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Activity Coefficients for Systems Sodium Toluenesulfonate–Xylose–Water and Sodium Toluenesulfonate–Urea–Water at 25°C from Isopiestic Measurements

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The osmotic and activity coefficients for the two ternary systems sodium *p*-toluenesulfonate–xylose–water and sodium *p*-toluenesulfonate–urea–water were measured by the isopiestic vapor pressure method at 25°C. The activity coefficients of sodium toluenesulfonate were increased by xylose and decreased by urea. The sulfonate increased the activity coefficients of xylose and decreased those of urea.

Many investigations have been made on the activity coefficients in aqueous ternary solutions because of their importance to the understanding of solute-solute interaction and solute-solvent interaction which includes water structure change by the solute. Thermodynamics of aqueous solutions of organic electrolytes arouse great interest as they generally have larger ionic radii than inorganic electrolytes and have hydrophobic parts in ions which interact peculiarly with water.

Concerning the ternary systems containing organic electrolytes, however, only a few systems have been investigated in which tetraalkylammonium halide (*14*) or sulfonate (*12*) has been one of the components. In the systems tetramethylammonium bromide–urea–water and tetrabutylammonium bromide–urea–water, Wen and Chen (*14*) noted that each solute component is salted in by the other and that the effect increases greatly with the cationic size of the tetraalkylammonium ion.

On the other hand, aromatic sulfonate ions are somewhat different from tetraalkylammonium ions in the locality of ionic charge, and the water-structure breaking effect of the sulfonic group outweighs the structure-making effect of the benzene ring (*13*).

Previously, we reported (*12*) the activity coefficients for the ternary systems, sodium benzenesulfonate–xylose–water and sodium benzenesulfonate–urea–water. In this paper, the osmotic and activity coefficients for the two ternary solutions sodium *p*-toluenesulfonate–xylose–water and sodium *p*-toluenesulfonate–urea–water were measured by the isopiestic vapor pressure method at 25°C. Sodium *p*-toluenesulfonate has a little larger hydrophobic part than sodium benzenesulfonate, and the difference may influence the activity coefficients in the ternary systems. These sulfonates are model compounds of sulfonic acid type of cation exchange resin. Therefore the data for the systems containing sulfonates and sugar will be useful for a thermodynamic description of purification of sugar by exchange resins.

EXPERIMENTAL

Materials. The purification and drying procedure for sodium *p*-toluenesulfonate (*10*), xylose (*12*) and urea (*12*) has been described elsewhere. Potassium chloride was analytical grade (Merck Co.) and was used without further purification. Solutions were made up in conductance water freed of air by boiling.

Measurements and Calculation of Activity Coefficients of Ternary Solutions. Osmotic and activity coefficients were determined with an apparatus similar to that employed by Robinson and Sotkes (*6*). A glass vacuum desiccator was set in a thermostat bath with rocking device at 25°C, controlled within 0.01°C. The desiccator contained a flat copper block, on which cylindrical silver dishes with lids were placed. Potassium chloride was used as the reference solute, and the osmotic coefficients for the salt solutions were taken from Robinson and Stokes (*5*). The initial concentration in the prepared solutions were adjusted by the method reported previously (*12*) so as to be reasonably close to their equilibrium concentrations. The time required for equilibrium to be attained was varied between 3 and 7 days according to the concentration of the solution. Concentration was measured by weighing dishes corrected to vacuum. More details were published elsewhere (*11*).

An experimental quantity, Δ, was calculated by the equation (*7*):

$$\Delta = 2\, m_R\phi_R - 2\, m_1\phi_1 - m_2\phi_2$$

where m_1 and m_2 are the molalities of solute 1 (1-1 electrolyte) and 2 (nonelectrolyte) in ternary solutions. ϕ_1 and ϕ_2 are the osmotic coefficients of solutes 1 and 2 in binary solutions. m_R and ϕ_R are the molality and osmotic coefficient of the reference solution in vapor pressure equilibrium with a ternary solution containing solutes 1 and 2 at molalities m_1 and m_2. The value of Δ can be calculated from the concentrations of the ternary solutions and reference solutions, provided the osmotic coefficients of reference solution and binary solutions of 1 and 2 are known.

The value of Δ/m_1m_2 is expressed by the following equation:

$$\frac{\Delta}{m_1m_2} = \mathrm{A} + \mathrm{B}m_1 + \mathrm{C}m_2 + \mathrm{D}m_1^2 + \mathrm{E}m_1m_2 + \mathrm{F}m_2^2 \qquad (1)$$

With Equation 1 and definition of Δ by osmotic coefficient of the ternary solutions, the activity coefficients for the 1-1 electrolyte in the ternary solution is given (*2*, *6*) by

$$\ln \gamma_1 = \ln \gamma_1^0 + \frac{\mathrm{A}}{2}m_2 + \frac{\mathrm{B}}{2}m_1m_2 + \frac{\mathrm{C}}{4}m_2^2 + \frac{\mathrm{D}}{2}m_1^2m_2 + \frac{\mathrm{E}}{3}m_1m_2^2 + \frac{\mathrm{F}}{6}m_2^3 \qquad (2)$$

and that of the nonelectrolyte is given by

$$\ln \gamma_2 = \ln \gamma_2^0 + \mathrm{A}m_1 + \frac{\mathrm{B}}{2}m_1^2 + \mathrm{C}m_1m_2 + \frac{\mathrm{D}}{3}m_1^3 + \frac{2\mathrm{E}}{3}m_1^2m_2 + \mathrm{F}m_1m_2^2 \qquad (3)$$

Table I. Ternary Isopiestic Data at 25°C for Systems Sodium p-Toluenesulfonate–Xylose–Water and Sodium p-Toluenesulfonate–Urea–Water

m_R	m_1	m_2	Δ/m_1m_2 Exptl	Δ/m_1m_2 Calcd	Diff, %
		Sodium *p*-Toluenesulfonate–Xylose–Water			
1.1244	0.60787	0.89460	0.09530	0.10055	0.14
	0.86620	0.49440	0.08715	0.09354	0.14
1.4389	0.93726	0.91107	0.08380	0.08522	0.05
	1.1545	0.59518	0.08198	0.08160	−0.01
1.5132	1.3080	0.50578	0.07904	0.07860	−0.01
	1.3111	0.50521	0.07361	0.07853	0.12
1.9622	0.42143	2.5877	0.13538	0.11191	−0.71
	0.79699	2.0019	0.09556	0.08562	−0.44
	1.1175	1.5354	0.08095	0.07179	−0.44
	1.4802	1.0436	0.07039	0.06482	−0.24
	1.8891	0.50372	0.09316	0.06768	−0.67
2.2408	0.51085	2.9260	0.09738	0.10877	0.41
	0.92477	2.3111	0.06285	0.07879	0.83
	1.3344	1.7268	0.05528	0.06170	0.36
	1.8265	1.0936	0.04439	0.05620	0.57
2.6080	1.3901	2.2899	0.05213	0.05648	0.29
	1.7972	1.7709	0.04401	0.04682	0.19
	2.2141	1.2655	0.03769	0.04787	0.59
3.0004	1.2078	3.2115	0.05702	0.06709	0.69
	1.5741	2.7259	0.04952	0.04819	−0.10
	1.9493	2.2620	0.04401	0.03813	−0.46
	2.3529	1.7780	0.04057	0.03729	−0.24
	2.7269	1.3507	0.03295	0.04527	0.81
3.2936	1.6513	3.1492	0.04637	0.04539	−0.08
	2.0534	2.6583	0.04145	0.03267	−0.77
	2.3712	2.2811	0.03857	0.02987	−0.76
	2.7227	1.8761	0.03379	0.03397	0.01
		Sodium *p*-Toluenesulfonate–Urea–Water			
0.78874	0.51896	0.55062	−0.12531	−0.13368	−0.17
1.3928	0.37085	2.0964	−0.13056	−0.12459	0.18
	0.62624	1.6383	−0.12369	−0.11979	0.16
	0.83545	1.2602	−0.12114	−0.11628	0.20
	1.0380	0.89171	−0.11726	−0.11326	0.15
	1.2333	0.53752	−0.11069	−0.11065	0.00
1.6976	0.40221	2.7230	−0.11849	−0.11730	0.04
	0.67087	2.2454	−0.11227	−0.11230	−0.00
	0.91231	1.8108	−0.10801	−0.10838	−0.02
	1.2074	1.2820	−0.10444	−0.10422	0.01
	1.4544	0.84395	−0.10059	−0.10124	−0.03
2.0242	0.55892	3.2028	−0.10364	−0.10667	−0.15
	0.97394	2.4685	−0.09810	−0.09973	−0.11
	1.2955	1.9008	−0.09491	−0.09533	−0.03
	1.6398	1.3000	−0.09137	−0.09150	−0.01
	1.8903	0.87412	−0.08890	−0.08921	−0.01
2.3023	0.59640	3.8057	−0.09439	−0.09902	−0.25
	0.96027	3.1677	−0.09025	−0.09294	−0.19
	1.2740	2.6147	−0.08629	−0.08861	−0.18
	1.7456	1.8000	−0.08163	−0.08345	−0.13
	2.2181	1.0115	−0.08107	−0.07986	0.06
2.7477	0.84092	4.5114	−0.08316	−0.08255	0.05
	1.3600	3.6115	−0.07707	−0.07522	0.18
	1.8625	2.7383	−0.06985	−0.07024	−0.04
	2.3908	1.8435	−0.06515	−0.06703	−0.16
	2.8391	1.0959	−0.06745	−0.06598	0.09
3.0244	1.1792	4.6440	−0.07180	−0.06949	0.22
	1.5132	4.0573	−0.06701	−0.06554	0.16
	1.9470	3.3165	−0.06266	−0.06155	0.13
	2.1455	2.9723	−0.05961	−0.06030	−0.08
	2.6088	2.1957	−0.05754	−0.05837	−0.08

where, γ_1, and γ_2 are the molal activity coefficients of solutes 1 and 2 in a ternary solution containing solutes 1 and 2 with molalities m_1 and m_2, respectively. γ_1^0 and γ_2^0 are the molal activity coefficients, respectively, of binary solutions containing only solute 1 at molality m_1 or solute 2 at molality m_2. The values of osmotic and activity coefficients for sodium toluenesulfonate solutions were taken from the data of Robinson and Stokes (*7*). The values of osmotic and activity coefficients for xylose solutions were taken from Uedaira and Uedaira (*11*) and the values for urea solutions, from Ellerton and Dunlop (*2*).

Table II. Constants for Equation 1 in Ternary Solutions Sodium p-Toluenesulfonate–Xylose–Water (I) and Sodium p-Toluenesulfonate–Urea–Water (II) at 25°C

Coefficients	I	II
$A \times 10$	1.4296	−1.5750
$B \times 10^2$	−5.9737	3.8313
$C \times 10^2$	−1.1202	0.8424
$D \times 10^2$	1.4235	−0.3593
$E \times 10^3$	−9.190	0.710
$F \times 10^3$	4.570	0.224

RESULTS AND DISCUSSIONS

The isopiestic data for the systems sodium *p*-toluenesulfonate–xylose–water and sodium *p*-toluenesulfonate–urea–water are shown in Table I. The first column gives the molality of the reference potassium chloride solution, and second and third columns give the values of the molalities of sodium *p*-toluenesulfonate and xylose or urea in the ternary solutions which were in equilibrium with the reference solution. The values of the experimental quantities Δ/m_1m_2 are given in the fourth column. The values of Δ/m_1m_2 calculated from Equation 1 with coefficients listed in Table II are shown in the fifth column. The last column gives the percentage error in the molality of the reference solution which would account for the difference between the experimental and the computed values (*6*).

In these systems the values of the compositions of solutions in vapor pressure equilibrium are nearly linear, and the coefficients of linear terms are almost equal in the same system as in many other systems reported previously (*12*). So, this relationship was utilized for the preparation of the initial solutions, the concentrations of which should be fairly close to equilibrium values.

Table II showed the coefficients of Equation 1 calculated from the experimental values of Δ/m_1m_2 by the method of least squares with a HITAC 8400 computer for both systems I and II. Activity coefficients of the solutes in these systems can be calculated using Equations 2 and 3 together with the parameters in Table II.

The activity coefficients of the salt and xylose are increased by the other mutually. The only explanation of the increase is that the solute-solvent interaction is increased by adding other solutes defined by Samoilov (*8*) as structure salting out. The activity coefficients of urea are lowered by sodium toluenesulfonate, and those of the salt are also lowered by urea. In the same concentration range of urea, activity coefficients of urea are also lowered by sodium chloride (*1*) and by sodium benzenesulfonate (*13*). The degree of the lowering effect of the salts is in order of the structure-breaking action of these salts (*9, 13*), which is in agreement with the structure salting in theory by Frank (*3, 4*) and Samoilov (*8*).

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