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**“Evaluation of Norrish equation for correlating the water activity of
highly concentrated solutions of sugars, polyols
and polyethylenglycols”**

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Running head: **Modeling water activity concentrated solutions**

Summary

Norrish's equation, ($a_w = X_w \exp (-K X_s^2)$), where a_w is water activity, X_w and X_s molar fractions of water and solute, respectively, and K is the correlating constant), has been widely used to predict a_w of aqueous non-electrolyte solutions in connection with development of intermediate moisture foods, i.e. food having $a_w \geq 0.85$.

Present work evaluated the ability of Norrish's equation to model the water activity of solutions of sugars, polyols and some polyethyleneglycols, in a wide range of concentration; i.e. from low to highly concentrated solutions.

For sugar and polyols a relatively small modification of the "most accepted" literature parameters K , allowed to fit the data for the whole range of solute concentrations (range of a_w 0.99 to 0.3/0.4) with high accuracy. However, a modified Norrish's model needs to be used to model the behavior of polyethyleneglycols 400 and 600 up to water activities as low 0.4/0.5.

Keywords : Norrish, water activity, non-electrolytes, sugars, polyols, polyethyleneglycol

Introduction

In the past decades, the interest in water activity (a_w) control in intermediate moisture foods stimulated research into the prediction of the water activity in single and mixed electrolyte and non-electrolyte aqueous solutions of interest to the food area (Ross, 1975, Sloan and Labuza, 1976, Chirife et al., 1980, Ferro Fontán and Chirife, 1981, Chirife et al, 1982).

For practical applications the most widely used equation for prediction of water activity in binary non-electrolyte solutions of food interest, is the one of Norrish. In 1966 Norrish proposed a very simple equation for correlating a_w data in non-electrolyte solutions, which may be written in the form,

$$a_w = X_w \cdot \exp (-K X_s^2), \quad \text{eqn. 1}$$

where X_w and X_s are molar fractions of water and solute, respectively and K is a correlating constant, which is supposed to be somewhat related with the chemical structure of non-electrolyte solute. Norrish (1966) developed eqn. (1) on the basis of a very simple equation for calculation of activity coefficients proposed by Hildebrand and Scott (1962) which states that for an aqueous solution,

$$\ln \gamma = K X_s^2 \quad \text{eqn. (2)}$$

where γ is the activity coefficient of water and K is a constant for each solute, and X_s the mole fraction of solute.

Several authors used experimental data of water activity of aqueous non-electrolyte solutions to evaluate the parameter K (eqn. 1) for a number of sugars, polyols, amino acids, etc. and concluded that water activity of binary non-electrolyte solutions may be very well described by Norrish's equation. It is to be noted however, that the equation was tested generally at water activities above 0.85, which as a matter of fact, is the range most concerned with development of intermediate moisture foods (Chirife et al., 1980, 1982).

It is the purpose of present paper to evaluate the usefulness of Norrish equation to describe water activity of highly concentrated (in some cases supersaturated) binary aqueous non-electrolyte solutions of sugars, polyols, polyethylenglycol 400 (PEG 400)

and polyethyleneglycol 600 (PEG 600) from high to very low water activities (i.e. as low as 0.3/0.4).

Materials and Methods

Preparation of solutions

Solutions of glycerol, polyethyleneglycol 400 (PEG 400), and fructose were prepared by adding distilled water to the pure chemicals. Moisture content of glycerol was checked by the Karl-Fisher method (AOAC, 1983) and found to be 0.5 % (this was taken into account in the preparation of corresponding solutions). Some of the fructose solutions were supersaturated and were prepared by heating the sugar and water in hermetically sealed flasks, and then allowing to cool to room temperature.

Glycerol was obtained from Ciccarelli (Buenos Aires, Argentina) and PEG 400 and fructose were from Anedra (Buenos Aires, Argentina).

Determination of water activity

Water activity for aqueous solutions of non-electrolytes were either measured or data obtained from literature. Table 1 gives the source of experimental data for all non-electrolytes studied.

In present work, water activity was determined at 24-26°C using an electronic dew-point water activity meter Aqualab CX2 (Decagon Devices, Pullman, Washington, USA). The equipment was calibrated with saturated salt solutions in the water activity range of interest (Favetto et al., 1983). For each determination three replicates were obtained and the averaged reported. In the case of supersaturated solutions precautions were taken to assure that no crystallization occurred during sample measurement (Zamora et al., 2006).

Statistical analysis

Norrish's parameter K was estimated for each solute using nonlinear least-squares regression according to the downhill simplex method proposed by Nelder and Mead (1965) followed by the Levenberg-Marquardt method (Press et al., 1986). In the case of PEG 400 and PEG 600, and using the above mentioned methodology two parameters of Norrish equation were estimated: constant K and the exponent of X_s .

Models were compared using the coefficient of determination R^2 and the coefficient of variation of the estimation CV%, defined as the standard error of the estimate (i.e. root mean squared error) expressed as percentage of the mean. Data were analyzed using statistical software Infostat version 2007 (Universidad Nacional de Córdoba, Argentina).

Results and discussion

As reported by Rahman (1995), Bell and Labuza (2000) and Sereno et al., (2001) “most accepted” literature values for sucrose, fructose, sorbitol, glycerol, xylitol, PEG 400 and 600 are, 6.47, 2.25, 1.65, 1.16, 1.66, 26.6 and 56, respectively (Chirife et al., 1980, Chirife et al 1982, Alzamora et al., 1994, Chirife and Ferro Fontán, 1980). It is to be noted however, that experimental data used to obtain the above values of parameter K corresponded to relatively high water activities, i.e. $a_w > 0.85$.

Figure 1 (A, B, C) compares experimental and predicted a_w data for glycerol, xylitol and sorbitol solutions at 25°C ; predicted curves were calculated either using the “most accepted” literature parameter K (for each solute), or the K values were calculated in present work using all available experimental data up to very high concentrations (see Table 1).

In the case of xylitol no data at very high concentrations (i.e. supersaturated) were found, so only the predicted curve using the “most accepted” parameter K was shown. As expected, “most accepted” values gives a fairly good description of data for solutions of up to about 60 % w/w, but at higher concentrations (the case of glycerol and sorbitol solutions) predictions showed some deviation from actual data . In the case of xylitol since no data at very high concentrations (i.e. supersaturated) were found, the predicted curve using the “most accepted” value worked very well. Glycerol and sorbitol predictions were improved when corresponding parameters K were calculated using all collected data (up to very high concentrations, see Table 1). This improved fitness was particularly noticed in the case of sorbitol solutions.

Figure 2 (A,B) compares experimental and predicted a_w data for fructose and sucrose at 25°C ; predicted ones being calculated using either the “most accepted” literature K parameters, or K values calculated in present work from experimental data up to very high concentrations (see Table 1). In the case of fructose solutions “most accepted” values gives a fairly good description of data for almost all solutions,

although predictions are slightly improved when the new K values derived from all collected experimental data (Table 1).

The case of sucrose solutions deserves special consideration: either the “most accepted” K value or the one calculated in present work are able to give an excellent description of sucrose behaviour up to 90 % solutions.

Table 2 gives quantitative information of the goodness of fit of Norrish’s equation to predict experimental data up to very high concentrations of binary solutions of sucrose (up to 90 %), fructose (up to 85 %), sorbitol (up to 90 %), glycerol (up to 90 %) and xylitol (up to 65 %) ; using either the “most accepted” values of parameter K (originally obtained from data up to limited concentrations) and those determined here using data up to very high concentrations. As reflected in the value of coefficient of variation, values for parameter K obtained from data at all concentrations (Table 1) give a somewhat better fitness, when the whole range of concentrations is considered. In the case of sorbitol the fitness improvement is noticeable.

Figure 3 (A,B) compares predicted and experimental a_w data for PEG 400 and PEG 600 solutions at 25°C. Predictions using the “most accepted” K parameters are very good up to about 60 % concentration ; however, above this value deviations are quite important. Predictions made using K values calculated from experimental data from low to high concentrations were not sufficient to improve modelling of data for the whole curve.

Table 3 gives the corresponding quantitative information of the goodness of fit of Norrish’s equation to predict experimental data up to very high concentrations of binary solutions of PEG 400 and PEG 600 ; neither the “most accepted” K values or those determined here using all data, allowed to describe the behaviour of PEG’s for the whole range of concentrations. This implies that original Norrish’s equation can not describe a_w data for the whole range of concentrations. However, if the exponent of X_s is assumed to be different from 2, the statistical analysis may be used to evaluate simultaneously not only the best value of K, but also the best exponent of X_s . Under this condition the quality of prediction improved dramatically; as observed in **Table 3**, an exponent value close to 1 instead of 2 (as in the original Norrish equation) allowed a much better modelling of data.

According to Norrish (1966) the parameter K might be correlated with the number of –OH groups in the molecules of sugars and polyols. Chirife et al (1980) found a linear relationship between parameter K and the number of –OH groups for glycerol, erythritol and sorbitol. However, they also noted that this simplifying assumption ignores the influence of groups different from –OH and/or the spatial conformation of the molecule on the K parameter. In addition to the number of –OH groups and spatial configuration, other functional groups also play a role in the a_w -lowering characteristics of a solute molecule. For example, Alzamora et al. (1994) noted that the behaviour of propylenglycol was different from that of polyols (glycerol, erythritol, arabitol, sorbitol) but resembled that of butylene glycols. PEG 400 and 600 are linear chain polymers of oxyethylene units and this may be a main reason for the different behaviour of these glycols at very high solute concentrations as compared to sugars and polyols.

Conclusions

Confirming previous literature results, Norrish's equation with "most accepted" values of parameter K can be satisfactorily used to describe the water activity lowering behaviour up to about 60-65 % concentration for non-electrolytes studied. However, when highly concentrated sugar and polyol solutions were considered, a somewhat different value of parameter K (as calculated in present work) allowed to model the data more accurately along the whole range of water activity.

PEG 400 and PEG 600, however, did not follow Norrish's equation above about 60 % concentration, even when different values of parameter K were used ; a "modified" form of this equation (eqn. 1) in which the exponent of X_s is allowed to be different from the value of 2, had to be used.

Table 1. Source of experimental data for water activity of non-electrolytes solutions *

Solute	Authors	Solute concentration range (% w/w)	N	Total n
Glycerol	Scatchard et al. (1938)	1-56	35	87
	Teng and Lenzi (1974)	4-56	24	
	Ninni et al. (2000)	5-85	17	
	present work	10-90	11	
Xylitol	Comesaña et al. (2001)	14-52	15	28
	Ninni et al. (2000)	5-65	13	
Sorbitol	Teng and Lenzi (1974)	8-42	8	49
	Comesaña et al. (2001)	14-54	16	
	Ninni et al. (2000)	5-65	13	
	Peng et al. (2001)	46-90	12	
Fructose	Peng et al. (2001)	8-58	15	40
	Zamora et al. (2006)	75-83	15	
	present work	10-85	10	
Sucrose	Scatchard et al. (1938)	3-69	24	71
	Teng and Lenzi (1974)	15-51	6	
	Bubnik et al. (1995)	50-90	41	
PEG 400	Ninni et al. (1999)	5-90	11	22
	present work	10-90	11	
PEG 600	Ninni et al. (1999)	5-90	11	11

n: number of experimental data utilized for each non-electrolyte

Table 2 – Calculated parameters of Norrish’s equation for highly concentrated solutions* of sugars and polyols

Solute	Parameter K, () 95 % confidence interval		R ²	CV %**
Glycerol	“Most accepted”	1.16	0.9931	1.43
	Present work	0.81 (0.77-0.84)	0.9984	0.70
Xylitol	“Most accepted”	1.66	0.9989	0.19
Sorbitol	“Most accepted”	1.65	0.9004	4.62
	Present work	0.35 (0.28-0.43)	0.9947	1.07
Fructose	“Most accepted”	2.25	0.9880	2.11
	Present work	1.77 (1.72-1.82)	0.9988	0.68
Sucrose	“Most accepted”	6.47	0.9982	0.75
	Present work	6.01 (6.00-6.03)	0.9999 7	0.10

* in some cases, supersaturated solutions

** coefficient of variation

Table 3 – Calculated parameters of Norrish’s equation evaluated from highly concentrated solutions of polyethyleneglycol (PEG) 400 and 600

Solute	Norrish constant K () 95 % confidence interval		Exponent of X_s		R^2	CV %*
PEG 400	“Most accepted”	26.6		2	0,1879	18.25
	Present work	7.29 (5.52-8.86)		2	0,9036	6.44
	Present work	1.49 (1.19-1.80)	Present work	0.98	0.9916	1.94
PEG 600	“Most accepted”	56		2	0,0383	17.20
	Present work	12.88 (7.82-17.95)		2	0,8659	6.49
	Present work	1.98 (1.29-2.68)	Present work	0.94	0.9889	1.97

* Variation coefficient

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REFERENCES

- Alzamora, S.M., Chirife, J. , & Gerschenson, L.N. (1994). Determination and correlation of the water activity of propylene glycol solutions. *Food Research International*, 27, 65-67.
- AOAC (2003). *Official methods of analysis of AOAC International* (17th ed.). Gaithersburg, MA: AOAC International.
- Bell, L.N., & Labuza, T.P. (2000). Moisture sorption- Practical aspects of isotherm measurement and use. *Amer. Association of Cereal Chemists, Inc.* (second edition).
- Bubnik, Z., Kadlec, P., Urban, D., & Bruhns, M. (1995). *Sugar Technologists Manual*, Verlag Dr.Albert Bartens, pp162. Berlin, Germany.
- Comesaña, J.F., Correa, A., & Sereno, A. (2001). Water activity at 35 °C in sugar + water and sugar + sodium chloride + water systems. *International Journal of Food Science and Technology*, 36, 655-661.
- Chirife, J., Favetto, G., & Ferro Fontán, C. (1982). The water activity of fructose solutions in the intermediate moisture range. *Lebensm. Wiss. U-Technologie*, 15, 159-160.
- Chirife, J., & Ferro Fontán, C. (1980). A study of water activity lowering behavior of polyethylene glycols in the intermediate moisture range. *J. Food Science*, 45, 1717 -
- Chirife, J., Ferro Fontán, C., & Benmergui, E.A. (1980). The prediction of water activity in aqueous solutions in connection with intermediate moisture foods. *J. Food Technology*, 15, 59-70

- Favetto, G. J., Resnik, S. L., & Ferro Fontán, C. (1983). Statistical evaluation of water activity measurements obtained with the Vaisala Humicap humidity meter. *Journal of Food Science*, 487, 534-538.
- Ferro Fontán, C. & Chirife, J. (1981). The evaluation of water activity in aqueous solutions from freezing point depression. *J. Food Technology*, 16: 21-30.
- Hildebrand, J.H., & Scott, R.L. (1962). *Regular Solution*. Prentice Hall, Inc. Englewood Cliffs, N.J.
- Nelder, J.A., & Mead, R. (1965) Downhill simplex method in multidimensions. *Computer Journal*, 7, 308-315.
- Ninni, L., Camargo, M.S., & Meirelles, A.J.A. (1999). Water activity in polyethylene glycol aqueous solutions. *Termochimica Acta*, 328, 169-176.
- Ninni, L., Camargo, M.S., & Meirelles, A.J.A. (2000). Water activity in polyol systems. *J. Chem. Eng. Data*, 45, 654-660.
- Norrish, R.S. (1966). An equation for the activity coefficients and equilibrium relative humidities of water in confectionery syrups. *J. Food Technology*, 1, 25-39.
- Peng, C., Chow, A.H.L., & Chan, C.K. (2001). Hygroscopic study of glucose, citric acid, and sorbitol using an electrodynamic balance : Comparison with UNIFAC predictions. *Aerosol science and Technology*, 35, 753-758.
- Press, W.F., Flannery, P., & Vetterling, W.T. (1986). *Numerical Recipes*. Cambridge University Press.
- Rahman, S. (1995). *Food properties Handbook*, CRC Press, Boca Raton, USA
- Ross, K. D. (1975). Estimation of water activity in intermediate moisture foods. *Food Technology*, 29 (3), 26.

- Scatchard, G., Hamer, W.J., & Wood, E. (1938). Isotonic solutions. I. The chemical potential of water in aqueous solutions of sodium chloride, potassium chloride, sulphuric acid, sucrose, urea and glycerol at 25 °C. *J. Am. Chem. Soc.*, 60, 3061-3070.
- Sereno, A.M., Hubinger, M.D., Comesaña J.F., & Correa, A. (2001). Prediction of water activity of osmotic solutions. *Journal of Food Engineering*, 49, 103-114.
- Sloan, A.E., & Labuza, T.P. (1976). Prediction of water activity lowering ability of food humectants at high a_w . *J. Food Science*, 41, 532-5.
- Teng, T.T., & Lenzi, F. (1974). Water activity data representation of aqueous solutions at 25 °C
- Zamora, M.C., Chirife, J., & Roldán, D. (2006). On the nature of the relationship between water activity and % moisture in honey. *Food Control*, 17, 642-647.

LEGENDS FOR FIGURES

Figure 1

A: Comparison of predicted and experimental a_w data for glycerol solutions at 25°C.

(a) predicted using literature value of K; (b) predicted using K value calculated from all experimental data.

Experimental data: ▲ Scatchard et al. (1938); ✕ Teng and Lenzi (1974); ◆ Ninni et al (2000); ○ present work.

B: Comparison of predicted and experimental a_w data for xylitol solutions at 25°C.

(a) predicted using literature value of K ; (b) predicted using K value calculated from all experimental data.

Experimental data: ○ Comesaña et al. (2001); ◆ Ninni et al (2001).

C: Comparison of predicted and experimental a_w data for sorbitol solutions at 25°C.

(a) predicted using literature value of K; (b) predicted using K value calculated from all experimental data.

Experimental data: ✕ Teng and Lenzi (1974); ▲ Comesaña et al. (2001); ◆ Ninni et al (2001); ○ Peng et al. (2001).

Figure 2

A: Comparison of predicted and experimental a_w data for fructose solutions at 25°C.

(a) predicted using literature K value; (b) predicted using K value calculated from all experimental data.

Experimental data: ▲ Peng et al. (2001); ◆ Chirife and Zamora (2006); ○ present work.

B: Comparison of predicted and experimental a_w data for sucrose solutions at 25°C.

(a) predicted using literature K value; (b) predicted using K value calculated from all experimental data.

Experimental data: ○ Scatchard et al. (1938); ◆ Teng and Lenzi (1974); ▲ Bubnik et al. (1995).

Figure 3

A: Comparison of predicted and experimental a_w data for PEG 400 solutions at 25°C.

(a) predicted using K value from literature; (b) predicted using K value calculated from all experimental data; (c) predicted using K value and exponent of X_2 calculated from all experimental data.

Experimental data: ♦ Ninni et al (2001); ○ present work.

B: Comparison of predicted and experimental a_w data for PEG 600 solutions at 25°C.

(a) predicted using K value from literature; (b) predicted using K value calculated from all experimental data; (c) predicted using K value and exponent of X_2 calculated from all experimental data.

Experimental data: ○ Ninni et al (2001).

Fig. 1

Fig. 2

Fig. 3