Table I. Properties of *N-o*-Tolylbenzohydroxamic Acids[a]

Compd no.	Benzohydroxamic acid	Mol formula	Mp, °C	% yield	Color	IR spectra (cm^{-1}) ν_{O-H}	$\nu_{C=O}$	ν_{N-O}
I	*N-o*-Tolyl-*o*-fluoro-	$C_{14}H_{12}NO_2F$	130	70	White	3165	1625	935
II	*N-o*-Tolyl-*p*-fluoro-	$C_{14}H_{12}NO_2F$	140	70	White	3160	1620	930
III	*N-o*-Tolyl-*o*-bromo-	$C_{14}H_{12}NO_2Br$	110	60	White	3175	1620	930
IV	*N-o*-Tolyl-*m*-bromo-	$C_{14}H_{12}NO_2Br$	90	65	White	3175	1625	925
V	*N-o*-Tolyl-*p*-bromo-	$C_{14}H_{12}NO_2Br$	155	65	White	3180	1620	923
VI	*N-o*-Tolyl-*p*-iodo-	$C_{14}H_{12}NO_2I$	140	60	Light pink	3200	1625	930
VII	*N-o*-Tolyl-*o*-nitro-	$C_{14}H_{12}N_2O_4$	150	70	Light yellow	3170	1615	930
VIII	*N-o*-Tolyl-*m*-nitro-	$C_{14}H_{12}N_2O_4$	101	70	Light yellow	3165	1600	920
IX	*N-o*-Tolyl-*p*-nitro-	$C_{14}H_{12}N_2O_4$	170	65	Light yellow	3175	1620	925
X	*N-o*-Tolyl-3,5-dinitro-	$C_{14}H_{11}N_3O_6$	140	65	Light yellow	3125	1630	920

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review.

fine suspension of 12.6 g (0.15 mol) of sodium bicarbonate in 25 ml of water were added. After the mixture was cooled to 0 °C, 23.12 g (0.1 mol) of *O*-fluorobenzoyl chloride dissolved in 50 ml of diethyl ether was added dropwise over a period of 1 h. Then an additional time of 30 min was allowed and the temperature was maintained at 0 °C or lower. Some of the product was precipitated as white solid while the ether layer was separated and the ether removed under vacuum. The light yellow residue was combined with the precipitated white solid, triturated for about 15 min on a porcelain mortar with a saturated solution of sodium bicarbonate to remove the acid impurities, filtered, and washed with cold water. The yield of air dried product, mp 135 °C, was 70%. Two crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave white needles, mp 140 °C.

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Solubility of Hydrogen Sulfide and Carbon Dioxide in an Aqueous Diisopropanolamine Solution

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The solubility of H_2S and CO_2 individually in a 2.5 kmol m^{-3} DIPA solution has been determined at 40 and 100 °C for partial pressures of H_2S ranging from 2.0 to 3207 kPa and for partial pressures of CO_2 ranging from 2.7 to 5888 kPa.

Aqueous alkanolamine solutions are widely used for the removal of the acid gases (H_2S and CO_2) from natural gas and synthesis gas streams. The most commonly used amine is monoethanolamine (MEA). Its primary advantage is its low molecular weight. Since the acid gases and amines react on an equivalent rather than a weight basis MEA requires lower circulation rates than other higher molecular weight amines. As well MEA is a stronger base than other alkanolamines. However, MEA reacts irreversibly with carbonyl sulfide (COS) and for this reason diethanolamine (DEA) solutions are commonly employed for natural gases containing COS and for refinery gases (*3*).

Diisopropanolamine (DIPA) has been widely used in Europe for the removal of the acid gases from synthesis gas and refinery gases and liquids. It is used in the Adip process, the Sulfinol process, and the SCOT process, all licensed by Shell. The Adip process was originally described by Bally (*1*) and recent developments and operating data have been provided by Klein (*2*). DIPA solutions are reported to be less corrosive than MEA or DEA solutions, have a greater selectivity for H_2S over CO_2 than either MEA or DEA, and as well are able to remove COS with excessive degradation of the solution. Another advantage claimed for DIPA solutions is that they require less heat in the regeneration of the solution.

In the Sulfinol process, aqueous DIPA is in combination with the physical solvent sulfolane (a typical Sulfinol solution contains 40% DIPA, 40% sulfolane, 20% water). The SCOT process, a tail-gas treating process employs a DIPA solution in order to effect a selective removal of H_2S from a stream containing H_2S and CO_2. DIPA is regarded as the best compromise among the alkanolamines (*8*).

Few solubility data for the acid gases in DIPA solutions have been published. Bally (*1*) presented a small-scale plot showing

Table I. Experimental Data for the Solubility of CO_2 in 2.5 kmol m^{-3} DIPA Solution

T/°C	p^a	α^b	T/°C	p	α
40	5629.5	1.111	100	5888.0	0.832
	3647.2	1.071		3488.0	0.721
	2451.0	1.011		2336.6	0.645
	2437.2	1.009		1407.8	0.565
	1767.1	0.964		1257.3	0.533
	1348.6	0.926		964.5	0.502
	784.6	0.861		670.8	0.452
	631.5	0.819		432.9	0.397
	544.6	0.807		414.3	0.391
	481.2	0.799		319.2	0.358
	278.5	0.722		217.8	0.322
	234.4	0.709		133.7	0.274
	164.7	0.677		95.1	0.240
	126.1	0.651		71.7	0.210
	103.4	0.626		46.8	0.199
	86.8	0.607		20.6	0.147
	78.5	0.590		15.8	0.119
	56.5	0.551		12.4	0.109
	48.2	0.538		7.5	0.090
	28.2	0.492		2.7	0.067
	17.2	0.458			
	15.8	0.438			
	12.4	0.446			
	8.9	0.421			
	6.2	0.419			

[a] p, partial pressure of CO_2 in kPa. [b] α, mole ratio in liquid, CO_2/DIPA.

Table II. Experimental Data for the Solubility of H_2S in 2.5 kmol m^{-3} DIPA Solution

T/°C	p^a	α^b	T/°C	p	α
40	2152.5	1.414	100	3207.4	1.249
	1199.6	1.215		2209.7	1.100
	903.2	1.092		880.4	0.849
	450.9	0.962		462.6	0.651
	179.9	0.824		211.6	0.476
	97.2	0.750		155.8	0.388
	73.7	0.728		82.7	0.300
	72.3	0.706		50.4	0.221
	47.5	0.671		31.6	0.176
	27.5	0.562		38.1	0.167
	22.7	0.473		12.1	0.098
	15.8	0.409			
	9.6	0.349			
	6.8	0.289			
	2.0	0.132			

[a] p, partial pressure of H_2S in kPa. [b] α, mole ratio in liquid, H_2S/DIPA.

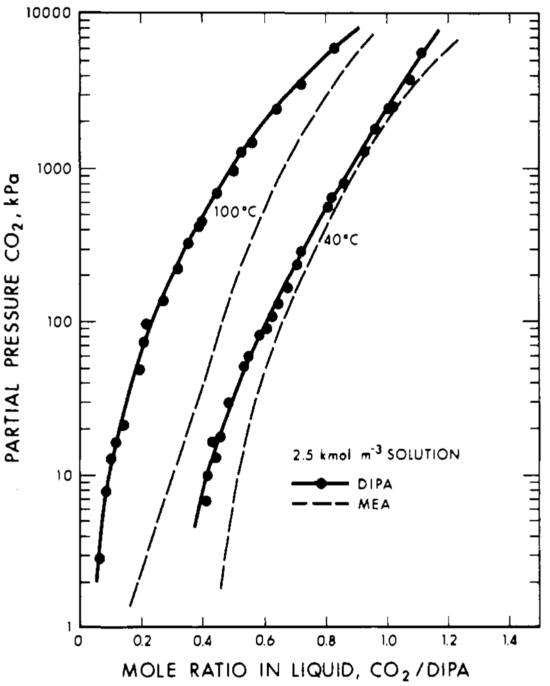

Figure 1. Solubility of CO_2 in 2.5 kmol m^{-3} DIPA and MEA solutions.

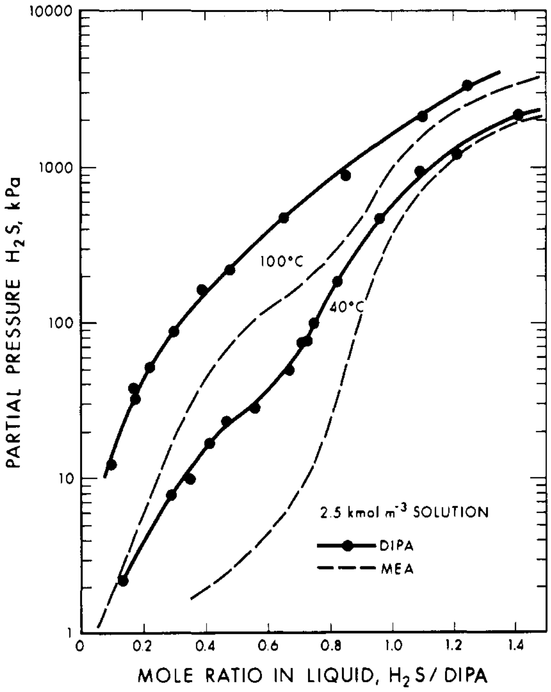

Figure 2. Solubility of H_2S in 2.5 kmol m^{-3} DIPA and MEA solutions.

the partial pressures of H_2S over DIPA solution, but neither the temperature or the concentration of the solution was indicated. To provide a rational basis for selection of amine treating solutions, this investigation of the solubility of H_2S and CO_2 in DIPA solutions was undertaken. A concentration of 2.5 kmol m^{-3} DIPA was selected so as to facilitate direct comparison with the MEA solutions.

Experimental Section

The apparatus used in this study is the same as that used for previous studies of H_2S–CO_2–MEA and H_2S–CO_2–DEA systems in this laboratory (*4–7*). 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 120 °C.

The DIPA solution (ca. 150 ml) was charged into the cell and H_2S or CO_2 was added in amounts determined by observation of the pressure. Nitrogen was added, when necessary, to ensure that the total gauge pressure was always greater than 600 kPa.

The vapor was circulated through the liquid for at least 4 h to ensure equilibrium had been reached.

Samples of the vapor were withdrawn from the top of the cell and passed through 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.

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 burette of 250-ml capacity. 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 amine in the liquid phase was calculated. The data are estimated to be accurate to about 0.02 mole ratio or 4%, whichever is larger, in liquid concentration at a given partial pressure of acid gas.

Results and Discussion

Experimental measurements of the equilibrium solubility of CO_2 and H_2S in 2.5 kmol m^{-3} DIPA solution have been made at 40 and 100 °C. Partial pressures of CO_2 ranged from 2.7 to 5888 kPa while partial pressures of H_2S ranged from 2.0 to 3207 kPa. The results are presented in Tables I and II for the CO_2 and H_2S, respectively. No comparisons with data from the literature are possible for this solution, but comparisons with data for a 2.5 N MEA solution have been made. The data for CO_2 and H_2S in a 2.5 N MEA solution at 40 and 100 °C, taken from ref 6 are reproduced on Figures 1 and 2 together with the present DIPA data. It can be seen that the solubility of CO_2 in DIPA is about the same as that in MEA at 40 °C, but is significantly lower (by as much as half) at 100 °C. For H_2S the solubility in DIPA is much lower than that in MEA at both 40 and 100 °C. These observations show that MEA solutions have the primary advantages of low molecular weight and high equilibrium solubility. However, as pointed out by Ouwerkerk (*9*), in the selection of a treating process, the absorption step is only one factor to be considered. The economics of processes depend as well upon desorption of the acid gases which requires large amounts of energy. As well, other sulfur compounds such as COS and mercaptans must be reduced to low concentrations for certain applications. The data presented here for DIPA allow one facet of the process, the solvent/acid gas ratio, to be determined.

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Osmotic and Activity Coefficients of Aqueous Guanidine Hydrochloride Solutions at 25 °C

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Osmotic coefficients have been obtained by the isopiestic method for aqueous solutions of guanidine hydrochloride at 25 °C from 0.75 to 11.7 *m*. Activity coefficients were calculated and compared with previous results.

Although guanidine hydrochloride (GdnHCl) has been utilized extensively as an unfolding agent in protein conformational studies, there has been little work on its physicochemical properties in solution. A single average osmotic coefficient has been reported by Hade and Tanford (*2*) for the 9.6–15.7 *m* region. In addition, an equation based on the results of Hade has been published (*1*) which gives the activity as a function of GdnHCl molarity. The experimental data and the uncertainties associated with the measurements are not available.

In conjunction with thermodynamic measurements of the interaction of GdnHCl with proteins, we required accurate osmotic coefficients for GdnHCl in water over a wide molality range. The resulting data comprise this paper.

Experimental Section

GdnHCl (Eastman or Aldrich) was recrystallized according to the method of Nozaki and Tanford (*3*), i.e., initial recrystallization from hot absolute ethanol followed by a second recrystallization from water at 40 °C using vacuum evaporation. The purified GdnHCl was dried under vacuum and stored over anhydrous $Mg(ClO_4)_2$ until needed. Reagent grade NaCl (Baker) was dried overnight at 120 °C and stored over $Mg(ClO_4)_2$. Doubly distilled water, boiled to remove residual CO_2, was used in all runs.

The isopiestic apparatus has been described previously (*5*). Silver cups were used to contain the sodium chloride reference solutions while glass cups placed inside silver cups contained the GdnHCl solutions. All samples were run in triplicate. The dishes were placed on top of a copper block inside a heavy-glass desiccator which was subsequently evacuated, and rocked in a constant temperature bath held at 25.00 ± 0.01 °C.

Vapor phase equilibrium was normally obtained in 6 days although, for runs below 2 *m*, 10 days to 2 weeks were required. As a check on equilibrium additional drops of water were added to one or two of the solutions of each salt. Nonequilibration was evidenced by an increase in the usual values of the uncertainly calculated for each set of solutions. The average standard deviation of the mean of a set of determinations for any run was 0.02%.

Results and Discussion

Osmotic coefficients determined for GdnHCl are given in Table I together with the equilibrium molalities of GdnHCl and NaCl.