PREDICTION OF HENRY'S CONSTANT BY GAS CHROMATOGRAPHY

A. H. N. MOUSA

Department of Chemical Engineering, University of Kuwait, Kuwait

Key Words: Pulse Gas Chromatography, Henry's Constant, Solubility, Olive Oil, Nitrobenzene

Introduction

Gas chromatography is a particularly convenient technique for determination of the solubility of gases in non-volatile liquids. The measurement of solubility data by conventional methods is fairly time-consuming. Battino and Clever²⁾ and Wilhelm and Battino¹⁶⁾ have reviewed and reported much solubility data. Hildebrand and co-workers^{4,5)} have studied the nature of solubility of gases in liquids. Almost all the solubility data reported in the literature is at 25°C.

Ng, Harris and Prausnitz⁸⁾ and Fredenslund, Jones and Prausnitz³⁾ have shown how it is possible to determine Henry's constant for a wide range of temperatures using gas chromatography. Schneider and Smith^{12,13)} have used gas chromatography in measuring adsorption rate constants and surface diffusion and obtained reasonable results. Mousa⁷⁾ used the pulse technique to predict Henry's constant and also obtained reasonable results.

The objective of this work is to use gas chromatography to measure Henry's constant for the solubility of gases in liquids.

Theory

The solubility of nonreacting gases in solvents can be predicted by a number of methods.^{9,11)} The solubility of a gas in a liquid solvent is most conveniently expressed by Henry's law:

$$H = C_G / C_L \quad (1)$$

This equation is valid for low pressure for which the Poynting correction may be neglected. So H will be a function of temperature only. But if the pressure is high, (above 5×10^5 Pa), the extended form due to Krichevsky-Kasavnovsky¹⁰⁾ must be used.

According to Andrieu and Smith,¹⁾ the first moment of the response to a pulse input of a gas into a column containing a stationary liquid phase can be expressed as

$$\mu_1 = \frac{\varepsilon_g L}{u} \left[1 + \frac{1}{H} \frac{\varepsilon_L}{\varepsilon_g} \right] = \tau_g \left[1 + \frac{1}{H} \frac{\varepsilon_L}{\varepsilon_g} \right] = \frac{1}{Q} \left[V_g + \frac{V_L}{H} \right] \quad (2)$$

The basic assumptions made in deriving the above equations are that Henry's law is valid, that pressure and temperature in the column are constant and that there are no radial concentration gradients. The first moment is defined as:

$$\mu_1 = \frac{\int_0^\infty C(t) t dt}{\int_0^\infty C(t) dt} \quad (3)$$

When a gas sample is injected in the carrier gas, the chromatogram obtained is a representation of the concentration vs. time graph. So at different times the concentration can be measured and Eq. (3) can be integrated to get (μ_1) , which is the experimental first moment, i.e. $(\mu_1)_{\text{exp}}$.

The value of the first moment measured experimentally, $(\mu_1)_{\text{exp}}$, must be corrected by considering the dead volume between the injection point and the packed column and the detector. The dead volume correction, $(\mu_1)_{\text{dv}}$, is found by dividing the total dead volume by Q . Also the time of injection of the pulse (t_0) must be taken into consideration. The result of these corrections gives the true first moment (μ_1) as

$$(\mu_1) = (\mu_1)_{\text{exp}} - (\mu_1)_{\text{dv}} - \frac{t_0}{2} \quad (4)$$

Apparatus and Procedure

The apparatus used is shown in **Fig. 1**. The packed columns were made of stainless steel, 0.42 cm in inside diameter and 30 cm long. The solid particles used were red fire-brick with an average diameter of 0.71 mm. The liquid loading (weight of liquid divided by weight of liquid plus solid) was 0.2.

Acetone was added to the liquid in a large beaker, then the solids were added to the mixture. The beaker with its contents was heated in an oven at 60°C for 24 h to evaporate all the acetone. Then the solids,

Received April 2, 1983. Correspondence concerning this article should be addressed to A. H. N. Mousa.

Fig. 1. Schematic drawing of apparatus. 1, helium cylinder; 2, hydrogen cylinder; 3, needle valves; 4, rotameter; 5, flow regulator; 6, pressure gauge; 7, six-port injection valve; 8, flow meters; 9, packed column; 10, hp5840A gas chromatograph.

coated with the liquid, were loaded into the column with slight vibration to eliminate nonuniform bed porosity. Helium was used as the carrier gas. When the apparatus was at steady state (i.e. about four hours from turning the apparatus on) pulses of 1.0 ml of the gas to be studied were introduced into the helium carrier gas with a six-way injection valve. The pulse passes through the packed column which is fixed inside a gas chromatograph with a thermal conductivity detector. The response curve (the chromatogram) was used to calculate the experimental first moment $(\mu_1)_{\text{exp}}$. Values of the time (t) and the corresponding concentration $C(t)$ were taken from the chromatogram and the integration was done analytically, using a UNIVAC computer.

The gases used in this work were hydrogen and nitrogen. The liquids used were olive oil and nitrobenzene.

At a fixed temperature of the column (i.e. a fixed temperature of the oven) the carrier gas flow rate (Q) was varied and for each value the corresponding first moment (μ_1) was calculated. Then according to Eq. (2) a plot of (μ_1) versus $1/Q$ will give a straight line with slope equal to $(V_g + V_L/H)$. Thus Henry's constant (H) can be calculated from the slope of the line.

Results

The solubility of nitrogen in nitrobenzene was studied at temperatures of 30, 35 and 40°C. Plots of the first moment (μ_1) versus $1/Q$ are shown in Fig. 2. The least square method was used to find the slope of the lines. From the slopes the values of Henry's constant found are listed in Table 1.

The solubility of nitrogen in olive oil was examined at temperatures of 30, 36 and 40°C. Plots of the first moment (μ_1) versus $1/Q$ at these temperatures are shown in Fig. 3. Using the least square method the slopes of these lines were calculated and the cor-

Fig. 2. Nitrogen-nitrobenzene.

Table 1. Henry's constant (H) in [(g mol/ml gas)/(g mol/ml liquid)]

System	Temperature [°C]	H
Nitrogen-nitrobenzene	30	0.062
	35	0.074
	40	0.095
Nitrogen-olive oil	30	0.079
	36	0.106
	40	0.15
Hydrogen-nitrobenzene	27	0.101
	35	0.139
	40	0.171

Fig. 3. Nitrogen-olive oil.

responding values of Henry's constant were calculated and are included in Table 1.

Similarly, the solubility of hydrogen in nitrobenzene was studied at temperatures of 27, 35 and 40°C. Plots of the first moment (μ_1) versus $1/Q$ at these temperatures are shown in Fig. 4. The calculated values of Henry's constant are also given in Table 1.

Discussion and Conclusions

The use of gas chromatography in evaluating solubilities of gases in relatively non-volatile solvents has been used by Yow and Smith¹⁷⁾ and they obtained satisfactory results. Smith¹⁹⁾ found the accuracy of

Fig. 4. Hydrogen-nitrobenzene.

this technique to be $\pm 7\%$.

No recent solubility values for the systems studied here have been found in the literature. Stephen and Stephen¹⁵⁾ have reported the solubility of hydrogen and nitrogen in nitrobenzene as ml of gas at 0°C and 760 mmHg in ml of nitrobenzene. For hydrogen at 20 and 25°C they gave the values of 0.0353 and 0.0371, respectively. For nitrogen at 20 and 25°C they gave the values of 0.06082 and 0.06255, respectively.

Linke⁶⁾ reported the solubility of nitrogen in olive oil as ml of gas at 0°C and 760 mmHg in 100 ml of olive oil. At temperatures of 21.5, 22 and 37°C he reported solubility values of 6.44, 5.2 and 6.7, respectively.

It is difficult to compare these literature values with values obtained in this work, since the bases of calculations are different and the temperatures are different. Nevertheless, the trends of the values indicate that the results obtained can be considered to be reasonable ones.

Acknowledgment

The author would like to thank Prof. J. M. Smith for his great help and valuable discussions. The author would like also to thank Miss Tagreed Mahmoud for her help in running the experiments. Thanks are also due to the Research Council of the University of Kuwait for its financial support.

Nomenclature

$C(t)$	= concentration of gas at any time (t) obtained from chromatogram	[mol/cm ³]
C_G	= gas-phase concentration	[mol/cm ³]
C_L	= liquid-phase concentration	[mol/cm ³]
H	= Henry's constant	
L	= column length	[cm]
Q	= carrier gas flow rate	[cm ³ /s]
V_g	= volume of gas in column	[cm ³]
V_L	= volume of liquid in column	[cm ³]
u	= superficial velocity in column	[cm/s]
μ_1	= first moment	[s]
ε_g	= gas hold-up in column	
ε_L	= liquid hold-up in column	

Literature Cited

- Andrieu, J. and J. M. Smith: *Chem. Eng. J.*, **20**, 211 (1980).
- Battino, R. and H. L. Clever: *Chem. Rev.*, **66**, 395 (1966).
- Fredenslund, A., R. L. Jones and J. M. Prausnitz: *AIChE J.*, **21**, 1086 (1975).
- Hildebrand, J. H. and R. L. Scott: "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing, New York (1950).
- Hildebrand, J. H., J. M. Prausnitz and R. L. Scott: *Regular and Related Solutions*, Van Nostrand Reinhold Co., New York (1970).
- Linke, W. F., Editor, "Solubilities of Inorganic and Metal-Organic Compounds," Vol. II, 4th ed., American Chemical Society, Washington, D.C. (1965).
- Mousa, A. H. N.: CHISA '81, 7th International Congress of Chem. Eng., Praha, Czechoslovakia, August 31-Sept 4 (1981).
- Ng, S., H. G. Harris and J. M. Prausnitz: *J. Chem. Eng. Data*, **14**, 482 (1969).
- Prausnitz, J. M. and F. H. Shair: *AIChE J.*, **7**, 682 (1961).
- Prausnitz, J. M.: "Molecular Thermodynamics of Fluid-Phase Equilibria," p. 357, Prentice Hall, Englewood Cliffs, N. J. (1969).
- Preston, G. T. and J. M. Prausnitz: *Ind. Eng. Chem. Fundam.*, **10**, 389 (1971).
- Schneider, P. and J. M. Smith: *AIChE J.*, **14**, 762 (1968).
- Schneider, P. and J. M. Smith: *AIChE J.*, **14**, 886 (1968).
- Smith, J. M.: personal communication.
- Stephen, H. and T. Stephen (ed.): "Solubilities of Inorganic and Organic Compounds," Vol. 1, Part 1, Pergamon Press, London (1963).
- Wilhelm, E. and R. Battino: *Chem. Rev.*, **73**, 1 (1973).
- Yow, J. and J. M. Smith: submitted for publication.