**Registry No.** Methane, 74-82-8; diethylene glycol, 111-46-6.

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# Solubility of Carbon Monoxide in Aqueous Mixtures of Allyl Alcohol, Diethylamine, and Triethylamine

**Mirza M. Taqui Khan* and Shivappa B. Halligudi**

*Homogeneous Catalysis Group, Coordination Chemistry Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India*

**The solubility of carbon monoxide (CO) in water–allyl alcohol, water–diethylamine, and water–triethylamine has been determined in a temperature range of 343–403 K and at a equilibrium CO pressure of 3.202 × $10^3$ kPa. The values of the enthalpy change of solution and Henry's coefficient have been determined. Solubility dependence on temperature and concentration in the liquid phase has been correlated by using the equation $\ln H = a + b/T + c(X)(1/303) - (1/T) + d \ln (1 + X)$, and the values of constants have been calculated for each system. The values predicted by using the above equation agreed well with the experimentally determined values within 3–5% error.**

## Introduction

In any study of the intrinsic kinetics of gas–liquid reactions, data on the solubility of the gas-phase reactant in the liquid medium are essential. In recent years, the study on the gas–liquid reactions involving CO using metal complex catalysts in solution has gained considerable importance (*1–4*). Data on the solubility of CO particularly at higher temperatures and pressures are not available in the literature. The objective of the present work, therefore, was to determine solubility of carbon monoxide (CO) in different solvent mixtures involved in industrial carbonylation process such as carbonylation of allyl alcohol, diethylamine, and triethylamine (*5*). As the data on the solubility of CO in the solvent mixture, which we had studied, were not available in literature at the desired pressures and temperatures, it was decided to determine these solubilities experimentally.

## Experimental Section

The solubility of a gas in a liquid at higher pressures and temperatures is generally obtained by taking out a known amount of saturated solution and measuring the dissolved gas in the liquid usually by the volumetric method. This method was used to determine the solubility of CO in aqueous mixtures of allyl alcohol, diethylamine, and triethylamine, as this method has been found to be quite accurate by many investigators (*6*, *7*). The apparatus and procedure to determine the solubility of CO has been described elsewhere (*7*). The carbon monoxide gas used in our studies was obtained from BOC, U.K., and GC analysis shows a purity greater than 99.6%. The solvents used were of A.R. grade and distilled before use. The purities of the solvents were greater than 99.5% as checked by GC. The pressure autoclave (3 × $10^{-4}$ $m^3$) obtained from Parr Instruments Co., USA, was used in the investigations.

The solubility of CO was calculated from the observed volume of gas desorbed from a known amount of liquid withdrawn from the autoclave after equilibration by using the relationship

$$Z = \frac{V - V_1}{V_1}\left[\frac{P - P_w - \dfrac{h}{13.6}}{101.3}\right]\frac{273}{T_w} \tag{1}$$

As the solubility of the CO measured excludes the solubility of CO at atmospheric pressure, the following equation was used to obtain the actual solubility under the conditions employed to equilibrate the gas with the solvent.

$$S = Z + S_1 \tag{2}$$

In this equation $S_1$ is the term used for correction.

The reproducibility of the data was also verified by conducting the same experiment twice and the reproducibility was within 2–3% error. The solubility determination of CO was also conducted at a particular chosen pressure using a pressure gauge with the range (0–1.37) × $10^4$ kPa (0–2000 psi) and different temperatures, varying the liquid-phase composition. The errors in the measurements of $P$, $V$, $T$ are estimated to be around 3 kPa, 1 × $10^{-6}$ $m^3$, and 0.1 K respectively.

The vapor pressures are calculated from Antoine's equation

$$\ln P_{vap} = A - \frac{B}{(T + C)} \tag{3}$$

where $A$, $B$, and $C$ are Antoine's constants which were taken from the literature (*8*). Since these are predicted values, and previous experience shows that the equation has an accuracy

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**Table I. Solubility Data for CO + Allyl Alcohol + Water at a CO Total Pressure of 3.202 × 10$^3$ kPa**

| | 373 K | | 383 K | | 393 K | | 403 K | | |
|---|---|---|---|---|---|---|---|---|---|
| mole fracn of allyl alcohol | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $\Delta H$, kJ/mol |
| 0 | 3.101 | 6.19 | 3.059 | 6.75 | 3.004 | 7.31 | 2.932 | 7.86 | 1.25 |
| 0.05 | 3.100 | 7.66 | 3.058 | 8.34 | 3.003 | 9.02 | 2.931 | 9.69 | 1.29 |
| 0.10 | 3.099 | 9.13 | 3.057 | 9.92 | 3.002 | 10.72 | 2.929 | 11.52 | 1.56 |
| 0.15 | 3.098 | 10.60 | 3.056 | 11.51 | 3.001 | 12.43 | 2.928 | 12.35 | 1.26 |
| 0.20 | 3.097 | 12.07 | 3.055 | 13.10 | 3.000 | 14.14 | 2.927 | 15.17 | 1.01 |
| 0.50 | 3.096 | 20.88 | 3.052 | 22.63 | 2.994 | 24.38 | 2.921 | 26.13 | 1.23 |
| 0.80 | 3.092 | 29.69 | 3.047 | 32.16 | 2.989 | 34.63 | 2.914 | 37.09 | 1.22 |
| 1.00 | 3.090 | 35.56 | 3.045 | 38.51 | 2.985 | 41.46 | 2.909 | 44.40 | 1.22 |

**Table II. Solubility Data for CO + Diethylamine + Water System at a CO Total Pressure of 3.202 × 10$^3$ kPa**

| | 343 K | | 353 K | | 363 K | | 373 K | | |
|---|---|---|---|---|---|---|---|---|---|
| mole fracn of diethylamine | $P_{CO} \times 10^{-13}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $\Delta H$, kJ/mol |
| 0 | 3.171 | 6.00 | 3.155 | 6.07 | 3.132 | 6.13 | 3.101 | 6.19 | 0.15 |
| 0.05 | 3.165 | 9.76 | 3.146 | 9.10 | 3.121 | 10.24 | 3.087 | 10.47 | 0.32 |
| 0.10 | 3.158 | 13.52 | 3.138 | 13.94 | 3.110 | 14.34 | 3.074 | 14.75 | 0.40 |
| 0.15 | 3.152 | 17.29 | 3.129 | 17.87 | 3.099 | 18.45 | 3.061 | 19.03 | 0.44 |
| 0.20 | 3.145 | 21.06 | 3.121 | 21.81 | 3.089 | 22.55 | 3.047 | 23.30 | 0.47 |
| 0.50 | 3.106 | 43.64 | 3.070 | 45.42 | 3.024 | 47.19 | 2.966 | 48.97 | 0.53 |
| 0.80 | 3.067 | 66.23 | 3.019 | 68.62 | 2.960 | 71.00 | 2.886 | 73.39 | 0.47 |
| 1.00 | 3.041 | 81.29 | 2.985 | 84.77 | 2.916 | 88.25 | 2.832 | 91.74 | 0.56 |

**Table III. Solubility Data for CO + Triethylamine + Water at a CO Total Pressure of 3.2023 × 10$^3$ kPa**

| | 343 K | | 353 K | | 363 K | | 373 K | | |
|---|---|---|---|---|---|---|---|---|---|
| mole fracn of triethylamine | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times 10^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $P_{CO} \times$ 10$^{-3}$, kPa | $H \times 10^6$, kmol/(m$^3$ kPa) | $\Delta H$, kJ/mol |
| 0 | 3.171 | 6.00 | 3.155 | 6.06 | 3.132 | 6.13 | 3.101 | 6.19 | 0.15 |
| 0.01 | 3.171 | 6.55 | 3.155 | 6.64 | 3.133 | 6.72 | 3.101 | 6.81 | 0.18 |
| 0.02 | 3.171 | 7.10 | 3.154 | 7.21 | 3.132 | 7.32 | 3.100 | 7.43 | 0.21 |
| 0.03 | 3.171 | 7.654 | 3.154 | 7.78 | 3.131 | 7.92 | 3.099 | 8.05 | 0.23 |
| 0.05 | 3.171 | 8.76 | 3.154 | 8.93 | 3.130 | 9.11 | 3.099 | 9.28 | 0.27 |
| 1.00 | 3.149 | 61.12 | 3.127 | 63.39 | 3.097 | 65.57 | 3.063 | 67.95 | 0.49 |

of 5%, we believe that the values predicted are of the same accuracy. These values were taken into consideration for correcting the partial pressure of CO in the autoclave.

## Results and Discussion

The solubility of CO was determined for (1) CO–water–allyl alcohol, (2) CO–water–diethylamine, and (3) CO–water–triethylamine systems. The needed Henry's coefficients were obtained by using Henry's equation at constant temperature as

$$S = HP \tag{4}$$

where $S$ is the solubility in kmol/m$^3$ and $P$ partial pressure of CO at equilibrium in kPa.

Hence, Henry's coefficient $H$ can be expressed in terms of $S$ and $P$ as

$$H = S/P \tag{5}$$

The unit of Henry's coefficients obviously is kmol/(m$^3$ kPa). The liquid-phase composition was also varied and the effect of temperature on solubility was determined. The results are shown in Tables I–III.

The effect of temperature on solubility of CO was studied for all the systems described above in the temperature range 340–403 K. It was observed that the solubility of CO increased with increase in temperature, for all the systems studied. For each system Henry's coefficient was calculated and a least-squares straight line fitting of ln $H$ vs $1/T$ was done using the HP-1000/45 computer system. The slope of this straight line fit is equal to $\Delta H/R$ from which the values of the enthalpy change of solution $\Delta H$ were calculated. These data are also accommodated in Tables I–III.

**Table IV. Constants of Eq 6**

| system | $a$ | $b$ | $c$ | $d$ | % error |
|---|---|---|---|---|---|
| allyl alcohol + water | −11.82 | −249.23 | −25.89 | 3.52 | 3.6 |
| diethylamine + water | −11.10 | −190.23 | −21.33 | 3.21 | 4.2 |
| triethylamine + water | −11.45 | −200.12 | −28.45 | 3.35 | 2.9 |

Among the systems studied, it was found that the solubility of CO was highest in diethylamine, followed by triethylamine, allyl alcohol, and water.

The correlation of data for the systems studied for the variation of liquid-phase composition and temperature was also done using the following empirical equation which was found to represent the solubility data satisfactorily.

$$\ln H = a + \frac{b}{T} + c(X)\left(\frac{1}{303} - \frac{1}{T}\right) + \text{d} \ln (1 + X) \tag{6}$$

which is the type of equation normally used for correlation of solubility data (*9*, *10*). Solubility data were fitted to eq 6 by using a linear least-squares analysis program and the values of the constants were evaluated. Table IV lists the values of the constants $a$, $b$, $c$, and $d$ for the systems, the predicted solubilities obtained by using eq 6, and the experimentally determined solubilities as well as the percentage errors between the estimated and predicted values, which are around 4%.

## Glossary

| | |
|---|---|
| $Z$ | solubility of CO, m$^3$/m$^3$ |
| $h$ | height of the water column in the gas desorption apparatus, m |

| | |
|---|---|
| $S_1$ | solubility of CO at atmospheric pressure and room temperature, $m^3/m^3$ |
| $S$ | solubility of CO, $kmol/m^3$ |
| $H$ | Henry's coefficient of solubility, $kmol/(m^3\ kPa)$ |
| $P$ | barometric pressures, kPa |
| $P_w$ | vapor pressure of water at temperature $T_w$, kPa |
| $P_{vap}$ | vapor pressure of solvent in eq 3, kPa |
| $P_{CO}$ | partial pressure of CO in the autoclave, kPa |
| $T$ | temperature in the autoclave, K |
| $T_w$ | temperature in the gas buret, K |
| $V$ | volume of water displaced by the desorbed CO gas, $m^3$ |
| $V_1$ | volume of the liquid sample withdrawn from autoclave, $m^3$ |
| $X$ | mole fraction of the organic component in water |

**Registry No.** CO, 630-08-0; allyl alcohol, 107-18-6; diethylamine, 109-89-7; triethylamine, 121-44-8.

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# Evaluation of Pitzer Ion Interaction Parameters of Aqueous Mixed Electrolyte Solutions at 25 °C. 2. Ternary Mixing Parameters

**Hee-Taik Kim and William J. Frederick, Jr.***

*Department of Chemical Engineering, Oregon State University, Corvallis, Oregon 97331*

**The Pitzer mixing parameters $\theta_{ij}$ and $\psi_{ijk}$ were evaluated for 49 ternary mixtures with common ions at 25 °C. The Harvie and Weare model, which is based on Pitzer equations for aqueous mixed electrolyte solutions, was used for these evaluations. Evaluation of these parameters for mixed electrolyte solutions required only the single-salt parameters and experimental values of ln $\gamma_\pm$ or $\phi$ for ternary mixtures with common ions. The effects of the higher order electrostatic terms were considered for all asymmetrical mixtures of electrolytes. The mean standard deviation for the calculated ln $\gamma_\pm$ or $\phi$ values is 0.0070 when compared with the experimental values used to obtain the ternary mixing parameters.**

## Introduction

In recent years there has been increasing interest in the thermodynamic properties of aqueous mixed electrolyte solutions, especially at high concentrations. In fields such as sea water desalination, geothermal energy recovery, chemical oceanography, hydrometallurgy, and pulp and paper chemistry, it is essential to have accurate data on the thermodynamic properties of mixed electrolyte solutions.

The nonideality of a single electrolyte solution is conventionally represented in terms of the mean activity coefficient, $\gamma_\pm$.

Activity coefficients are of primary importance in describing accurately the thermodynamic behavior of aqueous mixed electrolyte solutions. The lack of accurate activity coefficient predictions can result in large errors when calculating the solubility of inorganic species in aqueous multicomponent ionic solutions of high ionic strength even when only a few chemical species are present.

Among recently developed models of electrolyte solutions, ionic interaction models provide the simplest and most coherent procedures for calculating the thermodynamic properties of electrolyte components. They use a single set of equations to describe the activity and osmotic coefficients of the components of aqueous single and mixed electrolyte solutions. An ion interaction model for predicting activity coefficients of mixed electrolyte solutions was developed by Pitzer and co-workers (*1–4*) in the early 1970s. The Pitzer model extended the Debye–Hückel method, using a virial expansion to account for the ionic strength dependence of the short-range forces in binary and ternary ion interactions. The virial expansion approach accurately represents the compositional dependence of the thermodynamic properties in most multicomponent electrolyte solutions to high ionic strengths. Also, these equations can be used in iterative calculations since the ion interaction parameters are expressed as explicit functions of ionic strength, and only a few parameters are needed to evaluate properties of both single and mixed electrolyte solutions. Many publications (*5–11*) have shown that the Pitzer model results in excellent solubility prediction.

The purpose of this work is to obtain Pitzer mixing ion interaction parameters, $\theta_{ij}$ and $\psi_{ijk}$, from experimental data on aqueous mixed electrolyte solutions with common ions. The $\theta$-terms summarize interaction between ions of like charged sign that are independent of the common ion in a ternary mixture and the $\psi$-terms account for the modifying influence of the common ion on these interactions. The mixing ion interaction parameters from our results are stored in a computer as a database with single-salt parameters, and activity or osmotic coefficients for mixed electrolyte solutions can be calculated simply by identifying the salt and defining the appropriate ionic strength.

## General Equation for Mixed-Electrolyte Solutions

Recently Harvie and Weare (*5*) have developed a chemical equilibrium model for calculating mineral solubilities in brines from zero to high ionic strengths at 25 °C. This model was based on the semiempirical equations of Pitzer and co-workers

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