineering Journal, 1999, 3 (2), 121-129;

[8] Papagianni, M., Mattey, M.: Modeling the mechanisms of glucose transport through the cell membrane of Aspergillus niger in submerged citric acid fermentation processes, Biochemical Engineering Journal, 2004, 20 (1), 7-12;

[9] Papanikolaou, S., Galiotou-Panayotou, M., Fakas, S., Komaitis, M., Aggelis, G.: Citric acid production by Yarrowia lipolytica cultivated on olive-mill wastewater-based media, Bioresource Technology, 2008, 99 (7), 2419-2428;

[10] Imandi, S.B., Bandaru, V.V.R., Somalanka, S.R., Bandaru, S.R., Garapati, H.R.: Application of statistical experimental designs for the optimization of medium constituents for the production of citric acid from pineapple waste, Bioresource Technology, 2008, 99 (10), 4445-4450;

[11] Khosravi-Darani, K., Zoghi, A.: Comparison of pretreatment strategies of sugarcane baggase: Experimental design for citric acid production, Bioresource Technology, 2008, 99 (15), 6986-6993;

[12] Kumar, D., Jain, V.K., Shanker, G., Srivastava, A.: Citric acid production by solid state fermentation using sugarcane bagasse, Process Biochemistry, 2003, 38 (12), 1731-1738;

[13] Kumar, D., Jain, V.K., Shanker, G., Srivastava, A.: Utilisation of fruits waste for citric acid production by solid state fermentation, Process Biochemistry, 2003, 38 (12), 1725-1729;

[14] Sassi, G., Ruggeri, B., Specchia, V., Gianetto, A.: Citric acid production by A. niger with banana extract, Bioresource Technology, 1991, 37 (3), 259-269;

[15] Jianlong, W., Xianghua, W., Ding, Z.: Production of citric acid from molasses integrated with in-situ product separation by ion-exchange resin adsorption, Bioresource Technology, 2000, 75 (3), 231-234;

[16] Kurita, O., Fujiwara, T., Yamazaki, E.: Characterization of the pectin extracted from citrus peel in the presence of citric acid, Carbohydrate Polymers, 2008, 74 (3), 725-730;

[17] Vriesmann, L.C., Teófilo, R.F., Lúcia de Oliveira Petkowicz, C.: Extraction and characterization of pectin from cacao pod husks (Theobroma cacao L.) with citric acid, LWT - Food Science and Technology, 2012, 49 (1), 108-116;

[18] Mosqueda-Melgar, J., Raybaudi-Massilia, R.M., Martín-Belloso, O.: Non-thermal pasteurization of fruit juices by combining high-intensity pulsed electric fields with natural antimicrobials, Innovative Food Science & Emerging Technologies, 2008, 9 (3), 328-340;

[19] Schirmer, B.C., Heiberg, R., Eie, T., Møretrø, T., Maugesten, T., Carlehøg, M., Langsrud, S.: A novel packaging method with a dissolving CO2 headspace combined with organic acids prolongs the shelf life of fresh salmon, International Journal of Food Microbiology, 2009, 133 (1–2), 154-160;

[20] Behm, F.M., Schur, C., Levin, E.D., Tashkin, D.P., Rose, J.E.: Clinical evaluation of a citric acid inhaler for smoking cessation, Drug and Alcohol Dependence, 1993, 31 (2), 131-138;

[21] Stops, F., Fell, J.T., Collett, J.H., Martini, L.G., Sharma, H.L., Smith, A.-M.: The use of citric acid to prolong the in vivo gastro-retention of a floating dosage form in the fasted state, International Journal of Pharmaceutics, 2006, 308 (1–2), 8-13;

[22] Schilling, S.U., Bruce, C.D., Shah, N.H., Malick, A.W., McGinity, J.W.: Citric acid monohydrate as a release-modifying agent in melt extruded matrix tablets, International Journal of Pharmaceutics, 2008, 361 (1–2), 158-168;

[23] Yokoyama, A., Yamamoto, S., Kawasaki, T., Kohgo, T., Nakasu, M.: Development of calcium phosphate cement using chitosan and citric acid for bone substitute materials, Biomaterials, 2002, 23 (4), 1091-1101;

[24] Vieira, M.G.A., da Silva, M.A., dos Santos, L.O., Beppu, M.M.: Natural-based plasticizers and biopolymer films: A review, European Polymer Journal, 2011, 47 (3), 254-263;

[25] Chung, E.J., Sugimoto, M.J., Ameer, G.A.: The role of hydroxyapatite in citric acid-based nanocomposites: Surface characteristics, degradation, and osteogenicity in vitro, Acta Biomaterialia, 2011, 7 (11), 4057-4063;

[26] Chen, Y.X., Lin, Q., Luo, Y.M., He, Y.F., Zhen, S.J., Yu, Y.L., Tian, G.M., Wong, M.H.: The role of citric acid on the phytoremediation of heavy metal contaminated soil, Chemosphere, 2003, 50 (6), 807-811;

[27] Ibeh, B., Zhang, S., Hill, J.M.: Effect of citric acid on the synthesis of tungsten phosphide hydrotreating catalysts, Applied Catalysis A: General, 2009, 368 (1–2), 127-131;

[28] Rinaldi, N., Kubota, T., Okamoto, Y.: Effect of citric acid addition on the hydrodesulfurization activity of MoO3/Al2O3 catalysts, Applied Catalysis A: General, 2010, 374 (1–2), 228-236;

[29] Li, H., Li, M., Chu, Y., Liu, F., Nie, H.: Essential role of citric acid in preparation of efficient NiW/Al2O3 HDS catalysts, Applied Catalysis A: General, 2011, 403 (1–2), 75-82;

[30] aSimion, A.I., Dobrovici, P., Grigoraş, C.G., Rusu, L.: Modeling of the Thermo-Physical Properties of Aqueous Sucrose Solutions I. Density and Dynamic

and Kinematic Viscosity, Annals. Food Science and Technology, 2011, 12 (2), 225-232;

[31] bSimion, A.I., Dobrovici, P., Rusu, L., Gavrilă, L.: Modeling of the Thermo-Physical Properties of Grapes Juice III. Viscosity and Heat Capacity, Scientific Study & Research - Chemistry & Chemical Engineering, Biotechnology, Food Industry, 2011, XII (4), 409-420;

[32] cSimion, A.I., Grigoraş, C.G., Rusu, L., Dabija, A.: Modeling of the Thermo-Physical Properties of Aqueous Sucrose Solutions II. Boiling Point, Specific Heat Capacity and Thermal Conductivity, Food and Environment Safety, 2011, X (4), 49-56;

[33] Kharat, S.J.: Density, viscosity, conductivity, ultrasonic velocity, and refractive index studies of aqueous solutions of citric acid at different temperatures, International Journal of Applied Chemistry, 2008, 4 (3), 223-235.