

presented in Table III. Tables IV-VI gives the density, the kinematic viscosity, and the dynamic viscosity of the under-saturated ternary system sodium sulfate-water-methanol.

Glossary

x	methanol concentration, kg of CH ₃ OH/kg of (CH ₃ OH + H ₂ O)
Y	salt concentration, kg of Na ₂ SO ₄ /kg of (CH ₃ OH + H ₂ O)
ρ	density, kg/m ³
ν	kinematic viscosity, m ² /s
η	dynamic viscosity, kg/ms
ϑ	temperature, °C

Registry No. Na₂SO₄, 7757-82-6; CH₃OH, 67-56-1.

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Solubility of Carbon Dioxide, Hydrogen Sulfide, and Methane in Pure and Mixed Solvents[†]

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The solubility of carbon dioxide has been measured at 25 and 50 °C in *N*-methylpyrrolidone and propylene carbonate and in mixtures of these solvents individually with monoethanolamine and diethanolamine at two different concentrations. The solubility of hydrogen sulfide and methane was measured at 25 °C in *N*-methylpyrrolidone and in mixtures of this solvent with monoethanolamine also at two different concentrations. The solubility of methane was also determined at 25 °C in a mixture of *N*-methylpyrrolidone with diethanolamine.

Introduction

The study of the solubility of gaseous solutes in solvents is of great interest from both theoretical and practical points of view. The efficient removal of acid gases (e.g., CO₂ and H₂S) from industrial and natural gases is a continuous need. The design and operation of absorption and stripping equipment require reliable equilibrium data of the solubility of carbon dioxide, hydrogen sulfide, and light hydrocarbons in absorbing liquids, pure or mixed, as a function of temperature and concentration.

Aqueous alkanolamine solutions are used extensively for the removal of acid gases in gas mixtures. However, the present interest in energy conservation and pollution control has led to the search for more efficient and economical methods of removing acid gases. The use of physical solvents may offer some advantages (1) over the use of chemical solvents to remove CO₂, H₂S, and other sulfur compounds. There exist several absorption processes which use a physical solvent such as Rectisol (2), Purisol (2), Fluor Solvent (3, 4), Selexol (5), etc.

However, it is also possible to combine the advantages of using a chemical solvent and a physical solvent to remove acid

gases with great efficiency at reduced operating costs as in the sulfinol process (6, 7). We report in this work solubility data for carbon dioxide, hydrogen sulfide, and methane in pure physical solvents and in mixtures of physical solvent with a chemical solvent as part of a study to evaluate mixtures of solvents which could be used as substitutes for the ones traditionally used in industry. The physical solvents considered here are *N*-methylpyrrolidone (NMP) and propylene carbonate (PC) whereas the chemical solvents are monoethanolamine (MEA) and diethanolamine (DEA).

Experimental Section

Materials. The pure samples of NMP, PC, MEA, and DEA are the same as those used in a study of liquid densities as a function of temperature (ϑ) and their purity was always better than 99.5 mol %. The CO₂ was obtained from Infra S.A. with a reported purity of 99.7 mol %. The H₂S and CH₄ were obtained from Matheson with a reported purity of 99.5 and 99.99 mol %, respectively.

Apparatus and Procedure. The measurements of solubility were carried out in a vapor-liquid equilibrium system with circulation of the vapor phase. Figure 1 is a schematic diagram of the experimental apparatus which consists essentially of equilibrium glass cell 1, magnetic pump 2, gas-storage cylinder 3, pressure gauge 4, pressure transducer 5, digital temperature indicator 6, and proportional temperature controller 7.

The 170-cm³ equilibrium cell was made of Pyrex glass with an inlet gas tube ending in a fine fritted glass disk to disperse the gas bubbles into the bulk of the solvent. A magnetic Teflon-coated bar was used for continuous agitation of the liquid phase to ensure thermal equilibrium during measurements. Additionally a magnetic pump was used to circulate the vapor phase from the top of the cell into the liquid through the fritted glass disk. The equilibrium cell, the magnetic pump, and the gas-storage cylinder were placed in an air bath controlled within ± 0.1 °C by a proportional controller using a thermistor for air

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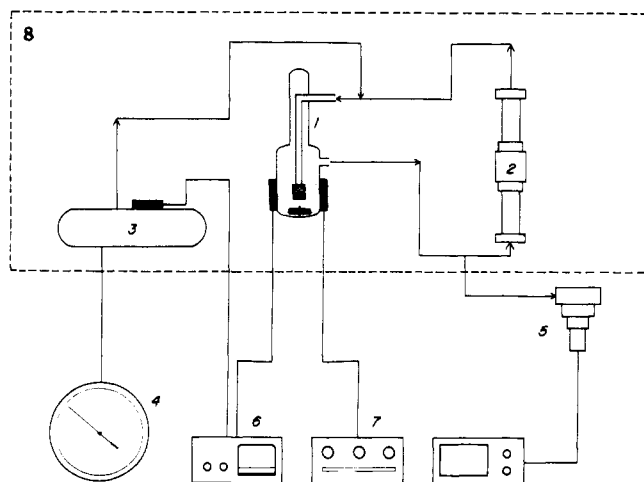


Figure 1. Schematic diagram of the solubility apparatus: 1, equilibrium cell; 2, magnetic pump; 3, gas-storage cylinder; 4, pressure gauge; 5, pressure transducer; 6, digital temperature indicator; 7, proportional temperature controller; 8, air bath.

Table I. Comparison of Henry's Law Constants for CO₂ and H₂S

gas	solv	t/°C	H _{1,2} /atm	
			this work	lit. ^a
CO ₂	NMP	25	68.5	66.0
		50	100.2	98.7
CO ₂	PC	25	78.8	82.8
		50	116.7	123.1
H ₂ S	NMP	25	7.4	7.5

^a Reference 9.

as sensor. The measurements of temperature were carried out with surface thermistors on the equilibrium cell and gas cylinder with a digital thermometer calibrated periodically against a H-P quartz thermometer. The equilibrium pressure in the cell was measured with a calibrated stainless steel pressure transducer used in the absolute fashion whereas the pressure in the gas cylinder was measured with a Bourdon tube gauge, both with an accuracy of $\pm 0.1\%$ in the pressure range used here.

The amount of solvent, pure or mixed, charged to the cell at the beginning of a run was determined by weight in an analytical balance. Degassing was carried out in situ by freezing–evacuating–thawing cycles. A known amount of the solute was added to the cell after this had reached thermal equilibrium and the magnetic pump started to circulate the vapor phase. The equilibrium was achieved in approximately 30 min once the pressure in the equilibrium cell remained constant. For each solute–solvent system at a given constant temperature six different equilibrium points were determined in the range 0.2–2.0 atm.

Results and Discussion

As a check on the experimental technique the solubility of CO₂ in NMP and PC was determined at 25 and 50 °C; also the solubility of H₂S in NMP was determined at 25 °C. We believe that the present results are no more than 5% inaccurate; a comparison with recent values from the literature (9, 10) affords a measure of our accuracy. Table I shows this comparison for the Henry's law constants of the systems mentioned above.

Experimental data for the solubility of CO₂ in mixtures of NMP with MEA and DEA were obtained at 25 and 50 °C at partial pressures of CO₂ from 0.2 to 2.0 atm. The concentration of the chemical solvent (i.e., MEA or DEA) was 5.1 and 14.3 wt %. These results are given in Table II and plotted in figures

Table II. Experimental Data for the Solubility of CO₂ in Pure and Mixed Solvents

X _{CO₂}	P _{CO₂} /atm	X _{CO₂}	P _{CO₂} /atm
NMP, 25 °C		NMP + 5.1 wt %	
0.003	0.226	MEA, 50 °C	
0.006	0.410	0.041	0.179
0.010	0.675	0.050	0.439
0.014	0.979	0.056	0.701
0.019	1.276	0.061	1.042
0.023	1.557	0.065	1.360
0.026	1.788	0.069	1.662
0.030	2.018	0.071	1.909
NMP + 5.1 wt %		NMP + 14.3 wt %	
MEA, 25 °C		MEA, 50 °C	
0.052	0.182	0.095	0.158
0.060	0.446	0.108	0.443
0.066	0.720	0.114	0.694
0.070	0.977	0.119	0.977
0.075	1.295	0.123	1.337
0.079	1.588	0.127	1.634
0.083	1.844	0.130	1.894
NMP + 14.3 wt %		NMP + 5.1 wt %	
MEA, 25 °C		DEA, 50 °C	
0.113	0.254	0.009	0.221
0.121	0.453	0.016	0.495
0.127	0.691	0.023	0.835
0.132	0.984	0.028	1.196
0.137	1.332	0.033	1.523
0.142	1.675	0.038	1.896
NMP + 5.1 wt %		NMP + 14.3 wt %	
DEA, 25 °C		DEA, 50 °C	
0.023	0.220	0.026	0.188
0.030	0.471	0.039	0.412
0.035	0.693	0.048	0.663
0.042	1.005	0.054	0.933
0.047	1.315	0.061	1.273
0.053	1.655	0.066	1.629
0.058	1.952	0.070	1.893
NMP + 14.3 wt %		PC, 25 °C	
DEA, 25 °C		0.002	0.200
0.057	0.189	0.005	0.403
0.067	0.412	0.008	0.663
0.075	0.727	0.012	0.927
0.082	1.038	0.016	1.279
0.087	1.360	0.019	1.509
0.092	1.649	0.024	1.911
0.096	1.922	PC + 5.1 wt %	
NMP, 50 °C		MEA, 25 °C	
0.002	0.252	0.004	0.211
0.005	0.465	0.007	0.449
0.007	0.722	0.010	0.697
0.010	0.979	0.013	0.934
0.013	1.323	0.016	1.248
0.017	1.620	0.020	1.559
0.019	1.905	0.024	1.864
		PC + 14.3 wt %	
		MEA, 25 °C	
		0.005	0.211
		0.007	0.433
		0.010	0.720
		0.012	0.974
		0.015	1.275
		0.017	1.539
		0.020	1.908

2 and 3 as the partial pressure of CO₂ against its mole fraction in the liquid phase. Figure 2 also includes data from ref 9 for CO₂ in NMP with 5 wt % MEA.

The above results show that at constant temperature the solubility of CO₂ increases as the concentration of the chemical solvent increases. For a given concentration of the chemical solvent the solubility of CO₂ decreases as the temperature increases. Overall, the solubility of CO₂ is greater in mixtures of NMP with MEA than in mixtures of NMP with DEA at the tem-

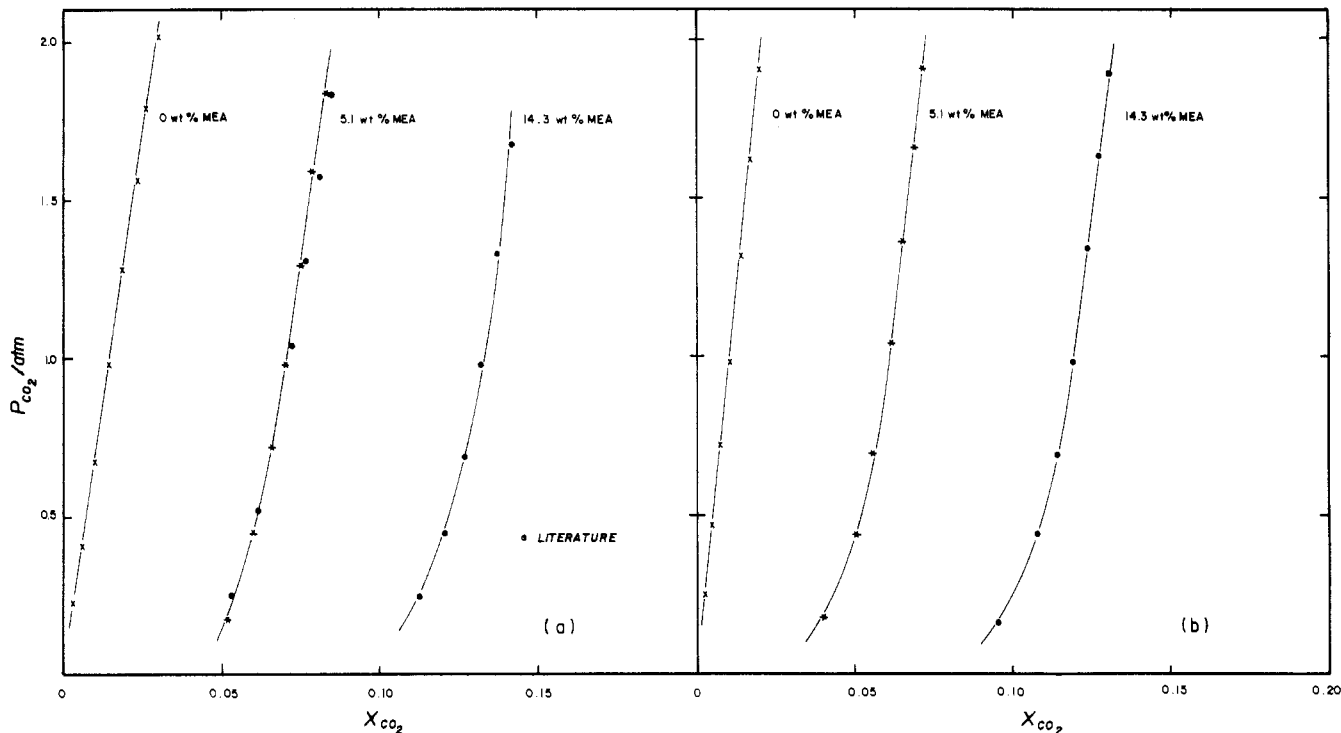


Figure 2. Solubility of CO₂ in mixtures of NMP with MEA: (a) at 25 °C; (b) at 50 °C.

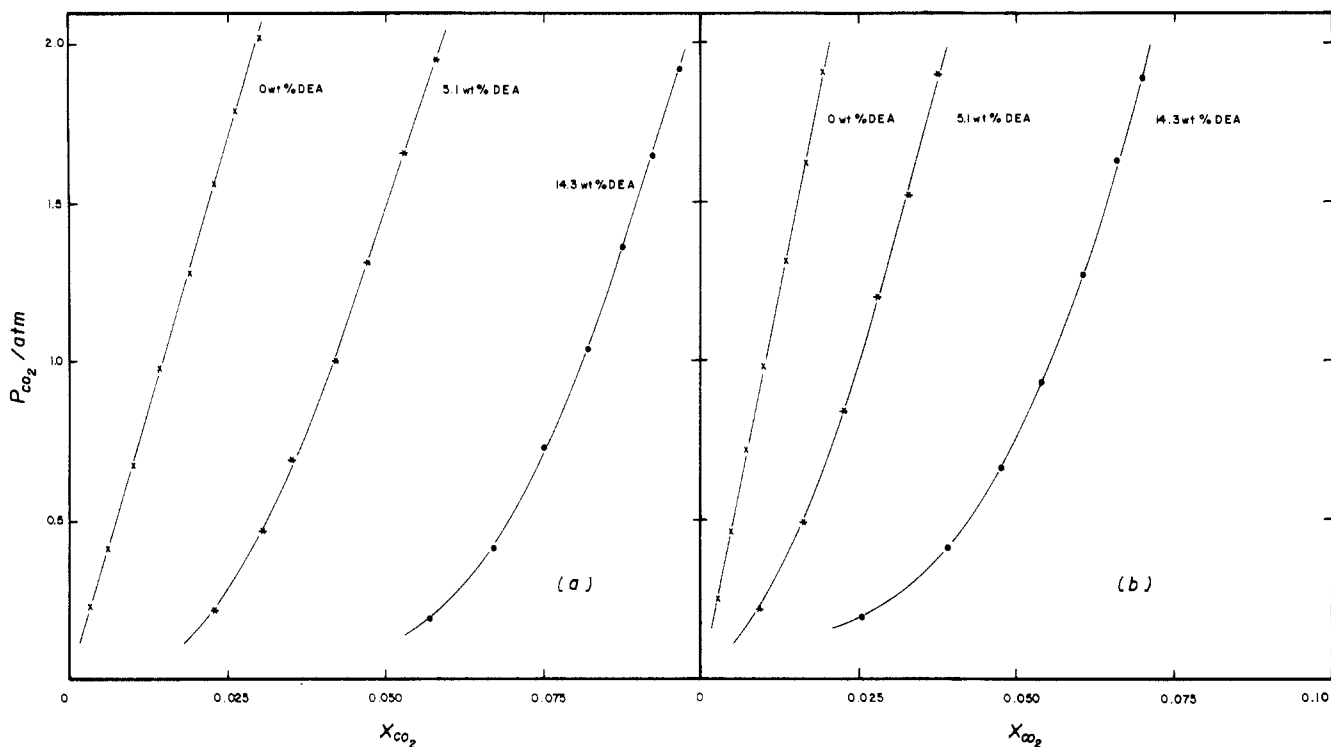


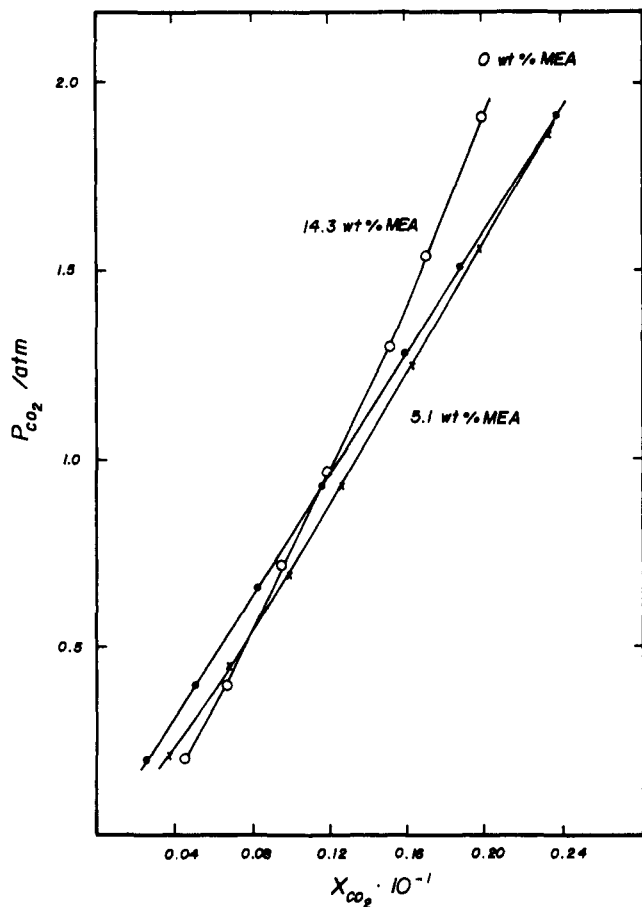
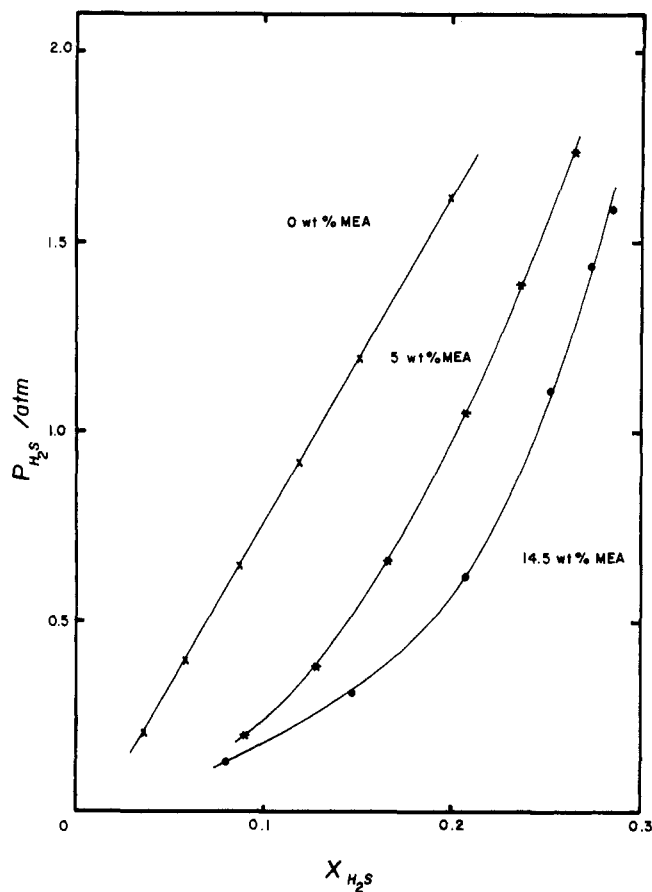
Figure 3. Solubility of CO₂ in mixtures of NMP with DEA: (a) at 25 °C; (b) at 50 °C.

peratures and concentrations studied here. The result that the mixtures with MEA are more efficient in solubilizing CO₂ is somewhat unsurprising since MEA is the most commonly used alkanolamine in aqueous solutions in separation processes due to its high reactivity with acid gases.

In order to investigate whether the combination of MEA with some other physical solvent would increase its reactivity we determined the solubility of CO₂ in mixtures of PC with 5.1 and 14.3 wt % MEA at 25 °C. These results are included in Table

II and shown in Figure 4. The change in concentration of MEA from 5.1 to 14.3 wt % seems to have a negligible effect on the solubility of CO₂. Furthermore, the presence of PC does not increase the solubility of CO₂ as compared with the results corresponding to the mixtures of NMP with MEA.

The solubility of H₂S in mixtures of NMP with 5.1 and 14.3 wt % MEA was determined at 25 °C to establish any possible selectivity of these mixtures for either CO₂ or H₂S. The experimental data are given in Table III and also shown in Figure

Figure 4. Solubility of CO_2 in mixtures of PC with MEA at 25 °C.Figure 5. Solubility of H_2S in mixtures of NMP with MEA at 25 °C.Table III. Experimental Data for the Solubility of H_2S in Pure and Mixed Solvents at 25 °C

$X_{\text{H}_2\text{S}}$	$P_{\text{H}_2\text{S}}/\text{atm}$
NMP	
0.034	0.207
0.057	0.395
0.087	0.638
0.119	0.911
0.150	1.191
0.192	1.619
NMP + 5.1 wt % MEA	
0.089	0.199
0.129	0.377
0.167	0.661
0.208	1.052
0.237	1.387
0.264	1.735
NMP + 14.3 wt % MEA	
0.080	0.134
0.147	0.308
0.207	0.619
0.252	1.108
0.274	1.439
0.285	1.586

5. The solubility of H_2S in mixtures of NMP with MEA, at a given temperature, is greater than the solubility of CO_2 in the same mixtures.

Since CH_4 is the main component of natural gas, it is necessary to know its solubility in mixtures that may be used for the removal of acid gases. We determined the solubility of CH_4 in pure NMP and in mixtures of this physical solvents with 5.1 and 14.3 wt % MEA and 14.3 wt % DEA at 25 °C. The results are given in Table IV and shown in Figure 6. The solubility of

Table IV. Experimental Data for the Solubility of CH_4 in Pure and Mixed Solvents at 25 °C

X_{CH_4}	$P_{\text{CH}_4}/\text{atm}$
NMP	
0.000 ₆	0.269
0.001 ₀	0.489
0.001 ₃	0.687
0.001 ₇	0.937
0.002 ₀	1.213
0.002 ₄	1.578
0.002 ₇	1.942
NMP + 5.1 wt % MEA	
0.000 ₇	0.258
0.001 ₄	0.466
0.002 ₁	0.686
0.002 ₆	0.937
0.003 ₃	1.247
0.004 ₀	1.594
0.004 ₆	1.938
NMP + 14.3 wt % MEA	
0.000 ₈	0.274
0.001 ₃	0.486
0.001 ₇	0.702
0.002 ₂	0.948
0.002 ₄	1.158
0.003 ₀	1.468
0.003 ₃	1.694
0.003 ₄	1.946
NMP + 14.3 wt % DEA	
0.000 ₆	0.270
0.001 ₀	0.468
0.001 ₄	0.721
0.001 ₇	0.937
0.002 ₂	1.238
0.002 ₆	1.582
0.003 ₂	1.955

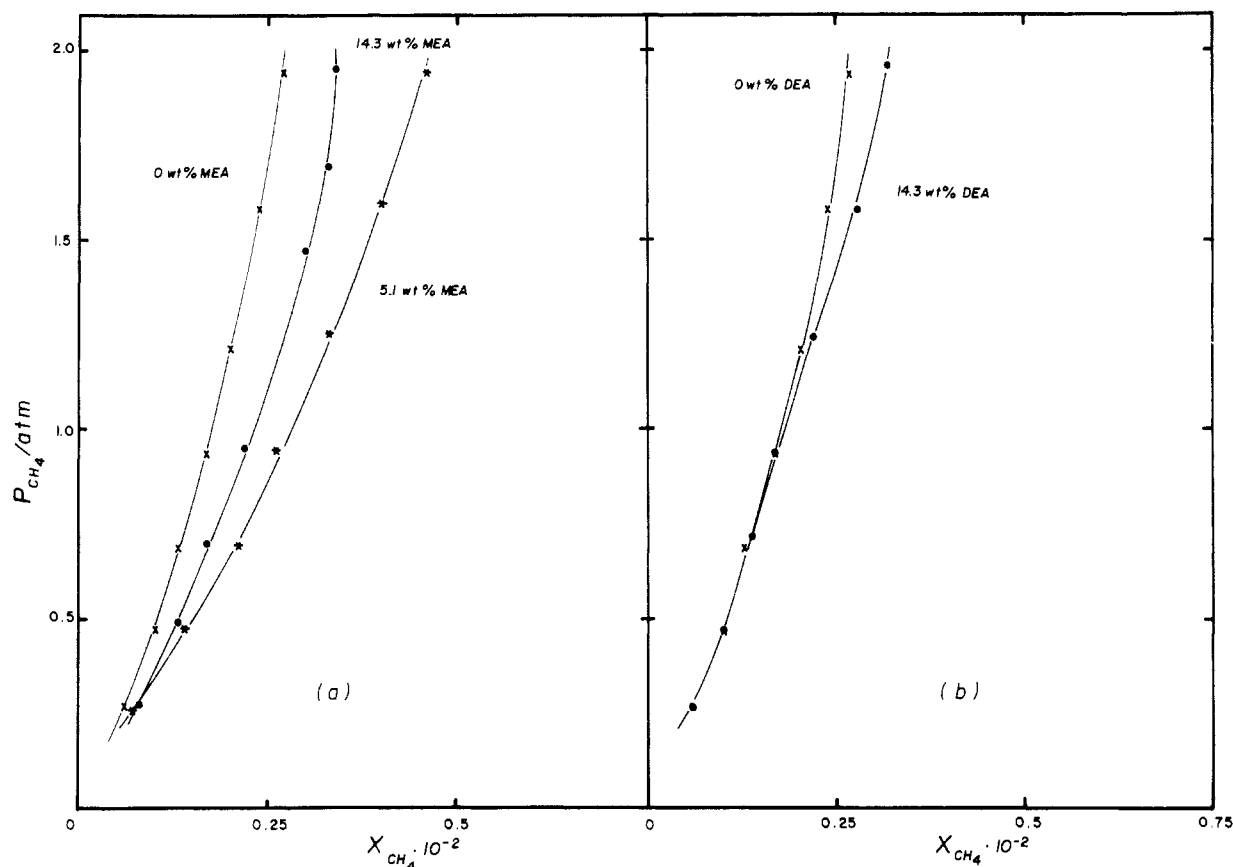


Figure 6. Solubility of CH_4 at 25 °C: (a) mixtures of NMP with MEA; (b) mixtures of NMP with DEA.

CH_4 is comparatively low in the mixtures of NMP with MEA; furthermore, as the concentration of MEA increases, the solubility of CH_4 decreases, which is highly favorable since the solubility of both CO_2 and H_2S varies in the opposite way. Thus, the mixtures of NMP with MEA present good efficiency to remove acid gases and at the same time low selectivity for CH_4 .

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 NMP with MEA may prove to be rather appropriate.

Registry No. CO_2 , 124-38-9; CH_4 , 74-82-8; H_2S , 7783-06-4; NMP, 872-50-4; MEA, 141-43-5; DEA, 111-42-2; PC, 108-32-7.

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Molar Volumes of Binary Solutions of Nitrobenzene in Halogenated and Nonhalogenated Solvents

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The molar volume as a function of composition is measured at 25.00 ± 0.01 °C for the following systems: toluene, α, α, α -trichlorotoluene, α, α, α -trifluorotoluene, cumene, *tert*-butylbenzene, ethanol, 2,2,2-trichloroethanol, 2,2,2-trifluoroethanol, acetic acid, trifluoroacetic acid, acetic anhydride, and trifluoroacetic anhydride with nitrobenzene as the second component. Preliminary study shows no obvious correlation between V^E and the molecular structure of the various solution constituents.

Introduction

The work presented here is a continuation of our effort to establish a data bank for volumetric behavior of liquid solutions. The data will be employed in deriving and testing semiempirical methods for predicting the volumetric behavior of liquid solutions from the volumetric behavior of the pure solution constituents. In the absence of rigorous thermodynamic methods, such semiempirical approaches are of great importance in predicting the volumetric behavior of liquid solutions. Such theories are