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MODELS AND CHARTS FOR ESTIMATION OF SOLUTIONS OF SULPHURIC ACID AS GENERATOR OF CONSTANT RELATIVE HUMIDITY AND CORRESPONDING WATER ACTIVITY VALUES IN AN ENCLOSED CONSTANT TEMPERATURE ENVIRONMENT

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Abstract

This paper seeks to comprehensively provide quantitative models and system of charts developed by computerized regression and interpolation for using solution of sulphuric acid as a sole and cost-efficient desiccant, which at different concentrations (from 0 to 100%) and temperatures (from 0 to 100°C), can be employed to generate and maintain reliable relative humidity (R.H.%) and corresponding water activity (a_w) values to achieve any desired experimental test- environment within a sealed hygrostatic container in a constant temperature incubator. The models and charts developed were successfully verified and validated. Therefore, the models and charts are rationally good for estimating solutions of sulphuric acid (in % concentration) for generating desired constant relative humidity (R.H.%) and corresponding water activity (a_w) environments.

Keywords: Models, Charts, Sulphuric Acid, Relative Humidity, Water Activity

Introduction

The need often arises in food and allied laboratories for generating and maintaining constant relative humidity and temperature experimental-test environments. Examples of this abound in shelf-life storage studies for food products, trial-tests for food packages and in experiments for equilibrium moisture isotherm determination (Covance Inc., 2013; Medallion Labs, 2017). For this purpose, a range of relatively expensive chemicals of questionable long-term storage stability, with varying temperature-dependent hygroscopicity, are employed in sealed hygrostatic containers held at constant temperature in an incubator. Stocking the significant array of chemicals involved for extended periods of time is not only expensive but could pose safety challenges in storage. As a stable, low-cost, readily available and easy-to-store desiccant-chemical, sulphuric acid provides a robust response to these challenges. It is a sole and relatively inexpensive chemical with demonstrated capacity for generating relative humidity (R.H.%) and corresponding water activity (a_w) values in the full-range (0 to 100%) at temperatures(0 to 100 ^{0}C) well within the range normally encountered in food storage tests. It is therefore convenient and cost-effective to use. Wilson's (1921) comprehensive work served to establish the properties of sulphuric acid solutions as universal agents for relative humidity generation and maintenance in test environments, facilitating its usage for this purpose in laboratories in the US. The objective of this short research report is to provide a template for the application of sulphuric acid for generating R.H. (%) on a comprehensive and universalized basis derived from computer-aided regressions and re-plotting of the data of Wilson (1921). This is done and presented to ease routines in laboratories employing sulphuric acid for relative humidity and corresponding water activity generation.

Methodology

Generation of Data and Curves that Relate Relative Humidity (%) and % Solution of Sulphuric Acid (H_2SO_4) in the Temperature Range, 0 to 100 ^{0}C

From the data of Wilson (1921) relating relative humidity (%) and % solution of sulphuric acid (H_2SO_4) at temperatures of 0, 25, 50 and 75 ^{0}C, the values of R.H. (%) were regressed against the specified temperature range at 0% solution of H_2SO_4acid using Microsoft Excel ™.From the curve produced, values of R.H. (%) corresponding to 40, 45 and 100 ^{0}C were generated by interpolation and recorded. This process was repeated at 5 to 80 R.H. (%). The data obtained were used to plot curves relating R.H. (%) and % solution of H_2SO_4acid at 0, 25, 40, 45, 50, 75 and 100^{0}C.

Generation of Data and Curves Relating Specific Gravity (SG) and % Solution of Sulphuric Acid (H_2SO_4) in the Temperature Range, 0 to 100 ^{0}C

The procedure applied in the previous methodology was repeated in respect of the values of specific gravity (SG) instead of R.H. (%). However, unknown values of SG at various % solution of H_2SO_4 acid were generated using computerized regression of SG against % solution of H_2SO_4 acid at each selected temperature. The resulting data were used to plot curves relating SG and % solution of H_2SO_4 acid for the following temperatures: 0, 25, 40, 45, 50, 75 and 100 ^{0}C.

Analysis of Data

Based on the nature of the generated curves, Equations 1 and 2 were selected as models to describe the functional relationships between R.H. (%) and % solution of H_2SO_4; and between SG and % solution of H_2SO_4 acid, respectively at different temperatures:

$Y_1 = a\text{x}^3 + b\text{x}^2 + c\text{x} + d$ ……………....1

$Y_2 = n.\text{e}^{m.\text{x}}$……………….....................2

Where: Y_1 = relative humidity (%), Y_2 = specific gravity (SG), x = % solution of H_2SO_4 acid and *a, b, c* are coefficients; *d* and *n* are constants; and *m* = slope.

Data were fitted into the models using Statistical Package for Social Scientists (SPSS) Version 20. Each model and its respective regression coefficients and constants were found.

Verification and Validation of Models

The models were verified and validated using the following statistical computations and analyses:

(i) Regression analysis to compute the coefficient of determination (R^2) and coefficient of correlation (r), which are embedded in SPSS (Frank and Altheon, 1995).

(ii) Analysis based on reduced Chi-square (χ_c^2), mean bias error (MBE), root mean square error (RMSE), coefficient of residual mass (CRM) and modelling efficiency (EF) (Loague and Green, 1991; Legates and McCabe Jr., 1999; Dermir *et al*., 2004; Arumuganathan *et al.*, 2009).

These values were obtained using Equations 3 to 7:

Reduced Chi-square (χ_c^2):

$$(\chi_c^2) = \frac{\sum_{\text{i}=1}^{\hat{\text{N}}}(\text{MR}_{\text{exp}} - \text{MR}_{\text{pre}})}{\hat{\text{N}} - \text{Z}} \quad …………………3$$

Mean bias error (MBE):

$$\text{MBE} = \frac{1}{\hat{\text{N}}}\sum_{\text{i}=1}^{\hat{\text{N}}}(\text{MR}_{\text{exp}} - \text{MR}_{\text{pre}})^2 \quad ..………4$$

Root mean square error (RMSE)

$$\text{RMSE} = (\text{MBE})^{1/2} ……………………….5$$

Coefficient of residual mass (CRM)

$$\frac{\sum_{\text{i}=1}^{\hat{\text{N}}}\text{MR}_{\text{exp}} - \sum_{\text{i}=1}^{\hat{\text{N}}}\text{MR}_{\text{pre}}}{\sum_{\text{i}=1}^{\hat{\text{N}}}\text{MR}_{\text{exp}}} \quad ………………6$$

Modelling efficiency (EF)

$$\text{EF} = 1 - \frac{\sum_{\text{i}=1}^{\hat{\text{N}}}(\text{MR}_{\text{exp}} - \text{MR}_{\text{pre}})^2}{\sum_{\text{i}=1}^{\hat{\text{N}}}(\text{MR}_{\text{exp}} - \text{MR}_{\text{exp.mean}})^2} \quad …....7$$

Assuming that the computational data = the experimental values

Where: MR_{exp}= experimental values, MR_{pre} = predicted values, $\text{MR}_{\text{exp.mean}}$ = mean experimental values, $\hat{\text{N}}$ = number of observations, and Z = number of constants; For accurate goodness of fit, the value of R^2 must be equal to r, and also greater than the values ofχ_c^2, MBE and RMSE. Besides, the value of CRM must be close to zero and EF approximately equal to 1 (Dermir *et al*., 2004; Arumuganathan *et al.*, 2009).

Results and Discussion

The data obtained from computerized regression, interpolation and re-plotting of Wilson's (1921) data are presented in Tables 1 (i) and (ii) as well as Figure 1, while the linearized curve of SG against % solution of sulphuric acid, that would aid easy usage, is presented in Appendix 1. It was observed generally that, at constant temperature, % solution of sulphuric acid increased with decrease in R.H(%). At constant % solution of sulphuric acid, increase in temperature increased R.H. (%); whereas at constant % solution of sulphuric acid, specific gravity (SG) decreased with increase temperature. However, at constant temperature, % solution of sulphuric acid increased with increase SG. This implies that any variation in temperature within the incubator will definitely affect relative humidity and the corresponding water activity.

Besides, the regression coefficients, constants and R-squared values of the selected model Equations 1 and 2 at various temperatures were found and are presented in Tables 2 (i) and 2 (ii), respectively.

The functional relationship between R.H. (%) and % solution of sulphuric acid is a typical polynomial of degree 3 (i.e. a cubic curve). Within the temperature range of 0 to 100 ^{0}C, coefficients *a* calculated ranged from 0.00050 to 0.00034; *b* ranged from -0.0615 to -0.0490; *c* ranged 0.5620 to 0.5713; and *d* ranged from 97.562 to 97.826. As observed, the SG varied exponentially with % solution of sulphuric acid, and with constant *n,* which ranged from 0.9748 to 1.0027; and slope (*m*) from 0.0064 to 0.0069 within the temperature range of 0 to 100 ^{0}C.Furthermore, the predicted values obtained using model Equations 1 and

2 with their corresponding regression coefficients and constants in the attempt to verify and validate the models, are as shown in Table 3i and ii. However, statistical parameters for goodness of fit for model Equations1 and 2 are as presented in Table 4.

Table 1i: Tabulation of relationship between % concentrated H_2SO_4 acid and its relative humidity (R.H.%) derived from computerized regression and re-plotting of the data of Wilson (1921)

% H_2SO_4	0 ^{0}C	25 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C	75 ^{0}C	100 ^{0}C
0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
5	98.4	98.5	98.5	98.5	98.5	98.6	98.6
10	95.9	96.1	96.2	96.3	96.3	96.5	96.7
15	92.4	92.9	93.2	93.3	93.4	93.8	94.3
20	87.8	88.5	89.0	89.1	89.3	90.0	90.8
25	81.7	82.9	83.5	83.7	84.0	85.0	86.2
30	73.8	75.6	76.7	76.8	77.2	78.6	80.3
35	64.6	66.8	68.0	68.4	68.9	70.8	73.0
40	54.2	56.8	58.2	58.7	59.3	61.6	64.2
45	44.0	46.8	48.3	48.9	49.5	52.0	54.8
50	33.6	36.8	38.6	39.2	39.9	42.8	46.0
55	23.5	26.8	28.7	29.4	30.0	33.0	36.4
60	14.6	17.2	18.9	19.5	20.0	22.8	25.5
65	7.8	9.8	11.2	11.6	12.0	14.2	16.3
70	3.9	5.2	6.2	6.5	6.7	8.3	9.7
75	1.6	2.3	3.0	3.2	3.2	4.4	5.2
80	0.5	0.8	1.1	1.2	1.2	1.8	2.2

Table 1ii: Tabulation of relationship between % concentrated H_2SO_4 acid and its specific gravity (SG) derived from computerized regression and re-plotting of the data of Wilson (1921)

% H_2SO_4	0 ^{0}C	25 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C	75 ^{0}C	100 ^{0}C
0	1.000	0.987	0.987	0.986	0.986	0.982	0.975
10	1.074	1.068	1.055	1.054	1.054	1.048	1.039
20	1.151	1.143	1.128	1.127	1.127	1.118	1.108
30	1.233	1.223	1.206	1.206	1.206	1.193	1.181
40	1.321	1.309	1.290	1.289	1.289	1.274	1.259
50	1.416	1.401	1.379	1.379	1.379	1.359	1.342
60	1.517	1.500	1.475	1.474	1.474	1.450	1.431
70	1.625	1.606	1.577	1.576	1.576	1.548	1.526
80	1.741	1.719	1.687	1.685	1.685	1.652	1.627

Table 2: Values of regression coefficients/ constants and R-squared values of model equations 1 and 2

(i)	Values	0 ^{0}C	25 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C	75 ^{0}C	100 ^{0}C
	A	5.0 E-4	4.5 E-4	4.3 E-4	4.2 E-4	4.1 E-4	3.8 E-4	3.4 E-4
	B	-0.0615	-0.0586	-0.0570	-0.0560	-0.0550	-0.0520	-0.0490
	C	0.5620	0.5713	0.5710	0.5628	0.5710	0.5590	0.5670
	D	97.826	97.730	97.698	97.722	97.664	97.674	97.562
	R^2	0.9990	0.9990	0.9990	0.9990	0.9990	0.9990	0.9980
(ii)	Values	0 ^{0}C	25 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C	75 ^{0}C	100 ^{0}C
	n	1.0027	0.9975	0.9868	0.9861	0.9861	0.9820	0.9748
	m	0.0069	0.0068	0.0067	0.0067	0.0067	0.0065	0.0064
	R^2	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997

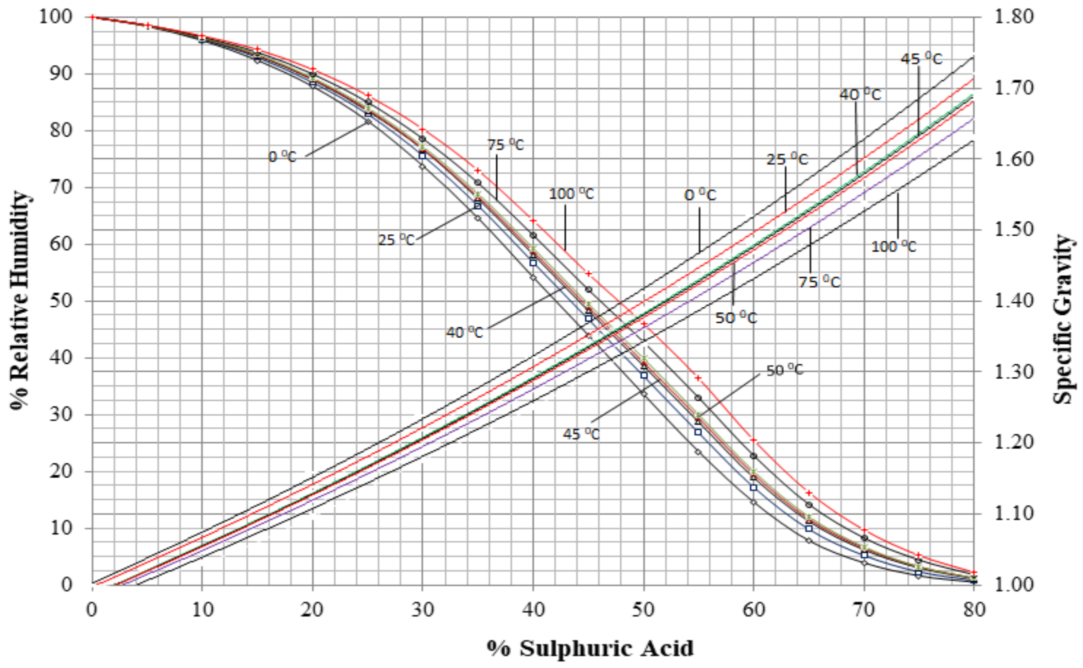

Figure 1: Superimposed curves from relationship between % concentrated H_2SO_4 acid and its (i) specific gravity (SG), and (ii) relative humidity (%).

From Tables 4(i) and (ii), all the values of coefficient of determination (R^2) were approximately equal the coefficient of correlation (r), which showed that $R^2 \approx 1$, and were higher than all the values of root mean square error (RMSE), mean bias error (MBE) and reduced Chi-square (χ_c^2), except χ_c^2 value at 0 ^{0}C for model Equation 1. Values of the coefficient of residual mass (CRM) were almost equal to zero while that of modeling efficiency (EF) was approximately equal 1. These are good properties of a satisfactory quality fit. Therefore, the charts and model Equations 1 to 2 are considered to be reasonably good for estimating values of % solution of sulphuric acid as generator of constant relative humidity R.H. (%) and corresponding water activity (a_w) environment.

Conclusion

Quantitative models and Charts were developed from computerized regression, interpolation and re-plotting of the data of Wilson (1921), which relate % solution of sulphuric acid desiccant with % relative humidity and specific gravity. These models and charts were verified and validated using tools of statistical computation and analyses. The results showed that the models and charts developed are rationally good for estimating % solution of sulphuric acid as a reliable generator of constant relative humidity (R.H.%) and corresponding water activity (a_w) environment.

Table 3i: Tabulation of relationship between % concentrated H_2SO_4 acid and its specific gravity (SG) derived from computerized regression and re-plotting of the data of Wilson (1921)

% H_2SO_4	0 ^{0}C	25 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C	75 ^{0}C	100 ^{0}C
0	1.003	0.998	0.987	0.986	0.986	0.982	0.975
10	1.074	1.068	1.055	1.054	1.054	1.048	1.039
20	1.151	1.143	1.128	1.127	1.127	1.118	1.108
30	1.233	1.223	1.206	1.206	1.206	1.193	1.181
40	1.321	1.309	1.290	1.289	1.289	1.274	1.259
50	1.416	1.401	1.379	1.379	1.379	1.359	1.342
60	1.517	1.500	1.475	1.474	1.474	1.450	1.431
70	1.625	1.606	1.577	1.576	1.576	1.548	1.526
80	1.741	1.719	1.687	1.685	1.685	1.652	1.627

Table 3ii: Tabulation of relationship between % concentrated H_2SO_4 acid and its relative humidity (R.H.%) derived from computerized regression and re-plotting of the data of Wilson (1921)

% H_2SO_4	0 ^{0}C	25 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C	75 ^{0}C	100 ^{0}C
0	97.8	97.7	97.7	97.7	97.7	97.7	97.6
5	99.2	99.2	99.2	99.2	99.2	99.2	99.2
10	97.8	98.0	98.1	98.2	98.3	98.4	98.6
15	94.1	94.6	94.9	95.0	95.2	95.6	96.1
20	88.5	89.3	89.8	89.9	90.4	91.1	91.9
25	81.2	82.4	83.1	83.4	84.0	85.1	86.2
30	72.8	74.3	75.1	75.5	76.4	77.9	79.4
35	63.6	65.2	66.3	66.8	67.9	69.8	71.6
40	53.9	55.6	56.9	57.5	58.7	61.2	63.1
45	44.1	45.8	47.2	47.9	49.3	52.2	54.2
50	34.7	36.0	37.5	38.4	40.0	43.1	45.2
55	25.9	26.8	28.2	29.2	30.9	34.3	36.2
60	18.1	18.2	19.6	20.6	22.5	26.1	27.6
65	11.8	10.9	12.1	13.0	15.0	18.7	19.5
70	7.3	4.9	5.9	6.8	8.8	12.3	12.3
75	5.0	0.8	1.3	2.1	4.1	7.4	6.2
80	5.2	-1.2	-1.3	0.6	1.3	4.2	1.5

Table 4(i): Statistical Parameters for Goodness of Fit for the Model Equation 1

	Values at Various Temp. (^{0}C)						
Parameters	0	25	40	45	50	75	100
R	0.9995	0.9995	0.9995	0.9995	0.9995	0.9995	0.9995
R^2	0.9990	0.9990	0.9990	0.9990	0.9990	0.9990	0.9990
χ_c^2	-1.8000	-0.2000	-0.3000	0.7000	-0.4000	0.1800	-0.4000
MBE	0.7760	0.4040	0.3260	0.1510	0.5240	0.5740	0.6840
RMSE	0.8809	0.6356	0.5710	0.7141	0.7239	0.7576	0.8270
CRM	-0.0049	-0.0006	-0.0010	0.0025	-0.0016	0.0023	-0.0015
EF	0.9983	0.9995	0.9998	0.9995	0.9994	0.9944	0.9993

Table 4(ii): Statistical Parameters for Goodness of fit for the Model Equation 2

	Values at Various Temp. (^{0}C)						
Parameters	0	25	40	45	50	75	100
R	0.9998	0.9998	0.9991	0.9993	0.9996	0.9992	0.9983
R^2	0.9997	0.9996	0.9982	0.9986	0.9992	0.9985	0.9967
χ_c^2	-0.0004	-0.0016	0.0000	0.0000	0.0000	0.0000	0.0000
MBE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
RMSE	0.0010	0.0037	0.0000	0.0000	0.0000	0.0000	0.0000
CRM	-0.0002	-0.0009	0.0000	0.0000	0.0000	0.0000	0.0000
EF	1.0000	0.9998	1.0000	1.0000	1.0000	1.0000	1.0000

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