Table II. Smoothed Values for γ_1

T (°C)	Smoothed ΔT	N_2	N_1	P_1^0 (mmHg)	γ_1
105	5	0.068	0.932	906.07	0.8999
110	10	0.125	0.875	1074.56	0.8083
115	15	0.180	0.820	1267.98	0.7309
120	20	0.230	0.770	1489.14	0.6628
125	25	0.280	0.720	1740.93	0.6063
130	30	0.330	0.670	2026.16	0.5598
135	35	0.380	0.620	2347.26	0.5222
140	40	0.412	0.588	2710.92	0.4767
145	45	0.470	0.530	3116.76	0.4600
150	50	0.520	0.480	3570.48	0.4434
155	55	0.570	0.430	4075.88	0.4336
160	60	0.610	0.390	4636.00	0.4203

using data for 40 salt–water systems. From the results it is concluded that, in general, the degree of dissociation of these salts in boiling, saturated, aqueous solution appears to be sufficiently small that its effect on the BPR is not significant. This apparent behavior at saturation is in marked contrast to the strong dissociation tendencies of many of these salts at lower concentrations.

The behavior of boiling saturated solutions can be useful in elucidating solvent and solution structure. If the information obtained can be generalized, prediction of salt behavior in mixed, as well as single, solvents may become possible.

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Solubility of Hydrogen Sulfide and Carbon Dioxide in a Sulfinol Solution

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The solubility of H_2S and CO_2 individually in a Sulfinol solution (40 wt % DIPA, 40 wt % sulfolane, 20 wt % water) has been measured at 40 and 100 °C. Partial pressures of H_2S ranged from 5 to 3900 kPa while partial pressures of CO_2 ranged from 2.4 to 5700 kPa.

The removal of the acid gases (H_2S and CO_2) from natural and refinery gases is commonly accomplished by absorption in a suitable solvent. Many processes employ an aqueous alkanolamine solution and are classed as "chemical" processes. They have the advantage of being able to reduce the concentrations of H_2S and CO_2 to low levels, even at low total pressures of the gas stream. However, the alkanolamine solutions do not remove mercaptans and other sulfur compounds readily, and require the application of large quantities of heat for regeneration. These disadvantages have led to the development of "physical" processes which employ a solvent, usually nonaqueous, to remove the H_2S, CO_2, and other sulfur compounds and which require little energy for regeneration, as most of the absorbed gases come out of solution upon reduction of the pressure. In some cases, though, the physical processes are unable to reduce H_2S to pipeline specifications without excessively large circulation rates. Factors to be considered in the selection of processes have been discussed recently by Richardson and O'Connell (*10*).

The Sulfinol process (*1–3*), patented by Shell, was devised to combine the advantages of the chemical and physical processes. The solvent consists of sulfolane, a physical solvent, together with diisopropanolamine (DIPA) and water, a chemical solvent. DIPA has the advantages of being less corrosive (*3, 9*) and less sensitive to degradation (*2*) than primary amines. The relative amounts of these components can be varied in a given treating process. Little solubility data for the acid gases in Sulfinol solution have been released. Operating details have been provided in various publications (*1–4, 6*), but only qualitative solubility data were presented. The present investigation was undertaken to provide equilibrium solubility data for CO_2 and H_2S in a typical Sulfinol solution. These data may be useful in comparisons of alternate treating processes.

Experimental Section

The apparatus used in this study is the same as that used for previous studies of H_2S–CO_2–monoethanolamine, H_2S–CO_2–diethanolamine, and H_2S–CO_2–DIPA systems in this laboratory (*5, 7, 8*). The equilibrium cell consisted of a Jerguson gauge and a gas reservoir (250-mL capacity) mounted at the top. A magnetic pump was used to circulate the gas phase from the reservoir to the bottom of the gauge. The temperature of the cell was measured by ten-junction copper–Constantan thermopiles which had been calibrated at the ice and steam points. The pressure of the cell was measured by a Heise bourdon tube gauge. The equilibrium cell was housed in a constant temperature air bath controlled within ±0.5 °C. The chromatograph used in this work had a 10-ft long, ¼-in. o.d. column packed with Chromosorb 104. It was operated isothermally at 100 °C.

The Sulfinol solution, composed of 40 wt % DIPA, 40 wt % sulfolane (tetrahydrothiophene 1,1-dioxide), and 20 wt % water,

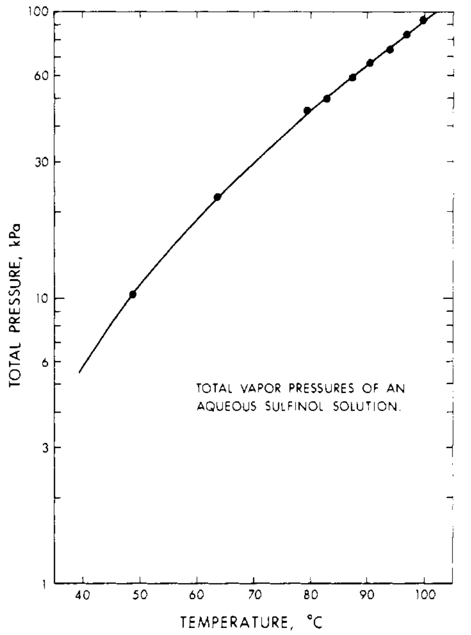

Figure 1. Total vapor pressures of aqueous Sulfinol solution.

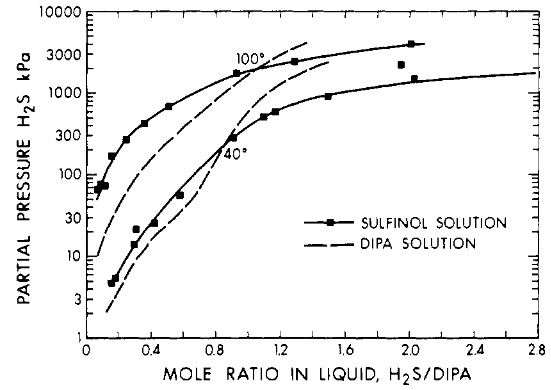

Figure 2. Solubility of H_2S in Sulfinol and DIPA solutions.

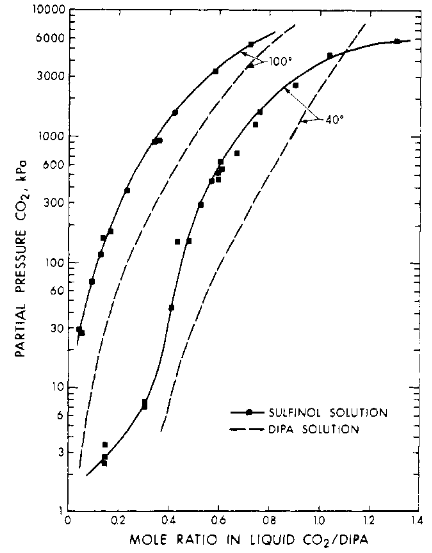

Figure 3. Solubility of CO_2 in Sulfinol and DIPA solutions.

Table I. Experimental Data for the Solubility of CO_2 in Aqueous Sulfinol Solution[a-c]

T/°C	P	α	T/°C	P	α
40	5688.0	1.302	100	5469.6	0.719
	4410.6	1.035		5371.6	0.717
	2597.5	0.901		3339.6	0.573
	1544.6	0.758		1534.8	0.419
	1232.6	0.743		935.0	0.356
	736.8	0.666		887.8	0.338
	539.0	0.604		364.5	0.229
	628.1	0.600		175.4	0.166
	521.4	0.592		157.0	0.134
	452.7	0.590		117.7	0.126
	439.6	0.566		69.6	0.091
	288.2	0.526		27.9	0.047
	147.7	0.474		29.3	0.041
	149.3	0.430			
	42.1	0.405			
	7.5	0.308			
	6.9	0.305			
	2.6	0.148			
	3.4	0.146			
	2.4	0.146			

[a] 40 wt diisopropanolamine and 40 wt % sulfolane. [b] α, mole ratio in liquid, CO_2/DIPA. [c] P, partial pressure of CO_2 in kPa.

Table II. Experimental Data for the Solubility of H_2S in Aqueous Sulfinol Solution[a-c]

T/°C	P	α	T/°C	P	α
40	2291.3	4.429	100	3862.3	1.988
	2051.2	3.339		2405.9	1.283
	1410.3	2.022		1748.8	0.929
	1081.9	1.598		1122.6	0.733
	865.6	1.492		658.7	0.510
	585.3	1.173		419.5	0.352
	502.3	1.091		262.1	0.243
	277.6	0.901		165.0	0.150
	55.9	0.582		71.7	0.119
	25.3	0.424		76.4	0.083
	20.3	0.308		63.7	0.074
	13.8	0.297			
	5.2	0.175			
	4.6	0.152			

[a] 40 wt % diisopropanolamine and 40 wt% sulfolane. [b] α, mole ratio in liquid, H_2S/DIPA. [c] P, partial pressure of H_2S, kPa.

was charged into the cell and H_2S or CO_2 was added in amounts determined by observation of the pressure. The DIPA and sulfolane were obtained from commercial suppliers and had minimum purities of 97 and 99%, respectively. Nitrogen was added, when necessary, to ensure that the total pressure was always greater than 350 kPa. The presence of nitrogen did not visibly alter the solubility behavior, even at low partial pressures of H_2S or CO_2. The vapor was circulated through the liquid for at least 8 h to ensure that equilibrium had been reached.

Samples of the vapor were withdrawn from the top of the cell and passed to the gas chromatograph for analysis. The partial pressure of CO_2 or H_2S was calculated from the analysis and a consideration of the gauge, barometric, and vapor pressures. The latter was measured by the boiling point method (*11*); the results are presented in Figure 1.

Liquid samples were withdrawn from the bottom of the cell and passed into a sample bottle containing 7 M H_2SO_4. Upon contact with the H_2SO_4, the acid gas evolved and was collected in a buret of 250 mL capacity. To ensure more complete evolution of the acid gas, the sample bottle was then heated to 100 °C. The pressure of the evolved gases was adjusted to atmospheric and their temperature was measured. From the P-V-T data the amount of gas which evolved was determined and the ratio of CO_2 or H_2S to DIPA in the liquid phase was calculated. The data are estimated to be accurate to about 0.02 or 4%, whichever is larger, in liquid concentration at a given partial pressure of acid gas.

Results and Discussion

Experimental measurements of the solubility of CO_2 and H_2S in a Sulfinol solution have been made at 40 and 100 °C. Partial pressures of CO_2 ranged from 2.4 to 5688 kPa while partial pressures of H_2S ranged from 4.6 to 3862 kPa. The results are presented in Tables I and II for CO_2 and H_2S, respectively. No comparisons with data from the literature are possible for this solution, but comparisons with a 2.5 kmol m^{-3} DIPA solution are shown on Figures 2 and 3 for H_2S and CO_2, respectively. The amount of DIPA in the Sulfinol solution is equivalent to that in a 3.4 kmol m^{-3} solution so that the somewhat lower solubility in the Sulfinol solution is consistent with the effect of amine concentration on solubility behavior. At high partial pressures, however, the effect of the physical solvent, sulfolane, becomes paramount and leads to high solubilities of the acid gases in the liquid. The present results are consistent with the statement (*4*) that Sulfinol solutions are attractive solvents at acid gas partial pressures of 760 kPa or greater.

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Vapor–Liquid Equilibria at 25 °C for Nine Alcohol–Hydrocarbon Binary Systems

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Solution vapor pressures at 25 °C were measured over the complete composition range for the nine alcohol–hydrocarbon binary systems formed among methanol, ethanol, 1-propanol, *n*-hexane, cyclohexane, and benzene. Vapor compositions and excess Gibbs energies were calculated from these data by the method of Mixon, Gumowski, and Carpenter. Heat-of-mixing data from the literature were combined with the present data to permit presentation of complete information on the excess properties G^E, H^E, and S^E for each system.

Recent interest in prediction of the phase behavior of nonideal solutions has led to the introduction of numerous models to represent this behavior. To develop and/or evaluate such models, especially those of the group-contribution type, requires accurate, systematic data on homologous series of substances with limited numbers of functional groups. Such data are surprisingly scarce. The present study was designed to produce data on the behavior of normal alcohols with an aliphatic, a naphthenic, and an aromatic six-carbon hydrocarbon. The particular systems were selected, in part, because heat-of-mixing data are available for each system, thus rather complete excess properties (G^E, H^E, S^E) could be calculated from the combined data.

Experimental Section

Apparatus. Detailed description of the experimental work is given elsewhere (*7*). Basically, the apparatus is similar in many features to that used by Gibbs and Van Ness (*5*). As shown in Figure 1, the major components of the system included a degassing assembly and storage bulb for each component of a binary system under study, a liquid measurement and injection assembly, an equilibrium cell, and a pressure measurement facility. All components other than the degassing assemblies were housed in a constant-temperature air bath where temperature was controlled at 26.0 ± 0.2 °C. The equilibrium cell was further immersed in a liquid (water) bath where the temperature was controlled at 25.0 ± 0.01 °C. Temperatures were measured by mercury-in-glass thermometers which had been calibrated against an NBS-certified platinum-resistance thermometer.

The equilibrium cell (Figure 2) is patterned after that of Gibbs and Van Ness. However, the pressure measurement and liquid measurement and injection apparatus differed from their design. Pressures were measured by a mercury manometer with levels determined by cathetometer. The manometer was maintained at a temperature of 28–29 °C to prevent condensation of vapor

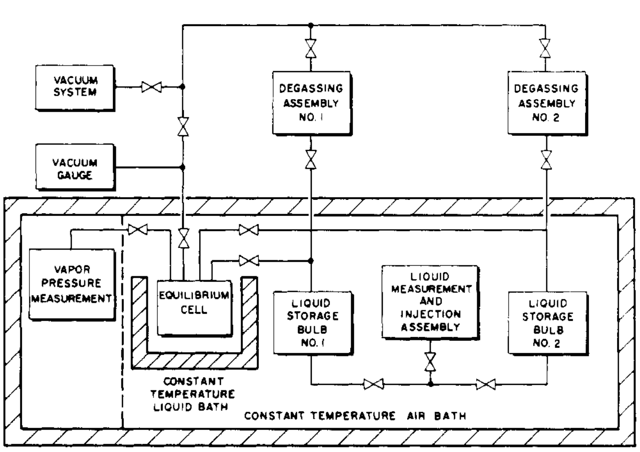

Figure 1. Schematic diagram of apparatus.