Water Activity in Polyol Systems

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Water activities of binary and ternary mixtures containing polyols were measured using an electronic hygrometer with temperature ranging from (10 to 35) °C. The concentrations of the mixtures varied according to the solubility limit for each polyol (D-sorbitol, D-mannitol, xylitol, *meso*-erythritol, and glycerol). Results were compared with the group contribution-based models ASOG and UNIFAC. The predictions using parameters from the literature were poor, probably as a consequence of the strongly polar hydroxyl groups bounded to consecutive carbon atoms in the polyol molecule. Better agreement was obtained by readjusting some of the interaction parameters. The data bank used in this procedure included water activity data as well as polyol solubility data taken from the literature. The best results were achieved using the UNIFAC−Larsen model with an average relative deviation of 0.9% for water activity and solubility data.

Introduction

Polyols are polyhydroxy alcohols or sugar alcohols used in many diverse fields including foods, pharmaceuticals, and cosmetics. The knowledge of the phase equilibria in systems containing biological products, such as polyols, is an important support for modeling and designing industrial processes like concentration and purification in a separation unit. Thermodynamic models have been used for calculating some physicochemical properties—such as water activity—in food systems containing amino acids, sugars, organic salts, and other solutes (Velezmoro and Meirelles, 1998; Ninni et al., 1999a, 1999b; Velezmoro et al., 2000). Water activity is an important physical chemical property in food engineering, since many chemical, enzymatic, and microbiological reactions that influence food stability are dependent on the availability of water.

Group contribution-based models such as UNIFAC (Fredenslund et al., 1975) and ASOG (Kojima and Tochigi, 1979) are considered to provide good results for estimating activity coefficients in the liquid phase. Correa et al. (1994) studied the behavior of some aqueous polyol solutions: water activities (a_w) of binary (polyol + water) and ternary (urea + polyol + water and urea + sugar + water) solutions were measured and results compared with those of the ASOG group contribution model. New specific groups were defined: glucose and fructose rings, urea, polyalcohol, and cyclic polyalcohol. The results showed that readjustment of binary interaction parameters provided better agreements between the model and experimental a_w values when compared with the predictions using the original parameters from Kojima and Tochigi (1979). Recently, Peres and Macedo (1997) have shown that the UNIFAC−Larsen model can be successfully used for calculating thermodynamic properties of aqueous and nonaqueous solutions containing sugars.

In this work, water activity has been measured for the binary (polyol + water) and ternary (polyol + polyol + water) systems using an electronic hygrometer. Furthermore, new parameters for the UNIFAC−Larsen and ASOG models were determined, allowing the calculation of water activity, solubility, and freezing point data of aqueous polyol solutions with low deviations between experimental and calculated values.

Experimental Section

Water activities of binary and ternary aqueous polyol systems were determined from (10 to 35) °C. The following polyols were used: D-sorbitol, D-mannitol, xylitol, *meso*-erythritol, and glycerol. They were analytical grade reagents from SIGMA with purity > 99%. The solutions were prepared by mass percent with distilled water using an analytical balance (Sartorius, Goettingen, Germany) with ±0.1 mg accuracy. The compositions were accurate to ±0.01% approximately in mass fraction. Before these solutions were prepared, the water content in the solid polyols was determined by Karl Fischer titration (Metrohm, Herisau, Switzerland). The amount of water varied from 0.08 to 0.64 mass %, and it was considered for calculating the water concentration in solutions.

An electronic hygrometer AQUA-LAB CX-2 (DECAGON Devices Inc., Pullman, USA) previously calibrated with saturated salt solutions was used for measuring a_w. The temperature inside the hygrometer was regulated at the desired value ± 0.1 °C by circulation of thermostated water from a water bath (Cole Parmer Instrument Co., Chicago, IL). Measurements were made in triplicate with a reproducibility of ±0.001 a_w units.

Results and Discussion

Water Activity. The experimental water activity data obtained in this work for the binary and ternary mixtures are given in Tables 1 and 2, respectively. The concentrations are in mass fraction. For the same mass concentration, it was observed that the polyols with low molecular weight are better water activity depressors than those with high molecular weight. This difference is well visualized at high solute concentrations. The change of a_w with

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10.1021/je990303c CCC: $19.00

Table 1. Water Activity in Binary Polyol Solutions As a Function of Mass Fraction of Polyol (w_2)

water (1) + sorbitol (2)						water (1) + mannitol (2)			
10.0 °C		25.0 °C		35.0 °C		25.0 °C		35.0 °C	
w_2	a_w	w_2	a_w	w_2	a_w	w_2	a_w	w_2	a_w
0.0519	0.996	0.0497	0.997	0.0495	0.996	0.0510	0.996	0.0501	0.995
0.0992	0.992	0.0993	0.992	0.0995	0.991	0.1036	0.991	0.0751	0.992
0.1986	0.979	0.1491	0.986	0.1985	0.978	0.1263	0.987	0.1035	0.989
0.2965	0.960	0.1978	0.977	0.2982	0.961	0.1501	0.985	0.1246	0.987
0.3966	0.934	0.2485	0.970	0.3953	0.937	0.1750	0.982	0.1467	0.983
0.4918	0.899	0.2980	0.960	0.4944	0.901			0.1745	0.980
0.5952	0.844	0.3478	0.949	0.5706	0.862				
		0.3974	0.935	0.6946	0.755				
		0.4468	0.919						
		0.4966	0.897						
		0.5466	0.872						
		0.5955	0.843						
		0.6457	0.803						

water (1) + xylitol (2)						water (1) + erythritol (2)			
10.0 °C		25.0 °C		35.0 °C		25.0 °C		30.0 °C	
w_2	a_w	w_2	a_w	w_2	a_w	w_2	a_w	w_2	a_w
0.0502	0.996	0.0501	0.993	0.0502	0.994	0.0500	0.992	0.0486	0.993
0.1020	0.989	0.0997	0.988	0.1011	0.987	0.1095	0.982	0.0966	0.985
0.2005	0.974	0.1499	0.981	0.1510	0.980	0.1547	0.973	0.1501	0.975
0.3009	0.951	0.1997	0.972	0.2033	0.971	0.2002	0.963	0.2022	0.964
0.3906	0.925	0.2496	0.963	0.2504	0.962	0.2524	0.950	0.2334	0.956
0.5021	0.876	0.2983	0.951	0.2996	0.951	0.2996	0.936	0.2914	0.940
0.5423	0.854	0.3496	0.937	0.3479	0.938	0.3470	0.922	0.3345	0.926
		0.3995	0.921	0.3990	0.922	0.3690	0.912		
		0.4492	0.901	0.4489	0.903				
		0.4995	0.878	0.4969	0.880				
		0.5489	0.849	0.5533	0.850				
		0.5991	0.816	0.5670	0.840				
		0.6490	0.774	0.5993	0.818				

water (1) + glycerol (2)			
25.0 °C		35.0 °C	
w_2	a_w	w_2	a_w
0.0506	0.991	0.0498	0.990
0.0999	0.980	0.1001	0.979
0.1498	0.967	0.1499	0.967
0.1999	0.952	0.1996	0.953
0.2502	0.936	0.2496	0.937
0.3002	0.918	0.2995	0.919
0.3495	0.896	0.3494	0.897
0.3994	0.872	0.3995	0.874
0.4497	0.844	0.4491	0.847
0.4992	0.812	0.4986	0.816
0.5491	0.775	0.5489	0.780
0.5993	0.733	0.5970	0.740
0.6495	0.683	0.6487	0.689
0.6989	0.628	0.6987	0.632
0.7489	0.557		
0.7986	0.483		
0.8487	0.399		

temperature is small. As can be seen in Figure 1, the experimental data for the system containing glycerol are in very good agreement with the available literature data (Scatchard et al., 1938), which were measured using the isopiestic method. The mean relative deviation between these two data sets is 0.1%. Such a result confirms the accuracy of the experimental a_w data measured using the AQUA-LAB CX-2 (DECAGON Devices Inc., Pullman, USA). Similar results were also reported by Velezmoro et al. (2000) and Ninni et al. (1999a) for sugar solutions and poly(ethylene glycol) solutions, respectively. The work of Roa and Daza (1991) also emphasizes the good performance of a prior version of this electronic hygrometer (AQUA-LAB CX-1) for measuring water activity for various kinds of food systems.

The prediction of water activity using different versions of the UNIFAC model (Fredenslund et al., 1975; Larsen et al., 1987) and the ASOG model (Kojima and Tochigi, 1979) was carried out as a first estimate. The group assignments utilized for the polyols in the various attempts are summarized in Table 3. It was observed that the models were not sufficiently accurate to predict values of a_w at high solute concentrations. This poor estimation is attributed to the effect of strongly polar hydroxyl groups bounded to consecutive carbon atoms in the molecule. This suggests that there is an intramolecular proximity effect between these constituent groups, as proposed by Wu and Sandler (1991a, 1991b) and Abildskov et al. (1996). Another reason, also relative to the chemical structure of the polyols, could be referred to the models being unable to distinguish

Table 2. Water Activity in Ternary Polyol Solutions at 25.0 °C

water (1) + xylitol (2) + sorbitol (3)			water (1) + glycerol (2) + mannitol (3)			water (1) + glycerol (2) + sorbitol (3)		
w_2	w_3	a_w	w_2	w_3	a_w	w_2	w_3	a_w
0.0264	0.0249	0.993	0.0254	0.0250	0.991	0.0254	0.0254	0.993
0.0494	0.0491	0.988	0.0376	0.0383	0.988	0.0511	0.0501	0.984
0.0765	0.0756	0.981	0.0509	0.0511	0.982	0.1002	0.1152	0.961
0.1005	0.0994	0.973	0.0610	0.0605	0.979	0.1491	0.1490	0.938
0.1259	0.1245	0.965	0.0770	0.0761	0.974	0.2105	0.1958	0.897
0.1493	0.1485	0.954	0.0872	0.0866	0.970	0.2626	0.2389	0.848
0.1764	0.1779	0.940				0.3039	0.2960	0.780
0.1911	0.1904	0.932				0.3501	0.3480	0.684
0.2266	0.2229	0.908						
0.2494	0.2482	0.887						
0.3013	0.2974	0.827						
0.3262	0.3226	0.787						

water (1) + glycerol (2) + xylitol (3)			water (1) + xylitol (2) + mannitol (3)			water (1) + erythritol (2) + mannitol (3)		
w_2	w_3	a_w	w_2	w_3	a_w	w_2	w_3	a_w
0.0255	0.0251	0.992	0.0249	0.0250	0.993	0.0249	0.0250	0.994
0.0525	0.0505	0.982	0.0499	0.0500	0.987	0.0499	0.0498	0.987
0.1029	0.1023	0.960	0.0749	0.0750	0.980	0.0750	0.0749	0.979
0.1498	0.1503	0.895	0.0999	0.0999	0.972	0.0999	0.1004	0.971
0.2040	0.1977	0.871	0.1248	0.1249	0.964	0.1246	0.1245	0.959
0.2988	0.2998	0.772	0.1398	0.1399	0.957	0.1397	0.1398	0.953
0.3246	0.3249	0.726						

Table 3. Group Assignments for Polyols

	UNIFAC[a]	UNIFAC[b]	ASOG[c]	
	ν_k^i	ν_k^i	ν_k^i	ν_i^{FH}
glycerol	1CHOH, 2CH$_2$OH	2CH$_2$, 1CH, 3OH	2.8CH$_2$, 3POH	6
meso-erythritol	2CHOH, 2CH$_2$OH	2CH$_2$, 2CH, 4OH	3.6CH$_2$, 4POH	8
xylitol	3CHOH, 2CH$_2$OH	2CH$_2$, 3CH, 5OH	4.4CH$_2$, 5POH	10
D-mannitol	4CHOH, 2CH$_2$OH	2CH$_2$, 4CH, 6OH	5.2CH$_2$, 6POH	12
D-sorbitol	4CHOH, 2CH$_2$OH	2CH$_2$, 4CH, 6OH	5.2CH$_2$, 6POH	12

[a] CH$_2$OH and CHOH are groups proposed by Wu and Sandler (1991a,b). [b] CH$_2$, CH, and OH are groups proposed by Skjold-Jorgensen et al. (1979). [c] POH is a group proposed by Correa et al. (1994). ν_k^i is the number of groups k in molecule i. ν_i^{FH} is the number of atoms (other than hydrogen atoms) in molecule i.

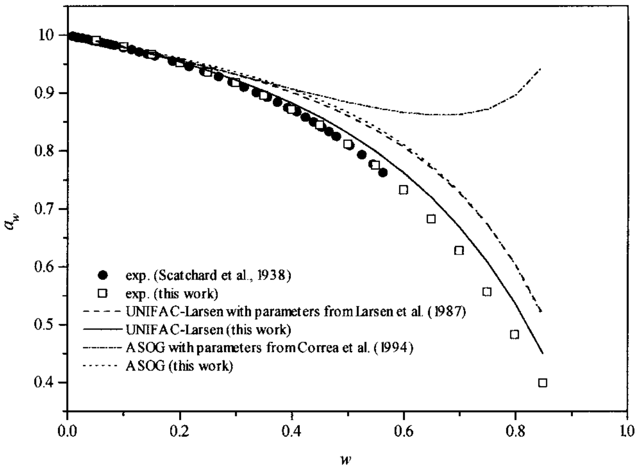

Figure 1. Prediction of water activities in the glycerol−water system.

between the molecular structures of isomers (mannitol and sorbitol).

For the ASOG model with parameters from Correa et al. (1994), the predictions were similarly poor. This could be a consequence of using a restricted range of solute concentrations for the adjustment of the parameters. This was well observed in the system containing glycerol, which presented a mean deviation of 0.8% in a restricted range of water activity (0.998 to 0.875) but a high deviation (15.6%) for the whole concentration range studied in this work (see Figure 1).

Table 4. UNIFAC−Larsen Interaction Parameters

	CH$_2$	CH	OH	H$_2$O
CH$_2$		0.0	972.8[b]	1857.0[b]
CH	0.0		972.8[b]	1857.0[b]
OH	637.5[b]	637.5[b]		278.7[a]
H$_2$O	410.7[b]	410.7[b]	−175.9[a]	

[a] Parameters readjusted in this work. [b] Parameters obtained from Larsen et al. (1987).

An average relative deviation, including all experimental a_w values from this work and from the literature (Scatchard et al., 1938; Robinson and Stokes, 1961; Bower and Robinson, 1963), was found as 2.1% for the ASOG model (with parameters from Correa et al. (1994)), 1.2% for the original UNIFAC model (Skjold-Jorgensen et al., 1979), and 1.8% when the UNIFAC−Larsen model (Larsen et al., 1987) was used in the predictions.

On the basis of these results and considering the proximity effect of the hydroxyl groups, some of the UNIFAC and ASOG interaction parameters were readjusted.

Readjustment of Group Interaction Parameters. To readjust some of the interaction parameters of the UNIFAC and ASOG models, different strategies were used. In the UNIFAC model, we have used the original equation and the UNIFAC−Larsen version. For each version we have assumed two alternatives for the division of groups: the first one proposed by Wu and Sandler (1991a,b) and the second one suggested by Skjold-Jorgensen et al. (1979) (see Table 3). For the ASOG model we have used the group

Table 5. ASOG Interaction Parameters

	CH_2	POH	H_2O	
CH_2		2434.7[a]	−277.3[b]	*n*
		−9.0831[a]	−0.2727[b]	*m*
POH	−2.3184[a]		−42.76[a]	*n*
	−3.2184[a]		−0.2868[a]	*m*
H_2O	−2382.7[b]	257.5[a]		*n*
	0.5045[b]	−0.6705[a]		*m*

[a] Parameters readjusted in this work. [b] Parameters obtained from Kojima and Tochigi (1979).

Table 6. Systems Used for Readjusting the Group Interaction Parameters

aqueous system	temp range/°C	reference data
		Water Activity
D-sorbitol	10−35	this work
D-sorbitol	25	Bower and Robinson, 1963
D-mannitol	25−35	this work
D-mannitol	25	Robinson and Stokes, 1961
xylitol	10−35	this work
meso-erythritol	25−30	this work
		Solubility
D-sorbitol	0−50	Mullin, 1993; Billaux et al., 1991
D-mannitol	0−100	Mullin, 1993; Billaux et al., 1991
xylitol	20−50	Billaux et al., 1991
erythritol	20−25	Röper et al., 1993

assignment proposed by Correa et al. (1994). The binary interaction parameters readjusted in this work are given in Tables 4 and 5 for the UNIFAC−Larsen and ASOG models, respectively.

The other group interaction parameters were set equal to the values available in the literature (Kojima and Tochigi, 1979; Skjold-Jorgensen, 1979; Larsen et al., 1987), and they are also given in Tables 4 and 5 for the UNIFAC−Larsen and ASOG models. To readjust some of the parameters, the Marquardt method (Marquardt, 1963) was used for minimizing the following objective function (OF)

$$\mathrm{OF} = \frac{\sum_{n} |a_{\mathrm{w,calc}} - a_{\mathrm{w,exp}}|}{a_{\mathrm{w,exp}}} + \frac{\sum_{k} |\mathrm{sol}_{\mathrm{calc}} - \mathrm{sol}_{\mathrm{exp}}|}{\mathrm{sol}_{\mathrm{exp}}} \qquad (1)$$

where *n* and *k* are the number of experimental water activity and solubility data, respectively; sol is the solubility; and the subscripts calc and exp mean calculated and experimental values. The systems used for readjusting the interaction parameters are given in Table 6.

The best results were obtained using the UNIFAC−Larsen model with the group assignment proposed by Skjold-Jorgensen et al. (1979). The results calculated by both the UNIFAC−Larsen and ASOG models are shown in Figures 2−4 for the binary systems of xylitol, D-sorbitol, and D-mannitol. The UNIFAC−Larsen model was capable of providing good results even at high solute concentrations. Moreover, in comparison with the obtained results from Correa et al. (1994), the readjustment of the ASOG parameters between the POH group and the other mixture constituent groups improved the calculated a_w values for these systems. In these cases, the use of a wide range of solute concentrations and different types of polyols makes it possible to attain significant interaction parameters for use in calculation of the thermodynamical properties studied.

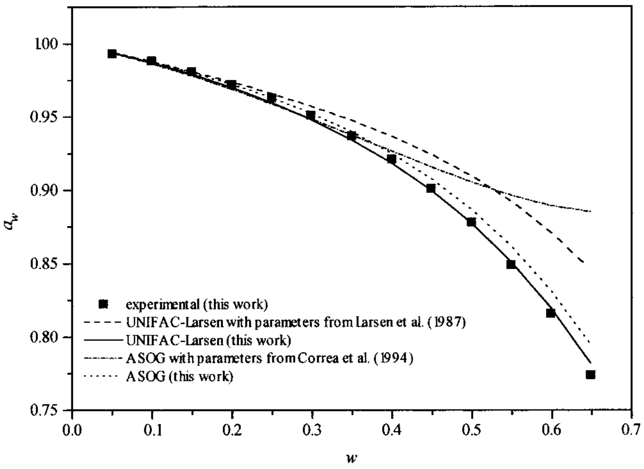

Figure 2. Experimental and calculated water activities for xylitol solutions at 25.0 °C.

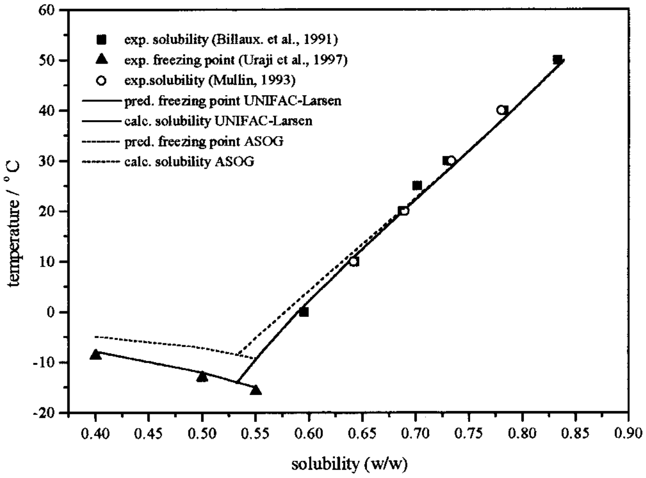

Figure 3. Solid−liquid equilibria for sorbitol aqueous solutions (solubility and freezing point depression).

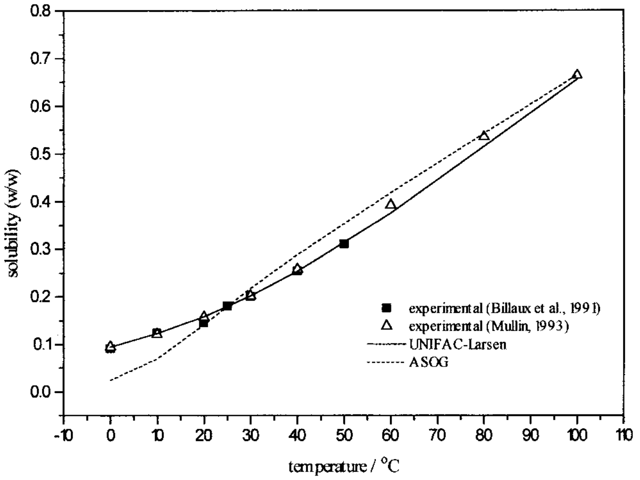

Figure 4. Experimental and calculated solubilities for D-mannitol at different temperatures.

Table 7 shows a comparison between the average relative deviations obtained in this work and those from the literature for water activities. The deviations between experimental and calculated solubilities using the sets of parameters adjusted in this work are given in Table 8.

For the calculation of polyol solubility in water the same equation adopted by Peres and Macedo (1996, 1997) was used. The thermodynamic properties needed for the determination of solubilities are reported in Table 9 as well as the data used for water in the calculations of the freezing

Table 7. Mean Relative Deviations between Experimental and Calculated a_w Data Points

	% deviation				
	UNIFAC−Larsen		ASOG		
aqueous system	Larsen et al. (1987)	this work	Correa et al. (1994)	this work	reference
D-sorbitol	2.51	0.51	3.04	0.64	this work
D-sorbitol	0.68	0.23	0.35	0.12	Bower and Robinson, 1963
D-mannitol	0.08	0.17	0.30	0.16	this work
D-mannitol	0.11	0.06	0.19	0.02	Robinson and Stokes, 1961
xylitol	2.01	0.26	2.11	0.76	this work
meso-erythritol	0.69	0.19	0.42	0.60	this work
avg deviation	1.01	0.24	1.07	0.38	

Table 8. Mean Relative Deviations between Experimental and Calculated Solubility Data

		% deviation		
aqueous system	temp range/°C	UNIFAC−Larsen	ASOG	reference
D-sorbitol	0−50	0.91	1.32	Mullin, 1993; Billaux et al., 1991
D-mannitol	0−100	1.86	20.80	Mullin, 1993; Billaux et al., 1991
xylitol	20−50	0.51	0.80	Billaux et al., 1991
erythritol	20−25	3.23	4.22	Röper et al., 1993
avg		1.63	6.79	

Table 9. Thermodynamic Data of Polyols and Water

polyol	melting temp, T_m/K	enthalpy of fusion, $\Delta_{fus}H$/kJ·mol^{-1}	ΔC_p(25 °C)/ J·K^{-1}·mol^{-1}
sorbitol	**366.5**[a]	30.2	191[a]
mannitol	**439.1**[a]	**56.1**[a]	191[a]
	433.2[b]	53.58,[b], 52.8[c]	290.36[b]
xylitol	**365.7**[a]	**37.4**[a]	157[a]
	367.0[d]	38.0[c]	
erythritol	**390.9**[a]	**39.4**[a]	122[a]
	391.6[b]	42.36[b]	155.42[b]
		40.3[c]	
water	**273.15**[e]	6.002[e]	38.03[e]

[a] Barone et al. (1990). [b] Spaght et al. (1932) (the values for ΔC_p are results from regression of the experimental data). [c] Raemy and Schweizer (1983). [d] Fassman (1975). [e] Daubert and Danner (1985) (the ΔC_p for water was considered constant with temperature).

Table 10. Values of ΔA and ΔB for the Calculations of ΔC_p with Linear Temperature Dependency

	UNIFAC−Larsen		ASOG	
	ΔA	ΔB	ΔA	ΔB
polyol	J·K^{-1}·mol^{-1}	J·K^{-2}·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}
D-sorbitol	214.9	−2.9712	215.7	−4.1643
D-mannitol	215.0	0.0618	225.8	−0.2073
xylitol	128.0	3.3261	124.5	2.7738
meso-erythritol	117.2	1.0924	115.8	1.9598

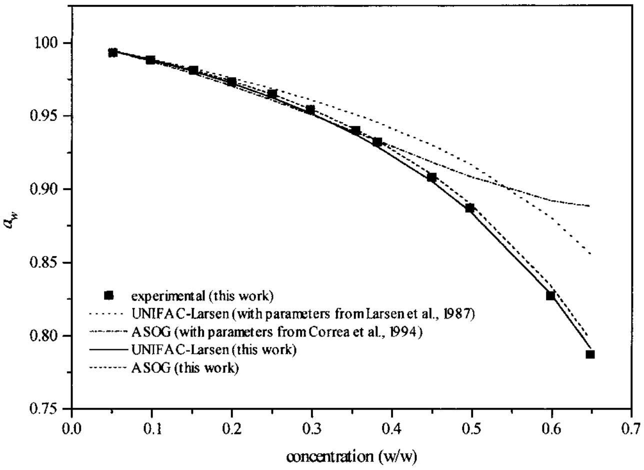

Figure 5. Predictions of water activities for the ternary system water−xylitol−sorbitol at 25.0 °C.

point depression of sorbitol and xylitol solutions. The values in bold type were used in this work. Table 9 also indicates published values for ΔC_p from the literature, and excluding the data for mannitol and erythritol, values were measured at only one temperature. There is only one literature source in which experimental C_p values were measured for a wide range of temperatures. These are for the solid and liquid phases of erythritol and mannitol (Spaght et al., 1932). The other cited literature (Barone et al., 1990) used a group contribution approach to estimate the C_p values for the liquid polyol. Moreover, in some cases, the experimental values taken from distinct literature sources are expressively different. For these reasons we opted for estimating ΔC_p as a linear function of temperature. This assumption was already used in previous works from Catté et al. (1994) and Peres and Macedo (1996, 1997) for systems containing sugars. The expression for representing the difference between the heat capacities of the pure liquid and those of the pure solid polyols (ΔC_p) is given below:

$$\Delta C_p = \Delta A + \Delta B(T - T_{ref}) \qquad (2)$$

where T_{ref} is a reference temperature which was set equal to 25 °C and where ΔA and ΔB are two adjustable parameters. The parameters ΔA and ΔB were adjusted for each polyol using the experimental solubilities at various temperatures taken from the literature (Billaux et al., 1991; Mullin, 1993; Röper, 1993). The values for ΔA and ΔB are presented in Table 10. It should be observed that the ΔA values estimated in this work are relatively close to the experimental ΔC_p values at 25 °C. For instance, in the case of the UNIFAC−Larsen model (with the groups CH_2, CH, OH, and H_2O), a mean relative deviation of about 16% was found between the calculated values and the ΔC_p experimental data at 25 °C. In general, these deviations were higher for the other models used in this work. For example, in the case of the original UNIFAC model, the deviation between the ΔA and ΔC_p values amounts to approximately 35%. Furthermore, the minimum values for the deviation concerning solubility data were obtained for the UNIFAC−Larsen model (with the groups CH_2, CH, OH, and H_2O), as can be seen in Table 8.

It must be stressed that, for the UNIFAC−Larsen model, we readjusted only two temperature-independent interaction parameters between the groups OH/H_2O and H_2O/OH. Otherwise, for the ASOG model, better results were

Table 11. Water Activity Prediction in Polyol Mixtures

		% deviation			
		UNIFAC−Larsen		ASOG	
polyol mixture	a_w range	Larsen et al. (1987)	this work	Correa et al. (1994)	this work
xylitol + sorbitol	0.993−0.787	2.10	0.23	2.16	0.27
glycerol + mannitol	0.991−0.970	0.16	0.08	0.08	0.18
glycerol + sorbitol	0.993−0.684	3.99	0.95	6.21	2.63
glycerol + xylitol	0.992−0.726	4.48	1.87	6.33	3.65
xylitol + mannitol	0.993−0.957	0.35	0.09	0.17	0.14
erythritol + mannitol	0.994−0.953	0.37	0.13	0.16	0.12
glycerol	0.990−0.399	6.30	2.55	15.60	6.40
glycerol[a]	0.998−0.762	2.20	0.88	2.94	2.54
avg		2.49	0.85	4.21	1.99

[a] Scatchard et al. (1938).

Table 12. Experimental and Calculated Eutetic Points of Xylitol and Sorbitol Aqueous Solutions

	experimental[a]		ASOG		UNIFAC−Larsen	
	T/°C	conc/(w/w)	T/°C	conc/(w/w)	T/°C	conc/(w/w)
xylitol	−12.2	0.43	−5.3	0.43	−10.8	0.44
sorbitol	−15.5	0.54	−8.5	0.53	−13.9	0.53

[a] Uraji et al. (1997).

achieved only after the readjustment of four pairs of temperature-dependent interaction parameters.

Predictions with the New Set of Parameters. The experimental freezing point data available in the literature as well as the a_w values of the ternary systems and of the binary system containing glycerol were used only for comparison with predicted values. For freezing point calculations, an expression proposed by Ferro Fontan and Chirife (1981) was used. Table 11 indicates the average mean deviations obtained for the water activities of the ternary mixtures and the binary systems containing glycerol. It can be noted that the deviations for glycerol were higher than those for the ternary systems but significantly lower in comparison to the predictions with parameters from the literature (see Figure 1). Correa et al. (1994) have already commented about the difficulties in obtaining good results for the systems with glycerol. Figure 5 shows calculated and experimental a_w values for the ternary mixture xylitol−sorbitol−water at 25 °C. However, the predictions of freezing point depression did not present the same accuracy, with mean deviations of 10% for the UNIFAC−Larsen model and 47% for the ASOG model. The experimental data are from Uraji et al. (1997), and the results achieved for sorbitol are also presented in Figure 3. The prediction of the eutetic points for xylitol and sorbitol aqueous solutions was also performed. These results are given in Table 12 for the ASOG and UNIFAC−Larsen models. Note that a good prediction for the eutetic point concentration was obtained for both systems.

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Received for review November 11, 1999. Accepted April 10, 2000. This work was supported financially by research grants from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP−Proc. 95/02617-5 + 98/12302-3) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq−Proc. 521011/95-7).

JE990303C