194 *J. Chem. Eng. Data* **2000,** *45,* 194−201

Solubility of H_2S in (H_2O + CH_3COONa) and (H_2O + CH_3COONH_4) from 313 to 393 K and at Pressures up to 10 MPa

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New experimental results for the solubility of gaseous hydrogen sulfide in (about 4 or 6 molal) aqueous solutions of either sodium acetate or ammonium acetate at temperatures from 313 K to 393 K and total pressures up to about 10 MPa are reported. The experimental results are used to parametrize a thermodynamic model for calculating such gas solubilities.

Introduction

The solubility of sour gases is of interest in many applications, for example, in the chemical industry, in the oil and gas industries, and in environmental protection. In the course of an extended research project, the solubilities of the sour gases carbon dioxide, hydrogen cyanide, sulfur dioxide, and hydrogen sulfide in water and aqueous solutions of strong electrolytes were determined experimentally and modeled applying an extension of Pitzer's expression for the Gibbs excess energy of an aqueous electrolyte solution (Rumpf et al., 1992, 1993a,b, 1994a,b, 1997, 1998; Xia et al., 1999a−e). The present paper extends those investigations by studying the solubility of hydrogen sulfide in about 4 and 6 molal aqueous solutions of the single salts sodium acetate and ammonium acetate. The temperature range extends from about 313 K to about 393 K. The maximum molality of hydrogen sulfide in the aqueous phase was limited by the appearance of a second liquid but hydrogen sulfide-rich phase. The maximum pressure was close to 10 MPa.

Experimental Section

The experimental arrangement was exactly the same as that in some recent investigations (Rumpf et al., 1998; Xia et al., 1999a−e), and therefore no details are repeated here.

The mass of the charged gas (up to about 2.8 g) is determined by weighing with an uncertainty of ±0.008 g. The volume of the aqueous solvent needed to dissolve the gas is determined by measuring the position of the high-pressure displacer piston before and after each experiment. The mass of the solvent is calculated—with a relative uncertainty of ≤0.7%—from its known density (either from Washburn (1928) or from our own measurements). Three pressure transducers (WIKA GmbH, Klingenberg, Germany) for pressures ranging to 0.6 MPa, to 4 MPa, and to 10 MPa, respectively, were used to determine the solubility pressure. Before and after each series of meaurements, the transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The maximum uncertainty in the pressure measurement is about 1 kPa in the pressure range up to 0.5 MPa, and 4 kPa at higher pressures. The temperature is determined with two calibrated platinum resistance thermometers placed in the heating jacket of the cell with an estimated maximum uncertainty of about ±0.1 K.

The aqueous salt solutions were prepared in a storage tank. The molality of the salt in the aqueous solution was determined gravimetrically with a relative uncertainty not surmounting 0.1%.

Substances

Hydrogen sulfide (≥98 mol %, from Messer-Griesheim, Ludwigshafen, Germany) was used without further purification. Deionized water was degassed by vacuum distillation. Sodium acetate (≥ 99 mass %) and ammonium acetate (≥99 mass %) were purchased from Riedel de Haën AG, Seelze, Germany, and were degassed and dried under vacuum.

Experimental Results

The solubility of hydrogen sulfide in aqueous solutions of sodium acetate ($\bar{m}_{CH_3COONa} \approx 4$ and 5.8 mol/kg) was measured at 313, 333, 353, and 393 K. The solubility of hydrogen sulfide in aqueous solutions of ammonium acetate ($\bar{m}_{CH_3COONH_4} \approx 6$ mol/kg) was measured at 313, 353, and 393 K. The maximum ratio of hydrogen sulfide to water in the equilibrium cell was about 4.1 mol/kg for the system $H_2S + H_2O + CH_3COONa$ and 4.4 mol/kg for the system $H_2S + H_2O + CH_3COONH_4$. The total pressure ranged up to about 10 MPa. The experimental results are given in Tables 1 and 2. For the investigated systems, the formation of a second (hydrogen sulfide-rich) liquid phase was observed at higher concentrations of hydrogen sulfide. Therefore, the number of observed phases π is also given in Tables 1 and 2. When there are three phases, the number given for $\bar{m}_{H_2S}$ in those tables (and also in the corresponding figures) is no longer the solubility of H_2S in the aqueous solution, as all numbers for $\bar{m}_{H_2S}$ are the ratio of (moles of) hydrogen sulfide to (kilograms of) water in the equilibrium cell.

The experimental results for the total pressure above an aqueous, about 4 molal solution of sodium acetate are plotted in Figure 1 versus the amount of hydrogen sulfide per kilogram of water in the equilibrium cell. As was to be expected, the pressure nearly linearly increases at constant temperature with the amount of dissolved hydrogen sulfide until a second liquid, hydrogen sulfide-rich phase appears. The slope of such an isotherm in the two-phase region increases with increasing temperature, thus indicating the

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10.1021/je990233+ CCC: $19.00

Table 1. Experimental Results for the Solubility of Hydrogen Sulfide (2) in Aqueous Solutions of Sodium Acetate (1)

T/K	$\bar{m}_2$/mol·kg^{-1}	$\bar{m}_1$/mol·kg^{-1}	10p/MPa	π
313.14	0.153	3.968	1.834	2
313.15	0.453	3.968	7.07	2
313.16	0.477	3.968	7.58	2
313.14	0.814	3.968	14.29	2
313.13	1.166	3.968	21.78	2
313.14	1.185	3.968	22.20	2
313.16	1.371	3.968	26.84	2
313.15	1.750	3.968	28.29	3
313.16	1.959	3.968	28.29	3
333.15	0.121	3.968	1.62	2
333.16	0.406	3.968	7.82	2
333.15	0.424	3.968	7.97	2
333.15	0.889	3.968	19.34	2
333.14	1.173	3.968	26.72	2
333.15	1.447	3.968	35.38	2
333.16	1.534	3.968	38.03	2
333.15	1.782	3.968	42.68	3
333.16	1.868	3.968	42.68	3
353.16	0.111	3.968	1.822	2
353.15	0.337	3.968	7.07	2
353.17	0.414	3.968	8.96	2
353.17	0.876	3.968	21.92	2
353.17	1.201	3.968	32.39	2
353.16	1.441	3.968	41.29	2
353.15	1.765	3.968	53.38	2
353.16	2.034	3.968	61.58	3
353.16	2.158	3.968	61.58	3
393.18	0.000	3.968	1.684	2
393.16	0.244	3.968	6.62	2
393.18	0.289	3.968	7.90	2
393.19	0.676	3.968	19.84	2
393.16	0.889	3.968	27.94	2
393.18	1.450	3.968	49.60	2
393.18	1.872	3.968	68.67	2
393.20	1.978	3.968	73.67	2
393.18	2.302	3.968	91.24	2
313.16	0.209	5.730	2.378	2
313.15	0.488	5.730	7.72	2
313.15	0.508	5.730	7.97	2
313.16	0.891	5.730	15.62	2
313.14	1.037	5.730	18.98	2
313.15	1.111	5.730	20.82	2
313.14	1.163	5.730	21.94	2
313.14	1.416	5.730	28.30	3
313.14	1.443	5.730	28.30	3
313.17	1.774	5.730	28.31	3
313.16	1.781	5.730	28.31	3
313.16	1.932	5.730	28.31	3
313.15	2.269	5.730	28.31	3
333.13	0.250	5.730	3.685	2
333.15	0.492	5.730	8.82	2
333.15	0.495	5.730	8.92	2
333.14	0.511	5.730	9.55	2
333.15	0.820	5.730	17.61	2
333.15	0.934	5.730	20.67	2
333.15	1.068	5.730	23.70	2
333.14	1.430	5.730	35.24	2
333.15	1.636	5.730	41.39	2
333.13	1.949	5.730	42.60	3
333.14	2.072	5.730	42.60	3
353.15	0.093	5.730	1.281	2
353.15	0.469	5.730	9.60	2
353.15	0.987	5.730	24.94	2
353.14	1.139	5.730	30.68	2
353.15	1.596	5.730	47.05	2
353.15	1.740	5.730	53.22	2
353.14	2.727	5.730	61.68	3
353.14	4.084	5.730	61.62	3
353.15	0.223	5.769	3.616	2
353.16	0.463	5.769	9.72	2
353.15	1.192	5.769	31.94	2
353.15	1.766	5.769	53.58	2
353.15	1.946	5.769	61.85	3
353.16	3.447	5.769	61.85	3
393.16	0.000	5.730	1.556	2
393.16	0.000	5.769	1.546	2
393.15	0.353	5.769	8.51	2
393.15	0.404	5.769	10.19	2
393.16	0.426	5.769	11.02	2
393.16	0.942	5.769	28.47	2
393.16	1.004	5.769	30.60	2
393.16	1.166	5.769	37.96	2
393.16	1.490	5.769	50.97	2
393.18	1.721	5.769	62.45	2
393.18	1.933	5.769	73.05	2
393.17	2.046	5.769	79.12	2
393.17	2.402	5.769	97.08	2

increase of the Henry's constant of hydrogen sulfide in the salt-containing aqueous phase (as well as in pure water).

Figure 2 demonstrates the influence of the cation of the acetate salt on the solubility of hydrogen sulfide in the aqueous phase. While the solubility of hydrogen sulfide in aqueous solutions is always reduced by the presence of sodium sulfate, sodium chloride (Xia et al., 1999d), and sodium nitrate (Xia et al., 1999e), that is, "salting out" is observed, sodium acetate has a somewhat different influence on the solubility of hydrogen sulfide. At low partial pressures, sodium acetate increases the solubility of hydrogen sulfide whereas the inverse behavior is observed at high partial pressures. So an inversion from "salting-in" to "salting-out" is observed with increasing concentration of hydrogen sulfide in the aqueous phase. When the ammonium ion replaces the sodium ion in sulfate, chloride, nitrate, or acetate salts, the "salting-out" effect reduces and even a change to "salting-in" is observed not only for ammonium acetate (cf. Figure 2) but also for ammonium nitrate (Xia et al., 1999e). With ammonium acetate there is no inversion in the salt effect on the solubility of hydrogen sulfide in water. Such an inversion from "salting-in" to "salting-out" observed for the solubility of hydrogen sulfide in aqueous solutions of sodium acetate is due to the fact that hydrogen sulfide and acetic acid are both rather weak acids. Therefore, when hydrogen sulfide is dissolved in an aqueous solution of an acetate, the bisulfide ion and the acetate ion compete for the cation. So hydrogen sulfide can be dissolved also chemically (as bisulfide or sulfide) and acetate can be converted to acetic acid, which has a smaller Henry's constant and therefore exerts a smaller partial pressure than hydrogen sulfide. However, with increasing amount of dissolved hydrogen sulfide, the "salting-out" of both sodium acetate and sodium bisulfide overcompensate that first effect and "salting-out" is the predominant phenomenon. When sodium is replaced by ammonium in the acetate, the "salting-out" due to the presence of a salt is reduced (maybe even converted to "salting-in") and the inversion from "salting-in" to "salting-out" is not observed any longer.

As can also be seen from Figure 2, the experimental results for the pressure at the three-phase equilibrium are the same in the salt-free as in the salt-containing systems. The same behavior was observed for aqueous solutions of sulfates, chlorides, and nitrates (Xia et al., 1999d,e). This indicates that the second liquid phase contains no or very little salt.

Modeling

Figure 3 shows a scheme of the model applied to correlate the new data for the solubility of hydrogen sulfide in aqueous solutions containing sodium acetate or ammonium acetate. Due to chemical reactions in the liquid

Table 2. Experimental Results for the Solubility of Hydrogen Sulfide (2) in Aqueous Solutions of Ammonium Acetate (1)

T/K	$\bar{m}_2$/mol·kg^{-1}	$\bar{m}_1$/mol·kg^{-1}	$10p$/MPa	π
313.15	0.248	6.006	2.003	2
313.15	0.556	6.006	5.408	2
313.15	0.569	6.006	5.472	2
313.16	0.576	6.006	5.528	2
313.18	0.964	6.006	10.10	2
313.18	1.309	6.006	14.48	2
313.15	1.731	6.006	20.32	2
313.16	1.769	6.006	20.50	2
313.17	1.950	6.006	23.51	2
313.16	2.486	6.006	28.48	3
313.16	2.849	6.006	28.50	3
353.16	0.186	6.006	2.60	2
353.15	0.460	6.006	6.81	2
353.15	0.507	6.006	7.52	2
353.16	1.321	6.006	23.73	2
353.15	1.954	6.006	37.90	2
353.15	2.522	6.006	52.25	2
353.16	3.476	6.006	61.73	3
353.16	4.404	6.006	61.71	3
393.15	0.000	6.006	1.77	2
393.15	0.110	6.006	3.82	2
393.13	0.408	6.006	9.78	2
393.14	0.425	6.006	10.12	2
393.14	1.065	6.006	26.17	2
393.14	1.216	6.006	29.97	2
393.15	1.747	6.006	44.47	2
393.15	2.212	6.006	58.94	2
393.15	2.378	6.006	63.97	2
393.15	3.104	6.006	88.24	2

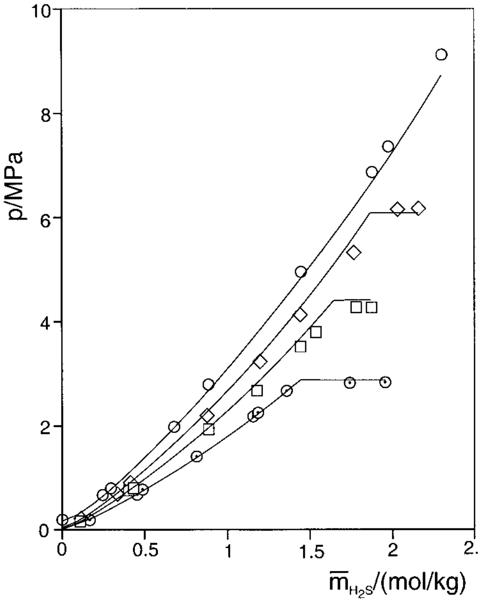

Figure 1. Solubility of hydrogen sulfide in an aqueous solution of sodium acetate ($\bar{m}_{CH_3COONa}$ = 4 mol/kg): (○, ◇, □, ⊙) exp results, this work (○, 393 K; ◇, 353 K; □, 333 K; ⊙, 313 K); (—) calculations, this work.

phase, hydrogen sulfide is present not only in molecular but also in ionic, nonvolatile form. It is assumed that sodium acetate and ammonium acetate are only present in the aqueous phase where they are completely dissociated. As acetic acid and hydrogen sulfide compete for the sodium (or ammonium) ions, acetate ions might be converted to (weak) acetic acid, which can be present also in molecular form, that is, as undissociated molecules. However, as the amount of molecular acetic acid is rather small and no information on the solubility of acetic acid in liquid hydrogen sulfide is available, the presence of acetic acid in the hydrogen sulfide-rich liquid is neglected.

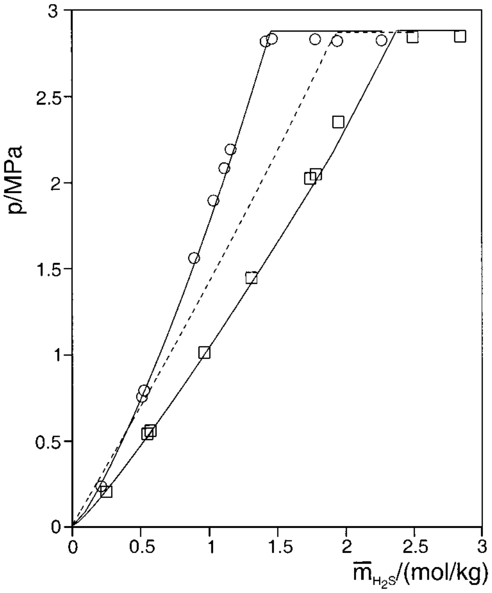

Figure 2. Solubility of hydrogen sulfide in aqueous solutions of either sodium or ammonium acetate at 313 K: (○, □) exp results, this work (○, $\bar{m}_{CH_3COONa}$ = 5.8 mol/kg; □; $\bar{m}_{CH_3COON4}$ = 6 mol/kg); (—) calculated results, this work; (- - -) calculated results for the system $H_2S + H_2O$.

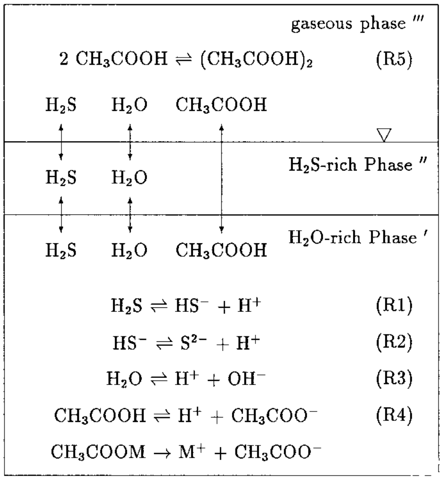

Figure 3. Scheme of modeling vapor–liquid–liquid equilibrium in aqueous solutions of hydrogen sulfide and sodium or ammonium acetate (M = Na^+ or NH_4^+).

Four chemical reactions are considered in the aqueous phase: the formation and dissociation of bisulfide, the autoprotolysis of water, and the dissociation of acetic acid:

$$H_2S \rightleftharpoons H^+ + HS^- \tag{R1}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \tag{R2}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{R3}$$

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \tag{R4}$$

Furthermore, the dimerization of acetic acid in the vapor phase is taken into account:

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2 \tag{R5}$$

whereas that dimerization is neglected in the liquid phase.

The second liquid phase is treated as a binary mixture of hydrogen sulfide and water.

Table 3. Henry's Constants of Hydrogen Sulfide and Acetic Acid in Pure Water

$$\ln \frac{H_{i,w}^{(m)}(T,p_w^s)}{(\mathrm{MPa{\cdot}kg{\cdot}mol^{-1}})} = A_i + \frac{B_i}{(T/\mathrm{K})} + C_i(T/\mathrm{K}) + D_i \ln(T/\mathrm{K})$$

i	A_i	B_i	C_i	D_i
H_2S	340.292	−13236.8	0.0595651	−55.0551
CH_3COOH	52.9967	−8094.25	0	−6.41203

Table 4. Second Virial Coefficients and Partial Molar Volumes of H_2S (1) at Infinite Dilution in Water (2)

T/K	B_{11}/ $\mathrm{cm^3{\cdot}mol^{-1}}$	B_{12}/ $\mathrm{cm^3{\cdot}mol^{-1}}$	B_{22}/ $\mathrm{cm^3{\cdot}mol^{-1}}$	$v_{1,2}^{\infty}$/ $\mathrm{cm^3{\cdot}mol^{-1}}$
313.15	−182	−381	−945	35.9
333.15	−162	−318	−737	37.2
353.15	−145	−270	−585	38.9
393.15	−118	−203	−389	43.7

Vapor−Liquid Equilibrium. The vapor−liquid equilibrium conditions for water, hydrogen sulfide, and acetic acid are

$$p_w^s \varphi_w^s \exp\left[\frac{v_w(p - p_w^s)}{RT}\right] a'_w = p y_w \varphi'''_w \tag{1}$$

$$H_{i,w}^{(m)}(\mathrm{T},p_w^s) \exp\left[\frac{v_{i,w}^{\infty}(p - p_w^s)}{RT}\right] a_i^{(m)} = p y_i \varphi'''_i \qquad i = \mathrm{CH_3COOH, H_2S} \tag{2}$$

$H_{i,w}^{(m)}(T,p_w^s)$ denotes Henry's constant for the solubility of component i in pure water on the molality scale. They were adopted from Edwards et al. (1978) and Rumpf et al. (1998), respectively (cf. Table 3). The influence of pressure on the Henry constant of hydrogen sulfide was considered using the partial molar volume of hydrogen sulfide in water as given by Brelvi and O'Connell (1972) (cf. Table 4), whereas for acetic acid it had to be neglected, as no data for the partial molar volume of molecular acetic acid in water at high dilution are available. The vapor pressure and liquid density of water were calculated from the equations of Saul and Wagner (1987).

The condition for chemical equilibrium for the dimerization of acetic acid in the vapor phase yields:

$$\bar{K}_p(T) = \frac{y_{(\mathrm{CH_3COOH})_2} \varphi'''_{(\mathrm{CH_3COOH})_2}}{(y_{\mathrm{CH_3COOH}} \varphi'''_{\mathrm{CH_3COOH}})^2} \cdot \frac{p°}{p} \tag{3}$$

The equilibrium constant was taken from Büttner and Maurer (1983, cf. Table 5). The vapor-phase fugacity coefficients were calculated from the virial equation of state truncated after the second virial coefficient. The second virial coefficient of pure water $B_{w,w}$ was calculated from a correlation based on the data collection by Dymond and Smith (1980, cf. Table 4). The second virial coefficient of pure hydrogen sulfide and the mixed second virial coefficient were estimated as recommended by Hayden and O'Connell (1975, cf. Table 4). All other second virial coefficients, that is, coefficients involving acetic acid monomers or dimers, were set to zero due to the lack of experimental information.

The presence of acetic acid in the vapor phase was included for the sake of completeness. However, the final phase equilibrium calculations revealed that the vapor-phase mole fractions of acetic acid monomers and dimers are very small (below about 0.05 mol %) and therefore their contribution to the total pressure above the aqueous phase is smaller than the uncertainty of the experimental results for the total pressure.

The condition for chemical reaction equilibrium in the aqueous phase is

$$K_R(T) = \prod_i a_i^{\nu_{i,R}} \quad (R = 1, ..., 4) \tag{4}$$

The balance equations for hydrogen sulfide, water, and the salt (sodium acetate or ammonium acetate) in the aqueous phase result in

$$\bar{n}_{\mathrm{H_2S}} = n'_{\mathrm{H_2S}} + n'_{\mathrm{HS^-}} + n'_{\mathrm{S^{2-}}} \tag{5}$$

$$\bar{n}_{\mathrm{H_2O}} = n'_{\mathrm{H_2O}} + n'_{\mathrm{OH^-}} \tag{6}$$

$$\bar{n}_{\mathrm{CH_3COOM}} = n'_{\mathrm{M^+}} \tag{7}$$

$$\bar{n}_{\mathrm{CH_3COOM}} = n'_{\mathrm{CH_3COO^-}} + n'_{\mathrm{CH_3COOH}} \tag{8}$$

The condition for liquid-phase electroneutrality is

$$n'_{\mathrm{H^+}} + n'_{\mathrm{M^+}} = n'_{\mathrm{OH^-}} + n'_{\mathrm{HS^-}} + 2n'_{\mathrm{S^{2-}}} + n'_{\mathrm{CH_3COO^-}} \tag{9}$$

Solving this set of equations for a given temperature and the overall mole numbers of mixed components (i.e. H_2S, H_2O, and CH_3COOM) results in the "true" composition of the liquid phase, that is, the molalities of true species i. This calculation requires knowledge of the temperature-dependent chemical equilibrium constants K_1 to K_4 as well as the activities a_i of all species present in the liquid aqueous phase. K_1 to K_3 were taken from Edwards et al. (1978); K_4 was calculated from data given by Brewer (1982) (cf. Table 5). A modified Pitzer model (Pitzer, 1973) for the excess Gibbs energy of aqueous solutions containing strong electrolytes is applied to calculate the activities of all species in the liquid phase:

$$\frac{G^E}{n_w RTM_w} = f_1(I) + \sum_{i \neq w} \sum_{j \neq w} m_i m_j [\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} f_2(x)] + \sum_{i \neq w} \sum_{j \neq w} \sum_{k \neq w} m_i m_j m_k \tau_{i,j,k} \tag{10}$$

Table 5. Chemical Equilibrium Constants

$$\ln K_R = A_R + \frac{B_R}{(T/\mathrm{K})} + C_R(T/\mathrm{K}) + D_R(T/\mathrm{K})^2 + E_R(T/\mathrm{K})^3 + F_R \ln(T/\mathrm{K})$$

R	A_R	B_R	10^2C_R	10^4D_R	10^7E_R	F_R
1	461.7162	−18034.72	9.19824	0	0	−78.07186
2	−214.5592	−406.0035	−5.411082	0	0	33.88898
3	140.932	−13445.9	0	0	0	−22.4773
4	−7.1741	44.0	−4.694733	1.93393	−2.67	0
5	−19.1001	7928.7	0	0	0	0

$f_1(I)$ is a modified Debye−Hückel term

$$f_1(I) = -A_\varphi \cdot \frac{4I}{b}\ln(1 + b\sqrt{I}) \tag{11}$$

where I is the ionic strength

$$I = \frac{1}{2}\sum_i m_i z_i^2 \tag{12}$$

b is 1.2 (kg/mol)$^{1/2}$ for all electrolytes. A_φ is the Debye−Hückel parameter for the osmotic coefficient

$$A_\varphi = \frac{1}{3}(2\pi N_A \rho_w)^{0.5}\left(\frac{e^2}{4\pi\epsilon_0 DkT}\right)^{1.5} \tag{13}$$

The dielectric constant of pure water is required for calculating $f_1(I)$. It was taken from Bradley and Pitzer (1979).

$\beta_{i,j}^{(0)}$ and $\beta_{i,j}^{(1)}$ are binary interaction parameters. The function f_2 is

$$f_2(x) = \frac{2}{x^2}[1 - (1 + x)e^{-x}] \tag{14}$$

where $x = 2\sqrt{I}$.

The activity of a dissolved species i is

$$\ln a_i^{(m)} = \ln m_i - A_\varphi z_i^2\left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln(1 + b\sqrt{I})\right] + 2\sum_{j\neq w} m_j[\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} f_2(x)] - z_i^2 \sum_{j\neq w}\sum_{k\neq w} m_j m_k \beta_{j,k}^{(1)} f_3(x) + 3\sum_{j\neq w}\sum_{k\neq w} m_j m_k \tau_{i,j,k} \tag{15}$$

where f_3 is

$$f_3(x) = \frac{1}{Ix^2}\left[1 - \left(1 + x + \frac{x^2}{2}\right)e^{-x}\right] \tag{16}$$

The activity of water follows from the Gibbs−Duhem equation

$$\ln a_w = M_w\left[2A_\varphi \cdot \frac{I^{1.5}}{1 + b\sqrt{I}} - \sum_{i\neq w}\sum_{j\neq w} m_i m_j(\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} e^{-x}) - 2\sum_{i\neq w}\sum_{j\neq w}\sum_{k\neq w} m_i m_j m_k \tau_{i,j,k} - \sum_{i\neq w} m_i\right] \tag{17}$$

As usual all parameters for interactions involving only species with the same sign of the electric charge were set to zero, that is, $\beta_{i,j}^{(0)} = \beta_{i,j}^{(1)} = \tau_{i,j,k} = 0$, when i, j, and k are either only cations or only anions.

For binary systems water + strong electrolyte $M_{\nu_+}X_{\nu_-}$ it is common practice to report $\beta_{M,X}^{(0)}$, $\beta_{M,X}^{(1)}$, and C_{MX}^{ϕ}. C_{Mx}^{ϕ} is the third osmotic virial coefficient, which contains the ternary parameters $\tau_{M,X,X}$ and $\tau_{M,M,X}$:

$$\frac{1}{3}C_{MX}^{\phi} = \left(\frac{\nu_+}{\nu_-}\right)^{1/2}\tau_{M,M,X} + \left(\frac{\nu_-}{\nu_+}\right)^{1/2}\tau_{M,X,X} \tag{18}$$

As there is usually no means to separate the influence of $\tau_{M,X,X}$ from that of $\tau_{M,M,X}$, one of those parameters is usually set to zero (here $\tau_{M,X,X} = 0$). For a 1:1 electrolyte C_{MX}^{ϕ} reduces to

$$\frac{1}{3}C_{MX}^{\phi} = \tau_{M,M,X} \tag{19}$$

For ternary systems water + strong electrolyte $M_{\nu_+}X_{\nu_-}$ + gas G it is common practice to neglect the parameters $\beta_{G,j}^{(1)}$ and $\beta_{G,k}^{(1)}$ (where j and k stand for both cation M and anion X) and to replace the parameters $\beta_{G,j}^{(0)}$ and $\tau_{G,j,k}$ by the parameters

$$B_{G,MX}^{(0)} = \nu_+\beta_{G,M}^{(0)} + \nu_-\beta_{G,X}^{(0)} \tag{20}$$

$$\Gamma_{G,MX,MX} = \nu_+^2\tau_{G,M,M} + 2\nu_+\nu_-\tau_{G,M,X} + \nu_-^2\tau_{G,X,X} \tag{21}$$

These equations follow from Pitzer's equation, provided that gas and electrolyte are nonreacting.

The expression for the Gibbs excess energy requires binary and ternary interaction parameters. Interaction parameters for the binary systems $H_2S + H_2O$ (i.e. $\beta_{H_2S,H_2S}^{(0)}$), $CH_3COOH + H_2O$ (i.e. $\beta_{CH_3COOH,CH_3COOH}^{(0)}$ and $\tau_{CH_3COOH,CH_3COOH,CH_3COOH}$), and $CH_3COONa + H_2O$ (i.e. $\beta_{Na^+,CH_3COO^-}^{(0)}$, $\beta_{Na^+,CH_3COO^-}^{(1)}$, and $C_{CH_3COONa}^{\phi}$) were taken from Kuranov et al. (1996), Rumpf et al. (1998), and Kim and Frederick (1988), respectively. All interaction parameters for the binary system $CH_3COONH_4 + H_2O$ were neglected. Rumpf et al. (1999) correlated vapor−liquid equilibrium data for the ternary system $NH_3 + H_2S + H_2O$ (cf. Table 6). The numbers for $B_{H_2S,NH_4HS}^{(0)}$, $\beta_{NH_4^+,HS^-}^{(0)}$, $\beta_{NH_4^+,HS^-}^{(1)}$, and $\tau_{NH_4^+,NH_4^+,HS^-}$ were taken from that publication. As in this system the concentrations of the NH_4^+ and HS^- ions are practically the same, $B_{H_2S,NH_4HS}^{(0)}$ was converted, applying eq 20, to

$$\beta_{H_2S,NH_4^+}^{(0)} = 0 \tag{22}$$

and

$$\beta_{H_2S,HS^-}^{(0)} = B_{H_2S,NH_4HS}^{(0)} \tag{23}$$

Combining eq 20 for $G \cong H_2S$ and $MX \cong Na_2SO_4$ and $(NH_4)_2SO_4$ with eq 22 gives

$$\beta_{H_2S,Na^+}^{(0)} = \frac{1}{2}[B_{H_2S,Na_2SO_4}^{(0)} - B_{H_2S,(NH_4)_2SO_4}^{(0)}] \tag{24}$$

The binary parameters $B_{H_2S,Na_2SO_4}^{(0)}$ and $B_{H_2S,(NH_4)SO_4}^{(0)}$ were taken from a correlation for the solubility of hydrogen sulfide in aqueous solutions of sodium sulfate and ammonium sulfate (Xia et al., 1999d).

All parameters for interactions where one species is either H^+ or OH^- or S^{2-} were set to zero, as those species are only present in very small amounts.

The System $H_2S-H_2O-CH_3COONa$. A sensitivity study revealed that among the remaining parameters $\beta_{H_2S,CH_3COO^-}^{(0)}$ and $\tau_{H_2S,Na^+,CH_3COO^-}$ are most important. All further remaining interaction parameters were set to zero. $\beta_{H_2S,CH_3COO^-}^{(0)}$ and $\tau_{H_2S,Na^+,CH_3COO^-}$ were fitted to the new experimental results for the total pressure above $H_2S + H_2O + CH_3COONa$. For the parameter determination, only vapor−liquid equilibrium data, that is, no experimental data in the three-phase region, were considered.

These parameters can be used to calculate the most common parameters $B_{H_2S,CH_3COONa}^{(0)}$ and $\Gamma_{H_2S,CH_3COONa,CH_3COONa}$.

$$B_{H_2S,CH_3COONa}^{(0)} = \beta_{H_2S,Na^+}^{(0)} + \beta_{H_2S,CH_3COO^-}^{(0)} \tag{25}$$

Table 6. Interaction Parameters for Pitzer's Equation for the Systems $H_2S + CH_3COONa + H_2O$ and $H_2S + CH_3COONH_4 + H_2O$

$$F(T) = q_{1,i} + \frac{q_{2,i}}{(T/K)}$$

parameter	$q_{1,i}$	$q_{2,i}$	T/K	subsystem	source
$\beta^{(0)}_{H_2S,H_2S}$	−0.26156	69.751	283−453	$H_2S + H_2O$	Kuranov et al. (1996)
$\beta^{(0)}_{CH_3COOH,CH_3COOH}$	−0.05761		298−363	$CH_3COOH + H_2O$	Rumpf et al. (1998)
$\tau_{CH_3COOH,CH_3COOH,CH_3COOH}$	0.00084				
$\beta^{(0)}_{Na^+,CH_3COO^-}$	0.13723		298	$CH_3COONa + H_2O$	Kim and Frederick (1988)
$\beta^{(1)}_{Na^+,CH_3COO^-}$	0.34195				
$C^{\phi}_{CH_3COONa}$	−0.00474				
$B^{(0)}_{H_2S,NH_4HS}$	0.05147	−21.2928	313−393	$NH_3 + H_2S + H_2O$	Rumpf et al. (1999)
$\beta^{(0)}_{NH_4^+,HS^-}$	−0.47256	174.8838			
$\beta^{(1)}_{NH_4^+,HS^-}$	6.4495	−2073.6627			
$\tau_{NH_4^+,NH_4^+,HS^-}$	0.03111	−10.83011			
$B^{(0)}_{H_2S,Na_2SO_4}$	−0.08436	115.72732	313−393	$H_2S + H_2O + Na_2SO_4$	Xia et al. (1999a)
$B^{(0)}_{H_2S,(NH_4)_2SO_4}$	0.14091	4.70824	313−393	$H_2S + H_2O + (NH_4)_2SO_4$	Xia et al. (1999a)
$\beta^{(0)}_{H_2S,CH_3COO^-}$	0.06859	−17.08745	313−393	$H_2S + H_2O + CH_3COONa$	fitted (this work)
$\tau_{H_2S,Na^+,CH_3COO^-}$	−0.00261				
$\tau_{H_2S,NH_4^+,CH_3COO^-}$	−0.00113	−0.09017	313−393	$H_2S + H_2O + CH_3COONH_4$	fitted (this work)

As τ_{H_2S,Na^+,Na^+} and $\tau_{H_2S,CH_3COO^-,CH_3COO^-}$ are both zero, applying eq 21 results in

$$\Gamma_{H_2S,CH_3COONa,CH_3COONa} = 2\tau_{H_2S,Na^+,CH_3COO^-} \quad (26)$$

The influence of temperature on any binary or ternary interaction parameter $F_i(T)$ was expressed by

$$F_i(T) = q_{1,i} + \frac{q_{2,i}}{(T/K)} \quad (27)$$

The numbers for $q_{i,1}$ and $q_{i,2}$ are given in Table 6.

The System $H_2S-H_2O-CH_3COONH_4$. The binary parameter $B^{(0)}_{H_2S,CH_3COONH_4}$ follows from eqs 20 and 22:

$$B^{(0)}_{H_2S,CH_3COONH_4} = \beta^{(0)}_{H_2S,CH_3COO^-} \quad (28)$$

$\beta^{(0)}_{H_2S,CH_3COO^-}$ was taken from the correlation presented above. Again, a sensitivity study revealed that among the remaining parameters $\tau_{H_2S,NH_4^+,CH_3COO^-}$ is most important. All other remaining interaction parameters were set to zero. $\tau_{H_2S,NH_4^+,CH_3COO^-}$ was fitted to the new VLE results above $H_2S + H_2O + CH_3COONH_4$.

As $\tau_{H_2S,NH_4^+,NH_4^+}$ and $\tau_{H_2S,CH_3COO^-,CH_3COO^-}$ are both zero, applying eq 21 results in

$$\Gamma_{H_2S,CH_3COONH_4,CH_3COONH_4} = 2\tau_{H_2S,NH_4^+,CH_3COO^-} \quad (29)$$

The influence of temperature on $\tau_{H_2S,NH_4^+,CH_3COO^-}$ was also expressed by eq 27. All nonneglected, that is, nonzero, interaction parameters are given in Table 6.

Vapor−Liquid−Liquid Equilibrium. The solubility of any salt as well as of acetic acid in the hydrogen sulfide-rich liquid phase is neglected. Therefore, that liquid is assumed to be a binary mixture of hydrogen sulfide and water. The phase equilibrium between the coexisting liquid phases is expressed by

$$K_i^{\prime\prime,\prime} = \frac{a_i''}{a_i'} = \exp\left[\frac{\mu_i^{ref,\prime} - \mu_i^{ref,\prime\prime}}{RT}\right] \qquad i = H_2S, H_2O \quad (30)$$

where $K_i^{\prime\prime,\prime}$ is the distribution coefficient of component i (hydrogen sulfide and water) between the water-rich (′) and the hydrogen sulfide-rich phases (″).

Table 7. Distribution Coefficients of Hydrogen Sulfide and Water in $H_2S + H_2O$

$$\ln K_i^{\prime\prime,\prime} = g_{1,i} + \frac{g_{2,i}}{(T/K)}$$

i	$g_{1,i}$	$g_{2,i}$
H_2S	−1.0711	173.1356
H_2O	3.44803	−2429.741

In the hydrogen sulfide-rich phase, concentrations are expressed through mole fraction, and the unsymmetric convention for normalization is chosen: For hydrogen sulfide the reference state is the pure liquid $\mu_{H_2S}^{ref,\prime\prime} = \mu_{H_2S}(T,p)_{pure\ liquid}$; for water it is the infinitly diluted solution $\mu_w^{ref,\prime\prime} = \mu^{\infty}_{w,H_2S}(T,p)$. As the second liquid phase is nearly pure hydrogen sulfide, it is assumed that this phase behaves like an ideal solution. Therefore, the activities of hydrogen sulfide and water were replaced by the mole fractions

$$a_i'' = x_i'' \qquad i = H_2S, H_2O \quad (31)$$

The distribution coefficients as taken from Xia et al. (1999a) are given in Table 7.

Comparison of Experimental Data with Model Calculations

Figure 1 shows a comparison between the new experimental results for the total pressure required to dissolve hydrogen sulfide in a 4 molal aqueous solution of sodium acetate and the correlation given above. Typically, the relative deviation in the total pressure is about 1 to 4%. However, as in a few cases relative deviations of >10% are observed, the absolute mean deviation is 4.2%. The maximum relative deviation is 18.1%. This is observed for 353 K at 0.1281 MPa, where the calculated pressure is too large by about 23 kPa. The correlation gives the pressure at the three-phase vapor−liquid−liquid equilibrium with an average deviation of 1.9%.

Figure 4 shows the calculated "true" molalities of the most important species when hydrogen sulfide is dissolved in a 6 molal aqueous solution of sodium acetate at 313 K.

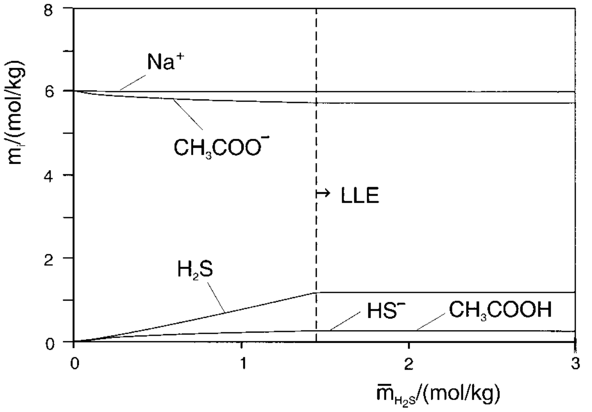

Figure 4. Predictions for species distribution in the system $H_2S + H_2O + CH_3COONa$ at 313 K, $\bar{m}_{CH_3COONa} = 6$ mol/kg.

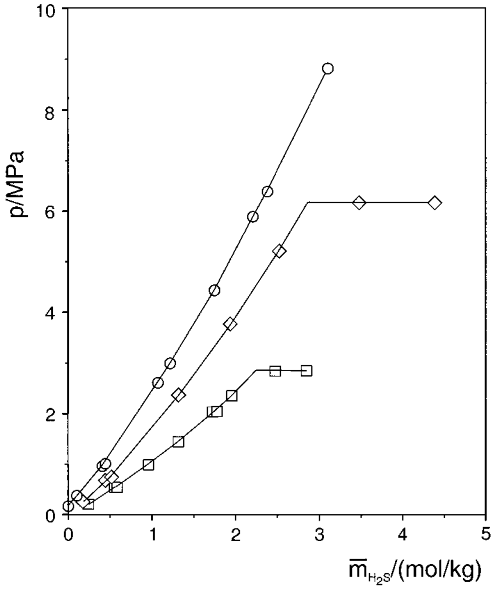

Figure 5. Solubility of hydrogen sulfide in aqueous solutions of ammonium acetate ($\bar{m}_{CH_3COON4} = 6$ mol/kg): (○, ◇, □) exp results, this work (○, 393 K; ◇, 353 K; □, 313 K); (—) calculated results, this work.

In accordance with the explanations given above, that figure shows that hydrogen sulfide competes with acetic acid for the sodium ions and consequently some acetate is converted to acetic acid.

The new experimental results for the total pressure required to dissolve hydrogen sulfide in an about 6 molal aqueous solution of ammonium acetate are compared to the results from the correlation in Figure 5. The absolute mean deviation between the experimental results for the total pressure and the results of the correlation is about 5.2%. The maximum relative deviation is nearly 24% (or 92 kPa) at 393 K and 0.382 MPa. The mean relative deviation between the measured and calculated pressures in the three-phase equilibrium is 1.0%.

Conclusions

The solubility of hydrogen sulfide in aqueous solutions containing the single salts sodium acetate and ammonium acetate was measured at temperatures from 313 to 393 K and at total pressures up to 10 MPa. The molalities were about 4 and 5.8 mol/kg for sodium acetate and about 6 mol/kg for ammonium acetate. In some experiments, that concentration was above the solubility limit for hydrogen sulfide and, therefore, a second (hydrogen sulfide-rich) liquid phase was observed. A thermodynamic model is used to describe the vapor−liquid and vapor−liquid−liquid equilibria. Interaction parameters for Pitzer's G^E equation were determined from the new experimental results. The model correlates most of the experimental data within the experimental uncertainty. It also gives reliable predictions for the three-phase (VLLE) pressure.

Nomenclature

$A_i...D_i$ = coefficients for the temperature dependence of Henry's constant for the solubility of component i in pure water
$A_R...F_R$ = coefficients for the temperature dependence of chemical equilibrium constants
A_φ = Debye−Hückel parameter
a_i = activity of component i
b = constant in modified Debye−Hückel expression
$B^{(0)}_{G,MX}$ = effective second osmotic virial coefficient for interactions between a gas G and a salt MX
C^ϕ = third osmotic virial coefficient in Pitzer's equation
D = relative dielectric constant of water
e = charge of proton
f_1, f_2, f_3 = functions in Pitzer's equation
F = function for the temperature dependence of an interaction parameter
g_i = coefficients for the temperature dependence of distribution coefficients
G = gas (here hydrogen sulfide)
G^E = excess Gibbs energy
$H^{(m)}_{i,w}$ = Henry's constant for the solubility of gas i in pure water (on molality scale)
I = ionic strength (on molality scale)
k = Boltzmann constant
K_i = distribution coefficient
K_R = equilibrium constant for chemical reaction R (on molality scale)
$\bar{K}_p$ = equilibrium constant for the dimerization of acetic acid in the vapor phase
M = cation M
M_w = molar mass of water in kg/mol
$\bar{m}_i$ = overall molality of component i in equilibrium cell
m_i = true molality of component i
$\bar{n}_i$ = overall number of moles of component i
n_i = true number of moles of component i
N_A = Avogadro's number
p = pressure
$p°$ = standard pressure ($p° = 0.1$ MPa)
q_i = coefficients for the temperature dependence of interaction parameters
R = universal gas constant
T = absolute temperature
v = partial molar volume
X = anion X
x = variable in Pitzer's equations
y = mole fraction in vapor
z_i = number of charges of component i

Greek Letters

$\beta^{(0)}$, $\beta^{(1)}$ = binary interaction parameters in Pitzer's equation
$\gamma^{(m)}$ = activity coefficient normalized to infinite dilution (on molality scale)
Γ = third osmotic virial coefficient
ϵ_0 = vacuum permittivity
μ_i = chemical potential of component i

$v_{i,R}$ = stoichiometric coefficient of component i in reaction R
ν_+, ν_- = number of cations and anions in salt $M_{\nu_+}X_{\nu_-}$
π = number of phases
ρ = mass density
τ = ternary interaction parameter in Pitzer's equation
φ = fugacity coefficient

Subscripts

G = gas
i, j, k = components i, j, k
R = reaction R
s = salt
w = water

Superscripts

(m) = on molality scale
s = saturation
∞ = infinite dilution
$'$ = water-rich liquid phase
$''$ = hydrogen sulfide-rich liquid phase
$'''$ = gas phase
ref = reference state

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Received for review August 18, 1999. Accepted November 8, 1999. Financial support of this investigation by the government of the Federal Republic of Germany (BMFT Grant No. 0326558 C) and by BASF AG, Ludwighafen, Bayer AG, Leverkusen, Degussa AG, Hanau, Hoechst AG, Frankfurt, Linde KCA, Dresden, and Lurgi AG, Frankfurt, is gratefully acknowledged. J.X. thanks the Deutscher Akademischer Austauschdienst (DAAD) for granting a scholarship.

JE990233+