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Samples of the vapor were withdrawn from the top of the cell and passed through the gas chromatograph for analysis.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Liquid samples were withdrawn from the bottom of the cell and passed into a sample bottle containing 7 M H_2SO_4.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.

Table I. Experimental and Calculated Osmotic Coefficients and Calculated Activity Coefficients for Aqueous GdnHCl Solutions at 25° C

m_{NaCl}	m_{GdnHCl}	ϕ_{exptl}	ϕ_{calcd}	$\gamma_{\pm calcd}$
0.6696	0.7511	0.8246	0.8255	0.5644
0.6793	0.7625	0.8242	0.8245	0.5623
0.6918	0.7766	0.8244	0.8232	0.5598
1.2343	1.5105	0.7716	0.7713	0.4647
1.2500	1.5342	0.7699	0.7700	0.4624
1.5649	2.0127	0.7463	0.7467	0.4231
2.0299	2.7745	0.7207	0.7198	0.3780
2.1768	3.0365	0.7122	0.7127	0.3659
2.5373	3.6937	0.6974	0.6982	0.3403
2.6707	3.9342	0.6950	0.6938	0.3324
2.6931	3.9855	0.6927	0.6929	0.3308
2.7778	4.1481	0.6902	0.6902	0.3259
2.9264	4.4414	0.6855	0.6856	0.3176
3.4498	5.5294	0.6713	0.6723	0.2921
3.6668	5.9818	0.6691	0.6683	0.2834
3.8805	6.4576	0.6653	0.6652	0.2754
3.9818	6.6794	0.6644	0.6640	0.2720
4.2345	7.2552	0.6614	0.6620	0.2640
4.8160	8.5966	0.6596	0.6593	0.2486
5.0150	9.0995	0.6574	0.6575	0.2433
5.8383	11.1681	0.6575	0.6575	0.2267

These osmotic coefficients were calculated using the relationships

$$2m_{GdnHCl}\phi_{GdnHCl} = -55.51 \ln a_w = 2m_{NaCl}\phi_{NaCl} \quad (1)$$

where ϕ_{NaCl} was obtained from the tabulation by Robinson and Stokes (*4*). The experimental data were fit by the method of least squares to the following equation

$$\phi_{GdnHCl} = 1 + C_1m^{1/2} + \sum_{i=2}^{i=8} C_im^{(i-1)} \quad (2)$$

The coefficients were: $C_1 = -2.643\ 06 \times 10^{-1}$; $C_2 = 9.042\ 70 \times 10^{-2}$; $C_3 = -3.203\ 60 \times 10^{-2}$; $C_4 = 1.328\ 47 \times 10^{-2}$; $C_5 = -3.044\ 47 \times 10^{-3}$; $C_6 = 3.830\ 30 \times 10^{-4}$; $C_7 = -2.476\ 28 \times 10^{-5}$; $C_8 = 6.407\ 30 \times 10^{-7}$. The overall standard deviation of the fit was 0.3%. Osmotic coefficients calculated from eq 1 are listed in column 4 of Table I.

Activity coefficients were calculated from the osmotic coefficients by means of the equation (*4*)

$$\ln \gamma_\pm = (\phi - 1) + \int_0^m \frac{(\phi - 1)\mathrm{d}m}{m} \quad (3)$$

Substituting $\phi - 1$ from eq 2 and integrating we obtain

$$\ln \gamma_\pm = 3C_1m^{1/2} + 2C_2m + \tfrac{3}{2}C_3m^2 + \tfrac{4}{3}C_4m^3 + \tfrac{5}{4}C_5m^4 + \tfrac{6}{5}C_6m^5 + \tfrac{7}{6}C_7m^6 + \tfrac{8}{7}C_8m^7 \quad (4)$$

Calculated values of $\gamma_\pm$ are given in column 5 of Table I.

The activity coefficients obtained here are larger than those calculated from the equation given by Aune and Tanford (*1*) by an average of 0.007 from 1 to 5 *m* and by 0.002 thereafter. The long region of near constancy of the osmotic coefficient exhibited here is similar to that observed for urea in water. Various association models have been invoked to explain the form of those data (*6*). It appears that the presence of the charge of the $GdnH^+$, while lowering the absolute value of the osmotic coefficient relative to urea, does not prevent $GdnH^+$ from undergoing both self interactions and interactions with water which are very similar to those of urea.

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Volumes and Heat Capacities of Mixtures of *N,N*-Dimethylformamide and Water at 298.15 K

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Densities and heat capacities of mixtures of *N,N*-dimethylformamide (DMF) and water (W) were measured at 298.15 K over the whole mole fraction range in two laboratories using a digital Anton Paar densimeter, a digital flow densimeter, an LKB precision calorimeter, and a Picker flow microcalorimeter. The data from both laboratories agree within the expected uncertainty of the various techniques. Excess thermodynamic functions and apparent and partial molal quantities of both components were calculated over the whole range. The concentration dependences of these functions for DMF are similar to those of other comparable solutes such as acetone. The corresponding functions for water do not change much with concentration; the standard partial molal volume of water is smaller than the molar volume by about 2.8 $cm^3\ mol^{-1}$ as expected from the loss of the open structure of the liquid, but the standard partial molal heat capacity of water is larger than the molar heat capacity by about 10 $J\ K^{-1}\ mol^{-1}$. A tentative explanation of the high values of $\bar{C}_{p,W}{}^\circ$ is given.

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