Prediction of water activity of osmotic solutions

A.M. Sereno a,*, M.D. Hubinger b, J.F. Comesana c, A. Correa c

a Department of Chemical Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal
b Faculty of Food Engineering, University of Campinas, 13.083-970 Campinas, S. Paulo, Brazil
c Department of Chemical Engineering, University of Vigo, Apdo. 874, 36200 Vigo, Spain

Received 1 June 2000; accepted 1 December 2000

Abstract

Models to correlate and predict water activity in aqueous solutions of single and multiple solutes, including electrolytes, relevant for osmotic processing of foods are reviewed. During the last decade a significant number of theoretical thermodynamic models that are applicable to these systems have been developed and published. Though their use is still limited, their performance is in general very good, similar to the best traditional empirical equations. Their predictive character together with built-in capabilities to work at different temperatures and in some cases pressure suggests that an increased effort to their wide use should take place. It was found that predictions of water activity in aqueous solutions may easily be made with average relative deviations of less than 2%; this value is of the same order or in some cases less than the typical error of current instrumentation available to measure water activity. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Osmotic dehydration; Vapour—liquid equilibria; Water activity; Sugars; Electrolytes; Aqueous solutions; Predictive models

1. Introduction

Osmotic treatments involve the contact of a material, usual of vegetal or animal origin, with a concentrated aqueous solution and include namely osmotic dehydration and solute impregnation processes. These constitute simple food processing operations conducted at ambient or near ambient temperature, which achieve a significant degree of dewatering without phase change and allowing some degree of product formulation and even restructuring.

A special mention should be made about the use of osmotic treatments in the preparation of intermediate moisture foods (IMF) and the so-called fourth generation or minimally processed foods. Such processes have been also referred to as dewatering and impregnation soaking (Raoult-Wack, Rios, Saurel, Giroux, & Guilbert, 1994) and are mainly being used as a pre-treatment introduced in any conventional fruit and vegetable processing, in order to improve quality, reduce energy costs or even formulate final products. Applications have been reported for fish and certain meat products (Collignan & Raoult-Wack, 1994; Bohuon, Collignan, Rios, & Raoult-Wack, 1998; Sabadini, Carvalho, Sobral, & Hubinger, 1998), as well as for fruit products, when the correct choice of solutes and a controlled ratio of water removal and impregnation allow to enhance their natural flavour and colour retention (Raoult-Wack et al., 1994; Guerrero, Alzamora, & Gerschenson, 1996; Alzamora, 1997; Forni, Sormani, Scalise, & Torregiani, 1997; Spiess & Behnilihan, 1998).

As a preliminary step to convective air drying, several studies are found in the recent literature as well as its influence on final food properties (Lenart, 1996; Del Valle, Cuadros, & Aguiler, 1998; Sá, Figueiredo, & Sereno, 1999; Salvatori, Andrés, Chiralt, & Fito, 1999; Lewicki & Lukaszuk, 2000; Krokida, Kiranoudis, Maroulis, & Marinos-Kouris, 2000). The combination of osmotic dehydration to some less common drying steps, such as microwave drying (Venkatachala- pathy & Raghavan, 1999) and freeze-drying (Karatheos, Anglea, & Karel, 1996) has also been described.

Osmotic pre-treatments may be used before vacuum frying, by immersion in solutions of high osmotic pressure (Spiess & Behnilihan, 1998), the effect on mass transfer rates of high hydrostatic pressure (HPP) processing, previous to osmotic treatment of vegetable tissues was also investigated (Rastogi & Niranjan, 1998; Rastogi, Angersbach, & Knorr, 2000).

* Corresponding author. Fax: +351-22-508-1440.
E-mail address: sereno@fe.up.pt (A.M. Sereno).

0260-8774/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S 0 2 6 0 - 8 7 7 4 ( 0 0 ) 0 0 2 2 1 - 1
The transfer of mass, water and solutes observed during the contact of a solid material with an osmotic solution is due to differences in chemical potential inside and outside the material, usually expressed in terms of the corresponding activity coefficients. As dehydration is the main objective of osmotic treatments, the activity of water in both the material and the solution and its prediction is of major importance. This relevance is particularly emphasised when mathematical models are used to describe the process. For cellular materials, as is the case of most foods, water transfer takes place in the vicinity of the cell through the semi-permeable cell membrane (Le Maguer, 1988); again difference of water activity in both sides governs its physical behaviour and mass transport.

The thermodynamic description of these osmotic solutions has been the object of intense research all along the last century, particularly those involving sugars and/or salts. Excellent reviews of such efforts have been written by Van den Berg and Bruin (1981) and Le Maguer (1992) to mention only two papers. Most thermodynamic models used to describe vapour-liquid equilibrium of osmotic solutions are based on relations involving Gibbs free energy of the system. Of particular interest is the excess Gibbs energy ($G^E$) and for each of the components the partial molar excess Gibbs energy ($g^E_i$), both allowing a convenient way to quantify the deviations from ideal behaviour.

From $G^E$, a large number of physical parameters may be calculated such as water and solute activities, partial equilibrium properties (solubility, relative volatility, etc.) and others (Le Maguer, 1989).

The activity of water in aqueous solutions is defined as (Prausnitz, Lichtenhaler, & Azevedo, 1986):

$$a_w(T,P,x) = \gamma_w(T,P,x)x_w = \frac{f_w(T,P,x)}{f_w^0(T,P^0,x^0)},$$

where $a_w$ is the water activity, $x_w$ is the mole fraction of water, $\gamma_w$ is the activity coefficient for water, $f_w$, $f_w^0$ are the fugacities of water in the system and at reference conditions, respectively.

It is usually assumed that under normal working conditions of ambient temperature and atmospheric pressure, gas phases behave ideally and so the ratio of fugacities can be taken as the ratio of partial pressures (Reid, Prausnitz, & Poling, 1987):

$$\frac{f_w}{f_w^0} = \frac{p_w}{p_w^0},$$

where $p_w$ and $p_w^0$ are the vapour pressures of water in the system and of pure liquid water at the same temperature, respectively. Under this assumption, from Eq. (1):

$$a_w = \frac{p_w}{p_w^0} = RH \frac{100}{100},$$

where $RH$ is the percent relative humidity of the air layer in equilibrium with the sample. The activity coefficient $\gamma_w$ may be calculated directly from the partial molar excess Gibbs energy of water, $g^E_w$ (Prausnitz et al., 1986):

$$g^E_w = RT \ln \gamma_w,$$

and for the total molar excess Gibbs energy, $g^E$:

$$g^E = RT \sum_i x_i \ln \gamma_i,$$

for an ideal solution all the activity coefficients, $\gamma_i(T,P,x)$, are equal to one, corresponding to an excess Gibbs energy equal to zero.

Several approaches have been used to calculate or estimate excess Gibbs energy in liquid solutions, including empirical models based on solution composition, the use of equations of state extended to the description of condensed phases and probably more often, different theories developed to describe solution structure and interactions among the chemical species. In Table 1 the major methodological groups used by published contributions to the prediction of water activity of solutions are indicated.

Most of the models included in Table 1 are general in themselves and may be used with food and related systems (Prausnitz et al., 1986; Le Maguer, 1992). The
Table 1
Different approaches to calculate $G^\circ$ and activity coefficients

**Empirical equations based on solution composition**
- Simple equations, often including semi-theoretical basis, which often produce reasonable predictions of liquid–vapour and liquid–liquid equilibria; served in some cases as the basis for more complex models: Margules equation, the Wohl expansion, Van Laar equation, Redlich–Kister equation, Scatchard–Hamner equation

**Use of equations of state (EOS)**
- Hu, Liu, Soane, and Prausnitz (1991): use double lattice (Freed & Flory-Huggins) to calculate Helmholtz energy of mixing, used to describe equilibrium in non-polar or slightly polar non-ideal systems
- Wu, Lin, Zhu, and Mei (1969): use modified version of Pitzer (1973) virial EOS with Fowler and Guggenheim (1939) instead of the more common Debye–Huckel contribution of long-range electrostatic forces
- Simonin (1999): uses McMillan–Mayer theory, assuming molecules as hard bodies interacting through van der Waals short range forces; to allow for the presence of polar molecules (alcohols) and weak electrolytes, and a volume exclusion contribution using Carnahan–Starling hard sphere EOS

**Solution theories**
- Van der Waals–van Laar theory: valid only for nearly ideal systems
- Regular solution theory (Hildebrand, 1929; Scatchard, Hamer, & Wood, 1938): systems without interactions among polar molecules (athermal), e.g. hydrocarbons
- Debye and Huckel (1923) introduced a successful description of long-range polar and ionic forces contribution
- Lattice theory due mostly to Guggenheim (1935, 1952) and Eyring and Marchi (1963)
- Flory (1941, 1942) and Huggins (1942) extension of lattice theory to polymer solutions
- Local-composition models, namely Wilson (1964); NRTL model of Renon and Prausnitz (1968); UNIQUAC model of Abrams and Prausnitz (1975)

Difficulties usually arise from the fact that as most food systems are not well characterised both from a chemical and structural point of view, and consequently thermophysical property data required to use (and fit) the models to such systems are not available. One way to overcome these difficulties in practical applications is to look for correlations between these thermodynamic properties and some easy method to measure physical properties. This approach produced a series of empirical and semi-empirical models which provide in many cases excellent results and constitute relevant contributions of widespread use in the food industry (Table 2).

All the models mentioned in Tables 1 and 2 refer to solutions, more specifically aqueous solutions. A parallel effort has been dedicated to the correlation and prediction of sorption isotherms in solid foods; a large number of equations and models used to describe and predict water activity and sorption isotherms of food systems containing solid phases (Van den Berg & Bruin, 1981; Iglesias & Chirife, 1982). Such models were not included here, as only aqueous solutions constituted the scope of this work.

An alternative approach to the use of empirical and semi-empirical equations consists in the application of group contribution methods, namely ASOG (analytical solutions of groups, Derr & Deal, 1969; Kojima & Tochigi, 1979) and UNIFAC (UNIQUAC functional group activity coefficients, Fredenslund, Jones, & Prausnitz, 1975; Larsen, Rasmussen, & Fredenslund, 1987). These two proposals probably constitute the only general accessible predictive technique for water activity of osmotic solutions. Their main advantage is to provide a technique for $a_w$ prediction for complex systems without requiring parameters for each specific compound, but instead characteristic interaction parameters for the chemical groups that constitute each molecule. The effect in the solution of each of such chemical group is assumed to be the same, irrespective of the molecule where it is contained.

The ASOG method, based on the Wilson model (Wilson, 1964), has been used for this purpose by Correa et al. (1994), who obtained good $a_w$ predictions for aqueous solutions of both sugar/polyol and sugar/urea. Kawaguchi et al. (1981, 1982) have combined the method with an hydration model of ionic species originated in aqueous solutions of electrolytes; later Correa et al. (1997) have redefined the groups in solution, obtaining improved predictions for several binary and multicomponent salt solutions.

Attempts to predict water activity using UNIFAC have also been extensively reported. Choudhury and Le Maguer (1986) used this method to predict $a_w$ in glucose solutions and Achard et al. (1992) described its use to estimate activity coefficients in aqueous systems containing sugars and polyols; Catté et al. (1995) used the same group typology as suggested by Correa et al. (1994) to characterise sugars, and successfully estimated several thermodynamic properties. Christensen et al. (1983) and Kikic et al. (1991) applied the same model to predict equilibria in salt solutions. Very interesting extensions to cover organic acids (Velezmaro & Meirelles, 1998), polyethylene glycol and other polyols (Ninni et al., 1999a, 2000), aminoacids (Ninni et al., 1999b) have been developed by Meirelles and co-workers.
Table 2
Models to calculate water activity in aqueous solutions relevant to food systems

1. Empirical equations

- Simple early formulas applicable to the candy industry: Grover and Nicol (1940), Money and Born (1951) and Dunning, Evans, and Taylor (1951).
- Zdanovskii (1936) and Stokes and Robinson (1966) proposed independently, equivalent models, valid, respectively, for electrolytes and non-electrolytes, whose merits were discussed in detail by Chen, Sangster, Teng, and Lenzi (1973).
- Several authors attempted to correlate water activities with freezing point depression, with moderate success: Ferro-Fontán and Chirife (1981), Lerici, Piva, and Rosa (1983) and Chen (1987).
- Lin, Zhu, Mei, and Yang (1996) proposed a simplified formula with two parameters per solute and one additional per binary interaction; Comesaña, Correa, and Sereno (2000) extended to sugars and salts.
- Roa and Tapia (1998) proposed a very simple yet reasonably successful formula with a single parameter per solute in mixed multicomponent solutions.

2. Semi-empirical equations

- A first group includes empirical approximation of deviations from Raoult’s law, Caurie (1985) and the very successful model by Chen (1989, 1990), which unfortunately involves three empirical parameters per solute.
- Based on the identity between equilibrium relative humidity and thermo-dynamic activity, Norrish (1966), developed one of the most successful equations applicable to non-ionic solutes; extensions were made by Chuang and Toledo (1976) and Chirife, Ferro-Fontán, and Bennerugi (1980) calculated an improved set of parameters which has been generally adopted since then.
- Based on the Gibbs–Duhem equation for multicomponent aqueous solutions, Ross (1975) proposed a simple and successful mixing rule to predict water activity of multicomponent solutions; extensions made by Ferro-Fontán, Chirife, and Boquet (1981) and Ruegg and Blanc (1981).

3. Local composition models

- WILSON model has been used in some models combined with other contributions and is the basis of ASOG group contribution method to predict thermodynamic equilibria. Sorrentino, Voilley, and Richon (1986), used it to predict activity coefficients of aroma compounds and Kawaguchi, Kanai, Kajiwara, and Ari (1981, 1982), of electrolytes; Correa, Comesaña, and Sereno (1994) applied to sugar/polysol/urea; later Correa, Comesaña, Correa, and Sereno (1997) applied to electrolyte solutions, introducing modifications to Kawaguchi’s approach.
- UNIFAC model was used by Le Maguer (1981), Saravacos and Marino-Kouri (1990) and Sander, Fredenslund, and Rasmussen (1986), combined with Debye–Hückel contribution and applied to electrolyte systems. Le Maguer (1992) proposed a building block concept to calculate individual molecular parameters. This model is the basis of the well-known UNIFAC group contribution method; Choudhury and Le Maguer (1986) used it with glucose solutions; Gabas and Laguérie (1992) with sugar solutions; Achar, Gros, and Dussap (1992) with sugars and polyols; Catté, Dussap, and Gros (1995) and Peres and Macedo (1997) introduced some improvements to describe sugars; Christensen, Sander, Fredenslund, and Rasmussen (1983) and Kikic, Fermeglia, and Rasmussen (1991) applied to electrolytes. Velezmore and Meirelles (1998) applied the concept to systems of organic acids; Ninini, Camargo, and Meirrelles (1999a, 2000), to polyethylene glycol and other systems with polyols; Ninini, Camargo, and Meirelles (1999b), to aminoacids.

These extensive and successful applications of the two major group contribution methods to predict water activity of osmotic solutions constitute an example, possibly one of the earliest, of the use of advanced thermodynamic models to describe the behaviour of food-related systems.

2. How group contribution methods work

The main principle underlying this technique is the assumption that all chemical functional groups in solution interact with other specific groups in a similar way, independent of the types of groups in presence and of the specific molecules where they are contained. To use the method the first step consists in ‘breaking’ the structure of the molecule in all its basic groups, for which interaction and individual geometric parameters are available. Since then, the method is applied as if the solution was made of known groups instead of unknown molecules.

Since their development the list of identified and well-characterised groups is increasing. Unfortunately some of the compounds found in food-related systems are too complex and sometimes new groups have to be identified and characterised. This happened with sugars. Sugars in aqueous solutions, both monosaccharides, like glucose and fructose, and disaccharides, like sucrose, adopt a cyclic structure made of pyranose and furanose unit rings (Fig. 1). To successfully describe such compounds by the ASOG method, Correa et al. (1994) defined three new groups named GR, FR and CPOH standing for ‘glucose ring’, ‘fructose ring’ and ‘cyclic-polyalcohol’ (OH groups linked to consecutive carbon atoms in a cyclic sugar structure). For polyhydric alcohols (e.g. glycerol, mannitol and sorbitol) a new group POH referring to OH groups linked to consecutive carbon atoms in a linear chain was also adopted. A fifth ‘group’ defined was UREA for the urea molecule, as it could not be adequately represented by a combination of available ASOG groups (Table 3).

The method uses two specific individual group parameters $v_i^{(H)}$ and $v_i$, and four interaction parameters for each binary pair of groups. Table 4 lists the values of these parameters for some relevant compounds.
3. Solutions with electrolytes

Although some of the general models included in Tables 1 and 2 have proved to be able to describe aqueous electrolyte solutions, this group of systems has deserved, from the early stages, a special separate attention. Effective empirical and semi-empirical equations were derived, but their contribution to the theoretical understanding of these systems has been minimal. Several reviews have been published during the last 20 years, focusing particular lines of research; a special mention about the work of Zemaitis, Clark, Rafal, and Scrivner (1986) where much of the published previous information including data are collected and that of Renon (1986). Lohe and Donohue (1997) give a list of such reviews together with a general broad view of recent advances.

Before 1985, most of the works have been conducted along the principles introduced by Debye and Huckel (1923) theories and their modification by Pitzer (1973), Bromley (1973) and Sandler (1977). In terms of new theoretical research on electrolyte systems, modern developments follow, according to Lohe and Donohue (1997), four major lines: (i) extensions to Debye–Huckel theories, which assume the system to be made of charged ions in a continuous dielectric medium, and employ different forms of the Poisson–Boltzman equations to calculate potential energies in the system; (ii) perturbation theories that use a series expansion of the Helmholtz free energy about a given reference state; (iii) integral equation theories that include solutions of the Ornstein–Zernicke equation, namely using the spherical approximation concept and (iv) fluctuation solution or

---

**Table 3**

New ASOG interaction groups

<table>
<thead>
<tr>
<th>Compound</th>
<th>v&lt;sup&gt;TH&lt;/sup&gt;</th>
<th>Groups: v&lt;sub&gt;i&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>POH</td>
<td>Polyalcohol</td>
<td>OH groups linked to consecutive carbon atoms in a linear chain</td>
</tr>
<tr>
<td>FR</td>
<td>Fructose ring</td>
<td>Furanose cyclic structure of fructose in water</td>
</tr>
<tr>
<td>GR</td>
<td>Glucose ring</td>
<td>Pyranose cyclic structure of glucose in water</td>
</tr>
<tr>
<td>CPOH</td>
<td>Cyclic polyalcohol</td>
<td>OH groups linked to consecutive carbon atoms in a cyclic sugar structure</td>
</tr>
<tr>
<td>UREA</td>
<td>Urea</td>
<td>Urea molecule</td>
</tr>
</tbody>
</table>

**Table 4**

Values of v<sup>TH</sup> and v<sub>i</sub> for some compounds considered

<table>
<thead>
<tr>
<th>Compound</th>
<th>v&lt;sup&gt;TH&lt;/sup&gt;</th>
<th>Groups: v&lt;sub&gt;i&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>12</td>
<td>GR:6</td>
</tr>
<tr>
<td>Fructose</td>
<td>12</td>
<td>FR:5</td>
</tr>
<tr>
<td>Sucrose</td>
<td>23</td>
<td>GR:6</td>
</tr>
<tr>
<td>Glycerol</td>
<td>6</td>
<td>POH:3</td>
</tr>
<tr>
<td>Urea</td>
<td>4</td>
<td>UREA:4</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>H2O:1.6</td>
</tr>
</tbody>
</table>

Partial list of ASOG group pair parameters, including the new groups

<table>
<thead>
<tr>
<th></th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>GR</th>
<th>FR</th>
<th>O</th>
<th>CPOH</th>
<th>CH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>OH</th>
<th>POH</th>
<th>Urea</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.7435</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–0.377</td>
</tr>
<tr>
<td>GR</td>
<td>0.4717</td>
<td>1.5856</td>
<td>–</td>
<td>0.8312</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–0.067</td>
</tr>
<tr>
<td>FR</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.5856</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–1.6816</td>
</tr>
</tbody>
</table>
Table 5
Equations for electrolyte solutions

1. Hydration models: ion–solvent interaction is modelled as producing solvated aggregates characterised through the use of solvating numbers and solvating energy; this approach has been applied for many years
- Zdanovskii (1936) and Stokes and Robinson (1966): based on a linear relation existing between the molalities of isopiestic systems of single or mixed solutes
- Robinson and Bower (1965): use specific expressions to describe hydration and association of ions in solution
- Pitzer (1973): a virial development of $G^E$ in terms of molalities of the solutions; is very widely used
- Meissner and TESTER (1972): use a relation of mean ionic activity coefficient and ionic force of the solution through a single parameter per salt
- Bromley (1973): improved previous model including extended Debye–Hückel equation
- Chirife et al. (1980): proposed a relation between solutions of mixed solutes and single solutes of same ionic strength
- Heyrovská (1989): considers the association degree and hydration number as parameters for direct correlation of equilibrium data
- Schoenert (1990a, b) and subsequent work: used expressions of $G^E$ of hydrated and associated ions, modifying Robinson and Stokes hydration model

2. Local composition models: model ion–solvent interaction on a local basis, trying then to generalise to the whole system
- Chen, Britt, Boston, and Evans (1982) and Chen and Evans (1986): use NRTL + Pitzer–Debye–Hückel; good for low and moderate concentrations of strong electrolytes
- Haghitalab and Vera (1991): two parameter non-random model to calculate $G^E$
- Cardoso and O’Connor (1987): combined UNIQUAC+Debye–Hückel contribution
- Kawaguchi et al. (1981, 1982) and Correa et al. (1997): use WILSON based ASOG group contribution coupled with hydration model for cations

3. Aqueous mixed electrolytes: concentrates in developing mixing rules that can be used with single solute models
- Clegg and Pitzer (1992) and Lu and Maurer (1993): combine Debye–Hückel with UNIQUAC for mean ionic activity and osmotic coefficient, proposing a mixing rule for mixed systems

4. Equation of state models: used mostly to predict the behaviour at high temperature and pressures
- Pitzer and Tanger (1989), Anderko and Pitzer (1993), and Economou, Peters, and Arons (1995): equations of state able to predict phase behaviour of electrolyte systems at high temperature
- Ikonomou and Donohue (1986) and Jin and Donohue (1988a, b): introduced the associated-perturbed-anisotropic-chain theory to describe aqueous halides between 200°C and 500°C
- Wu et al. (1969): combine Pitzer virial equation with Fowler and Guggenheim (1939), long-range contribution

Kirkwood–Buff theories, accounting for composition fluctuations in an open system.

From an applied engineering point of view recent results on electrolyte systems may be divided into three major groups (Loche & Donohue, 1997): (i) local composition and hydration models, (ii) empirical and semi-empirical equations of state for electrolyte systems and (iii) equations for mixed electrolytes and mixed solvents. These are summarised in Table 5.

4. Temperature effect on $a_w$

Dependence of activity coefficient on temperature may be expressed in terms of the excess partial molar enthalpy or the partial molar excess heat of mixing as (Prausnitz et al., 1986):

$$\left[ \frac{d \ln \gamma_i}{dT} \right]_\rho = \frac{h^E_i}{RT^2}. \quad (6)$$

After integration between two different temperatures, a form of the well-known Clausius–Clapeyron equation is obtained:

$$\ln \left( \frac{a_{w1}}{a_{w2}} \right)_T = -\frac{h^E_w}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right), \quad (7)$$

when $h^E_w$ is constant along the path $T_1$ to $T_2$.

In spite of this elegant way of expressing temperature dependence, some empirical equations have been proposed (e.g. Scott & Bernard, 1983; Kitic, Jardim, Favetto, Resnik, & Chirife, 1986), often involving a considerable number system specific parameters.

Those models which involve local composition based concepts (Wilson, NRTL, UNIQUAC) as well as equations of state have explicit dependence on temperature (and in some cases pressure), making this dependence automatic.

5. Comparing model predictions with experimental data

As all the required information to apply the models included in Tables 1, 2 and 5 is detailed in the original papers and some of the indicated reviews, they will not be reproduced here; the reader is invited to look at those papers for such information.

Several comparative studies have been presented in the past, most of them involving only a small group of models. It is apparent from these studies that for many systems of growing interest for the food industry, there is still a very important lack of reliable experimental data on thermophysical properties. Experimental techniques to measure them are delicate and very time consuming.
Table 6  
Prediction of water activity in glucose–water solutions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model/Equation</th>
<th>ARD (%)</th>
<th>RMS</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norrish (1966) and Chirife et al. (1980) (parameters)</td>
<td>Norrish (1966)</td>
<td>0.63</td>
<td>0.89</td>
<td>Stokes and Robinson (1966)</td>
</tr>
<tr>
<td>Chen (1989)</td>
<td>Chen (1989)</td>
<td>0.65</td>
<td>0.95</td>
<td>Stokes and Robinson (1966)</td>
</tr>
</tbody>
</table>

Table 7  
Prediction of water activity in sucrose–water solutions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model/Equation</th>
<th>ARD (%)</th>
<th>RMS</th>
<th>Experimental data</th>
</tr>
</thead>
</table>

Fig. 2. Water activity of aqueous glucose solution: experimental data (symbols) and predictive models (lines).

Fig. 3. Water activity of aqueous sucrose solution: experimental data (symbols) and predictive models (lines).

The use of more recent techniques, like group contribution methods or equations of state, has not yet been the object of extensive comparative studies, justifying thus this analysis targetting the case of osmotic solutions. For such a purpose, using some of the more successful models, predictions of water activity for two sugar solutions (glucose and sucrose, Tables 6 and 7 and Figs. 2 and 3), sodium chloride solution (Table 8, Fig. 4) and two mixed solute solutions (sucrose–sodium chloride and glucose–sodium chloride, Tables 9 and 10 and Figs. 5 and 6) were made and compared. These systems are believed to be the most common solutions for osmotic treatment processes.

The meaning of the statistical parameters ARD and RMS in the tables is as follows:

$$\text{ARD} = \frac{1}{n} \sum_{i=1}^{n} \frac{(a_{W_i})_{\text{calc}} - (a_{W_i})_{\text{exp}}}{1 - (a_{W_i})_{\text{exp}}} \times 100,$$  \hspace{1cm} (8)

$$\text{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{(a_{W_i})_{\text{calc}} - (a_{W_i})_{\text{exp}}}{1 - (a_{W_i})_{\text{exp}}} \times 100 \right)^2}.$$  \hspace{1cm} (9)

6. Conclusions

Analysis of the comparative performance of different predictive models for water activity has revealed that
good estimations may be obtained, not only from empirical equations with parameters fitted to experimental data but also from theoretical models derived from expressions of the excess Gibbs free energy and from equations of state.

It is somehow surprising how good the predictions made from group contribution models are. These truly predictive models use group interaction parameters not necessarily calculated from data involving the components of interest. Due to these capabilities, further effort and testing should be devoted to this group of techniques.

For practical applications of osmotic treatments, the most widely used equations for prediction of water activity in binary are the ones of Norrish (1966) and Ross (1975) (see also Lopez-Malo, Palou, Welti, Corte, & Argaiz, 1994; Guerero et al., 1996; Alzamora, 1997; Nieto, Salvatori, Castro, & Alzamora, 1998). Parameters calculated by Chirife et al., 1980 should be preferred for use with Norrish equation. For solutions containing electrolytes, Pitzer (1973) and Chen (1989, 1990) equa-

![Fig. 4. Water activity of aqueous sodium chloride solution: experimental data (symbols) and predictive models (lines).](image)

Table 8

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model/Equation</th>
<th>ARD (%)</th>
<th>RMS</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitzer (1973)</td>
<td>Pitzer (1973)</td>
<td>0.14</td>
<td>0.25</td>
<td>Robinson and Stokes (1965)</td>
</tr>
<tr>
<td>Correa et al. (1997)</td>
<td>ASOG</td>
<td>1.67</td>
<td>2.33</td>
<td>Robinson and Stokes (1965)</td>
</tr>
<tr>
<td>Chen (1989)</td>
<td>Chen (1989)</td>
<td>2.8</td>
<td>3.9</td>
<td>Robinson and Stokes (1965)</td>
</tr>
</tbody>
</table>

Table 9

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model/Equation</th>
<th>ARD (%)</th>
<th>RMS</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen (1990)</td>
<td>Chen (1989) and Ross (1975)</td>
<td>1.25</td>
<td>1.41</td>
<td>Robinson et al. (1970)*</td>
</tr>
<tr>
<td>Comesaña et al. (2000)</td>
<td>Lin et al. (1996)</td>
<td>1.78</td>
<td>1.92</td>
<td>Robinson et al. (1970)*</td>
</tr>
<tr>
<td>Correa et al. (1997)</td>
<td>ASOG</td>
<td>2.48</td>
<td>3.54</td>
<td>Robinson et al. (1970)*</td>
</tr>
</tbody>
</table>

*As reported by Teng and Seow (1981).

Table 10

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model/Equation</th>
<th>ARD (%)</th>
<th>RMS</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen (1990)</td>
<td>Chen (1990)/Ross</td>
<td>1.83</td>
<td>2.66</td>
<td>Comesaña et al. (2000)</td>
</tr>
<tr>
<td>This work</td>
<td>ASOG</td>
<td>8.4</td>
<td>9.3</td>
<td>Comesaña et al. (2000)</td>
</tr>
</tbody>
</table>
tions are recommended. For water activity of multicomponent mixtures good results are obtained using Ross (1975) equation with any of the already mentioned single solute models. Recently Roa and Tapia (1998) have proposed a simple equation, based on the first-order sum of molalities, with a reasonable predictive accuracy.

The use of UNIFAC and ASOG models as well as equations of state, although constituting a good and accurate tool to estimate the activity coefficients of non-electrolyte and electrolyte mixtures, are not yet widely used in everyday practical application of osmotic treatments. The development of computer-aided tools allowing a simpler manipulation of such complex models may contribute to their popularity and should be encouraged.

Acknowledgements

The authors acknowledge the support of project XI12, Programme CYTED, and EU project FAIR-CT96-1118 and of project XUGA 30101B98 of Xunta de Galicia.

References


Towards the extension of UNIFAC to mixtures with electrolytes. *Fluid Phase Equilibria*, 13, 297–309.


1. The chemical potential of water in aqueous solutions of sodium chloridenee potassium chloride, sulphuric acid, sucrose, urea and glycerol at 25°C. *Journal of the American Chemical Society*, 60, 3061–3070.


