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Limiting Activity Coefficients for Butyl Alcohols in Water, *n*-Octane, and Carbon Tetrachloride[†]

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Activity coefficients are reported for 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol in water, *n*-octane, and carbon tetrachloride, in the dilute solute region. Measurements were made at 20.0 °C by direct analysis of the vapor above the solutions. From these measurements at mole fractions of 0.0005–0.01, limiting activity coefficients, Henry's law constants, and standard Gibbs energies of transfer of solute from liquid to vapor were calculated.

Introduction

As part of a program to study the interfacial properties of systems related to the solvent extraction systems used in the reprocessing of nuclear fuel, we are measuring the adsorption of some alcohols at oil–water interfaces (*1*). To interpret these adsorption measurements, activity coefficients of these alcohols are needed in the low solute mole fraction regime for both the oil and the water. This work reports measurements of the activity coefficients of four isomeric alcohols in water and in two organic solvents, *n*-octane and carbon tetrachloride. The activity coefficients were measured by analyzing the vapor compositions in equilibrium with solutions of known composition (*2*).

Experimental Section

In this work, activity coefficients were measured by determining butanol concentrations in the vapor over dilute solutions of butanols using gas chromatography. The cell used was virtually identical with that described earlier by Milanová and Cave (*2*, *3*) and Afrashtehfar and Cave (*4*, *5*). This cell was a vertical cylindrical chamber, about 150 mm high by 50 mm in diameter, fitted with a sampling valve at the top end. This valve incorporated a rotatable head fitted with three calibrated sampling volumes. It was designed so that each volume, in turn, was opened to the vapor in the cell, swept out with a carrier gas, and evacuated prior to being opened to the cell again. The cell was placed in a water bath maintained at 20.00 ± 0.04 °C as measured by a Hewlett-Packard HP2804 quartz crystal thermometer.

Analyses were done using a Varian 1860 gas chromatograph fitted with both flame ionization detectors and thermal conductivity detectors. It was also equipped with a Hewlett Packard HP3390A reporting integrator. For most systems, a short 30-cm column of Porapak Q-S was used at temperatures between 115 and 160 °C. For separations from carbon tetrachloride (except for 2-methyl-2-propanol), it was necessary to use a 2-m column of 20% Carbowax 1540 on Super Support at 80 °C. The analysis system was calibrated by manual injections of 1-μL samples of dilute solutions of solute in solvent.

All chemicals were the best available grade supplied by Aldrich Chemical Co., except for *n*-octane, which was obtained from the Humphrey Chemical Co. All chemicals were of better than 99% purity, as checked by gas chromatography.

Table I. Activity Coefficients for the *n*-Hexane–Benzene Binary System at 20 °C

n-hexane mole fracn	activity coeff	
	n-hexane	benzene
0.0395	1.985	1.005
0.0410	1.862	1.008
0.0488	1.837	1.006
0.1216	1.757	1.039
0.1256	1.685	1.031
0.1410	1.640	1.021
0.1889	1.497	1.007
0.2018	1.550	1.026
0.2269	1.553	1.055
0.2514	1.440	1.071
0.2851	1.388	1.061
0.3250	1.391	1.132
0.3705	1.245	1.111
0.4146	1.117	1.076
0.4824	1.170	1.218
0.4887	1.173	1.218
0.5570	1.138	1.228
0.6043	1.087	1.262
0.6188	1.066	1.249
0.6823	1.032	1.277
0.7521	1.027	1.401
0.7832	1.024	1.382
0.8229	1.012	1.475
0.8257	1.009	1.443
0.8601	1.016	1.450

For any given system, the gas chromatograph was calibrated by injecting known, varying quantities of solute so that the peak areas were known as a function of the number of moles of solute. Samples of about 50 mL were then prepared by weight and placed in the cell, after retaining a small portion for analysis. The glass cell was then attached to the valve and the liquid degassed by the freeze–pump–thaw technique. A thermostat with water at 20.00 ± 0.04 °C was then placed around the cell, and the solution in the cell was stirred with a magnetic stirrer. Samples were taken at regular intervals until equilibrium was achieved. When equilibrium was reached, samples of the retained liquid were then injected into the gas chromatograph. From the calibration curve, solute concentrations in the vapor and the liquid were calculated, correcting the solute concentration in the liquid for solute evaporated into the cell, and correcting for the temperature difference between the cell at 20 °C and the sample loops at room temperature (~24 °C).

The gas chromatography measurements were reliable to within ±2%.

Results and Discussion

Activity coefficients, corrected for gas-phase nonidealities, were calculated by using eq 1 (*2*, *6*).

$$\ln \gamma_2 = \ln \frac{C_2}{X_2 C_{02}} + 2B_{22}(C_2 - C_{02}) + 2B_{12}C_1 \qquad (1)$$

In this equation, subscript 2 refers to solute and 1 to solvent. Thus, C_2 is the molar concentration of solute in the equilibrium vapor, corrected for the temperature difference between the sampling loop and the bath (20 °C). The molar concentration

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Table II. Activity Coefficients for Butyl Alcohols in Water, *n*-Octane, and Carbon Tetrachloride at 20 °C

solute	solvent	solute mole fracn	solute activity coeff
1-butanol	water	0.00137	42.3
1-butanol	water	0.00308	41.1
1-butanol	water	0.00487	43.0
1-butanol	water	0.00603	42.0
1-butanol	water	0.00697	40.6
1-butanol	water	0.00861	39.1
1-butanol	water	0.0115	38.6
1-butanol	water	0.0124	38.4
1-butanol	water	0.01343	38.1
1-butanol	water	0.0143	41.5
1-butanol	water	0.0165	41.0
1-butanol	water	0.0179	41.6
1-butanol	water	0.0192	40.7
1-butanol	*n*-octane	0.00145	32.5
1-butanol	*n*-octane	0.00251	31.4
1-butanol	*n*-octane	0.00493	28.8
1-butanol	*n*-octane	0.00721	25.8
1-butanol	*n*-octane	0.00883	24.3
1-butanol	*n*-octane	0.0265	14.4
1-butanol	*n*-octane	0.0417	9.40
1-butanol	*n*-octane	0.0607	5.90
1-butanol	*n*-octane	0.1147	4.44
1-butanol	*n*-octane	0.2279	2.45
1-butanol	*n*-octane	0.3164	2.03
1-butanol	*n*-octane	0.3535	1.70
1-butanol	*n*-octane	0.4250	1.66
1-butanol	*n*-octane	0.4556	1.65
1-butanol	*n*-octane	0.5782	1.55
1-butanol	*n*-octane	0.6202	1.49
1-butanol	*n*-octane	0.7052	1.14
1-butanol	*n*-octane	0.8365	1.08
1-butanol	carbon tetrachloride	0.00277	17.3
1-butanol	carbon tetrachloride	0.00386	15.8
1-butanol	carbon tetrachloride	0.00392	16.4
1-butanol	carbon tetrachloride	0.00508	16.2
1-butanol	carbon tetrachloride	0.00550	17.2
1-butanol	carbon tetrachloride	0.00714	16.9
1-butanol	carbon tetrachloride	0.00749	16.4
1-butanol	carbon tetrachloride	0.00880	15.1
2-methyl-1-propanol	water	0.00278	41.2
2-methyl-1-propanol	water	0.00321	39.4
2-methyl-1-propanol	water	0.00345	44.2
2-methyl-1-propanol	water	0.00404	40.9
2-methyl-1-propanol	water	0.00534	38.5
2-methyl-1-propanol	water	0.00662	35.4
2-methyl-1-propanol	water	0.00771	37.9
2-methyl-1-propanol	water	0.00948	33.4
2-methyl-1-propanol	water	0.01153	34.0
2-methyl-1-propanol	*n*-octane	0.00058	44.2
2-methyl-1-propanol	*n*-octane	0.00171	43.4
2-methyl-1-propanol	*n*-octane	0.00321	36.2
2-methyl-1-propanol	*n*-octane	0.00469	33.8
2-methyl-1-propanol	*n*-octane	0.00595	35.0
2-methyl-1-propanol	*n*-octane	0.00640	26.4
2-methyl-1-propanol	*n*-octane	0.00785	26.3
2-methyl-1-propanol	carbon tetrachloride	0.00204	17.6
2-methyl-1-propanol	carbon tetrachloride	0.00362	17.7
2-methyl-1-propanol	carbon tetrachloride	0.00378	17.7
2-methyl-1-propanol	carbon tetrachloride	0.00524	17.4
2-methyl-1-propanol	carbon tetrachloride	0.00630	16.4
2-methyl-1-propanol	carbon tetrachloride	0.008368	16.1
2-butanol	water	0.00407	22.0
2-butanol	water	0.00510	20.9
2-butanol	water	0.00614	20.2
2-butanol	water	0.00775	19.3
2-butanol	water	0.00901	19.2
2-butanol	water	0.0111	20.0
2-butanol	water	0.0138	19.8
2-butanol	water	0.0165	19.1
2-butanol	water	0.0181	18.8
2-butanol	water	0.0189	20.3
2-butanol	water	0.0212	20.4
2-butanol	*n*-octane	0.00242	25.3_0
2-butanol	*n*-octane	0.00334	23.9_5
2-butanol	*n*-octane	0.00398	23.3_5
2-butanol	*n*-octane	0.00590	22.16
2-butanol	*n*-octane	0.00674	21.8_4
2-butanol	*n*-octane	0.00852	20.3_4
2-butanol	carbon tetrachloride	0.00245	14.82
2-butanol	carbon tetrachloride	0.00333	14.88
2-butanol	carbon tetrachloride	0.00396	14.92
2-butanol	carbon tetrachloride	0.00580	14.70
2-butanol	carbon tetrachloride	0.00680	14.45
2-butanol	carbon tetrachloride	0.00773	14.45
2-methyl-2-propanol	water	0.000284	11.7
2-methyl-2-propanol	water	0.000592	12.0
2-methyl-2-propanol	water	0.00175	11.6
2-methyl-2-propanol	water	0.00331	11.2
2-methyl-2-propanol	water	0.00520	10.8
2-methyl-2-propanol	water	0.00717	11.3
2-methyl-2-propanol	water	0.00877	10.8
2-methyl-2-propanol	water	0.0120	11.4
2-methyl-2-propanol	water	0.0149	11.6
2-methyl-2-propanol	water	0.0167	11.3
2-methyl-2-propanol	water	0.0186	11.2
2-methyl-2-propanol	water	0.0217	11.6
2-methyl-2-propanol	water	0.0278	11.7
2-methyl-2-propanol	water	0.0319	12.0
2-methyl-2-propanol	water	0.0378	11.9
2-methyl-2-propanol	water	0.0560	10.67
2-methyl-2-propanol	water	0.0790	8.47
2-methyl-2-propanol	water	0.1086	6.26
2-methyl-2-propanol	water	0.1158	5.99
2-methyl-2-propanol	water	0.1605	4.24
2-methyl-2-propanol	water	0.1904	3.70
2-methyl-2-propanol	water	0.280	2.56
2-methyl-2-propanol	water	0.372	2.04
2-methyl-2-propanol	*n*-octane	0.00072	19.7
2-methyl-2-propanol	*n*-octane	0.0011	20.7
2-methyl-2-propanol	*n*-octane	0.0024	20.8
2-methyl-2-propanol	*n*-octane	0.0042	19.7
2-methyl-2-propanol	*n*-octane	0.0049	18.4
2-methyl-2-propanol	*n*-octane	0.0071	17.7
2-methyl-2-propanol	*n*-octane	0.0100	17.0
2-methyl-2-propanol	*n*-octane	0.0678	5.64
2-methyl-2-propanol	*n*-octane	0.1194	3.43
2-methyl-2-propanol	*n*-octane	0.1289	3.27
2-methyl-2-propanol	*n*-octane	0.200	2.58
2-methyl-2-propanol	*n*-octane	0.244	2.19
2-methyl-2-propanol	*n*-octane	0.318	1.82
2-methyl-2-propanol	*n*-octane	0.378	1.65
2-methyl-2-propanol	*n*-octane	0.432	1.39
2-methyl-2-propanol	*n*-octane	0.500	1.26
2-methyl-2-propanol	*n*-octane	0.532	1.14
2-methyl-2-propanol	carbon tetrachloride	0.0016	15.9
2-methyl-2-propanol	carbon tetrachloride	0.0027	15.6
2-methyl-2-propanol	carbon tetrachloride	0.0041	15.5
2-methyl-2-propanol	carbon tetrachloride	0.0062	14.7
2-methyl-2-propanol	carbon tetrachloride	0.0075	14.8
2-methyl-2-propanol	carbon tetrachloride	0.0086	14.1

of solute vapor over pure solute is C_{02}, and X_2 is, of course, the mole fraction of solute in the liquid. The solvent concentration in the vapor is C_1, and the second virial coefficients of the mixture and pure solute are B_{12} and B_{22}, respectively. The value of B_{12} was taken as the algebraic mean of B_{11}, the second virial coefficient of the solvent, and B_{22}. The virial coefficients used were taken from Dymond and Smith (*7*), or were estimated from virial coefficients of similar molecules. The activity coefficients have the usual standard state of unit activity for the pure component.

The system was tested by using the well-known system *n*-hexane/benzene. Activity coefficient measurements were made over the entire range of mole fractions, using the thermal conductivity detectors of the gas chromatograph. The results with this system are shown in Figure 1 and listed in Table I. Agreement with earlier results (*2*, *8*) is satisfactory.

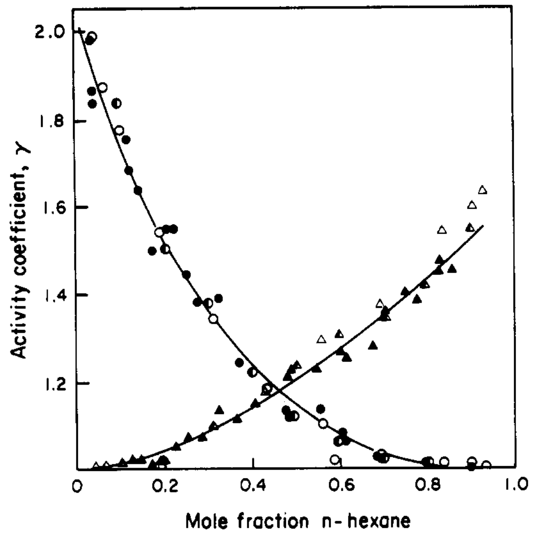

Figure 1. Activity coefficients for *n*-hexane (circles) and benzene (triangles) in *n*-hexane–benzene mixtures. Our results are given as filled symbols, those of Milanová and Cave (*2*) as open symbols, and of Smith and Robinson (*7*) as half-filled symbols.

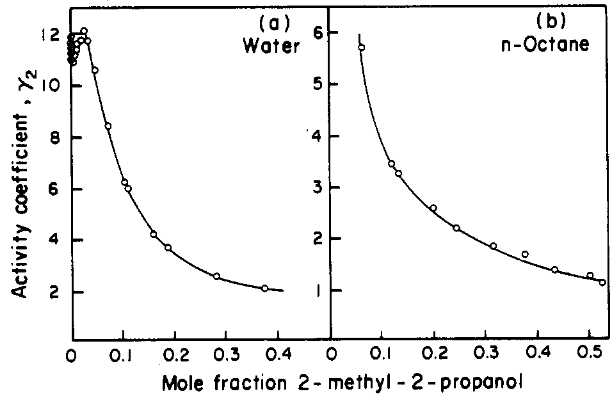

Figure 2. Activity coefficients for 2-methyl-2-propanol as a function of mole fraction in water (a) and in *n*-octane (b).

All the activity coefficients for the butyl alcohols in the three solvents, water, *n*-octane, and carbon tetrachloride, are listed in Table II. Errors in these activity coefficients are ±2%, at least, from errors in the gas chromatographic analyses. Errors in sample compositions are small by comparison.

We were primarily interested in activity coefficients in very dilute solutions. Nevertheless, some measurements were made over a more extended range of solute mole fraction. Figure 2, a and b, shows results for 2-methyl-2-propanol in water and *n*-octane, respectively. The results in *n*-octane show a high activity coefficient at low 2-methyl-2-propanol mole fractions, as expected, but the results with aqueous solutions are particularly interesting, as they suggest a maximum at 0.03 mole fraction 2-methyl-2-propanol. A maximum in this system at about the same mole fraction of water has also been noted recently by Kruus and Hayes (*9*) using a total vapor pressure technique. Their activity coefficients are somewhat lower than ours and we have no explanation for the discrepancy. Maxima have also been noted for other thermodynamic properties of this system (*9*, *10*) and are thought to result from aggregation of the alcohols in the water.

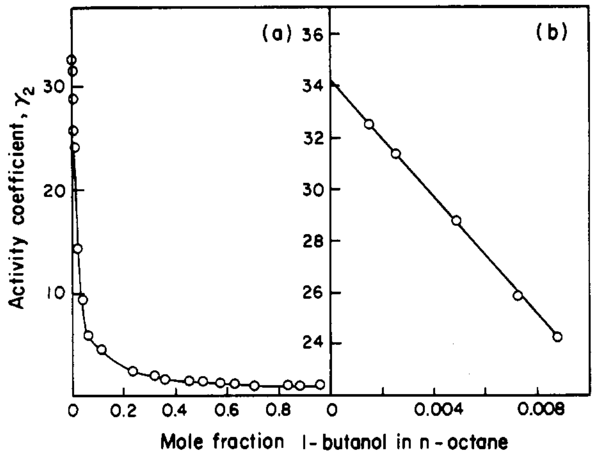

Figure 3. Activity coefficients for 1-butanol in *n*-octane shown over the whole region of mole fraction (a) and in the dilute solute region (b).

Table III. Limiting Activity Coefficients, Henry's Law Constants, and Gibbs Energies of Transfer (20 °C)

solute	solvent	γ_2^∞	k_H^∞, kPa	$\Delta_l^gG_2°$, kJ·mol^{-1}
1-butanol	H_2O	41.4	31.3	2.82
1-butanol	*n*-octane	34.2	25.9	3.30
1-butanol	CCl_4	17.3	13.1	4.96
2-methyl-1-propanol	H_2O	44.4	55.0	1.46
2-methyl-1-propanol	*n*-octane	46.0	57.0	1.37
2-methyl-1-propanol	CCl_4	18.5	22.9	3.59
2-butanol	H_2O	20.8	36.0	2.49
2-butanol	*n*-octane	26.7	46.3	1.88
2-butanol	CCl_4	15.2	26.3	3.25
2-methyl-2-propanol	H_2O	11.4	41.2	2.16
2-methyl-2-propanol	*n*-octane	20.6	74.3	0.72
2-methyl-2-propanol	CCl_4	16.4	59.3	1.27

Figure 3a shows activity coefficients for 1-butanol in *n*-octane, over a large mole fraction range in 3a, and in the very dilute mole fraction region in 3b. The results in the dilute region were obtained by using the flame ionization detector of the gas chromatograph. In this mole fraction range, the activity coefficients are quite linear with mole fraction and can be extrapolated back toward zero to obtain the solute activity coefficient at infinite dilution, γ_2^∞. The values of γ_2^∞ for all the systems investigated are listed in Table III. Henry's law constants, k_H^∞, can be obtained by multiplying the activity coefficient by the vapor pressure of the pure solute (*6*). Then, if the standard state for solute vapor is taken as 100 kPa, and the standard state for the solute in solution is taken as ideal solute mole fraction, the Gibbs energy of transfer of the solute to the gas is given by eq 2 where the superscript ∞ refers to

$$\Delta_l^gG_2° = -RT \ln (k_H^\infty/100) \qquad (2)$$

infinite dilution. Henry's law constants and Gibbs energies of transfer from the solution to the vapor are also listed in Table III.

From the Gibbs energies of transfer from an organic liquid to the vapor, and from water to vapor, Gibbs energies of transfer from the water to the organic may be obtained by simple subtraction. Thus, the Gibbs energy of transfer for 1-butanol from water to *n*-octane is 0.47 kJ·mol^{-1}, in excellent agreement with the 0.488 kJ·mol^{-1} obtained by Goffredi and Liveri (*11*) using a totally different calorimetric method.

The Gibbs energies of transfer to vapor from *n*-octane are roughly proportional to the relative surface area of the alkane portion of the alcohol, as noted by Rytting et al. (*12*). Gibbs energies of transfer from water are not easily attributable to any one single enthalpic or entropic factor, since there are known to be large compensating entropy and enthalpy contributions to the Gibbs energy of transfer from water (*9*).

Acknowledgment

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Registry No. 1-Butanol, 71-36-3; 2-methyl-1-propanol, 78-83-1; 2-butanol, 78-92-2; 2-methyl-2-propanol, 75-65-0; *n*-octane, 111-65-9; carbon tetrachloride, 56-23-5.

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Isopiestic Measurements of the Osmotic and Activity Coefficients for the System $HClO_4$–$Ba(ClO_4)_2$–H_2O at 25 °C

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Isopiestic measurements of the osmotic coefficients are presented for the system $HClO_4$–$Ba(ClO_4)_2$–H_2O. Parameters obtained from these results are used to calculate values of the osmotic coefficient and the activity coefficient of each component.

This paper is the third in a series on the Gibbs energies of mixed perchlorate solutions. The first paper (*1*) reported the results of isopiestic measurements on mixtures of univalent perchlorates. The second paper (*2*) reported the results of isopiestic measurements on mixtures of $HClO_4$ and $NaClO_4$ with $UO_2(ClO_4)_2$. This paper presents the results of such measurements on mixtures of $HClO_4$ and $Ba(ClO_4)_2$. The osmotic coefficient of $HClO_4$ increases strongly with ionic strength ($\phi = 4.39$ at $I = 15$) while that of $Ba(ClO_4)_2$ increases only slightly ($\phi = 1.79$ at $I = 15$). The mixture of these two should provide a good test of how well the osmotic coefficients of mixtures can be correlated.

Experimental Section

The experimental work described in this paper was performed in 1970. The delay in the analysis and presentation of the results was caused by a change in work assignment for the author.

Materials. The stock solution of H_2SO_4 was the same as used previously (*1*, *2*). The concentration was monitored by measuring the density to 5 parts in 100 000. The maximum change in molality from values used previously as indicated by these measurements was 0.06% over the course of these experiments.

The stock solution of NaCl was prepared from reagent grade crystals dried overnight at 200 °C. The concentration was calculated from the weight of the dried salt. Analysis by measurement of the density to 5 parts in 100 000 and comparison with the data of Wirth et al. (*3*) gave a difference in molality of 0.09%.

The stock solution of $HClO_4$ was prepared from reagent grade concentrated acid. The solution was analyzed by weight titration against Na_2CO_3. Analysis by measurement of the density to 5 parts in 100 000 and comparison with the data of Haase and Duecker (*4*) gave a molality 0.07% higher than the value obtained from the direct titration with Na_2CO_3.

The stock solution of $Ba(ClO_4)_2$ was prepared from reagent grade crystals. Flame photometric analysis of the solid crystals for strontium gave a value of 0.126% as Sr. Corrections were made for this impurity in all calculations. The concentration of the stock solution was determined by precipitation and weighing as $BaSO_4$ and determination of acid displaced from a H-form cation exchange resin. The molalities determined by these methods differed by 0.10%. A redetermination 2.5 years later by the $BaSO_4$ precipitation method gave a molality that was 0.23% higher than the earlier determination by this method. The concentration used was an average of the earlier and later measurements. Analysis by measurement of the density to 5 parts in 100 000 and comparison with the data of Kohner (*5*) and Willard and Smith (*6*) gave molalities that agreed by 0.01% for the earlier analyses and 0.08% for the later analyses.

Solutions of the various perchlorate mixtures were prepared by weight from the above solutions. Distilled water, passed through a mixed-bed ion-exchange column, was used for the preparation of all solutions.

Apparatus and Procedure. The apparatus and procedure have been described previously (*7*). The temperature of the bath varied 0.02 °C or less during the course of an equilibration. The temperature of the bath at equilibrium varied from one equilibration run to another within the range of 24.99–25.01 °C.

Following the weighing of the 12 dishes, the first dish was weighed again; the difference between the two weighings was less than 0.01% of the weight of the solution.

For each set of equilibrations there were at least two dishes containing the same solution. The maximum difference in concentration among the replicate dishes was 0.09%.

The reference material was NaCl up to the limit of its solubility and H_2SO_4 for higher concentrations. The osmotic coefficients for these electrolytes were taken from the tables given by Robinson and Stokes (*8*). The values used for the osmotic coefficient of NaCl differ from those derived from the results of Gibbard et al. (*9*) with an average deviation without regard to sign of 0.0012 and a maximum deviation of 0.0021. The values used for the osmotic coefficient of H_2SO_4 differ from those derived from the report of Staples (*10*) with an average deviation without regard to sign of 0.0045 and a maximum deviation of 0.0077.

Results

The concentrations at isopiestic equilibrium and the observed osmotic coefficients are given in Tables I–V. Concentrations are given as molality, *m*, and ionic strength on the molality