

however, does not display this regularity, decreasing for acetic acid and increasing for butyric acid. The apparent reversal with propionic acid caused by addition of isopropyl alcohol is beyond the limits of experimental uncertainty and seems especially anomalous. These observations serve to illustrate the complexity of ion-solvent interactions in multicomponent systems.

Registry No. Acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6.

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Solubility of CO₂ in an AMP Solution

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The solubility of CO₂ in a 2.00 mol/L solution of 2-amino-2-methyl-1-propanol (AMP) has been determined at 40 and 70 °C at partial pressures between 0.2 and 5279 kPa.

Introduction

Aqueous alkanolamine solutions are widely used for the removal of the acid gases H₂S and CO₂ from natural gases. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA) are those most commonly used (1, 2). Except for MDEA at high pressures, these alkanolamines have a relatively low maximum capacity for the acid gases. Sartori and Savage (3) discovered a new class of amines, sterically hindered amines. They are capable of high loadings of the acid gases because their carbamates are relatively unstable. AMP (2-amino-2-methyl-1-propanol) is a hindered primary alkanolamine that forms a carbamate with a much lower stability than the carbamates of MEA and DEA (4). The formation of bicarbonate becomes the only important reaction, and loadings approaching 1 mol of CO₂/mol of AMP are possible at moderate partial pressures.

The present work reports the solubility of CO₂ in a 2.00 M aqueous AMP solution at 40 and 70 °C over a wide range of pressures.

Experimental Details

An aqueous solution of AMP was prepared from distilled water and AMP, which was obtained from Matheson, Coleman, and Bell. The AMP had a purity of 98% and was used without further purification. The concentration in the resulting solution was determined by titration with standardized 1 N H₂SO₄ solution, using methyl red indicator. The carbon dioxide and nitrogen were obtained from Matheson and had purities greater than

Table I. Solubility of CO₂ in 2.00 mol/L AMP^a

at 40 °C			at 70 °C		
<i>P</i> /kPa	<i>p</i> /kPa	α	<i>P</i> /kPa	<i>p</i> /kPa	α
434.8	0.162	0.035	444.9	0.586	0.033
398.3	0.189	0.068	420.6	0.878	0.054
383.1	0.373	0.294	380.3	2.43	0.197
425.1	1.283	0.466	448.7	6.95	0.336
434.3	6.01	0.693	447.9	10.92	0.436
466.7	142.7	0.982	432.3	26.6	0.597
565.4	283.7	1.001	445.0	50.9	0.725
			463.3	87.6	0.817
			501.4	148.5	0.851
			566.0	224.4	0.883
			813.9	434.6	0.927
			669.7	641.0	0.971*
			1126.9	791.5	1.026
			1492.1	1461.6	1.099*
			2645.9	2615.0	1.176*
			3489.7	3458.0	1.205*
			5306.9	5279.0	1.265*

^a Abbreviations: *P* = total pressure; *p* = partial pressure, *yP*; *y* = mole fraction of CO₂ in the vapor phase; α = mole ratio in the liquid phase, CO₂/AMP. Values marked with an asterisk, no addition of N₂.

99%. The equipment used for the solubility measurements was essentially the same as that used previously in this laboratory (5). It consists of a windowed equilibrium cell into which the AMP solution and the CO₂ were introduced and brought to equilibrium. The cell had an internal volume of about 75 mL with a 250-mL cylindrical reservoir mounted on the top of the cell to increase the amount of vapor in equilibrium with the solvent. The vapor in the reservoir was recirculated through the solvent by means of a magnetically driven piston pump similar to that devised by Ruska et al. (6). The pump and cell were enclosed in an air bath, the temperature of which was controlled to within ± 0.5 °C. A Leeds and Northrup potentiometer was used to measure the output of an iron-constantan thermocouple, which extended through the wall of the cell into the fluid. The fluid pressure in the cell was measured by a calibrated Heise bourdon gauge. The gas was recirculated and bubbled through the solution for at least 8 h to allow the system

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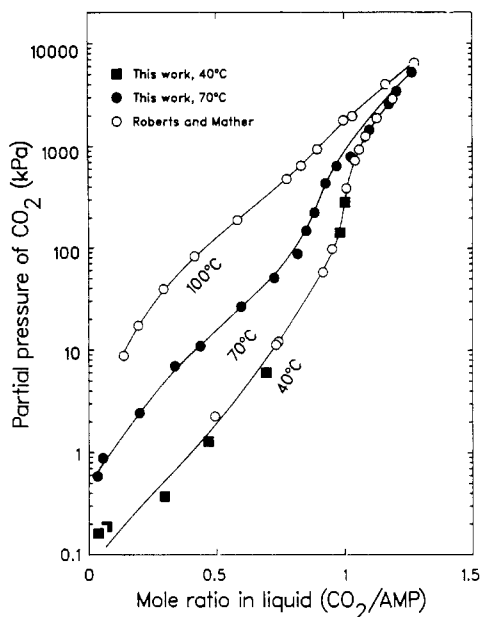


Figure 1. Solubility of CO₂ in a 2.0 mol/L AMP solution.

to reach equilibrium. At vapor-liquid equilibrium, the vapor phase was analyzed by means of a H-P gas chromatograph Model 5710A with a 3-m length, 6.35-mm o.d. column packed with Chromosorb 104. The response factors for the gases were as follows: N₂, 1.17; CO₂, 1.00. The partial pressure of the water over the aqueous AMP solution was calculated from Raoult's law:

$$p_w = x_w P_w^s \quad (1)$$

The partial pressure of water calculated in this way varied from 6.8 to 7.1 kPa at 40 °C and from 28.3 to 29.8 kPa at 70 °C.

A known amount of the loaded solution was withdrawn from the cell through the liquid sample line into a 1 N NaOH solution for analysis. The CO₂ content of the loaded solution was determined by mixing an aliquot of the sample solution with an excess of 0.1 N BaCl₂ solution to form BaCO₃ precipitate. The precipitate was then filtered, washed with distilled water, and titrated with standardized 0.1 N HCl solution by using methyl orange-xylene cyanol indicator.

A 40-cm³ high-pressure metal sampling bomb containing the 1 N NaOH solution was used for sampling at CO₂ loadings where the reaction rate was not fast enough to prevent pressure buildup over the basic solution. A 50-cm³ Erlenmeyer flask fitted with a rubber septum was used to collect liquid samples for partial pressures lower than 1000 kPa. The experimental error in the solution loading (moles of CO₂/mole of AMP) is estimated to be ±2-3%.

Results and Discussion

To test the analytical procedures and experimental technique, data were obtained at 40 °C for comparison with those of Roberts and Mather (7), who obtained data for a similar solution at 40 and 100 °C. Figure 1 shows that the new results are in good agreement with the previous work. Data were also obtained at 70 °C over the pressure range 0.6-5279 kPa. The experimental data are presented in Table I, and all the data for a 2.0 mol/L AMP solution are shown in Figure 1. The solubility of CO₂ in the AMP solution is indeed higher than that in comparable DEA or TEA solutions; at 70 °C and a partial pressure of 100 kPa, the corresponding α would be 0.52 and 0.22, respectively, compared with 0.81 for the AMP solution. At CO₂ loadings greater than unity, there is little effect of temperature on the solubility. This behavior is similar to that noted in MDEA solutions by Jou et al. (5).

Registry No. AMP, 124-68-5; CO₂, 124-38-9.

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Excess Molar Volumes, Excess Logarithmic Viscosities, and Excess Activation Energies of Viscous Flow for 2-Ethoxyethanol + γ -Butyrolactone and + Sulfolane at 303.15 K

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Densities, excess volumes, excess logarithmic viscosities, and excess activation energies of viscous flow are reported for binary mixtures of 2-ethoxyethanol + γ -butyrolactone and + sulfolane over the whole mole fraction range at 303.15 K. The excess volumes, excess logarithmic viscosities, and excess activation energies of viscous flow are all negative over the whole mole fraction range. The sulfolane system shows a larger negative deviation from ideality than that of the γ -butyrolactone system.

Introduction

In previous papers (1, 2), the excess molar volumes of 2-ethoxyethanol + a glycol and + morpholine derivatives were reported. Our interest in these solvents and their binary mixtures arose from their high efficiency for the extraction of monocyclic aromatic hydrocarbons from petroleum products. Although an extensive search in the literature was made, we could not trace any thermodynamic and spectroscopic data for these systems. In the present paper, we report the densities, excess volume viscosities, excess logarithmic viscosities, and