SOLUBILITY OF HYDROGEN AND CARBON MONOXIDE IN WATER AND SOME ORGANIC SOLVENTS

U. J. JÁUREGUI-HAZA [†*], E. J. PARDILLO-FONTDEVILA[†], A. M. WILHELM[‡] and

H. DELMAS [‡]

† Centro de Química Farmacéutica, Apdo. 16042, C. Habana, Cuba.
* ulises@cqf.co.cu
‡ Ecole Nationale Superieure d'Ingenieurs en Arts Chimiques et Technologiques, 118 route de Narbonne, 31077, Toulouse, France

Abstract— **The solubility of hydrogen and carbon monoxide in water, octene, toluene and nonanal in the range 298-373 K and 0.5-1.5 MPa was studied. The experimental values of the solubility of H_2 and CO at 353 K, 363 K and 373 K were determined by the absorption method as a function of gas pressure in the solvents. The estimation of solubility of gases in water and organic solvents was also accomplished. The proposed method is based on the theory of Regular Solutions by the correlations of Prausnitz-Shair and Yen-McKetta corrected by Lemcoff factor for polar solvents. The critical temperature was predicted by Group Interaction Contribution approach. The experimental results were compared with theoretical prediction of solubility and found to agree with an average relative error of 2.6 %.**

Keywords— **Gas Solubility, Hydrogen, Carbon Monoxide, Theory of Regular Solutions.**

I. INTRODUCTION

The solubility of gases in liquid media is an important parameter required for the interpretation of rate data in gas-liquid, gas-liquid-liquid and gas-liquid-solid reactions. Among them, the hydroformylation of alkenes and fine chemicals by biphasic and supported aqueous phase catalysis have gained considerable interest in recent years (Kuntz, 1975; Arhancet *et al.*, 1989; Jáuregui-Haza *et al.*, 2001). A large volume of solubility values of hydrogen and carbon monoxide in a variety of solvents is available (Pray, 1952; Crozier and Yamamoto, 1974; Sokolov and Polyakov, 1977; Young, 1981; Brunner, 1985; Cargill, 1990; Purwanto *et al.*, 1996; Lekhal, 1998; Nair *et al.*, 1999), but limited data are available at higher temperatures and pressures.

In the present work the solubility of hydrogen and carbon monoxide in water, octene, toluene and nonanal in the range 298-373 K and 0.5-1.5 MPa was studied. Taking into account that a few data of solubility for H_2 and CO at 353 K, 363 K and 373 K are available, they were experimentally determined. The estimation of the solubility of these gases in water and different organic solvents, using a model based on the theory of Regular Solutions, was also accomplished.

II. EXPERIMENTAL SECTION

The solvents octene, toluene and nonanal with a purity greater than 98 %, procured from Aldrich, were used as received. The solubility of H_2 and CO was determined by the absorption method as a function of the gas pressure in the solvents in a 5.0×10^{-4} m^3 capacity stirred autoclave (Autoclave Engineers). The experimental setup (Fig. 1) was described elsewhere (Purwanto *et al.*, 1996). The temperature of the liquid in the reactor was controlled within ± 1 K. A pressure transducer having a precision of ± 1 kPa was used to measure the pressure. Hydrogen, carbon monoxide and nitrogen with purity of 99 %, supplied by Prodair, were used. The solvents were degassed by three freeze-pump-thaw cycles using nitrogen.

In a typical experiment, a known volume of solvent was introduced into the autoclave and the contents were heated to a desired temperature. After the thermal equilibrium was attained, the void space in the reactor was carefully flushed with the gas and pressurized to the level required. The contents were then stirred for about 10 min to equilibrate the liquid phase with the gas. The pressure change in the autoclave was recorded on-line as a function of time till it remained constant, indicating saturation of the liquid phase. From the initial and final pressure readings, the solubility was calculated in mole fraction. Each experiment was carried out three times.

III. RESULTS AND DISCUSSION

A. Solubility Data

The solubility of hydrogen and carbon monoxide in water, octene, toluene and nonanal was measured at 353 K, 363 K and 373 K in a pressure range of 0.5-1.5 MPa. The effect of pressure was found to be linear for all the systems, according to the Henry's law. The same behavior of gas solubility with pressure at values lower than 10 MPa has been reported before (Brunner, 1985; Purwanto *et al.*, 1996; Lekhal, 1998; Nair *et al.*, 1999).
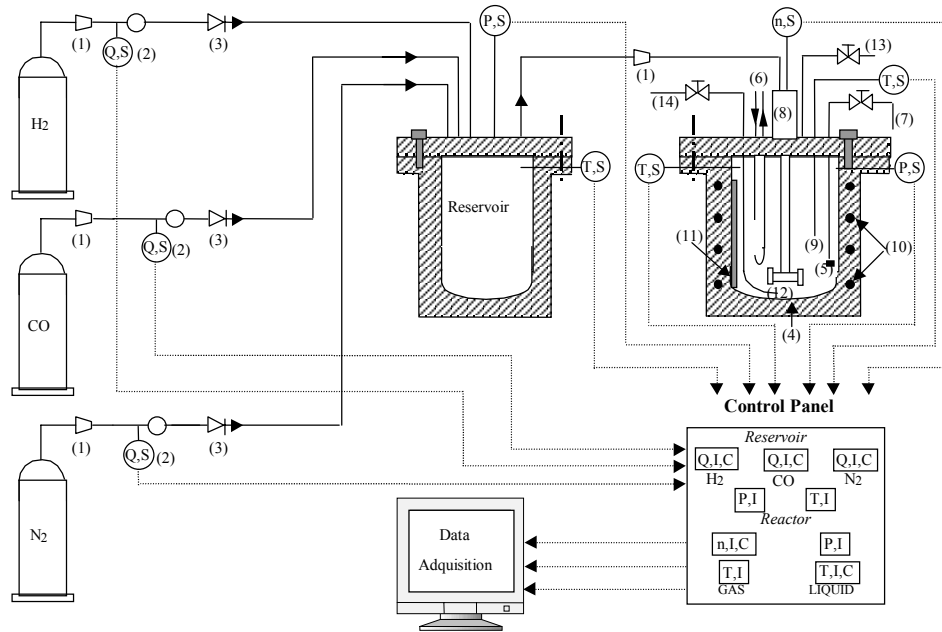
Fig. 1. Experimental setup: 1- pressure regulator; 2- mass flow controller; 3- nonreturn valve; 4- reactor; 5- filter for sampling; 6- cooling water; 7- sampling valve; 8- magnetic stirrer; 9- thermocouple; 10- electric furnace; 11- baffles; 12- impeller, gas induced; 13- vent; 14- liquid outlet; Q- flow; S- measure element; T- temperature; P- pressure; n- agitation speed; I- indicator; C- automatic control.

For this reason, the results are presented in Table 1 as Henry's law constant (K_H), which was calculated as

$$K_H = \frac{P}{c_2} \qquad (1)$$

Table 1. Solubility of hydrogen and carbon monoxide in different solvents $(K_H,$ MPa m^3/kmol).

	Hydrogen		
	353 K	363 K	373 K
water	141.36±3.02 (141.70[1])	141.53±1.96 (141.89[1])	141.64±2.11 (141.78[1])
toluene	27.12±0.95 (26.80[2])	25.64±0.84	24.89±1.26 (24.35[3])
1-octene	21.58±0.38	21.12±0.47	20.86±0.67
nonanal	38.76±1.23	37.42±0.88	36.15±1.52
	Carbon monoxide		
	353 K	363 K	373 K
water	128.79±2.01	130.02±0.95	131.54±2.16
toluene	11.61±0.18 (11.53[2])	11.51±0.25	11.94±0.27
1-octene	11.76±0.37	11.42±0.23	11.85±0.42
nonanal	17.65±0.47	17.02±0.31	16.57±0.63

1- Pray *et al.* (1952), 2- Nair *et al.* (1999), 3- Brunner (1985)

where P represents the partial pressure of the solute gas and c_2 is the concentration of the solute gas in the solvent. The relative uncertainties were less than 5.5 %. A comparison of these results with literature data indicated an agreement within 0.1 % to 2.5 %, as shown in Table 1. The solubility of CO, in all cases, is higher than the solubility of hydrogen. On the other hand, the solubility of both gases is much higher in organic solvents than in water.

B. Estimation of the Solubility of Hydrogen and Carbon Monoxide in Water and Organic Solvents

Among the developed models for estimating the behavior of gas solubility in liquids, those based on the theory of Regular Solution are widely used. Here we present a procedure based on correlation proposed by Prausnitz-Shair (1961) and Yen-McKetta (1962). This semi-empirical correlation for the solubility of gases in pure, nonpolar solvents at atmospheric pressure is given below:

$$-\ln x_2 = \ln(f_2^L / f_2^0) + \phi_1^2 v_2 (\delta_1 - \delta_2)^2 / RT \qquad (2)$$

where x_2 represents the mole fraction of solute gas in the liquid phase; f_2^L y f_2^0 are the fugacity of the pure gas and hypothetical liquid solute at atmospheric pressure; ϕ_1 is the volume fraction of solvent; v_2 is the molar liquid volume of solute gas; δ_1 and δ_2 are the solubility parameters for the solvent and the solute gas, respectively, R is the universal gas constant and T is the temperature. According to the postulates of the regular solution theory, activity coefficients are proportional to $1/T$. This means that the product $\phi_1^2 v_2 (\delta_1 - \delta_2)^2$ is constant with temperature. Then the solubility parameters for gas and molar volume of solutes were kept constant, using the values reported by Prausnitz and Shair (1961) and Katayama and Nitta (1976), specifically:

$\delta_{H_2} = 7.835 \cdot 10^3 \, J^{0.5} m^{-1.5}$; $\delta_{CO} = 6.403 \cdot 10^3 \, J^{0.5} m^{-1.5}$;

$v_{H_2} = 3.73 \cdot 10^{-5} \, m^3 mol^{-1}$ and

$v_{CO} = 3.21 \cdot 10^{-5} \, m^3 mol^{-1}$. The parameter f_2^L was calculated from the Eqs. (3) and (4) proposed by Yen and McKetta (1962) for the temperature interval from 273 K to 373 K:

- for hydrogen:

$\ln f_{H_2}^L$ = -7.4246 10^{-2} + 4336 T^{-1} − 9.3595 10^5 T^{-2} + 6.3853 10^7 T^{-3} (3)

- for carbon monoxide:

$\ln f_{CO}^L$ = 4.7475 + 588.52 T^{-1} − 1.3151 10^5 T^{-2} (4)

The solubility parameter for solvent was calculated from the heat of vaporization as:

$$\delta_1 = (\Delta H_v − RT)/v_1 \tag{5}$$

where ΔH_v represents the heat of vaporization and v_1 the molar volume of the solvent. The heat of vaporization is mainly reported at boiling temperature (T_e), so for calculating it at 298 K the correlation proposed by Watson (1943) was used:

$$\Delta H_{v,T} = \Delta H_{v,T_e} \left(\frac{1-Tr}{1-Tr_{T_e}} \right)^{0.375} \tag{6}$$

being:

$$Tr = T/T_c \tag{7}$$

and

$$Tr_{T_e} = T_e/T_c \tag{8}$$

where T_c is the critical temperature of the solvent. T_c for the organic solvents was calculated using the Group-Interaction Contribution approach (Pardillo-Fontdevila and González-Rubio, 1998):

$$T_c = (a + b \cdot n_A − \Sigma)^{-2} \tag{9}$$

where n_A is the total number of atoms in the molecule; Σ is the sum of the products of interactions between the groups present in the molecule and their contributions and a and b are the parameters of the model. Equation 5 is valid only for non-polar solvents. Lemcoff (1977) proposed a correction factor to evaluate the value of the solubility factor for polar solvents (δ_1^p). Later, Radhakrishnan et al. (1983) proposed a new value of the gas solubility parameter depending on the type of solvent. They assumed that for any system, at least one solubility value must be known. The corrected solubility parameter δ_1^p was calculated as:

$$\delta_1^p = \delta_1 / F_c \tag{10}$$

where F_c, the correction factor, is determined by specific correlation for each compound (Purwanto et al., 1996). Taking into account that the model of Prausnitz-Shair and Yen-McKetta is valid at atmospheric pressure, once the value of x_2 is known, we proceed to calculate the Henry's constant (Eq. 1) at P = 0.1013 MPa, and

then the solubility of hydrogen and carbon monoxide is calculated at different working pressures.

The solubility values calculated using Eq. 2 and the above correlations were compared with the experimental data obtained in this work (see Table 1) and with data available in the literature in the temperature range from 298 K to 373 K (Purwanto et al., 1996; Pray et al., 1952; Crozier and Yamamoto, 1974; Lekhal, 1998; Brunner, 1985; Nair et al., 1999). Figures 2 and 3 show the comparison of experimental and predicted values of solubility of H_2 and CO in studied solvents.
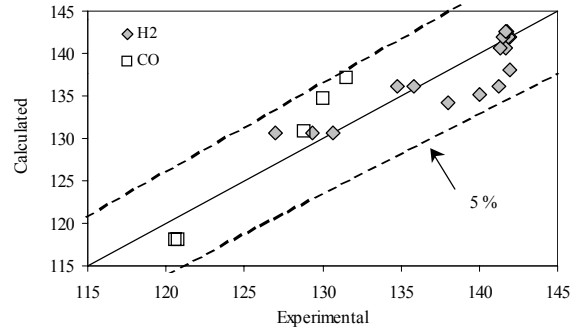
Fig. 2. Comparison of experimental and calculated solubility $(K_H,$ MPa m^3/kmol) in water.

The theoretical predictions of solubility were found to be within a maximum error of ± 7.5 % for all the solvents except for one value reported by Purwanto et al. (1996) for carbon monoxide at 323 K (25 %). However, Lekhal (1998) found at same conditions an experimental solubility, which corresponds with the estimated value within error of ± 7.5 %. The average error of estimation was 2.6 % lower than the 3 % and 10 % reported for the methods proposed by Nair et al. (1999) and Purwanto et al. (1996), respectively.
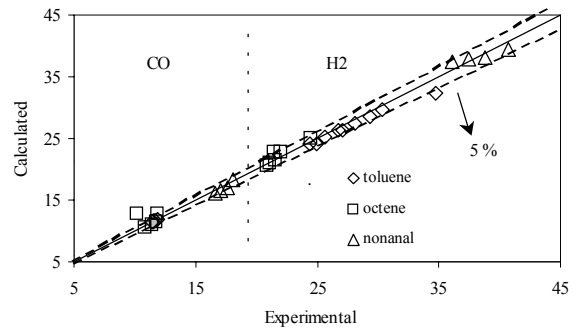
Fig. 3. Comparison of experimental and calculated solubility $(K_H,$ MPa m^3/kmol) in organic solvents.

IV. CONCLUSIONS

The solubility of hydrogen and carbon monoxide in water, octene, toluene and nonanal are reported in the range 353-373 K and 0.5-1.5 MPa. The solubility of CO, in all cases, is higher than the solubility of hydrogen. On the other hand, the solubility of both gases is much higher in organic solvents than in water. The estimation of solubility of gases in water and organic sol-

vents in the range 298-373 K was also accomplished, using a method based on the theory of Regular Solutions by the correlations of Prausnitz-Shair and Yen-McKetta corrected by Lemcoff factor for polar solvents. The experimental results were compared with theoretical prediction of solubility and found to agree with an average relative error of 2.6 %.

REFERENCES

Arhancet, J.P., M.E. Davis, S.S. Merola, B.E. Hanson, "Hydroformylation by supported aqueous-phase catalysis: a new class of heterogeneous catalysts," *Nature* **399**, 454-455 (1989).

Brunner, E., "Solubility of hydrogen in 10 organic solvents at 298.15 and 373.15 K," *J. Chem. Eng. Data* **30**, 269-273 (1985).

Cargill, R. W. *IUPAC Solubility Series. Vol. 43. Carbon Monoxide*, Pergamon Press: Oxford, U.K. (1990).

Crozier, T. E., S. Yamamoto, "Solubility of hydrogen in water, seawater and NaCl solutions," *J. Chem. Eng. Data* **19**, 242-244 (1974).

Jáuregui-Haza, U. J., M. Dessoudeix, Ph. Kalck, A. M. Wilhelm, H. Delmas, "Multifactorial analysis in the study of hydroformylation of oct-1-ene using supported aqueous phase catalysis", *Catalysis Today* **66**, 297-302 (2001).

Katayama, T., T. Nitta, "Solubilities of hydrogen and nitrogen in alcohols and n-hexane," *J. Chem. Eng. Data* **21**, 194-196 (1976).

Kuntz, E. Procédé d'hydroformylation des oléfines. Brevet francais No. 2314910, *Rhone-Poulenc Industries*. (1975).

Lekhal, A. *Etude du transfer de matiere gaz-liquide dans les systemes gaz-liquide-liquide: application a l'hydroformylation de l'octene-1 par catalyse biphasique*. Thèse de Doctorat, ENSIGC, Toulouse. (1998).

Lemcoff, N. O., "Liquid phase catalytic hydrogenation of acetone," *J. Catal.* **46**, 356-364 (1977).

Nair, V.S., S.P. Mathew, R. V. Chaudhari, "Kinetics of hydroformylation of styrene using homogeneous rhodium complex catalyst," *J. Mol. Catal.* **143**, 99-110 (1999).

Pardillo-Fontdevila, E., R. González-Rubio, "A group-interaction contribution approach. A new strategy for the estimation of physico-chemical properties of branched isomers," *Chem. Eng. Comm.* **163**, 245-254 (1998).

Prausnitz, J. M., F. H. Shair, "A thermodynamic correlation of gas solubilities," *AIChE J.* **7**, 682-687 (1961).

Pray, H. A., C. E. Schweickert, B. H. Minnich, "Solubility of hydrogen, nitrogen and helium in water at elevated temperatures," *Ind. Eng. Chem.* **44**, 1146-1152 (1952).

Purwanto, P, R. M. Deshpande, R. V. Chaudhari, H. Delmas, "Solubility of hydrogen, carbon monoxide, and 1-octene in various solvents and solvent mixture," *J. Chem. Eng. Data* **41**, 1414-1417 (1996).

Radhakrishnan, K., P.A. Ramachandran, P. H. Brahme, R.V. Chaudhari, "Solubility of hydrogen in methanol, nitrobenzene and their mixtures: experimental data and correlation," *J. Chem. Eng. Data* **28**, 1-4 (1983).

Sokolov, V. I., A. A. Polyakov, "Solubility of H_2 in n-decane, n-tetradecane, 1-hexane, 1-octene, iso-propyl benzene, 1-methyl naftalene and decalin," *Zh. Prikl. Khim.* **50**, 1403-1405 (1977).

Watson, K. M., "Thermodynamics of the liquid state. Generalyzed prediction of properties," *Ind. Eng. Chem.* **35**, 398-401 (1943).

Yen, C. L., J. J. McKetta, "A thermodynamic correlation of nonpolar gas solubilities in polar, non-associated liquids," *AIChE J.* **8**, 501-507 (1962).

Young, C. L. *IUPAC Solubility Series. Vol. 5/6. Hydrogen and Deuterium*, Pergamon Press: Oxford, U.K. (1981).