Solubility of Carbon Dioxide in Binary Mixtures of *N*-Methylpyrrolidone with Alkanolamines

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Gas solubility data have been determined for carbon dioxide in binary mixtures of physical plus chemical solvents. The physical solvent studied is *N*-methylpyrrolidone, whereas the chemical solvents are monoethanolamine and diethanolamine. The mixtures studied were *N*-methylpyrrolidone with monoethanolamine 15 wt % and with diethanolamine 15 and 30 wt %. The data were obtained at several temperatures ranging from 298 to 373 K in the pressure range 20–2200 kPa. The experimental results are reported as the partial pressure of carbon dioxide against its mole fraction in the liquid phase. Values of the enthalpy of solution of carbon dioxide were derived from the experimental data.

Introduction

Gas solubility is one of the fundamental properties of gas absorption processes in the chemical industry. Absorption with a polar solvent provides a convenient method for removal of undesirable components from gas mixtures; both chemical and physical solvents are commonly used. A large number of publications in the open literature give experimental data for gas solubilities of systems used in the development of theories to investigate liquid and solution structure. However, experimental information for systems of industrial interest is not plentiful, particularly at moderate to high pressure. In previous work from this laboratory dealing with the gas solubility of either hydrogen sulfide (H_2S) or carbon dioxide (CO_2) in pure physical solvents (*1*), it was concluded that *N*-methylpyrrolidone could be used in the removal of acid gases (i.e. H_2S and CO_2) in industrial processes. This result, together with low-pressure data previously reported (*2*) for the solubility of the same acid gases as above in mixtures of either *N*-methylpyrrolidone or propylene carbonate with monoethanolamine or diethanolamine, has prompted us to extend the study on the solubility of acid gases at moderate pressure in binary mixtures of *N*-methylpyrrolidone with alkanolamines in order to assess their absorption capacity and selectivity.

In the present study new data for the solubility of CO_2 in mixtures of *N*-methylpyrrolidone with monoethanolamine and with diethanolamine are reported. The data were obtained in mixtures of 15 wt % monoethanolamine and 15 and 30 wt % diethanolamine. The measurements were carried out in the temperature range 298–373 K and in the pressure range 20–2200 kPa. From the experimental data values of the enthalpy of solution ΔH_s were derived.

Experimental Section

***Materials*.** The solvent *N*-methylpyrrolidone was provided by Fluka with a quoted purity of 98 mol %. The samples of monoethanolamine and diethanolamine were obtained from J. T. Baker with reported purities of 99.6 and 98.5 mol %, respectively. Each of the three solvents was further purified using the same method reported in previous work (*3*). Analysis of the purified samples by gas–liquid chromatography showed no impurities with a lower limit of detection of impurities of 0.05 mol %. The CO_2 is the same as that used previously (*1*) with a reported purity of 99.7 mol %.

***Apparatus and Procedure*.** The determination of solubility data was performed in an experimental apparatus which has been described in detail by Murrieta-Guevara (*4*) and used in previous solubility studies from this laboratory (*1*, *5*). A schematic diagram of the apparatus is shown in Figure 1. The apparatus consists of a 190-cm^3 stainless steel equilibrium cell, two gas storage cylinders, a magnetic pump, a precision pressure gauge, a pressure transducer–digital indicator, two digital thermometers, and two constant temperature bath circulators.

The amount of solvents charged into the equilibrium cell at the beginning of a run was determined by weight in an analytical balance with a precision of ±0.0001 g. Degassing was carried out by freezing–evacuating–thawing cycles.

A known amount of the solute from the corresponding gas storage cylinder was added to the equilibrium cell after this had reached thermal equilibrium. Gas–liquid equilibrium is quickly attained by circulating the gas phase into the solvent with the magnetic pump.

The solubility or mole fraction of the solute in the liquid phase was derived through material balances and equations of equilibrium as discussed previously (*4*, *6*). Thus the precision of the results is ±2% for the mole fraction at a given partial pressure of CO_2. The temperature of equilibrium was controlled within ±0.02 K, and the equilibrium total pressure was measured with an accuracy of ±3.5 kPa.

Results and Discussion

Equilibrium solubilities were obtained for CO_2 in mixtures of known composition of *N*-methylpyrrolidone with either monoethanolamine or diethanolamine at 298.15, 323.15, and 373.15 K in the range of partial pressure of CO_2 of 20–2200 kPa. The concentration of monoethanolamine was 15 wt %, while that for diethanolamine was 15 and 30 wt %. The experimental partial pressure–composition results are given in Table I. Figure 2 presents solubility data at 323.15 K where we have also included previously reported data for CO_2 in pure *N*-methylpyrrolidone (*1*) and in mixtures of *N*-methylpyrrolidone with monoethanolamine or diethanolamine (14.3 wt % amine) at low partial pressures (*2*). It may be observed that the present data are consistent with the low-pressure data regardless of the small difference in concentration of the amine between both sets of results.

The behavior of the solubility data shown in Figure 2 is typical for all the systems studied; that is, the solubility of CO_2 increases as the pressure increases, and, for a given temperature and solvent concentration, the solubility of CO_2 is much higher in the mixtures of *N*-methylpyrrolidone with monoethanolamine or diethanolamine than in pure *N*-methylpyrrolidone at given temperature. Furthermore, the solubility of CO_2 is greater in *N*-methylpyrrolidone + monoethanolamine mixtures than in *N*-methylpyrrolidone + diethanolamine mixtures at the same concentration of the amine for a given temperature.

The result that the mixtures of *N*-methylpyrrolidone with monoethanolamine are more efficient in solubilizing CO_2 is not

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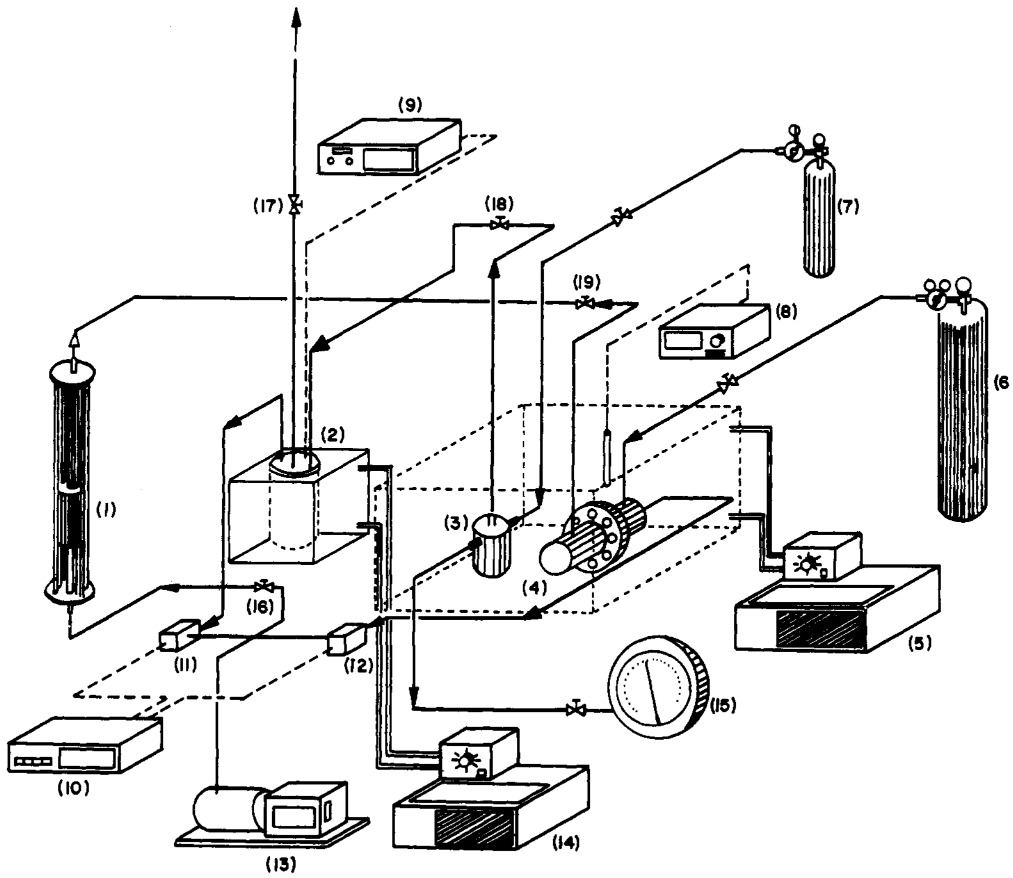

Figure 1. Schematic diagram of the solubility apparatus: (1) magnetic pump; (2) equilibrium cell; (3) storage vessel; (4) storage vessel; (5) constant temperature bath circulator; (6) gas cylinder; (7) gas cylinder; (8) thermometer gas storage; (9) thermometer equilibrium cell; (10) digital pressure indicator; (11) pressure transducer; (12) pressure transducer; (13) vacuum pump; (14) constant temperature bath circulator; (15) pressure gauge; (16) vacuum valve; (17) feed valve; (18) micrometer needle valve; (19) micrometer needle valve.

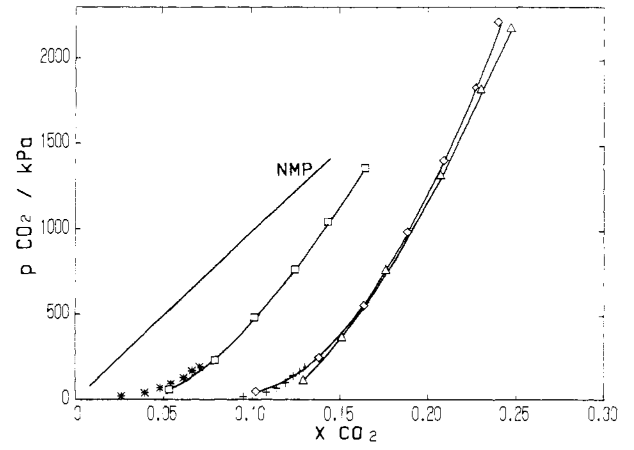

Figure 2. Partial vapor pressure p and mole fraction solubility X in pure N-methylpyrrolidone (NMP) and in mixtures of NMP with monoethanolamine (MEA) or diethanolamine (DEA) at 323.15 K: △, 15 wt % MEA; □, 15 wt % DEA; ◇, 30 wt % DEA; +, 14.3 wt % MEA; ✱, 14.3 wt % DEA.

surprising since monoethanolamine is stoichiometrically more active than diethanolamine.

The enhancement of the solubility of CO_2 when N-methylpyrrolidone is mixed with an alkanolamine is shown in Figure 3, where we have plotted solubility data of CO_2 in pure N-methylpyrrolidone at 298.15, 323.15, and 373.15 K (*1*), which are compared with solubility data in a mixture of N-methylpyrrolidone with 15 wt % monoethanolamine at the same temperatures. The larger absorption capacity of mixtures of solvents formed by a physical and a chemical solvent is a very useful property that several industrial processes apply for the sweetening of gas currents.

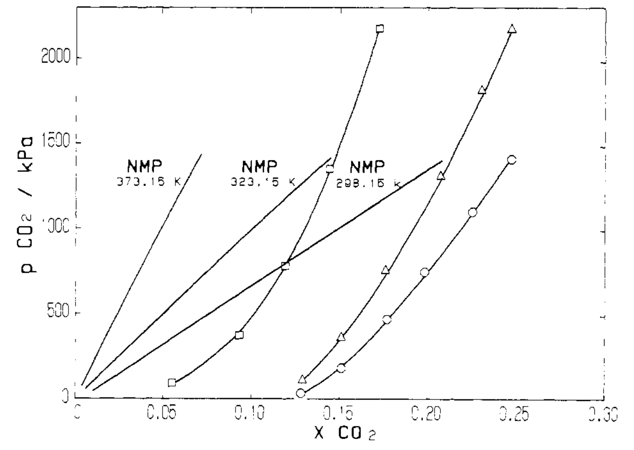

Figure 3. Partial vapor pressure p and mole fraction solubility X of CO_2 in pure N-methylpyrrolidone (NMP) and in mixtures of NMP with 15 wt % monoethanolamine: ○, 298.15 K; △, 323.15 K; □, 373.15 K.

The behavior described above has also been observed for the solubility of CO_2 in mixtures of sulfolane with alkanolamines (*5*) in the same temperature and pressure intervals as studied here.

Figure 4 shows a comparison between the solubility of CO_2 in mixtures of N-methylpyrrolidone with monoethanolamine or diethanolamine and in aqueous solutions of several alkanolamines: 3.5 N diethanolamine at 323.15 K (*7*), 15 wt % monoethanolamine at 313.15 K (*8*), 2.5 kmol m^{-3} diisopropanolamine at 313.15 K (*9*), sulfinol solution (40 wt % diisopropanolamine, 40 wt % sulfolane, 20 wt % water) at 313.15 K (*10*), and 60 wt % diglycolamine at 323.15 K (*11*). The comparison is carried out using α, the mole ratio of CO_2 and

Table I. Experimental Partial Pressure p and Mole Fraction X Results for CO_2 in Mixtures of N-Methylpyrrolidone (NMP) with Monoethanolamine (MEA) or Diethanolamine (DEA) at Temperature T

system	T/K	p/kPa	X_{CO_2}
NMP + 15 wt % MEA	298.15	33.8	0.128
		183.0	0.151
		467.5	0.177
		747.0	0.198
		1100.7	0.225
		1410.6	0.247
	323.15	113.5	0.129
		362.0	0.151
		756.6	0.176
		1310.8	0.207
		1819.3	0.230
		2178.9	0.247
	373.15	95.3	0.055
		374.0	0.093
		785.1	0.119
		1350.8	0.144
		2177.6	0.172
NMP + 15 wt % DEA	298.15	66.8	0.081
		250.0	0.109
		454.7	0.133
		721.6	0.161
		940.4	0.181
		1178.2	0.204
		1392.5	0.224
	323.15	61.1	0.053
		230.9	0.079
		483.4	0.101
		763.4	0.124
		1046.4	0.143
		1352.6	0.164
	373.15	71.8	0.008
		239.8	0.021
		553.2	0.042
		855.1	0.058
		1162.1	0.074
		1460.3	0.088
NMP + 30 wt % DEA	298.15	24.2	0.112
		215.0	0.153
		546.1	0.187
		956.1	0.216
		1480.6	0.250
		1856.2	0.273
		2174.5	0.290
	323.15	48.8	0.102
		247.6	0.138
		552.9	0.163
		981.1	0.188
		1400.3	0.209
		1828.6	0.227
		2211.0	0.240
	373.15	154.9	0.027
		347.7	0.052
		671.5	0.083
		1154.7	0.112
		1727.3	0.138

the amine, as a function of the partial pressure of the gas.

It can be seen that the mixture of N-methylpyrrolidone + monoethanolamine presents a higher absorption capacity for CO_2 than the other mixtures considered, except for water + monoethanolamine in the low partial pressure range, this however could be different if the comparison was done at the same temperature for both mixtures.

Since the solvent phase is essentially nonvolatile under the conditions of these experiments, approximate values of ΔH_s, the enthalpy of solution of CO_2 in the amine solutions, can be calculated from the following equation:

$$\frac{\Delta H_s}{R} = \frac{\bar{H}^l - H^*}{R} = \left[\frac{\partial \ln f}{\partial(1/T)}\right]_{P,\alpha} \qquad (1)$$

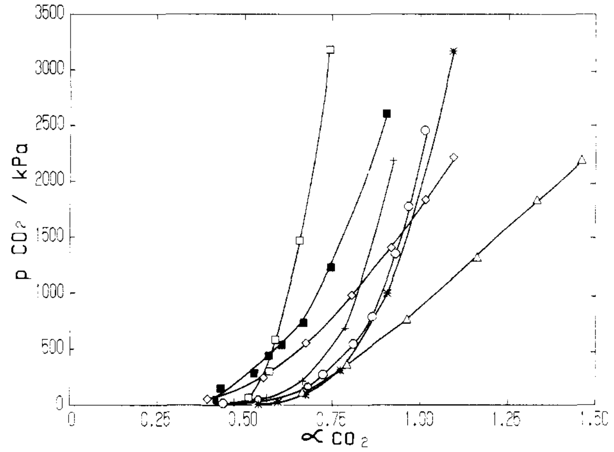

Figure 4. Partial vapor pressure p of CO_2 and mole ratio α of CO_2/amine in aqueous alkanolamine solutions: ✱, 15 wt % monoethanolamine (MEA) at 313.15 K; +, 3.5 N diethanolamine (DEA) at 323.15 K; ○, 2.5 kmol m^{-3} diisopropanolamine (DIPA) at 313.15 K; ■, 40 wt % DIPA and 40 wt % sulfolane at 313.15 K; □, 60 wt % diglycolamine at 323.15 K; △, N-methylpyrrolidone with 15 wt % MEA at 323.15 K; ◇, N-methylpyrrolidone with 30 wt % DEA at 323.15 K.

Table II. Enthalpy of Solution ΔH_s of CO_2 in Mixtures of N-Methylpyrrolidone (NMP) with Monoethanolamine (MEA) or Diethanolamine (DEA) as a Function of the Mole Ratio α of CO_2/Amine in the Liquid Phase in the Temperature Range 298–373 K

	$-\Delta H_s$/(kJ mol^{-1})		
α	NMP + 15 wt % MEA	NMP + 15 wt % DEA	NMP + 30 wt % DEA
0.1		71.7	113.2
0.2		66.7	88.8
0.3	121.7	59.0	70.1
0.4	89.1	50.6	53.1
0.5	67.5	42.3	40.3
0.6	49.4	35.8	31.7
0.7	36.1	32.5	28.0
0.8	26.9		
0.9	21.1		
1.0	17.9		

where $\bar{H}^l$ is the partial molar enthalpy, H^* is the enthalpy of the ideal gas state, f is the fugacity, T is the temperature of the system, P is the system pressure, α is the mole ratio in the liquid phase, CO_2/amine, and R is the gas constant.

The fugacity values were smoothed with a polynomial function to carry out interpolations at constant composition; the plots of ln f versus $1/T$ were linear within the accuracy of the data; and the average correlation coefficient was 0.997, indicating that ΔH_s is independent of temperature over the range of temperature studied. The uncertainty of the ΔH_s results is ±20%; thus the inclusion of the Poynting correction was not considered justified.

Table II contains values of ΔH_s for the systems studied in this work. It may be observed that the enthalpy of solution depends strongly on the loading of the acid gas in solution. Reported data of ΔH_s were not found for comparison.

Although the experimental data reported in this work are limited, it is possible to conclude that mixtures composed of a physical and a chemical solvent may be an excellent alternative to the aqueous solutions of alkanolamines for the removal of acid gases from gas streams. In particular the mixtures of N-methylpyrrolidone with monoethanolamine may prove to be rather appropriate.

The solubility of H_2S in mixtures of N-methylpyrrolidone with alkanolamines and the effect of adding small quantities of water to the mixture of solvents will be the subject of future reports.

Registry No. NMP, 872-50-4; MEA, 141-43-5; DEA, 111-42-2; CO_2, 124-38-9.

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Received for review July 30, 1990. Revised April 11, 1991. Accepted September 26, 1991.

High-Pressure Vapor–Liquid Equilibrium Phase Properties of the Octafluoropropane (K-218)–Chlorodifluoromethane (Freon-22) Binary System

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Vapor and liquid equilibrium phase compositions were determined at 50, 60, 70, and 75 °C for the octafluoropropane–chlorodifluoromethane system. Measurements were made at pressures from the vapor pressure of the two pure components to the higher of the azeotropic or critical pressure for the binary systems at each temperature. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The azeotropic compositions and pressures were measured at 50, 65, and 70 °C. The critical pressure was determined at 70 and 75 °C.

Introduction

For process engineering and design calculations, it is frequently necessary to have available a suitable method for calculating the thermodynamic properties and phase behavior of multicomponent gaseous and liquid systems. Many of these methods rely extensively on the availability of pure component properties and binary interaction parameters for use in equations of state or other fluid property models.

In view of the perceived dangers to the ozone layer caused by chlorinated hydrocarbons, a great deal of interest has developed in fluorinated hydrocarbons. Recently, information on the behavior of octafluoropropane–chlorodifluoromethane at temperatures of 0 and 25 °C was published by Leu and Robinson (*1*). The object of the work undertaken in this study was to extend the temperature range and thereby explore the possibility of azeotropic behavior at higher temperatures. The potential for this had been indicated by the shape of the pressure–composition phase envelopes at 0 and 25 °C.

Experimental Method

The experiments were carried out in a variable-volume vapor–liquid equilibrium cell consisting of a transparent sapphire cylinder mounted between two steel headers. This has been described in detail by Robinson et al. (*2*). The body of the cell had a 2.54-cm inside diameter with a length of 15.2 cm. The cell had an internal capacity of about 45 cm^3. The main cell and all the necessary auxiliary lead lines and valves were mounted inside a controlled-temperature bath. The method of operation was basically the same as those described previously by Leu and Robinson (*3*).

Prior to commencing an experimental run, the equipment was thoroughly cleaned and evacuated. A suitable amount of octafluoropropane was then added to the cell, followed by sufficient chlorodifluoromethane to achieve the desired pressure range at the chosen temperature. Equilibrium was attained by mechanically rocking the entire assembly about a horizontal axis. The gas phase was sampled first by continuously drawing off a vapor stream through the sample valve under isobaric isothermal conditions. The withdrawn vapor was mixed with a stream of heated helium and circulated through the chromatographic switching valve. Samples were taken for analysis through the switching valve at periodic intervals.

After the remainder of the vapor phase plus a small interface portion of the liquid was removed, the liquid phase was then sampled and analyzed by using a similar procedure. At the completion of each pressure point, a new set of conditions was established by adjusting pressure and/or adding more material. The equilibration and sampling sequence was then repeated.

The azeotropic or critical region was approached isothermally by using an iterative experimental procedure involving changes in pressure and/or composition. After the equilibration process had been completed, the critical pressure corresponding to a given experimental temperature was determined by performing isothermal compression and expansion on either side of the critical point to observe both the phase boundary and the color changes taking place within the system. The critical composition was determined by taking a sample as described above, but the isobaric sampling pressure was kept at least 0.14 MPa higher than the observed critical pressure to ensure the mixture remained in the single phase.

Temperatures were measured with iron–constantan thermocouples which had been calibrated against a platinum resistance thermometer. This thermometer was calibrated for use in the range $t = -189$ to $+500$ °C on the International Practical Temperature Scale of 1968 (IPTS-68), amended edition of 1975. Each temperature was read on a digtial voltmeter, such

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