J. Chem. Eng. Data **1992,** *37,* 291-293 291

Solubility of CO in 1,1,1-Trichloroethane, *N*,*N*-Dimethylacetamide, Dibutyl Phthalate, and Their Mixtures

Somiran Baruah, Narendra N. Dutta,* and Gajanan S. Patil

Chemical Engineering Division, Regional Research Laboratory, Jorhat-785 006 (Assam), India

The solubility of CO in 1,1,1-trichloroethane, *N*,*N*-dimethylacetamide, dibutyl phthalate, and their binary mixtures was measured using a simple volumetric method at temperatures up to 353 K and near atmospheric pressure. Henry's constants for pure solvents have been correlated by the equation $\ln H = a + b/T$ for the temperature dependence of CO solubility. The solubility of CO in binary mixtures could be represented by a simple expression of the type $\ln H = x_1 \ln H_1 + x_2 \ln H_2$ with reasonable accuracy.

Introduction

Data on CO solubility in different solvents have various applications. The most important use of CO solubility data is related to the studies of transition-metal-catalyzed carbonylation reactions for production of valuable chemicals and Fischer–Tropsch catalytic synthesis of hydrocarbons. In view of this, solubilities of CO in various reacting media and solvents have been studied by various researchers. Data on the solubility of CO in different types of solvents have been recently compiled (*1*). However, it does not include the solubility of CO in benzonitrile which has been reported elsewhere (*2*). Our interest in studies on CO solubility in the specific solvents under investigation stems from the need of such data in designing supported liquid membrane systems for selective permeation of CO. For such application, the solvent selection should be based on volatility and surface tension considerations and the membrane support should be microporous and thin (*3*). In other specific cases of carrier-facilitated transport of gases across liquid membranes, carrier solubility in the solvent is one of the important factors. We report here measurements of the solubility of CO in 1,1,1-trichloroethane (TCE), *N*,*N*-dimethylacetamide (DMA), and dibutyl phthalate (DBP) and their mixtures, as we found that these solvents were ideal for designing a suitable carrier-mediated facilitated transport system for CO (*4*).

Experimental Section

The solvents 1,1,1-trichloroethane (anhydrous and purity >99%), *N*,*N*-dimethylacetamide (anhydrous and purity >99%), and dibutyl phthalate (purity >99% and moisture content <0.005%) were obtained from Aldrich Chemical Co. Carbon monoxide having 99.98% purity was obtained from M/s Indian Oxygen Ltd., India. The solvents were used without further purification.

Table I. Henry's Constant *H* for CO in the Pure Solvents

T/K	H/(Pa m^3 mol^{-1}) DMA	TCE	DBP
293	22 400	28 100	38 000
303	26 500	22 500	38 500
313	30 400	18 700	43 200
323	37 800	16 100	48 100
333	53 100	14 500	65 000
343	78 200	13 800	90 100

Table II. Henry's Constant *H* for CO in Mixed Solvents at 303 K

x TCE + $(1 - x)$ DMA		x TCE + $(1 - x)$ DBP		x DMA + $(1 - x)$ DBP	
x	H/(Pa m^3 mol^{-1})	x	H/(Pa m^3 mol^{-1})	x	H/(Pa m^3 mol^{-1})
0.000	26 500	0.000	38 500	0.000	38 500
0.090	29 400	0.089	36 100	0.140	41 500
0.178	32 700	0.181	33 800	0.260	43 500
0.248	33 900	0.390	28 400	0.505	47 400
0.390	32 400	0.530	26 200	0.640	46 700
0.600	27 600	0.675	24 000	0.880	38 700
0.849	22 500	0.830	22 450	0.960	29 500
1.000	22 450	1.000	22 500	1.000	26 500

A simple procedure for measurement of the solubility was adopted. A glass vessel with a volume of 500 mL was used in which 100 mL of solvent was taken. This amount of liquid volume used in the measuring cell is thought to be adequate to eliminate any chance of error in solubility measurements (*5*). The solvent was degassed by means of a vacuum pump connected to the evacuation vessel, and the solvent was held under vacuum for some time until equilibrium was reached. The equilibrium pressure was measured with a micromanometer using a cathetometer. An adequate amount of dry gas was fed to the vessel slowly until a pressure of around 100 kPa was reached. Then the vessel was closed, and a magnetic stirrer was used to agitate the solvent. The change of pressure was recorded till an equilibrium value was reached. The solubility was calculated according to the relation

$$H = \frac{P_o - \Delta P - P_v}{\Delta P} RT \frac{V_g}{V_1} \tag{1}$$

The reproducibility between various experiments was within ±5%. Temperature control within ±1 K was achieved by placing the equilibrium vessel in a stirred water bath heated by a magnetic hot plate.

Results and Discussion

The solubility of CO was measured in the temperature range 293–353 K at near ambient pressure in the following systems: TCE, DBP, DMA, TCE + DMA, TCE + DBP, and DMA + DBT. However, for the binary mixture systems, data were obtained at 303 ± 1 K only. The results are given in Tables I and II and represented graphically by fitted lines in Figures 1 and 2. The vertical lines in Figures 1 and 2 represent the standard deviation of five measurements for each experimental value. Solubility values obtained for TCE are comparable with those reported elsewhere (*6*). The increase of solubility of CO with temperature in the case of TCE may be attributed to a decrease in solvent density as temperature increases. In the case of the DMA and DBP systems, solubilities of CO decreased with temperature, with the extent of decrease being higher for the latter system. It is believed that, in simple systems, gas solubility decreases with temperature when the density of the solvent is held constant (*7*), probably because of the large kinetic energy experienced by the gas at high temperature in relation to that

---

* To whom correspondence should be addressed.

0021-9568/92/1737-0291$03.00/0 © 1992 American Chemical Society

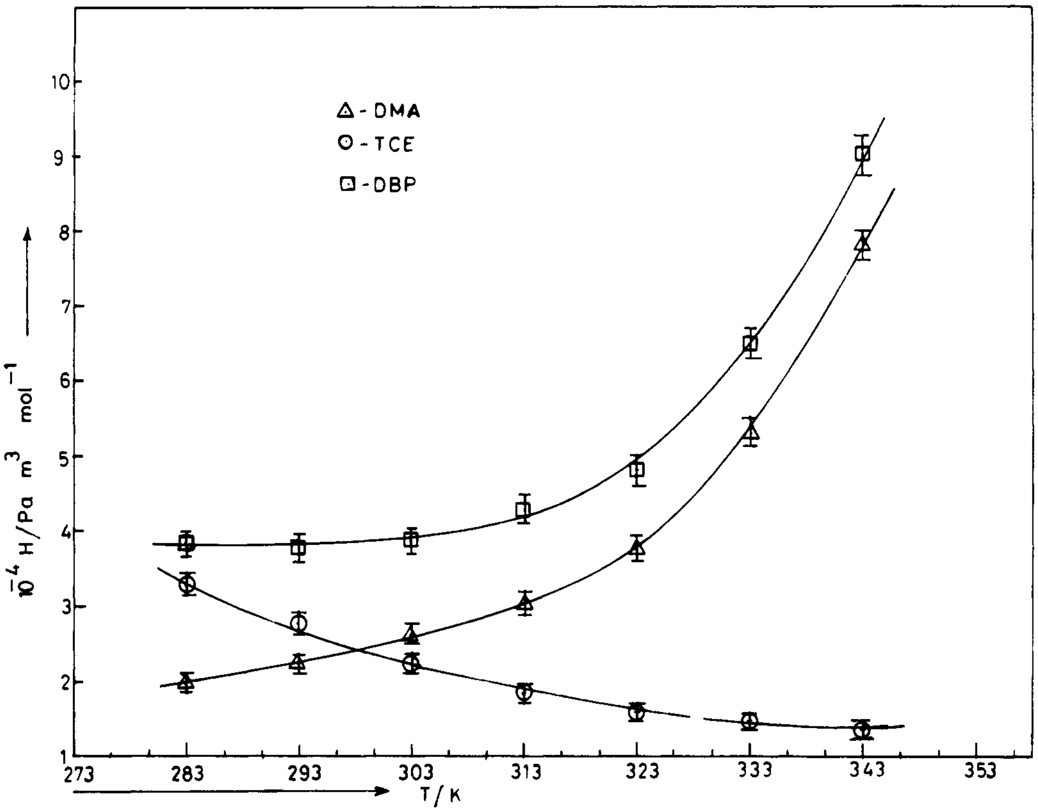

Figure 1. Variation of Henry's constant H for CO with temperature.

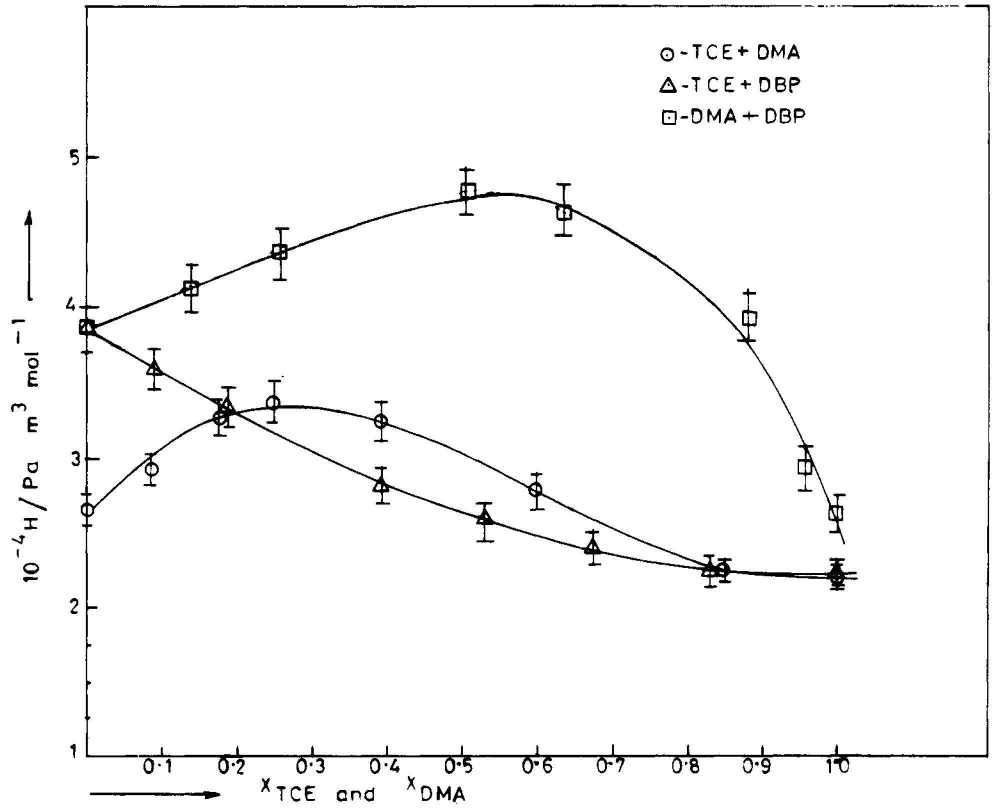

Figure 2. Henry's constant H for CO in mixed solvents at 303 K.

at its own boiling point. Very often solubilities of gases in solvents with higher density decrease with an increase of temperature. In our study with DMA and DBP, the trend in the decrease of solubility with an increase of temperature is found to be more pronounced for the denser solvent. This is in line with that reported for systems comprising gases like CO_2, N_2,

Table III. Constants of Equation 2 and Enthalpy of Solution ΔH

solvent	a	b	ΔH/(kJ mol^{-1})	std dev/%
DMA	11.6	−492.30	0.41	14
DBP	11.8	−262.29	0.22	18
TCE	9.4	184.60	−0.15	10

H_2, NH_3, CO, etc. and diphenylmethane, bicyclohexyl, and 1-methylnaphthalene as the solvents (*5*). The temperature-solubility relationship may be represented by the following empirical equation:

$$\ln (H/(\text{Pa m}^3\ \text{mol}^{-1})) = a + b/(T/\text{K}) \qquad (2)$$

A linear least-squares analysis was performed to obtain the values of the constants *a* and *b* as shown in Table III. The values of ΔH (enthalpy of solution, kJ mol^{-1}) calculated from the constant *b* have also been included in Table III.

The solubility data for the binary mixtures were obtained at 303 K only. The solubility of CO in mixed solvents is characterized by a maximum for TCE + DMA and DMA + DBP systems and a minimum for the TCE + DBP system. The results could be well described by the expression

$$\ln H = x_1 \ln H_1 + x_2 \ln H_2 \qquad (3)$$

which is the usual type of equation valid for ideal systems (*8*). The percent error between estimated (right-hand side of eq 3) and experimental values of *H* for the mixture was always less than ±3%.

Conclusion

The data presented in this paper are useful for the calculation of permeation parameters in the liquid membrane transport of CO and other design engineering calculations.

Glossary

a	empirical constant
b	empirical constant
H	Henry's constant
P_0	initial pressure
ΔP	pressure change due to absorption
P_v	vapor pressure of solvent
P_p	partial pressure of CO
R	gas constant
T	temperature
V_g	volume of gas
V_1	volume of liquid
x_1,x_2	mole fraction of components 1 and 2 in mixture

Registry No. CO, 630-08-0; TCE, 71-55-6; DMA, 127-19-5; DBP, 84-74-2.

Literature Cited

(1) Cargill, R. W., Ed. Carbon Monoxide. *Solubility Data Series*; Pergamon Press: Oxford, 1990; Vol. 43.
(2) Koval, C. A.; Noble, R. D.; Way, J. D.; Louie, B.; Reyes, Z. E.; Bateman, B. R.; Horn, G. M.; Reed, D. L. *Inorg. Chem.* **1985**, *24*, 1147.
(3) Nobel, R. D.; Way, J. D. In *Liquid Membranes, Theory and Applications*; Noble, R. D., Way, J. D., Eds.; ACS Symposium Series 347; American Chemical Society: Washington, DC, 1987; pp 1-26.
(4) Patil, G. S.; Baruah, S.; Dutta, N. N. *Gas Sep. Purif.* **1991**, *5*, 2.
(5) Tremper, K. K.; Prausnitz, J. M. *J. Chem. Eng. Data* **1976**, *21*, 295.
(6) Lyke, S. E.; Liiga, M. A.; Ozanich, R. M.; Nelson, D. A.; James, B. R.; Lee, C. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 517.
(7) Preston, G. T.; Funk, E. W.; Prausnitz, J. M. *Phys. Chem. Liq.* **1971**, *2*, 193.
(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; p 359.

Received for review August 1, 1991. Revised December 10, 1991. Accepted December 21, 1991. We thank the Department of Science and Technology, Government of India, for financial support under Grant No. III-4(1)/89-ET, September 1989.

Vapor–Liquid Equilibria at 760 mmHg for the System Vinyl Acetate–*n*-Decane

G. Ovejero Escudero,* A. de Lucas Martínez, and J. M. Moreno Rodríguez

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

Vapor–liquid equilibrium data for the vinyl acetate–*n*-decane system have been determined at 760 mmHg. The data were satisfactorily correlated by Wilson, UNIQUAC, and NRTL equations, and the appropriate parameters are reported.

Introduction

In the ethylene–vinyl acetate copolymer purification process, the liquid stream recycle is a mixture of vinyl acetate–*n*-decane which contains acetic acid as a major impurity.

Distillation is a good method to purify vinyl acetate. For the design and simulation of the distillation columns, phase equilibrium data are necessary. Binary vapor–liquid equilibrium (VLE) data were found in the literature for vinyl acetate–acetic acid (*1–5*) and acetic acid–*n*-decane (*6*). However, no VLE data were found for the vinyl acetate–*n*-decane.

In this work, we report experimental VLE measurements for vinyl acetate–*n*-decane. Among the different equations available in the literature for the correlation of binary equilibrium data, we have applied in this study the Wilson (*7*), UNIQUAC (*8*), and NRTL (*9*) liquid-phase activity coefficient models.

Table I. Refractive Indexes, *n*, and Normal Boiling Points, t_b, of the Pure Components

	n(20 °C)		t_b/°C	
component	this work	lit.	this work	lit.
vinyl acetate	1.3940	1.3941 (*12*)	72.9	72.84 (*13*)
n-decane	1.4115	1.4119 (*12*)	174.2	174.1 (*13*)

Experimental Section

Materials. Vinyl acetate (>99%), from Merck, was used without further purification. *n*-Decane (>95%), from FLUKA, was purified by distillation in a column (25-mm i.d. and 500 mm long) packed with 2.5 × 2.5 Dixon rings. Gas chromatography analysis after distillation showed less than 0.5% impurities. The properties of the components appear in Table I.

Apparatus and Procedure. The experimental apparatus is entirely made of glass and is schematically shown in Figure 1. In this apparatus, both the liquid and vapor phases are continuously recirculated in order to provide mixing of the phases and to ensure that equilibrium was established. The vapor

0021-9568/92/1737-0293$03.00/0