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Osmotic and Activity Coefficients of Some Nonelectrolytes

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Osmotic and activity coefficients are reported for solutions of dextrose, *sym*-dimethylurea, and *meso*-erythrytol at 25° and 37° C. Osmotic coefficients are also reported at 60° C. for concentrated solutions of these compounds. The solvation of certain alcohols and sugars is indicated to be directly related to the number of polar groups per molecule.

OSMOTIC and activity coefficients have been previously reported for certain nonelectrolytes at 25° C.—e.g., sucrose (*6*), sorbitol (*2*), and urea (*3*). These data are of interest as these coefficients in aqueous solutions for sucrose and sorbitol are greater than unity while they are less than unity for urea. The original intention of the authors was to investigate solutions for sucrose and urea at temperatures above 25° C. so as to furnish additional information on the relative importance of solute-solute and solute-solvent interactions for these substances. However, considerable hydrolysis occurred when solutions of either of these nonelectrolytes were maintained at temperatures of 35° C. or higher, and this necessitated a search for compounds of the same types whose aqueous solutions were stable at temperatures above 60° C. Data are reported for these compounds.

EXPERIMENTAL

All determinations of osmotic and activity coefficients in concentrated solutions have been made by the isopiestic method. Platinum-clad silver dishes were used for the measurements at 25° C. The experimental procedures which were used at the other temperatures have been described earlier (*1*). Sodium chloride was used as the reference electrolyte for these isopiestic comparisons. The Mecrolab Model 301A Vapor Pressure Osmometer was used to supplement the isopiestic data in dilute solutions. Nonelectrolyte osmotic coefficients were calculated by comparison of dekastat readings for these solutions with those of sodium chloride solutions of similar water activity. The isopiestic data at 25°, 37°, and 60° C. may be reproduced with precisions of 0.1, 0.2, and 0.3%, respectively. The precision of the vapor pressure osmometer measurements at 25° and 37° C. is approximately the same as for the isopiestic comparisons. No measurements using the vapor pressure osmometer were attempted at 60° C.

DISCUSSION

Osmotic and activity coefficients of sodium chloride solutions at 25° C. are known with great accuracy (*5*). There appears to be a considerable discrepancy, however, among values obtained by various experimental methods at other temperatures. Values of ϕ at 40° and 60° C. calculated from electromotive force and boiling point measurements (with reasonable extrapolations) appear to differ by as much as 0.01 unit. The values of γ have an even greater uncertainty. Smoothed values of ϕ and γ at 37° C., corresponding to those presented by Harned and Owen (*5*), and at 60° C. corresponding to those in Robinson and Stokes (*6*) have been used in the calculation of the nonelectrolyte osmotic and activity coefficients (Table I). However, the uncertainty

Table I. Osmotic Coefficient Corrections for NaCl Solutions

m	$\phi_{37^\circ} - \phi_{25^\circ}$	$\phi_{60^\circ} - \phi_{25^\circ}$
0.5	0.001	. . .
1.0	0.005	. . .
1.5	0.007	0.014
2.0	0.007	0.016
2.5	0.008	0.018
3.0	0.006	0.016
3.5	0.006	0.012
4.0	0.006	0.010
4.5	0.005	0.010
5.0	0.005	0.010

Data have been smoothed and extrapolated. Data at 37° from Harned and Owen (*5*, p. 492). Data at 60° from Robinson and Stokes (*6*, p. 480).

Table II. Isopiestic Solutions at 25° C.

m(NaCl)	m(Dextrose)	m(NaCl)	m(Erythrytol)	m(NaCl)	m(Dimethylurea)
2.105	3.809	0.9145	1.678	1.252	2.875
2.293	4.146	1.006	1.847	1.642	3.977
3.162	5.838	1.144	2.103	1.920	4.770
3.216	5.922	1.415	2.617	2.309	5.945
3.732	6.995	1.642	3.058	2.853	7.620
4.139	7.868	2.309	4.390	2.871	7.704
4.707	9.130	2.779	5.378	4.023	11.764
5.641	11.542	2.853	5.549	. . .	. . .
. . .	. . .	2.861	5.555	. . .	. . .

Table III. Osmotic and Activity Coefficients at 25° C.

	Dextrose		*sym*-Dimethylurea		*meso*-Erythrytol	
m	ϕ	γ	ϕ	γ	ϕ	γ
0.2	1.002	1.003	0.980	0.952	1.001	1.002
0.4	1.004	1.007	0.965	0.911	1.002	1.004
0.6	1.006	1.011	0.948	0.871	1.004	1.007
0.8	1.008	1.015	0.933	0.835	1.006	1.010
1.0	1.011	1.020	0.919	0.803	1.008	1.014
1.2	1.014	1.026	0.905	0.771	1.010	1.018
1.4	1.018	1.032	0.892	0.742	1.012	1.022
1.6	1.022	1.039	0.880	0.715	1.015	1.027
1.8	1.027	1.047	0.869	0.692	1.018	1.032
2.0	1.033	1.056	0.858	0.668	1.021	1.037
2.5	1.050	1.084	0.837	0.619	1.028	1.050
3.0	1.066	1.114	0.816	0.577	1.035	1.063
3.5	1.083	1.146	0.805	0.545	1.041	1.076
4.0	1.100	1.181	0.797	0.518	1.048	1.090
4.5	1.117	1.215	0.791	0.495	1.055	1.104
5.0	1.129	1.246	0.786	0.476	1.061	1.118
5.5	1.140	1.276	0.782	0.459	1.067	1.131
6.0	1.150	1.306	0.779	0.443	...	...
6.5	1.161	1.336	0.777	0.430	...	...
7.0	1.171	1.368	0.775	0.417	...	...
7.5	1.180	1.295	0.774	0.407	...	...
8.0	1.188	1.423	0.772	0.397	...	...
8.5	1.196	1.452	0.771	0.388	...	...
9.0	1.204	1.481	0.770	0.380	...	...
9.5	1.212	1.510	0.769	0.371	...	...
10.0	1.219	1.537	0.767	0.364	...	...

Table IV. Isopiestic Solutions at 37° C.

m(NaCl)	m(Dextrose)	m(NaCl)	m(Erythrytol)	m(NaCl)	m(Dimethylurea)
2.213	4.091	2.384	4.620	2.051	5.283
2.384	4.420	3.155	6.293	2.384	6.464
3.475	6.630	3.465	6.997	3.155	9.174
3.609	6.928	4.027	8.361	3.475	10.438
4.423	8.745	4.413	9.315	4.017	12.683
4.937	9.943	...	...	...	...

Table V. Osmotic and Activity Coefficients at 37° C.

	Dextrose		*sym*-Dimethylurea		*meso*-Erythrytol
m	ϕ	γ	ϕ	γ	ϕ
0.2	1.001	1.002	0.977	0.943	...
0.4	1.003	1.005	0.958	0.893	...
0.6	1.005	1.009	0.940	0.849	...
8.0	1.007	1.012	0.924	0.810	...
1.0	1.009	1.016	0.910	0.775	...
1.2	1.012	1.021	0.895	0.742	...
1.4	1.015	1.026	0.881	0.712	...
1.6	1.020	1.034	0.870	0.685	...
1.8	1.025	1.042	0.857	0.660	...
2.0	1.030	1.050	0.846	0.636	...
2.5	1.044	1.075	0.825	0.588	...
3.0	1.058	1.101	0.807	0.547	...
3.5	1.071	1.125	0.703	0.513	1.034
4.0	1.084	1.151	0.780	0.484	1.041
4.5	1.096	1.178	0.771	0.460	1.046
5.0	1.106	1.202	0.763	0.438	1.051
5.5	1.116	1.227	0.758	0.421	1.056
6.0	1.125	1.251	0.753	0.405	1.061
6.5	1.133	1.275	0.748	0.389	1.066
7.0	1.141	1.298	0.743	0.376	1.071
7.5	1.149	1.322	0.739	0.364	1.076
8.0	1.157	1.346	0.735	0.353	1.081
8.5	1.164	1.368	0.732	0.343	...
9.0	1.171	1.391	0.729	0.334	...
9.5	1.178	1.413	0.726	0.325	...
10.0	1.186	1.439	0.723	0.317	...

Table VI. Isopiestic Solutions at 60° C.

m(NaCl)	m(Dextrose)	m(NaCl)	m(Erythrytol)	m(NaCl)	m(Dimethylurea)
3.122	5.969	2.114	4.105	2.027	5.465
3.240	6.195	2.944	5.935	2.114	5.760
3.546	6.869	3.100	6.328	2.697	7.677
3.912	7.716	3.442	7.107	3.100	9.503
4.265	8.463	3.546	7.367	3.955	13.03
4.745	9.644	4.025	8.571	4.025	13.38
5.011	10.321	4.506	9.837	...	...
...	...	4.891	10.873	...	...

Table VII. Osmotic Coefficient, ϕ at 60° C.

m	Dextrose	*sym*-Dimethylurea	*meso*-Erythrytol
5.0	1.101	0.748	1.042
5.5	1.110	0.741	1.045
6.0	1.118	0.735	1.048
6.5	1.126	0.729	1.051
7.0	1.133	0.723	1.053
7.5	1.139	0.718	1.056
8.0	1.145	0.714	1.058
8.5	1.151	0.710	1.061
9.0	1.157	0.706	1.063
9.5	1.162	0.702	1.066
10.0	1.167	0.698	1.068

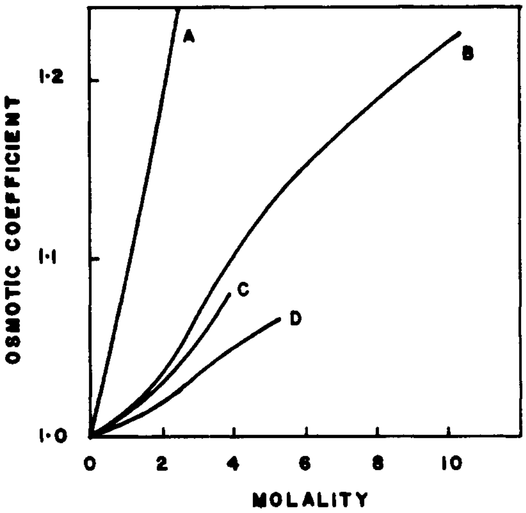

Figure 1. Osmotic coefficients of some sugars and alcohols at 25° C.

A, sucrose; B, dextrose; C, sorbitol; D, *meso*-erythrytol

in the sodium chloride values probably exceeds the experimental uncertainty of the isopiestic method, and the reported values for ϕ and γ for the nonelectrolytes at 37° and 60° C. may have an uncertainty of at least 0.005 unit.

It may be qualitatively observed that at 25° C. the osmotic and activity coefficients of dextrose like those of sucrose are greater than unity while the coefficients of both urea and *sym*-dimethylurea are less than unity (Tables II and III). This indicates that solute-solvent interactions are prevalent in dextrose solutions although probably not to as great an extent as in solutions of sucrose. Solute-solute interaction appears to be predominant in both solutions of urea and *sym*-dimethylurea although they appear to be stronger in the latter case. This may be a further manifestation (for dipole-dipole interactions between nonelectrolytes) of the phenomenon described by Diamond (*4*) for electrolytes as a structure enforced ion-pairing, since the substituted urea is the larger molecule and should cause a greater disruption of the water structure.

The osmotic and activity coefficients of both dextrose and *sym*-dimethylurea decrease as the temperature is increased, and this can be attributed in both instances to a decrease in hydration of the molecules (Tables IV to VII). This should favor the solute-solute interaction in *sym*-dimethylurea and probably accounts for the relatively larger effect of temperature on the coefficients of this compound.

Osmotic and activity coefficients for several alcohols and sugars are compared (Figure 1). The osmotic coefficients of these compounds at any given concentration are directly related to the number of hydrophilic groups contained by the molecule. The relative constancy of the function, $[\phi-1]/$ polar groups per molecule, at each concentration substantiates the role of solvation and indicates a possible problem in the use of colligative property measurements for the determination of the molecular weights of some polymers. These sugars and alcohols may be considered as polymers having a repeating hydrophilic (OH) group. The osmotic coefficient of a 2 molal solution of sorbital (having six such groups) is 3% greater than unity. Polymers of higher molecular weight which have a large number of lyophilic groups must, therefore, exhibit gross deviations from Raoult's Law.

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Ternary Systems of Liquid Ammonia

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This paper presents 60 new observed ternary or quaternary systems of liquid ammonia. Most of them involve two liquid phases in equilibrium under pressure. Graphs include several systems with isopycnics, iso-optics, twin density lines, or twin index lines; but none with solutropes, island curves, or those with two or three separate binodal curves. Systems with sulfur as a component show a deep purple color, the result of a reversible reaction, but only in the ammonia-rich phase. Other systems include urea, which is extremely soluble in ammonia. These solutions do not form adducts with straight chain paraffins. Liquids found miscible in all proportions with liquid ammonia at room temperature include water, benzonitrile, 2-butanone, butenes, Chlorex, diethanolamine, diethylene glycol, dioxane, ethanolamine, ethylene glycol, formamide, glycerol, isopropyl ether, nitrobenzene, pyridine, propylene, and aromatic hydrocarbons up to C_9.

LIQUID ammonia is a cheap, noncorrosive solvent operable for extractions at ordinary temperature and moderate pressures, and easily separable from hydrocarbon products. When pure, it is fairly selective for aromatic hydrocarbons and slightly so for some other hydrocarbon pairs.

Some misleading values for solubility in liquid ammonia appear in the early literature. Franklin and Kraus (*10*) list cuprous chloride as "sl. sol.," but indicate that toluene is only slightly soluble, ethylbenzene much less so, and higher aromatics not perceptibly soluble. Actually, cuprous chloride is insoluble, but all liquid aromatic hydrocarbons up to C_9 are miscible with liquid ammonia in all proportions (*3*). The discrepancy may be due to the presence of water (which also is miscible) in the ammonia used by the early workers. The water would decrease miscibility of hydrocarbons, and increase solubility of cuprous chloride. Their observations were at atmospheric pressure, and therefore at about −33° C. These and some unpublished observations of Franklin are reported by Bergstrom and coworkers (*1*). De Carli (*2*) likewise reported many solubilities of hydrocarbons in liquid ammonia, which are excessively low, probably because of the same low temperature.

Critical solution temperatures of liquid ammonia are listed in references *3*; *8*, pp. 221–2; *12*, *15*, and *20*. Extensive investigations of liquid ammonia as a selective solvent have been made by Ishida (*12–15*), and by Long (*17*). Fifteen of their ternary graphs (at various temperatures) are shown in Landolt-Börnstein (*16*), for hydrocarbon pairs. Also included as cosolvents are pyridine, thiophene, or methylamine. Four other systems of liquid ammonia are presented (*7*, graphs 8, 9, 34, 35).

EXPERIMENTAL

This paper presents observations on 60 additional ternary or quaternary systems (on 46 graphs) with ammonia as a component (Figure 1). Most of them show two or more liquid phases. As in the observations on liquid sulfur dioxide systems (*6*), a thick-walled glass tube was charged by weight with the nonvolatile components, and cooled in a cold bath. Ammonia was condensed into the tube, which was then sealed, warmed to room temperature, and weighed. When a hydrocarbon gas was a component also, it was charged in the same way, but with intermediate sealing and weighing. Additional ammonia as required was introduced similarly to titrate the mixture to a composition on a phase boundary. The resulting graphs are shown in concise form.

DISCUSSION

Pure liquid ammonia is not entirely satisfactory as a selective solvent for aromatics. Although it is completely miscible at ordinary temperatures with aromatic hydrocarbons boiling up to about 160°, it also dissolves moderate amounts of paraffins or cycloparaffins. Consequently, with pure ammonia as a solvent, an extract cannot be concentrated above about 85% benzene or toluene except at very low temperatures.

Dilution of the ammonia with water or an organic solvent such as ethylene glycol would diminish solubility of the

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