Water Activity in Sorbitol or Xylitol + Water and Sorbitol or Xylitol + Sodium Chloride + Water Systems at 20 °C and 35 °C

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Water activities of aqueous solutions of sorbitol and xylitol, and of these polyols with sodium chloride, were measured and correlated with a simple empirical equation. Parameters for the equation were obtained, and from them, values of water activity were calculated with an average relative deviation of <0.12% for all the systems studied.

Introduction

The importance of water activity (a_w) on food stability is well documented, and although its effects on microbial growth, chemical reactions, and enzyme activity have been described,[1,2] the concept of water activity has been questioned in recent years. One example of such criticism is the fact that food with medium or low moisture content may form systems that do not reach an equilibrium but remain in a metastable and amorphous state, sensitive to temperature changes and moisture contents; another important example is the different microbial response observed at a determined value of a_w, when such value is due to the presence of different solutes.

Chirife and Buera[3] carried out a detailed study of this problem and concluded that, despite the above-mentioned drawbacks, the concept of water activity is still valid, because there is in general a good correlation between its values and microbial growth as well as metabolic activity.

Because water is the major requirement for the already mentioned pernicious processes, it is important to reduce the a_w value in food. This may be achieved with the help of humectants such as some sugars, polyols, and salts.[4,5] Unfortunately some of them have a negative effect on taste and other organoleptic properties. Attempts to combine several solutes were made in order to reduce their individual amount. In other cases their combination can result in a mutual synergistic effect.[4]

In this work values of water activity for the systems sorbitol + water, xylitol + water, sorbitol + sodium chloride + water, and xylitol + sodium chloride + water were measured at 20 °C and 35 °C with an electric hygrometer and correlated with a simple empirical model.[6]

Experimental Section

All chemicals used in this work were analytical grade and were used directly without any further purification (sodium chloride, Merck 99.5% purity; sorbitol, Carlo Erba 98% purity; xylitol, Aldrich 99% purity). Distilled water was obtained from the MILLI-Q 185 PLUS system with a resistivity of 18.2 MΩ·cm. Reagents were previously dried in an oven at 105 °C and subsequently kept in a desiccator

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Table 1. Water Activities for the Systems Sorbitol + Water and Xylitol + Water

sorbitol (1) + water (2)		xylitol (1) + water (2)	
m_1/mol·kg^{-1}	a_w	m_1/mol·kg^{-1}	a_w
t = 20 °C			
1.0068	0.981	1.1055	0.979
1.4724	0.973	1.4689	0.971
2.0064	0.963	2.0278	0.963
2.3385	0.958	2.4178	0.956
2.7113	0.950	3.0146	0.944
3.0087	0.945	3.3405	0.937
3.3388	0.938	3.7092	0.930
3.7145	0.930	4.0716	0.924
3.9851	0.926	4.4729	0.915
4.3182	0.919	4.7516	0.911
5.0533	0.904	5.0783	0.905
5.3043	0.899	5.6611	0.892
5.6480	0.894	6.0230	0.888
6.0600	0.883	6.5786	0.877
6.5674	0.876	7.0017	0.869
7.0722	0.865		
t = 35 °C			
1.0652	0.980	1.1055	0.979
1.4958	0.971	1.4689	0.971
2.0495	0.961	2.0278	0.961
2.3989	0.955	2.4178	0.955
2.7152	0.949	3.0146	0.943
3.0178	0.943	3.3405	0.937
3.4803	0.933	3.7092	0.929
3.7738	0.927	4.0716	0.921
4.0608	0.920	4.4729	0.913
4.3516	0.916	4.7516	0.908
5.0588	0.901	5.0783	0.901
5.3822	0.895	5.6611	0.891
5.6994	0.888	6.0230	0.884
6.1780	0.878	6.5786	0.873
6.5674	0.872	7.0017	0.864
7.0722	0.862		

over silica gel until use. All solutions were prepared from water and reagents by mass using a Scaltec SBA31 analytical balance to 0.1 mg.

Water activities were measured with a Thermoconstanter electric hygrometer (Defensor-Novasina AG) as described by Stamp et al.[7] The hygrometer was previously calibrated using a_w standards supplied by the manufacturer, and this calibration was verified by means of saturated salt solutions at 20 °C[8] and 35 °C.[9] Under these conditions it was determined that an estimated uncertainty

Table 2. Water Activities for the Systems Sorbitol + Sodium Chloride + Water and Xylitol + Sodium Chloride + Water

sorbitol (1) + NaCl (2) + water (3)			xylitol (1) + NaCl (2) + water (3)		
m_1/ mol·kg^{-1}	m_2/ mol·kg^{-1}	a_w	m_1/ mol·kg^{-1}	m_2/ mol·kg^{-1}	a_w
t = 20 °C					
0.5065	0.5136	0.974	0.5005	0.5000	0.975
1.5064	0.5076	0.958	1.5130	0.5010	0.958
1.0138	1.1264	0.946	1.0333	1.0268	0.950
0.5228	1.5010	0.940	0.5003	1.5021	0.943
2.4737	0.5024	0.940	2.5018	0.5010	0.941
2.0026	1.0298	0.933	2.0323	1.0485	0.932
1.5008	1.6633	0.919	1.5021	1.5516	0.926
3.6357	0.5070	0.917	3.5142	0.5062	0.921
1.0090	2.0119	0.914	1.0270	2.0061	0.916
2.5093	1.5237	0.908	3.0002	1.0009	0.916
3.0190	1.2267	0.907	2.5089	1.5061	0.909
0.5022	2.5018	0.905	0.5293	2.5261	0.904
2.0000	2.0003	0.900	2.0001	2.0043	0.901
3.9075	1.0525	0.898	3.9490	1.0167	0.899
1.5017	2.5304	0.890	3.5055	1.5017	0.892
3.4686	1.5367	0.890	1.5045	2.5021	0.891
1.0274	3.0383	0.880	3.0370	2.0051	0.886
3.0296	2.1657	0.878	1.0546	3.0047	0.880
2.5014	2.5425	0.875	2.5019	2.5024	0.878
3.9078	2.0424	0.869	3.9011	2.0003	0.871
2.0066	3.0050	0.867	2.0293	3.0140	0.866
0.5028	3.5800	0.864	3.5338	2.5073	0.860
3.5105	2.5938	0.858	0.5096	3.6794	0.860
1.5668	3.5347	0.852	1.5068	3.5457	0.854
3.0172	3.0181	0.851	3.0059	3.0018	0.852
2.5280	3.5010	0.840	2.5033	3.5248	0.841
3.9018	3.0678	0.838	3.9018	3.0406	0.838
t = 35 °C					
0.5036	0.5293	0.974	0.5071	0.5067	0.974
1.5186	0.5552	0.954	1.5330	0.5472	0.954
1.0822	1.0083	0.949	1.0413	1.0015	0.949
0.5140	1.5467	0.939	0.5238	1.5397	0.939
2.0496	1.0552	0.931	2.5361	0.5141	0.937
2.5500	0.6783	0.930	2.0145	1.2330	0.922
1.6136	1.5282	0.919	1.5101	1.5327	0.921
3.5579	0.6247	0.916	3.5300	0.5190	0.918
1.0125	2.0113	0.915	1.1342	2.1286	0.905
3.1177	1.0295	0.910	3.0199	1.2356	0.904
2.6055	1.6178	0.903	0.5142	2.6178	0.897
2.0027	2.0683	0.895	2.5614	1.7080	0.897
4.0534	1.0022	0.894	3.9264	1.0292	0.895
0.6022	2.7659	0.892	2.0354	2.1138	0.892
1.6515	2.5813	0.885	3.5336	1.5117	0.887
3.5471	1.6956	0.883	1.4788	2.5714	0.883
3.0104	2.0162	0.880	3.0328	2.1490	0.875
1.0606	3.0140	0.878	2.5719	2.5257	0.870
2.5202	2.6218	0.867	3.9136	1.9193	0.868
4.0184	2.0368	0.865	1.0282	3.2198	0.866
2.0621	3.1182	0.858	0.5468	3.6268	0.857
0.5218	3.8081	0.852	3.5617	2.5384	0.854
3.6778	2.5940	0.852	2.0141	3.2011	0.853
1.5488	3.6383	0.844	3.0228	3.1507	0.839
3.0750	3.1622	0.840	1.8755	3.6372	0.839
2.5000	3.5505	0.835	1.0550	3.9456	0.837
			2.5185	3.5001	0.834

in a_w measurements of ±0.005 can be obtained, in agreement with the results reported by Troller.[10]

Samples of each solution (about 10 mL) were left in the hygrometer at (20 ± 0.2) °C and (35 ± 0.2) °C until equilibrium was reached after a period ranging from 5 h for the more concentrated solutions to 24 h for the less concentrated ones.
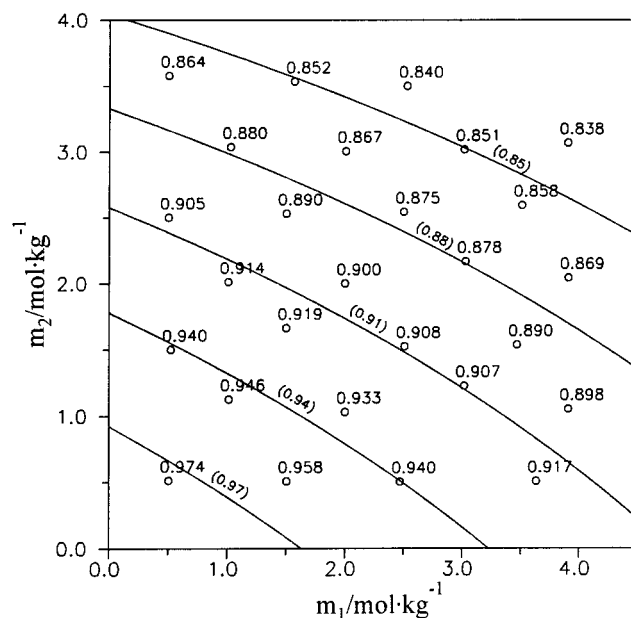

Figure 1. Calculated water isoactivity plot for sorbitol (1) + NaCl (2) + water (3) at 20 °C (○, water activity experimental).

Each water activity measurement was the average of three determinations, found to be sufficient to reach the indicated precision with the instrument for the a_w range studied.[11]

Results and Discussion

The water activities at (20 and 35) °C for the binary and ternary systems studied are reported in Tables 1 and 2. Due to the similarity in molecular structure of xylitol and sorbitol, values of water activity for similar concentrations do not differ much.

Values of water activity measured for the binary systems xylitol + water and sorbitol + water and those given by Pitzer et al.[8] and Kitic et al.[9] for the system sodium chloride + water at (20 and 35) °C, respectively, were correlated using the empirical equation proposed by Lin et al.:[6]

$$a_{wi} = 1 + C_i m_i + C_{ii} m_i^2 \tag{1}$$

where m_i represents solute molality and C_i and C_{ii} are adjustable empirical coefficients.

For the ternary systems, the Lin et al.[6] equation has the form

$$a_w - 1 = (a_{w1} - 1) + (a_{w2} - 1) + C_{12} m_1 m_2$$
$$= C_1 m_1 + C_{11} m_1^2 + C_2 m_2 + C_{22} m_2^2 + C_{12} m_1 m_2 \tag{2}$$

where m_i represents the molality of each solute and C_i, C_{ii}, and C_{12} are adjustable empirical coefficients; only the parameter C_{12} is obtained from ternary data. In this work the subscript 1 refers always to each of the polyols and the subscript 2 refers to sodium chloride. Values obtained for the parameters C_i, C_{ii}, and C_{12} are presented in Table 3.

With the parameters listed in Table 3, water activities for the ternary systems were calculated with an average relative deviation of 0.12% for the sorbitol system (20 °C), 0.10% for the xylitol system (20 °C), 0.11% for the sorbitol

Table 3. Parameters for Eq 2 for Polyol + Sodium Chloride + Water Systems

	parameter				
system	$10^2 C_1$	$10^4 C_{11}$	$10^2 C_2$	$10^3 C_{22}$	$10^3 C_{12}$
sorbitol + NaCl + water (20 °C)	−1.8099	−1.4770	−3.1076	−1.4873	1.5131
xylitol + NaCl + water (20 °C)	−1.8788	0.0625	−3.1076	−1.4873	1.7217
sorbitol + NaCl + water (35 °C)	−1.8880	−1.1123	−3.1648	−1.4048	1.4465
xylitol + NaCl + water (35 °C)	−1.8968	−0.5861	−3.1648	−1.4048	1.0992

system (35 °C), and 0.10% for the xylitol system (35 °C). Figure 1 compares experimental and calculated values of water activity for one of the ternary systems studied. The method proved to be simple to use and accurate for such systems.

To assess the corrective effect of the adjustable parameter C_{12}, values of a_w for pure binary solutions with the concentrations in Table 2 were calculated and, from them,
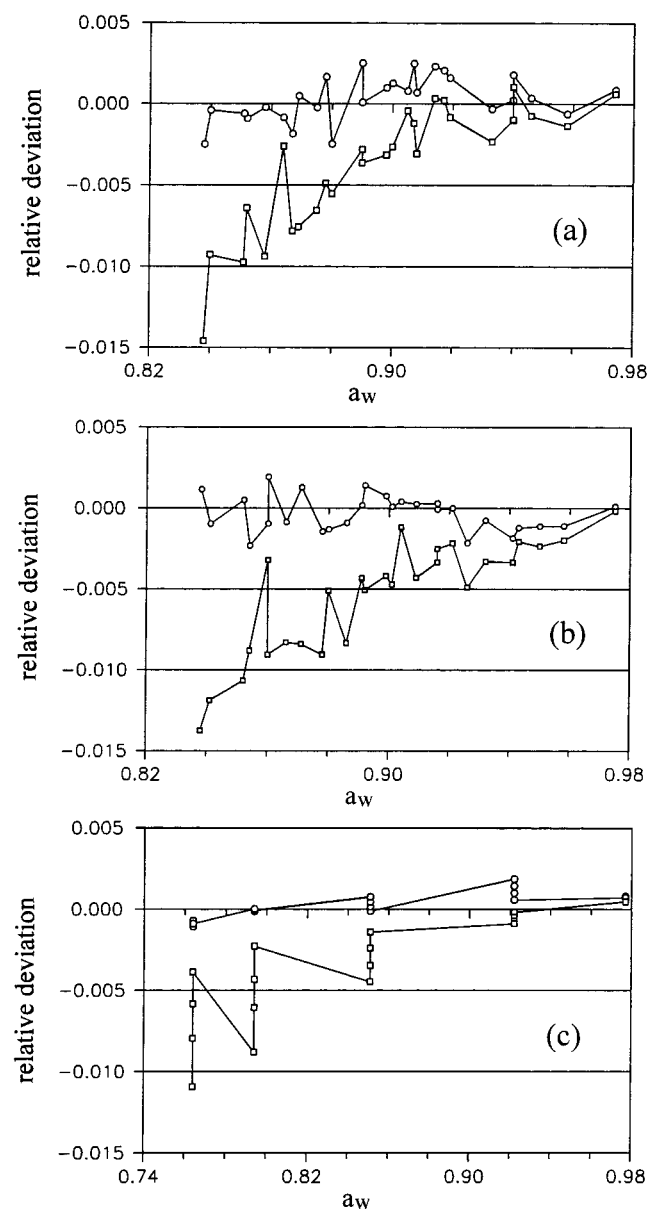

Figure 2. Residual diagrams of Lin's (○) and Ross' (□) models fitted to experimental ternary systems: (a) sorbitol + sodium chloride + water at 20 °C; (b) xylitol + sodium chloride + water at 20 °C; (c) sorbitol + sodium chloride + water at 25 °C (Bower and Robinson[14]).

a_w for the ternary polyol/salt/water solutions was estimated using the Ross[12] equation. This equation is commonly used for the estimation of water activity data in complex multisolute solutions from a_w values for each of the n binary systems present, with the same solute concentration as in the final multisolute solution:

$$a_w = \prod_{i=1}^{n} a_{wi} \tag{3}$$

The use of the Ross[12] equation is widespread and appears to provide a reasonable means of estimating the water activities of multicomponent aqueous mixtures over the intermediate and high water activity ranges.[13]

Results show that while for dilute solutions the Ross[12] equation is generally acceptable, important deviations occur for concentrated systems. Residual diagrams for the systems at 20 °C are graphically shown in Figure 2. The use of the Lin et al.[6] equation with the adjustable parameter C_{12} successfully reduces such deviation for concentrated systems, improving a_w values. A similar pattern of residuals was obtained when experimental data reported by Bower and Robinson[14] were analyzed in a similar way with both the Lin et al.[6] and Ross[12] equations, as shown in the same figure.

The effect of temperature on the water activities of NaCl + polyol aqueous solutions was evaluated by using empirical parameters obtained for the Lin et al.[6] equation at 20 °C and 35 °C to estimate water activities of ternary systems reported by Bower and Robinson.[14] Values calculated this way differed from experimental values at 25 °C reported by those authors by 0.12% and 0.24%, respectively, showing that temperature has a minor effect on the a_w values of these solutions in this temperature range.

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