V	true molar volume of alcohol solution
V_I^0	true molar volume of pure liquid
v_I^L	molar volume of pure liquid I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	coordination number equal to 10

Greek Letters

γ_I	liquid-phase activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid and vapor mole fractions
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
$\Phi_{I_1}^0$	monomer segment fraction of component I at pure alcohol reference state
ϕ_I	vapor-phase fugacity coefficient of component I
ϕ_I^s	vapor-phase fugacity coefficient of pure component I at its saturation pressure P_I^s and system temperature T

Registry No. Methanol, 67-56-1; 2-propanol, 67-63-0; chlorobenzene, 108-90-7.

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Osmotic and Activity Coefficients of Tris Sulfate from Isopiestic Vapor Pressure Measurements at 25 °C

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The gravimetric isopiestic technique, with reference standards of NaCl, has been used to determine the osmotic and activity coefficients of Tris sulfate, $(TH)_2SO_4$, where TH represents the protonated form of the base 2-amino-2-(hydroxymethyl)-1,3-propanediol, in the molality range from 0.2 to 6 mol kg^{-1} at 25 °C. The parameters of the Pitzer equation and the Rush-Johnson equation were determined from the results. Tris sulfate was found to be a strong electrolyte, with activity coefficients similar to those of the alkali sulfates.

Introduction

Tris(hydroxymethyl)aminomethane (2-amino-2-(hydroxymethyl)-1,3-propanediol, THAM, or Tris) is useful both as an acidimetric standard (*1*) and as the basis for buffer systems in the physiological pH region (*2*). A solid base, easily purified, it has also been applied extensively, along with its protonated form, to study salt effects and solvent effects on the dissociation of cationic acids (see, for example, ref *3-6*). Despite evidence of anomalous liquid-junction potentials under certain conditions (*7*), Tris buffers may be useful as standards near pH 8 (*8*, *9*).

Because the buffer range (approximately from pH 7 to pH 9 (*10*, *11*)) includes the pH of natural seawater, Tris buffers are also well suited as standards for pH in seawater (*11-13*). Nevertheless, the assignment of reference pH values, based on either an activity or molality scale, may be rendered uncertain by unforeseen interactions between the buffer substances and constituents of the seawater solvent. The synthetic seawater used as a vehicle for the standard buffer contains Na^+, K^+, Mg^{2+}, and Ca^{2+} cations along with Cl^- and SO_4^{2-} anions. A strong interaction between Tris and sulfate, for example, leading possibly to slightly dissociated ion pairs $(TH{\cdot}SO_4)^-$ would alter both the ionic strength and the buffer ratio.

For this reason, we have determined the stoichiometric activity coefficients and osmotic coefficients of Tris sulfate in aqueous solution. The gravimetric isopiestic vapor pressure method was used, with solutions of NaCl as standards. The results demonstrate that $(TH)_2SO_4$ is a strong electrolyte, with activity coefficients comparable with those of Na_2SO_4, K_2SO_4, and $(NH_4)_2SO_4$.

Experimental Section

Tris sulfate was prepared by neutralizing Tris ("Trizma Base" from Sigma Chemical Co., St. Louis, MO 63178) with AnalaR sulfuric acid, diluted to about 1 M and standardized by weight titration. Tris was purified by crystallization and was dried under vacuum, as described earlier (*14*). Stoichiometric amounts of solid Tris and the stock solution of H_2SO_4 were mixed to produce a solution of $(TH)_2SO_4$ of precisely known concentration. The molality of this solution was about 1.2 mol kg^{-1}.

The reference solutions for the isopiestic measurements were prepared from twice recrystallized reagent-grade NaCl. Stock solutions were standardized gravimerically for chloride content.

The gravimetric isopiestic equipment has been described elsewhere (*15*). Solutions were contained in gold-plated silver cups placed on a slab of gold-plated copper 2.5 cm thick inside a vacuum desiccator which was rocked gently in a water bath maintained at 25 ± 0.01 °C. Equilibration times varied from 2 days to 4 weeks, being longest for the most dilute solutions.

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Table I. Isopiestic Molalities of Solutions of Tris Sulfate ($(TH)_2SO_4$) and Reference Solutions of Sodium Chloride at 25 °C

m_{NaCl}	$m_{(TH)_2SO_4}$	ϕ	m_{NaCl}	$m_{(TH)_2SO_4}$	ϕ
0.1894	0.1550	0.7523	2.7849	2.4813	0.7717
0.37519	0.31716	0.7253	2.9782	2.6711	0.7760
0.48845	0.42110	0.7120	3.0016	2.6741	0.7823
0.61424	0.53601	0.7053	3.0097	2.6980	0.7779
0.72351	0.63557	0.7028	3.2860	2.9308	0.7957
0.8129	0.71715	0.7019	3.3385	2.9754	0.7990
0.9677	0.8648	0.6985	3.8178	3.4131	0.8217
1.1301	1.0138	0.6991	4.1287	3.7115	0.8340
1.3727	1.2295	0.7083	4.6926	4.2609	0.8569
1.6755	1.5109	0.7145	4.7610	4.3091	0.8636
1.9865	1.7861	0.7290	5.2303	4.8070	0.8772
2.1304	1.9128	0.7361	5.6222	5.2215	0.8908
2.1595	1.9369	0.7381	6.1330	5.7721	0.9090
2.5889	2.3204	0.7579	6.1411	5.7742	0.9103

Table II. Parameters of the Pitzer and Rush–Johnson Equations (Eq 2–4) for $(TH)_2SO_4$ at 25 °C

Equation 2	Equations 3 and 4
$\beta^{(0)} = 0.09393$	$A = 1.0369$
$\beta^{(1)} = 0.59829$	$B = -0.02656$
$C^{\phi} = -0.004316$	$C = 0.006544$
$s(\phi)^a = 0.0026$	$D = -4.254 \times 10^{-4}$
	$E = 9.266 \times 10^{-6}$
	$s(\phi)^a = 0.0020$

[a] Standard deviation of fit.

Equilibrium was assumed to be complete when duplicate samples of solution reached the same molality within 0.1%. There was no evidence of corrosion of the isopiestic cups.

Results and Calculations

The isopiestic molalities of Tris sulfate and NaCl are collected in Table I, together with the corresponding values of the osmotic coefficient ϕ of the Tris sulfate solutions. The latter were derived from the relationship

$$\phi = \nu_R m_R \phi_R / \nu m \qquad (1)$$

where the subscript R designates the reference NaCl solution and ν is the number of ions from one molecule of the electrolyte in question (2 for NaCl and 3 for $(TH)_2SO_4$). Values of ϕ_R were interpolated with the aid of the Pitzer equation (*16*) for an electrolyte $M_{\nu_M}{}^{z_M} X_{\nu_X}{}^{z_X}$

$$\phi = 1 - 0.392|z_M z_X| \left[\frac{I^{1/2}}{1 + 1.2I^{1/2}}\right] + (2\nu_M\nu_X/\nu)m\,[\beta^{(0)} + \beta^{(1)} \exp(-2I^{1/2})] + [2(\nu_M\nu_X)^{3/2}/\nu]C^{\phi}m^2 \qquad (2)$$

where I is the ionic strength and z is the charge of the ion designated by the subscript. The Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for NaCl have the values 0.076 69, 0.264 61, and 0.001 219 3, respectively (*17*). Equation 2 reproduces the values of ϕ for NaCl given by Robinson and Stokes (*18*) with a standard deviation of fit of 0.0007.

The osmotic coefficients given in Table I were expressed as a function of the molality of $(TH)_2SO_4$ by fitting them to eq 2 ($\nu_M = |z_X| = 2$, $\nu_X = |z_M| = 1$). The parameters of the best-fit equation, determined by nonlinear least-squares methods, are given in Table II, along with the standard deviation of fit. In a similar manner, the parameters A–E of the five-constant Rush–Johnson equation (*19*, *20*)

$$\phi = 1 - \frac{2S}{A^3 I}[(1 + AI^{1/2}) - (1 + AI^{1/2})^{-1} - 2 \ln (1 + AI^{1/2})] + BI + CI^2 + DI^3 + EI^4 \qquad (3)$$

where the slope S was assigned the value 1.172 02, were determined. They are also given in Table II.

Table III. Osmotic and Activity Coefficients of Tris Sulfate at Round Molalities at 25 °C

$m_{(TH)_2SO_4}$	ϕ	$\gamma_{\pm}$	$m_{(TH)_2SO_4}$	ϕ	$\gamma_{\pm}$
0.2	0.743	0.355	1.6	0.720	0.191
0.3	0.725	0.313	1.8	0.730	0.187
0.4	0.714	0.286	2.0	0.741	0.184
0.5	0.707	0.266	2.5	0.770	0.179
0.6	0.703	0.251	3.0	0.799	0.177
0.7	0.701	0.239	3.5	0.825	0.177
0.8	0.700	0.230	4.0	0.848	0.177
0.9	0.700	0.222	4.5	0.868	0.177
1.0	0.701	0.215	5.0	0.884	0.178
1.2	0.705	0.204	5.5	0.900	0.179
1.4	0.712	0.197	6.0	0.919	0.181

Table IV. Activity Coefficients of Sulfates of the Charge Type M_2SO_4 at 25 °C

	M			
$m/(\text{mol kg}^{-1})$	Na^+	K^+	NH_4^+	Tris·H^+
0.2	0.371	0.356	0.343	0.355
0.5	0.270	0.261	0.248	0.266
1.0	0.204		0.189	0.215
2.0	0.154		0.144	0.184
3.0	0.139		0.125	0.177
4.0	0.138		0.116	0.177

Inasmuch as eq 3 reproduces the experimental data somewhat better than does eq 2, it was used, with the parameters listed in Table II, to calculate osmotic and activity coefficients for Tris sulfate at round molalities. The results for the molality range 0.2–6.0 are given in Table III. The activity coefficient equation corresponding to eq 3 is

$$\ln \gamma_{\pm} = \frac{-2SI^{1/2}}{1 + AI^{1/2}} + 2BI + (3/2)CI^2 + (4/3)DI^3 + (5/4)EI^4 \qquad (4)$$

It is now possible to compare the activity coefficients of Tris sulfate with those of other sulfates of the same charge type which are generally regarded as nonassociated electrolytes. Such a comparison appears in Table IV, which includes data taken from the compilations of Robinson and Stokes (*18*). It is evident that the activity coefficients of $(TH)_2SO_4$ are close to those of the alkali sulfates and ammonium sulfate below $m = 1$ and are higher than those of Na_2SO_4 and $(NH_4)_2SO_4$ in the molality range 1–4 mol kg^{-1}. It may also be noteworthy that the individual Pitzer parameters for Tris sulfate given in Table II display a pattern not radically different from those for these other sulfates, as given by Pitzer and Mayorga (*16*). These results indicate that no strong "abnormal" interactions between Tris·H^+ and SO_4^{2-} exist.

Registry No. $(TH)_2SO_4$, 23654-78-6.

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Three-Phase Liquid–Liquid–Vapor Equilibria in the Methane + Ethane + *n*-Hexane and Methane + Ethane + *n*-Heptane Systems

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The three-phase L_1–L_2–V equilibria behavior of the ternary systems methane + ethane + *n*-hexane and methane + ethane + *n*-heptane is studied. Also presented are the results for the binary system methane + *n*-heptane. The compositions and molar volumes of the liquid phases are reported as functions of temperature and pressure within the immiscibility regions. The two ternary systems have constituent binaries that exhibit L_1–L_2–V immiscibility (methane + *n*-hexane and methane + *n*-heptane, respectively). The addition of the third component, ethane, promotes three-phase behavior in a region extending upward in temperature. The three-phase regions of both systems are bounded from above by a K-point (L_1–L_2 = V) locus and from below by a LCST (L_1 = L_2–V) locus. The system of methane + ethane + *n*-heptane, however, has a fourth boundary of Q points (S–L_1–L_2–V). For both systems, the K point and LCST point loci intersect at a tricritical point (L_1 = L_2 = V).

Introduction

We have undertaken an extensive study of liquid–liquid–vapor (L_1–L_2–V) phenomena in well-defined ternary prototype systems of liquefied natural gas (LNG) (*1–5*). Many of these ternary system studies have exhibited L–L–V immiscibility without having an immiscible constituent pair. Some of the nitrogen-rich ternary systems studied, however, contained either the immiscible pair nitrogen + propane (*6*) or nitrogen + ethane (*7*).

Only a few binary prototype LNG hydrocarbon systems exhibit L–L–V three-phase behavior, almost always very near the critical point of the more volatile component. For example, the binary system of methane + *n*-hexane exhibits L–L–V immiscibility terminating with a critical end point of type K (L_1–L_2 = V) at the high-temperature end and an LCST (L_1 = L_2–V, lower critical solution temperature) at the low-temperature end (*8*). The L–L–V locus of the binary system methane + *n*-heptane extends from a K point at the high-temperature end to a four-phase S–L_1–L_2–V point, or Q point (quadruple point), at the low-temperature end (*9*).

This paper presents the results of the L_1–L_2–V phase equilibria of the ternary systems of methane + ethane + *n*-hexane and methane + ethane + *n*-heptane. The liquid-phase compositions and molar volumes are reported for the L_1 and L_2 phases within the three-phase region including the critical boundaries. The addition of the ethane component to each of the two binary immiscible pairs extends their respective multiphase behavior upward in temperature and pressure from the binary three-phase locus, in the direction of the ethane pure component critical point. These two ternary systems are bounded by (1) the binary L_1–L_2–V locus; (2) a locus of K points (L_1–L_2 = V); (3) a locus of LCST points (L_1 = L_2–V). There is also a fourth boundary for the system of methane + ethane + *n*-heptane, a locus of Q points (S–L_1–L_2–V), where S is a solid *n*-heptane phase. For both systems, the intersection of the loci of K points and LCST points is an invariant point, the tricritical point. For a more complete discussion of the three-phase topography, the reader is directed to ref *10*.

Experimental Section

The experimental work was performed with the aid of an apparatus of the type similar to the one developed by Kohn (*11*), designed to measure accurately pressure, temperature, volume, and input compositions of the chemical species added to a glass equilibria visual cell. The details of the experimental procedures are discussed in ref *1* and *2*. Volumetric calibration of the visual cell permits accurate accounting of the phase volumes of the multiphase behavior under study. Combination of the stoichiometric and volumetric measurements allows the computation of the composition and molar volume of each liquid phase present.

Precise measurement of the amount of each chemical species introduced into the cell is essential in the stoichiometric procedure. This was achieved by accurate temperature, pressure, and input volume determination. The temperature was measured with a platinum resistance thermometer, calibrated to the IPTS-1968 standards and was estimated to be accurate ±0.03 K. The equilibrium cell pressure was monitored by means of a Heise bourdon tube gauge with an accuracy of about ±0.07 bar. The phase volumes of the equilibrium mixtures were measured from calibrated cell markings which can be read to about ±0.02 cm^3. The visual cell volumes are typically about 10 cm^3.

In order to account properly for the distribution of the input composition in the liquid phases present, the vapor space was assumed to be composed of only methane + ethane in both ternary systems. The vapor-phase mixture of methane + ethane was assumed to have a composition consistent with the methane + ethane binary vapor–liquid system reported by Wichterle and Kobayashi (*12*). With this information on com-

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