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Sweetening of Sour Natural Gases by Mixed-Solvent Absorption: Solubilities of Ethane, Carbon Dioxide, and Hydrogen Sulfide in Mixtures of Physical and Chemical Solvents

O. R. RIVAS
and
J. M. PRAUSNITZ
Chemical Engineering Department
University of California
Berkeley, California 94720

Solubilities of ethane, carbon dioxide, and hydrogen sulfide have been measured in propylene carbonate, N-methyl-2-pyrrolidone and tetramethylene sulfone (sulfolane); and in mixtures of these physical solvents with monoethanolamine and diglycolamine, in the range −10 to 100°C. Thermodynamically consistent equations are given for gas absorption with chemical reaction at equilibrium. Henry's law describes physical equilibrium between the acidic gas in the vapor phase and free acid solute in the liquid phase. Equilibrium constants describe chemical equilibria for the absorbed gas and the chemical solvent.

Preliminary design calculations for sweetening natural gases by absorption with mixed solvents suggest that, under some circumstances, mixed-solvent absorption may be more economical than using conventional aqueous alkanolamine.

SCOPE

Since natural gases frequently contain appreciable quantities of carbon dioxide and hydrogen sulfide, it is necessary to remove these acidic components. Absorption with a polar solvent provides a convenient method for removal; both chemical and physical solvents are commonly used. This work provides some fundamental solubility data for possible absorption processes using mixed solvents, i.e., an organic physical solvent mixed with a relatively small amount (5-15%) of chemical solvent. Solubility data in mixed solutions are reported for carbon di-

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oxide and for hydrogen sulfide in the region −10 to +100°C. Since the solvent should be selective for these acidic components, solubility data are also reported for ethane. Solubility data are correlated with a thermodynamic framework to account simultaneously for physical and chemical equilibria. Preliminary design calculations indicate process conditions where a mixed-solvent process may be economically advantageous.

CONCLUSIONS AND SIGNIFICANCE

The correlated solubility data are useful for designing an absorption process using a mixed solvent. Especially at high pressures, a suitably chosen non-aqueous mixed solvent may be superior to a pure solvent, with respect to both selectivity and capacity. The solvent pair must be chosen carefully; in some cases the organic physical solvent (e.g., propylene carbonate) may react with the chemical solvent, making the chemical solvent molecules unavailable for strong interaction with carbon dioxide and hydrogen sulfide. However, the major advantage of a mixed solvent follows from the solvent-recovery step. With rising steam costs, there may be substantial savings when an organic physical solvent (e.g., N-methyl-2-pyrrolidone or tetramethylene sulfone) contains also about 15% of a chemical solvent (e.g., monoethanol amine or diglycolamine).

In designing absorption systems to purify natural gases, it is necessary to know the solubilities of ethane, carbon dioxide and hydrogen sulfide in absorbing solvents as a function of temperature. The equilibrium solubilities of the acid gases determine the amount of solvent to be circulated and the maximum amount of residual acid gases which may be present in the regenerated solvent solution.

Removing carbon dioxide and hydrogen sulfide from natural gases by absorption is costly. However, removal is necessary to upgrade the heating value and avoid offensive odor. Further, hydrogen sulfide is toxic and corrosive; its combustion products are sulfur dioxide or trioxide. Hydrogen sulfide can be recovered to yield elemental sulfur.

Foremost among purification processes is the removal of acid gases by "chemical" absorption, with an aqueous alkanolamine solution. This process is used to remove hydrogen sulfide and carbon dioxide to very low levels, by strong chemical reaction with the amine. An alternate purification process is "physical" absorption with polar organic solvents. "Physical" processes are most economical for bulk removal of acid gases. However, when high-purity gas is required, the remaining acid impurities are usually removed with a "chemical" solvent, e.g., monoethanolamine.

An attractive alternative absorption process uses mixed solvents, one physical and one chemical. Such a mixed-solvent process is in some respects comparable to the aqueous ethanolamine process. However, the presence of the physical solvent appreciably enhances the solution capacity, especially when the gas stream to be treated is available at high pressure and the acidic components are present in high concentrations. One example is provided by Shell Oil's Sulfinol process, which uses as solvent a mixture of sulfolane (a physical solvent), diisopropanolamine (a chemical solvent), and water.

Very few fundamental data have been published for mixed-solvent absorption. In this work we report the solubilities of ethane, carbon dioxide and hydrogen sulfide in three physical solvents and in nonaqueous mixtures of these solvents with two chemical solvents. The solvents chosen reflect current industrial relevance. Solubilities were measured at pressures below 1 atm and in the temperature range −10 to 100°C. The experimental data are interpreted with a thermodynamic framework which enables us to interpolate with respect to temperature and solvent composition and to extrapolate with confidence to higher pressures. Finally, the correlated results are used to make preliminary design calculations, to compare absorption using mixed solvents with that using aqueous alkanolamine.

EXPERIMENTAL

The experimental apparatus and procedure are described elsewhere (Rivas and Prausnitz, 1979). A known amount of pure solvent (or solvent mixture of known composition) is continuously stirred in an equilibrium cell containing a quantity of solute whose magnitude is obtained from reading a gas buret. Temperature of the system is controlled in a thermostated bath to better than 0.05°C. Pressures in the gas buret and in the equilibrium cell are measured with high-precision Texas Instruments devices. The number of moles of solute absorbed by the solvent in the equilibrium cell is determined by subtracting the number of moles in the vapor space of the cell from the total moles of gas added. The number of moles in the vapor space is determined using the virial equation of state and experimental values for gas partial pressure, temperature, and vapor-space volume.

All gases and solvents (except diglycolamine) were obtained from standard laboratory-reagent suppliers with purities of at least 99%. Diglycolamine was obtained from the Jefferson Chemical Co. with a purity of at least 97%.

DATA REDUCTION

The solubility is calculated from material balances and equations of equilibrium for each one of the components of the system. Typically, we have three components in the system: the gas (1), the physical solvent (2), and the chemical solvent (3). The experimental measurements are: the total moles of each component in the equilibrium cell (N_{1t}, N_{2t}, N_{3t}), the vapor pressure of the degased solvent mixture (P_t^{sat}), the total pressure (P), and the temperature (T). We also know the total volume of the equilibrium cell (V_t), the density of the solvent mixture as a function of temperature, and the vapor pressure of each solvent.

For a three-component mixture, we have a closed system with 8 unknowns. These are the mole fractions and the total number of moles of the vapor and liquid phases (y_1, y_2, y_3; x_1, x_2, x_3; N_g, N_l). The above unknowns are related by 8 equations. These are:

$$\sum_i y_i = 1 \tag{1}$$

$$\sum_i x_i = 1 \tag{2}$$

$$N_g = \frac{PV_g}{RT + B_{\text{mix}}P} \quad (3)$$

$$N_g y_i + N_l x_i = N_{it}, \quad i = 1, 2, 3 \quad (4)$$

$$\phi_i y_i P = \gamma_i x_i P_i^{\text{sat}}, \quad i = 2, 3 \quad (5)$$

Where V_g is the volume of the vapor space in the equilibrium cell, ϕ_i is the vapor-phase fugacity for component i, B_{mix} is the second virial coefficient of the gas mixture, and γ_i is the activity coefficient. Note than in Equation (5) we do not include the equation of equilibrium for the solute.

The vapor-phase volume (V_g) is given by the difference between the total volume and the volume occupied by the solvent and by the gas absorbed in the liquid phase. Thus:

$$V_g = V_t - V_l \quad (6)$$

and

$$V_l = N_l v_l \quad (7a)$$

$$v_l = \Sigma \overline{v}_i x_i \quad (7b)$$

where $\overline{v}_i$ is the liquid-phase partial molal volume of component i. For each solvent, we set the partial molal volume equal to the molal volume of the pure component at the same temperature (Reid, Prausnitz and Sherwood 1977). The partial molal volume of the solute is set equal to that at infinite dilution (Lyckman et al. 1965).

The virial equation of state, truncated after the second virial coefficient, was used to relate ϕ_i to temperature, pressure and composition. The virial coefficients were calculated using the correlation of Hayden and O-Connell (1975).

Activity coefficients for the solute-free solvent mixture are calculated using the two-suffix Margules equation:

$$\ln \gamma_2 = \frac{A_{23}}{RT} x_3^2 \quad (8)$$

$$\ln \gamma_3 = \frac{A_{23}}{RT} x_2^2 \quad (9)$$

Coefficient A_{23} is determined from total-pressure data for the solute-free solvent mixture.

Equations (1) to (5) are solved to determine the solubility of the gas. These equations are highly nonlinear, and a trial-and-error procedure is needed to solve them. Details are given elsewhere (Rivas, 1978).

SOLUTE EQUILIBRIUM EQUATION

When the absorbing liquid is pure physical solvent, the equation of equilibrium for the solute is given by equating the fugacity in the vapor phase to that in the liquid phase:

$$f_1^V = f_1^L \quad (10)$$

At low pressures,

$$P y_1 \phi_1 = H_{12} x_1 \quad (11)$$

where Henry's constant is defined by:

$$H_{12} = \lim_{x_1 \to 0} \frac{f_1}{x_1} \quad (12)$$

Here f_1 is the fugacity of component 1. The limit in Equation (12) is achieved in our low-pressure experiments. (Additional gas was sometimes added to the cell at the same temperature to ensure that the ratio f_1/x_1 did not change.) Therefore, the solubility results obtained by the method outlined in the previous section are reported in terms of Henry's constants.

When the solute is absorbed by a solvent mixture containing a chemical and a physical solvent, the equation of equilibrium for the solute at low pressures is:

$$f_1 = H_{1M} z_1 \quad (13)$$

where H_{1M} is Henry's constant for the "free" (i.e., not complexed) solute in the solvent mixture and z_1 is the "true" mole fraction of the free solute in the liquid phase.

When ethane is the gas, there are no chemical reactions between solute and chemical solvent. In that case, z_1 is the same as x_1. However, when an acid gas is dissolved in a solvent mixture containing a chemical solvent, e.g., monoethanolamine in methyl pyrrolidone, the following reactions occur:

$$\text{Amine} + \text{Acid Gas} \overset{K_I}{\rightleftarrows} (\text{Complex})_I \quad \text{Reaction I}$$

$$2(\text{Amine}) + \text{Acid Gas} \overset{K_{II}}{\rightleftarrows} (\text{Complex})_{II} \quad \text{Reaction II}$$

Let 1 represent the free acid solute, 2 the physical solvent, 3 the chemical solvent, 4 $(\text{Complex})_I$ and 5 $(\text{Complex})_{II}$. The equilibrium constants are given by:

$$K_I = \frac{a_4}{a_3 a_1} = \frac{\gamma_4^*}{\gamma_3^* \gamma_1^*} \frac{z_4}{z_3 z_1} \quad (14)$$

$$K_{II} = \frac{a_5}{(a_3)^2 a_1} = \frac{\gamma_5^*}{(\gamma_3^*)^2 \gamma_1^*} \frac{z_5}{(z_3)^2 z_1} \quad (15)$$

Where a_i = activity of species i, z_i = "true" mole fraction of species i, γ_i^* = unsymmetrically normalized activity coefficient of species i ($\gamma_i^* \to 1$ as $x_i \to 0$ and $x_2 \to 1$).

In our experiments, the liquid-phase concentration of the acid solute was kept small. Therefore, we set $\gamma_1^* = \gamma_4^* = \gamma_5^* = 1$. Since z_1, z_4, and z_5 are very small compared to unity, the activity coefficient of component 3 is calculated using the two-suffix Margules equation.

$$\ln \gamma_3^* = \frac{A_{23}}{RT} (z_2^2 - 1) \quad (16)$$

By definition, $z_i = n_i/n_t$ where n_i is the number of moles of species i in the equilibrium liquid and $n_t = n_1 + n_2 + n_3 + n_4 + n_5$.

The number of moles of each species at equilibrium is given by stoichiometry in terms of the initial number of moles, $(n_i)_o$, and α_I and α_{II}, which represent, respectively, the fraction of the initial moles of the acid gas, $(n_1)_o$, which reacts according to reaction I and II. Thus

$$n_1 = (n_1)_o (1 - \alpha_I - \alpha_{II}) \quad (17a)$$

$$n_2 = (n_2)_o \quad (17b)$$

$$n_3 = (n_3)_o - (n_1)_o (\alpha_I + 2\alpha_{II}) \quad (17c)$$

$$n_4 = (n_1)_o \alpha_I \quad (17d)$$

$$n_5 = (n_1)_o \alpha_{II} \quad (17e)$$

$$n_t = (n_t)_o - (n_1)_o (\alpha_I + 2\alpha_{II}) \quad (17f)$$

If we set $(n_t)_o = 1$; $(n_1)_o$, $(n_2)_o$, and $(n_3)_o$ become x_1, x_2, and x_3, the "apparent" mole fractions of species 1, 2, and 3 respectively. Substituting Equations (17) into Equations (14), (15), and (16) gives:

$$K_I = \frac{[1 - x_1(\alpha_I + 2\alpha_{II})]\alpha_I}{\gamma_3^* [x_3 - x_1(\alpha_I + 2\alpha_{II})](1 - \alpha_I - \alpha_{II})} \quad (18)$$

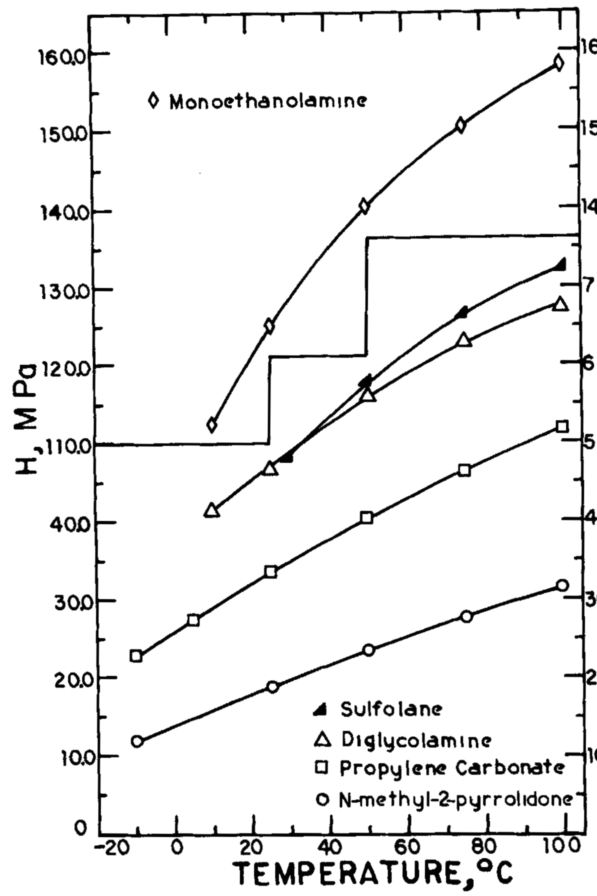


Figure 1. "Physical" Henry's constants for ethane.

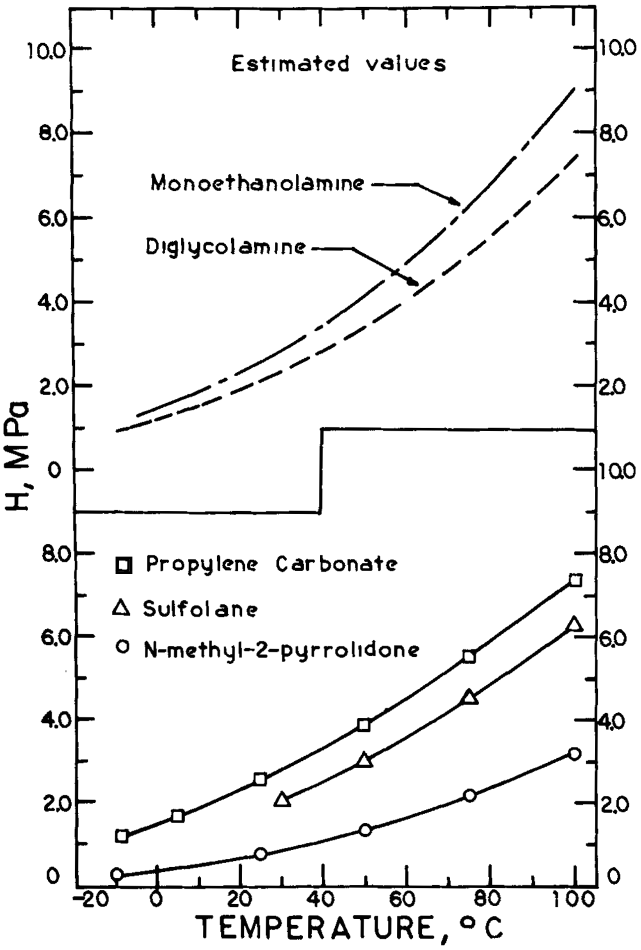


Figure 3. "Physical" Henry's constants for hydrogen sulfide.

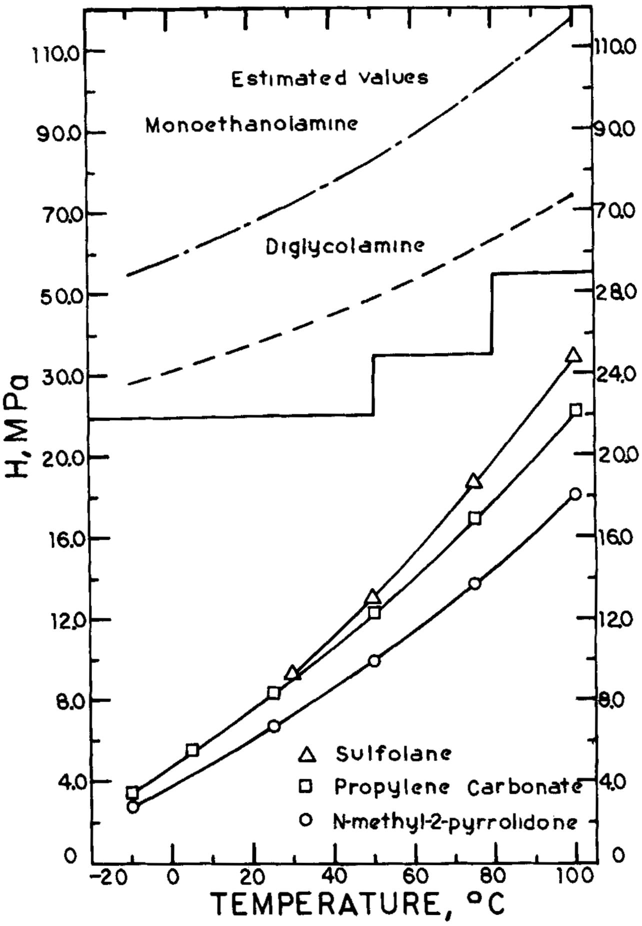


Figure 2. "Physical" Henry's constants for carbon dioxide.

$$K_{II} = \frac{[1 - x_1(\alpha_I + 2\alpha_{II})]^2\alpha_{II}}{(\gamma_3{}^*)^2[x_3 - x_1(\alpha_I + 2\alpha_{II})]^2(1 - \alpha_I - \alpha_{II})} \tag{19}$$

$$\ln \gamma_3{}^* = \frac{A_{23}}{RT}\left[\left(\frac{x_2}{1 - x_1(\alpha_I + 2\alpha_{II})}\right)^2 - 1\right] \tag{20}$$

At low pressures, the fugacity of the solute is given by

$$f_1 = H_{1M}\frac{x_1(1 - \alpha_I - \alpha_{II})}{[1 - x_1(\alpha_I + 2\alpha_{II})]} \tag{21}$$

Here Henry's constant refers to the free acid solute. Hence it is a "physical" Henry's constant, reflecting the solubility which would occur if no chemical complexes were formed.

For given values of K_I and K_{II}, it is possible to compute the values of α_I and α_{II} by simultaneous solution of Equations (18) to (20). Although algebraic solution in closed form is not possible, these equations can be solved easily by iteration. Once α_I and α_{II} are determined, the fugacity of the solute is given by Equation (21), if the value for H_{1M} is known.

For a system containing a physical solvent, a chemical solvent and an acid solute, we need K_I, K_{II} and H_{1M} to describe the system at equilibrium. Since the solvent mixture is rich in physical solvent, H_{1M} is determined primarily by H_{12}, which we have measured in single-solvent experiments. To reduce the number of adjustable parameters, we estimate H_{1M} and obtain only K_I and K_{II} from the experimental data, that is, from isothermal measurements of the solubility of the gas at different pressures and at different solvent-mixture compositions.

Table 1. Physical Henry's Constants for Three Gases in Five Polar Solvents (MPa)

Gas	Solvent	Temperature °C −10	25	30	50	75	100
Ethane	Propylene carbonate	22.88	33.81	—	40.76	46.96	52.42
	N-methyl-2-pyrrolidone	11.99	19.00	—	23.64	27.99	32.04
	Sulfolane	—	—	48.69	58.30	67.32	73.00
	Monoethanolamine	—	126.1	—	142.1	152.5	158.5
	Diglycolamine	—	47.13	—	57.05	64.14	68.46
Carbon dioxide	Propylene carbonate	3.66	8.39	—	12.47	17.12	22.35
	N-methyl-2-pyrrolidone	2.80	6.69	—	10.0	13.9	18.26
	Sulfolane	—	—	9.26	13.30	18.89	25.07
	Monoethanolamine*	—	71.37	—	82.78	101.8	120.4
	Diglycolamine*	28.76	40.34	—	48.51	61.05	74.79
Hydrogen sulfide	Propylene carbonate	1.17	2.56	—	3.91	5.55	7.48
	N-methyl-2-pyrrolidone	0.31	0.76	—	1.35	2.17	3.21
	Sulfolane	—	—	2.07	3.07	4.57	6.33
	Monoethanolamine*	—	2.64	—	4.20	6.35	9.19
	Diglycolamine*	0.98	2.17	—	3.43	5.20	7.51

* Estimated.

A non-linear regression technique was used to find the values of K_I and K_{II} which minimized the sum of squared deviations of calculated from experimental solute partial pressure.

The physical Henry's constant for the solute in the mixed solvent, H_{1M}, is estimated using an equation derived by O'Connell and Prausnitz (1964):

$$\ln H_{1M} = x_2 \ln H_{12} + x_3 \ln H_{13} - \frac{A_{23}}{RT} x_2 x_3 \quad (22)$$

where x_2 and x_3 are the mole fractions of the solute-free solvent mixture, H_{12} is Henry's constant in the physical solvent, and H_{13} is the physical Henry's constant in the chemical solvent.

In Equation (22), H_{12} and A_{23} are known measured quantities. On the other hand, H_{13} cannot be determined in our experimental apparatus. An estimate of H_{13}, however, can be made by using a correlation described elsewhere (Rivas, 1978). Fortunately, results are not sensitive to H_{13} or A_{23}; since $x_2 > x_3$, the leading term in Equation (22) is H_{12}.

RESULTS

Figures 1, 2, and 3 present Henry's constants in three physical solvents as a function of temperature. For ethane, Figure 1 also shows experimental Henry's constants in two amines, while for carbon dioxide and hydrogen sulfide, Figures 2 and 3 show estimated values of the physical Henry's constants in pure monoethanolamine and diglycolamine. Table 1 lists individual values. Experimental results are given for the temperature range −10 to 100°C, except for sulfolane which solidifies at 27°C.

For the three gases, Henry's constants are lowest in N-methyl-2-pyrrolidone indicating that the best physical solvent for absorbing the acid gases has the disadvantage that it also absorbs appreciable amounts of ethane.

Figures 4, 5, 6, 7, and 8 show the equilibrium constants which best fit the solubility data in solvent mixtures. Individual values are given in Tables 2 and 3. Table 4 presents Margules constants A_{23} for the solvent pairs.

Figures 9 and 10 show how adding a small amount of chemical solvent to a physical solvent affects the equilibrium partial pressure of absorbed carbon dioxide and hydrogen sulfide at 25°C. As expected, adding monoethanolamine to methyl pyrrolidone increases appreciably the solvent's capacity to absorb the acid gas; the solvent capacity is enhanced by the strong chemical reaction between the chemical solvent and the acid gas. The opposite effect, however, was observed when monoethanolamine was added to propylene carbonate. In this case, addition of the chemical solvent decreases the solvent's capacity to absorb the acid gas, because pro-

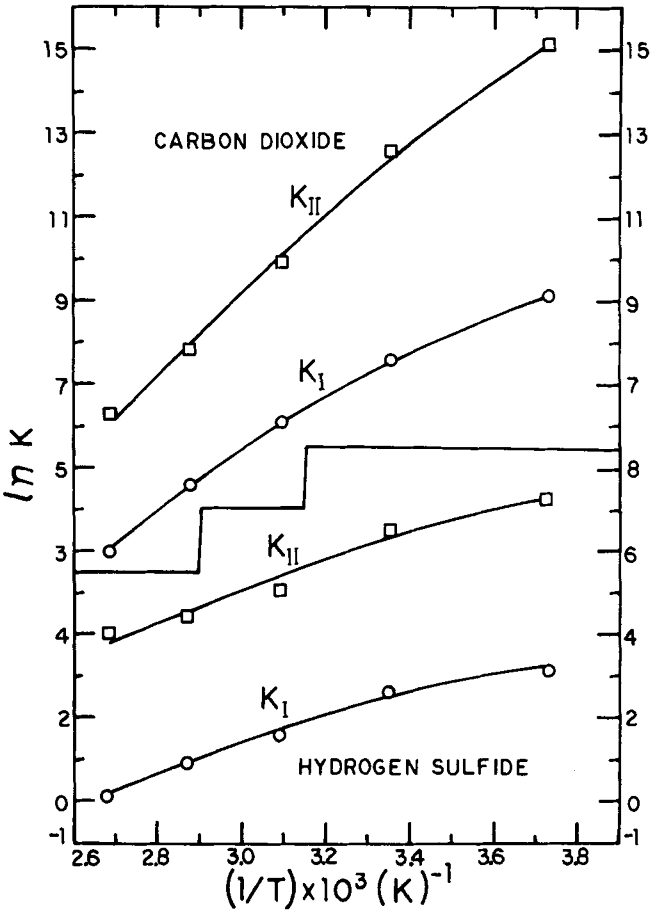


Figure 4. Equilibrium constants for the acid gas-monoethanolamine reaction in methyl pyrrolidone.

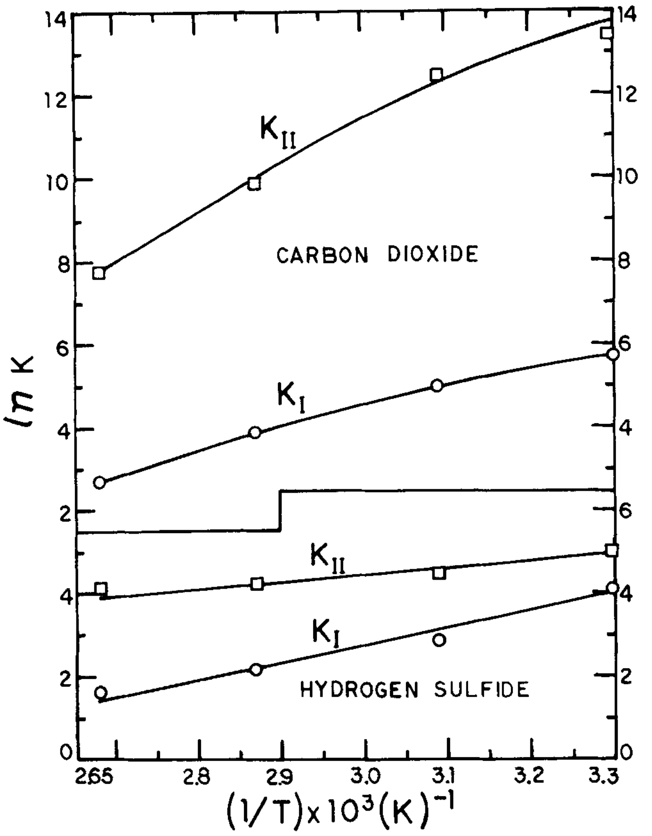


Figure 5. Equilibrium constants for the acid gas-monoethanolamine reaction in sulfolane.

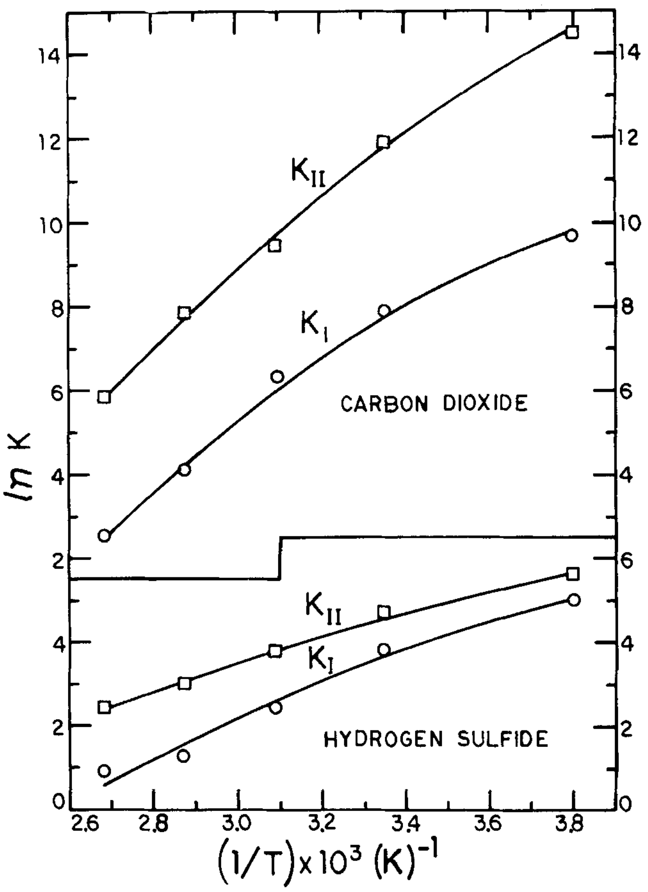
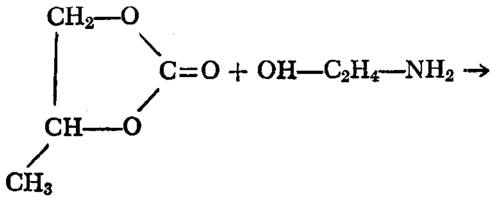


Figure 6. Equilibrium constants for the acid gas-diglycolamine reaction in methyl pyrrolidone.

pylene carbonate (an ester) reacts with monoethanolamine to produce a glycol carbamate according to



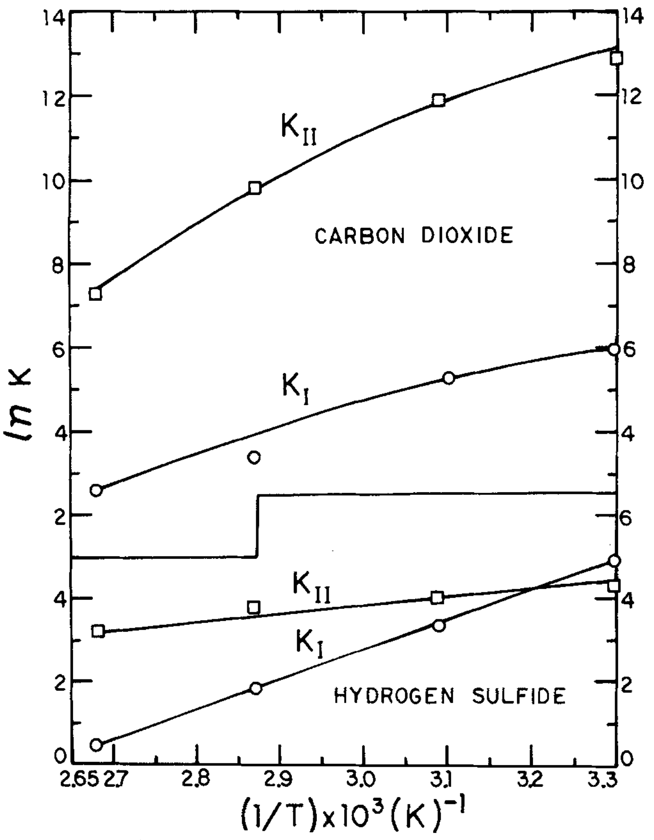


Figure 7. Equilibrium constants for the acid gas-diglycolamine reaction in sulfolane.

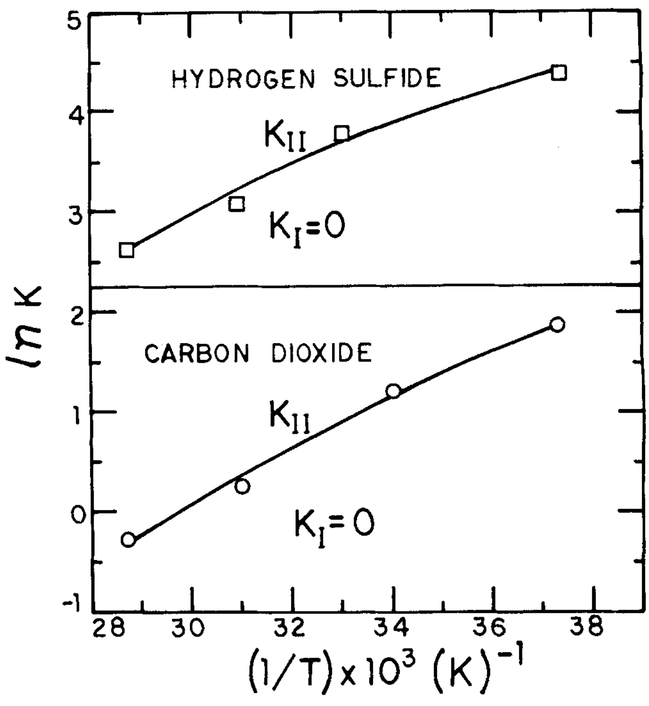


Figure 8. Equilibrium constants for the acid gas-monoethanolamine reaction in propylene carbonate.

Table 2. Equilibrium Constants for the Hydrogen Sulfide-Chemical Solvent Reaction in Physical Solvent
K_I (first line), K_{II} (second line)

Chemical solvent	Physical solvent	Temperature °C −10	−5	25	30	50	75	100
Monoethanolamine	N-methyl-2-pyrrolidone	—	22.3	14.0	—	4.7	2.3	1.2
		—	1400	650	—	153	80	57
	Sulfolane	—	—	—	60	17	8	5
		—	—	—	150	90	70	60
	Propylene carbonate	—	0	0	—	0	0	—
		—	80	45	—	22	14	—
Diglycolamine	N-methyl-2-pyrrolidone	150	—	44	—	11	3.5	2.5
		260	—	110	—	45	20	11.5
	Sulfolane	—	—	—	135	28	6	1.4
		—	—	—	70	55	42	25

Table 3. Equilibrium Constants for the Carbon Dioxide-Chemical Solvent Reaction in Physical Solvent
K_I (first line), K_{II} (second line)

Chemical solvent	Physical solvent	Temperature °C −10	−5	25	30	50	75	100
Monoethanolamine	N-methyl-2-pyrrolidone	—	9,260	2,000	—	450	100	20.2
		—	4×10^6	290,000	—	22,000	2,600	520
	Sulfolane	—	—	—	300	150	50	15
		—	—	—	700,000	260,000	20,000	2,500
	Propylene carbonate	—	0	0	—	0	0	—
		—	6.5	3.5	—	1.3	0.8	—
Diglycolamine	N-methyl-2-pyrrolidone	15,000	—	2,600	—	550	60	12.6
		2×10^6	—	160,000	—	13,000	2,720	340
	Sulfolane	—	—	—	400	200	30	10
		—	—	—	390,000	150,000	20,000	1,500

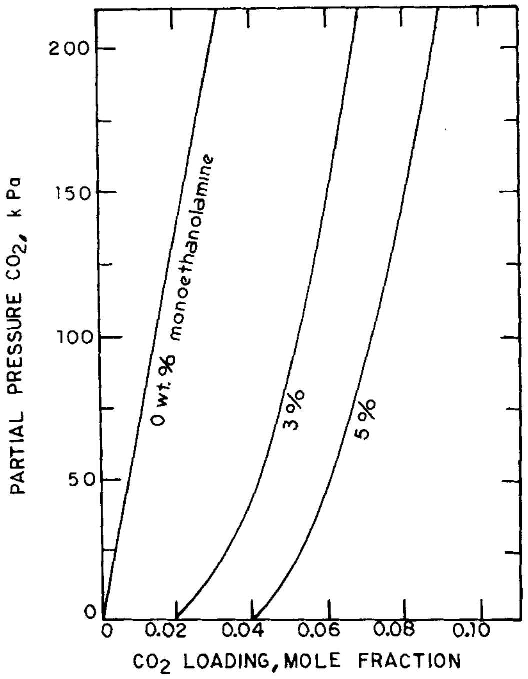


Figure 9. Solubility of carbon dioxide in methyl pyrrolidone-monoethanolamine mixtures.

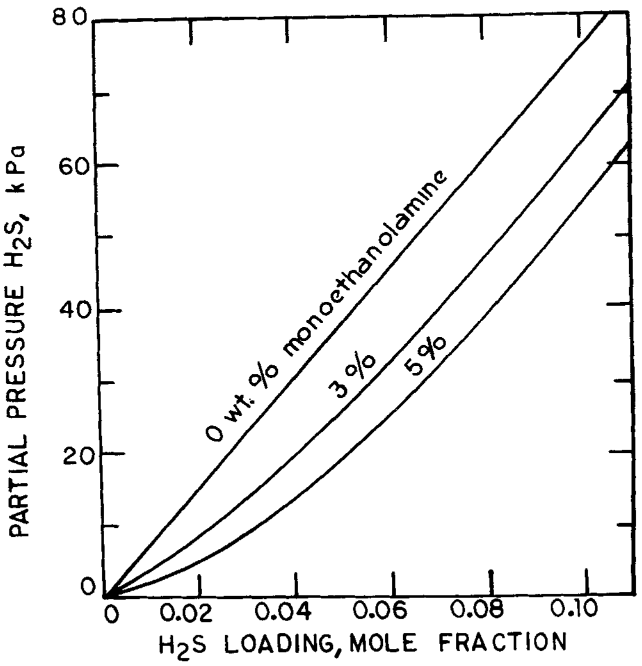


Figure 10. Solubility of hydrogen sulfide in methyl pyrrolidone-monoethanolamine mixtures.

Table 4. Margules Constants for Solvent Binary Pairs, Temperature Range: 25-100°C

Component 2	Component 3	A_{23} (J/mole)
N-methyl-2-pyrrolidone	Monoethanolamine	2,280
	Diglycolamine	1,400
Sulfolane	Monoethanolamine	2,010
	Diglycolamine	1,690
Propylene carbonate	Monoethanolamine	−929

$$\underset{\displaystyle\text{OH}}{C_2H_4}NHCOOCH_2\underset{\displaystyle\text{OH}}{CH}CH_3$$

This reaction prevents the amine from complexing significantly with the acid gas; the equilibrium constant shown in Figure 8 is very small. Affinity of propylene carbonate for monoethanolamine is also shown in Table 4 by the large negative value of A_{23} for this binary pair.

GAS SOLUBILITY AT HIGH PRESSURES

All solubility data reported here were obtained at pressures below 100 kPa. However, many natural-gas plants operate at pressures as high as 7 MPa. Therefore, it is necessary to develop a thermodynamic method for prediction of high-pressure solubility from the low pressure data.

For a solute in a physical solvent, we can write the equation of equilibrium for the solute using either the symmetrically or unsymmetrically normalized activity coefficient.

$$\phi_1 y_1 P = \gamma_1^* x_1 H_{12} \exp\frac{\bar{v}_1 P}{RT} = \gamma_1 x_1 f_1^{oL} \exp\frac{\bar{v}_1 P}{RT} \qquad (23)$$

where γ_1^* is the unsymmetrically normalized activity coefficient ($\gamma_1^* \to 1$ as $x_1 \to 0$); γ_1 is the symmetrically normalized activity coefficient ($\gamma_1 \to 1$ as $x_1 \to 1$); f_1^{oL} is the fugacity of pure liquid 1 at temperature T corrected to zero pressure, and $\bar{v}_1$ is the partial molal volume of component 1 in the liquid phase; ϕ_1 is the fugacity coefficient in the vapor phase.

In Equation (23), the major effect of the total pressure on the solubility is in the calculation of the fugacity coefficient and in the exponential term, i.e., the Poynting correction.

At low partial pressure of the acid gas, $\gamma_1^* = 1$. When the partial pressure of the acid gas is high, however, corrections due to changes of γ_1^* with liquid-phase composition may be taken into account. In practice, these corrections are usually small since the acid-gas partial pressure in natural-gas plants rarely exceeds 1 MPa.

For a solute dissolved in a physical solvent, changes of liquid-phase activity coefficients with composition may easily be taken into account. When x_1 is very small, we have the exact limiting relation

$$\gamma_1^\infty = \lim_{x_1 \to 0} \gamma_1 = \frac{H_{12}}{f_1^{oL}} \qquad (24)$$

We now assume that the symmetrically normalized activity coefficient of the solute is related to the liquid-phase composition by the two-suffix Margules equation.

$$\ln \gamma_1 = \frac{A_{21}}{RT} x_2^2 \qquad (25)$$

It follows that

$$\ln \gamma_1^\infty = \frac{A_{21}}{RT} \qquad (26)$$

Substituting in Equation (24) gives

$$\frac{A_{21}}{RT} = \ln \frac{H_{12}}{f_1^{oL}} \qquad (27)$$

The solubility of the gas at any pressure can now be calculated from Equation (23). The fugacity f_1^{oL} for the pure liquid is calculated readily as discussed elsewhere (Prausnitz, 1969). When the temperature of the system is somewhat (but not excessively) above the critical temperature of the solute, we can use the correlation of Lyckman et al. (1965) to estimate f_1^{oL}. The partial molal volume ($\bar{v}_1$) can be estimated using the correlation of Lyckman et al. (1965). In Equation (23) the partial molal volume is assumed to be independent of pressure. Vapor-phase fugacities are calculated from an equation of state as discussed elsewhere (Prausnitz, 1969).

For an acid gas in a mixed solvent, the equation of equilibrium at high pressures is:

$$\phi_1 y_1 P = H_{1M} x_1 \frac{(1 - \alpha_I - \alpha_{II})}{[1 - x_1(\alpha_I + 2\alpha_{II})]} \exp\frac{\bar{v}_1 P}{RT} \qquad (28)$$

where α_I and α_{II} are obtained by simultaneous solution of Equations (18), (19), and (20).

Equation (28) is strictly valid only for small x_1, mole fraction of the acid gas in the liquid phase. When x_1 becomes large, interactions among the different species (including complexes) have to be taken into account, as discussed elsewhere (Harris and Prausnitz, 1969).

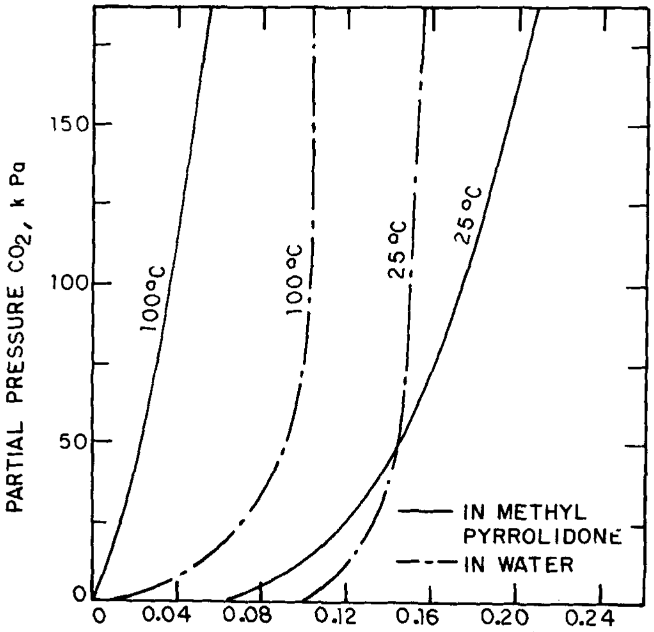


Figure 11. Solubility of carbon dioxide in two solutions containing 15 wt% monoethanolamine (Effect of temperature is larger for nonaqueous solvent, facilitating regeneration.)

COMPARISON OF MIXED SOLVENTS WITH AQUEOUS ALKANOLAMINES

Figure 11 shows the equilibrium solubility of carbon dioxide in a mixture containing 85 wt. % methyl pyrrolidone and 15% monoethanolamine. For comparison, Figure 11 also shows the solubility of carbon dioxide in 15% aqueous monoethanolamine. At 25°C and at low partial pressures of carbon dioxide, the capacity of the mixed solvent is inferior to that of aqueous monoethanolamine. However, as the partial pressure of carbon dioxide rises, the capacity of the mixed solvent continues to increase, while that of the monoethanolamine solution remains essentially constant.

The effect of temperature on solubility is much larger in the mixed solvent. Therefore, the mixed solvent can be regenerated more easily, requiring less steam or a smaller number of trays in the stripping column.

Tables 5 and 6 show the results of some preliminary design calculations for sweetening sour natural gases at two different pressures and acid-gas contents. Typical design and operating data for commercial installations were obtained from Kohl and Riesenfeld (1974). In the first case, we have a low-pressure natural gas with low acid-gas content; the natural gas is to be purified to a very low H_2S level. Typically, aqueous monoethanolamine has been used to purify natural gases under these conditions. As expected from Figure 11, the solvent flow rate using a mixed solvent is larger by a factor of about 1.5 than that for aqueous monoethanolamine. However, for the mixed solvent, the amount of steam used in the stripping column is substantially lower than that required for the aqueous amine.

In the second case we have a high-pressure natural gas. Here, both the solvent flow rate and the steam requirement are lower for the mixed-solvent process.

These results suggest that for high-pressure gases, the mixed-solvent process may be appreciably more economical than the aqueous monoethanolamine process. For low-pressure gases, the mixed solvent may be slightly inferior from the standpoint of solvent capacity. But this disadvantage may be more than offset by substantial savings in steam requirements for solvent regeneration. With the cost of steam running higher than \$6.60 per Mg (*Chem. Eng.*, April 24, 1978, p. 1), the use of the mixed solvent process may result in yearly savings of about \$1,700,000 for the high-pressure plant.

TABLE 5. DESIGN AND OPERATING RESULTS FOR LOW-PRESSURE NATURAL-GAS TREATING PROCESSES

Process variable	Process A	Process B	Process C
Gas feed, hm^{3***}	1.3	1.3	1.3
H_2S content, g/m^{3***}	4.1	4.1	3.9-4.1
CO_2 content, volume %	0.35	0.35	0.3-0.4
Outlet gas composition:			
H_2S, g/dam^{3***}	3.9	1.7	0.48-7.3
CO_2, volume %	0.014	0.014	—
Solvent solution:			
Composition, wt. %	17 MEA* 83 MP**	17 MEA* 83 water	17 MEA* 83 water
Rate of flow, dm^3/m^{3***} of treated gas	0.48	0.30	0.3-0.4
Absorber:			
No. of trays	19	19	23
Temperature, °C	25	25	—
Pressure, MPa	1.5	1.5	1.5
Stripper:			
No. of trays	21	21	20
Pressure, kPa	184	184	184
Temperature, °C			
top	127	116	116
bottom	116	121	121
Inert gas flow rate, dam^{3***}	7.0	—	—
Steam consumption, kg/dam^{3***} of gas treated	19.5	68.2	54 (max)

* MEA = monoethanolamine.
** MP = N-methyl-2-pyrrolidone.
*** At standard conditions (101.325 kPa, 0°C).
Process A: Mixed Solvent; Process B: Aqueous MEA; Process C: Aqueous MEA, design and operating data for a commercial plant, Kohl and Riesenfeld (1974).

The design calculations presented here are not optimized, since the operating variables are set somewhat arbitrarily. Solution flow rate and steam requirements are calculated such that the number of trays in the absorption and stripping columns is the same for the two processes. To calculate the number of trays, Murphree-efficiency data are needed for the simultaneous absorption of H_2S and CO_2 in the solvents. These data are not generally available. Efficiencies are determined to a major extent by the rate of reaction of the solutes with the chemical solvent in the liquid phase.

For aqueous ethanolamines, rough estimates of the efficiencies can be made using results presented by Kohl and Riesenfeld (1974). In our design calculations we assume that the Murphree vapor efficiencies in the mixed solvent are the same as those estimated for the aqueous monoethanolamine solutions. The equilibrium partial pressures of the acid gases in aqueous ethanolamine solutions are calculated using results presented by Kent and Eisenberg (1976).

TABLE 6. DESIGN AND OPERATING RESULTS FOR HIGH-PRESSURE NATURAL-GAS TREATING PROCESSES

Process variable	Process A	Process B	Process C
Gas feed, m^3/s***	11.01	11.01	11.01
H_2S, volume percent	15.0	15.0	15.0
CO_2, volume percent	10.0	10.0	10.0
Outlet gas composition:			
H_2S, g/dam^{3***}	0	0	6.8
CO_2, volume percent	0.0089	0.059	0.01
Solvent solution:			
Composition, wt. %	20 MEA* 80 MP**	20 MEA* 80 water	20 DEA† 80 water
Rate of flow, dm^3/s	62.0	69.4	97.2
Absorber:			
No. of trays	31	31	30
Temperature in °C	35.0	35.0	—
Temperature out °C	95.72	79.44	—
Pressure, MPa	7	7	7
Stripper:			
Number of trays	17	17	20
Pressure, kPa	270	270	270
Temperature, °C			
top	132	123	—
bottom	95	131	133
Inert gas flow rate, m^3/s***	2.4	—	—
Steam consumption, kg/s	3.7084	11.876	11.592

* MEA = monoethanolamine.
** MP = n-methyl-2-pyrrolidone.
*** At standard conditions (101.325 kPa, 0°C).
† DEA = diethanolamine.
Process A: Mixed Solvent; Process B: Aqueous MEA; Process C: Aqueous DEA, design and operating data for a commercial plant, Kohl and Riesenfeld (1974).

The energy requirements for the two processes are evaluated by making energy balances around the stripping tower. Most of the energy required in the aqueous alkanolamine process is used to evaporate the water which leaves the stripping column. In our design scheme for the mixed-solvent process, the rich-solvent solution is regenerated by stripping with inert gas (flue gases) at elevated temperatures. In this case, most of the energy is needed to provide the heat of reaction to dissociate the amine-acid gas complexes.

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NOTATION

A = Margules constant
a = activity
B = second virial coefficient
f = fugacity
H = Henry's constant
K = chemical equilibrium constant
N = number of moles in solubility apparatus
n = number of moles in the equilibrium liquid
P = pressure
R = gas constant
T = temperature
V = volume
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction in liquid
y = mole fraction in vapor
z = true mole fraction
α = fraction of initial number of moles that have reacted
ϕ = vapor-phase fugacity coefficient
γ = liquid-phase activity coefficient

Subscripts

g = gas phase
i = component
l = liquid phase
M = mixture
o = initial conditions, prior to reaction
t = total
$1, 2, 3, \ldots$ = components
I, II = complex

Superscripts

o = standard state
L = liquid phase
sat = saturation
$*$ = unsymmetric convention
∞ = infinite dilution

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The Influence of the Freeboard Region in a Fluidized Bed Catalytic Cracking Regenerator

HUGO I. DE LASA
and
JOHN R. GRACE

Department of Chemical Engineering
McGill University
Montreal, Canada H3A 2A7

A model is developed for a fluidized bed reactor with the dense phase region treated by conventional two-phase models. Conversion in the freeboard is obtained based on particle trajectories predicted from drag considerations. The model is applied to an industrial-scale catalytic cracking regenerator. It is shown that the freeboard region can have an important influence on the overall conversion in the unit.

SCOPE

Although fluidized beds are applied as reactors for many industrial heterogeneous and catalytic reactions, design and scale-up of fluidized bed reactors continues to be a difficult undertaking. Considerable effort has been devoted in the past two decades to models which describe the bubbling region of fluidized beds. Recent work shows that end effects may also be important. A significant portion of the reaction can take place in the grid region at the bottom of a fluidized bed, and in the freeboard region above the bed proper.

New address for J. Grace is: Department of Chemical Engineering, University of British Columbia, Vancouver, Canada, V6T 1W5.

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