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### Quantitation of Carbon Dioxide by High Performance Liquid Chromatography: The Key to Solubility Measurements in Liquefied Gas Solutions

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QUANTITATION OF CARBON DIOXIDE BY HIGH PERFORMANCE LIQUID  
CHROMATOGRAPHY: THE KEY TO SOLUBILITY MEASUREMENTS IN  
LIQUEFIED GAS SOLUTIONS

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ABSTRACT

A technique is described whereby solubility data may be obtained for systems employing liquefied carbon dioxide as the solvent. Analysis of the solution is effected by the direct injection of an aliquot of pressurized liquid into a modern liquid chromatograph fitted with a reversed-phase C<sub>18</sub> column. Detection of the carbon dioxide is accomplished by a differential refractometer. After the appropriate calibrations are performed, data are obtained which compare favourably with the literature value of the solubility of naphthalene in liquid carbon dioxide.

INTRODUCTION

Liquid carbon dioxide is assuming a role of increasing importance in the development of modern technology. Several processes which employ the solvent properties of this high pressure liquid are the extraction of essential ingredients from hops (1-3), pyrethrins from chrysanthemum flowers (4-5) and aroma ingredients from apples, pears, coffee and orange juice

(6-7). A novel application by the Commonwealth Industrial Gases Limited (Sydney, Australia) employs highly compressed carbon dioxide as both a solvent and a propellant for the aerosol dispensation of insecticides (8).

A feature common to all these applications is the need for reliable data on the solubility of the desired components in liquid carbon dioxide. Although several techniques for estimating these data have been described (9-12), these procedures are considered inadequate because of the difficulty in determining the mass of solvent present in solution (13).

A technique for the direct sampling and liquid chromatographic analysis of liquefied carbon dioxide-based solutions has been described in a previous report from this laboratory (13). The qualitative aspects of the liquid chromatography and detection of carbon dioxide have been investigated (14) and no barriers to the quantitation of carbon dioxide by reversed-phase liquid chromatography were found. This paper describes the third and final stage of the development of a technique which enables generation of accurate solubility data for systems comprising an organic substrate in equilibrium with a saturated liquid carbon dioxide-based solution.

## EXPERIMENTAL

### Chromatographic Apparatus

The instrument employed in this research comprised a Waters Associates model 6000A solvent delivery system, a model 440 absorbance detector monitoring at 254 nm and an R401 differential refractometer. Each detector was coupled to a Hewlett-Packard model 3390A reporting integrator. These integrators were modified to permit simultaneous remote starting upon the injection of a sample. Separations were effected on a Waters

Associates  $\mu$ -Bondapak C<sub>18</sub> 30 cm x 3.9 mm ID analytical column which was protected by a Brownlee Labs RP-8 guard cartridge. Mobile phases were prepared from water, which was freshly distilled from a glass apparatus, and Waters Associates HPLC-grade acetonitrile. Eluents were filtered to 0.45  $\mu$ m and thoroughly degassed before use.

#### Revised Sampling Procedure

One of the major difficulties encountered during the development of the basic sampling technique was that of partial gasification of the solvent carbon dioxide within the sample stream, and the corresponding irreproducibility of the solute peak height data in the liquid chromatographic analysis. This was overcome by the pressurization, with nitrogen, of the solution. However, when this technique was applied to the analysis of a solution which was saturated with a solid substrate, we again observed irreproducibility of the solute peak height data. The explanation of this irreproducibility lay in a phenomenon occurring in a system comprising a saturated solution and a two-component vapour phase: when a small volume of liquid is withdrawn from such a system, some solvent must vaporize in order to maintain constant the vapour-phase composition. In non-saturated systems containing a single-component vapour phase, this phenomenon accounts for the observed increase in solute concentration during the dispensation of liquefied carbon dioxide-based insecticide mixtures (15). In saturated systems, vaporization of solvent results in the dissolution of excess substrate and the subsequent entrainment of material in the sample stream. Therefore, the quantity of solute in solution is overestimated, furthermore, the analytical data are irreproducible.

In order to obviate this phenomenon of phase separation, a different method of solution pressurization was developed. Figure 1 presents a schematic diagram of the apparatus used in

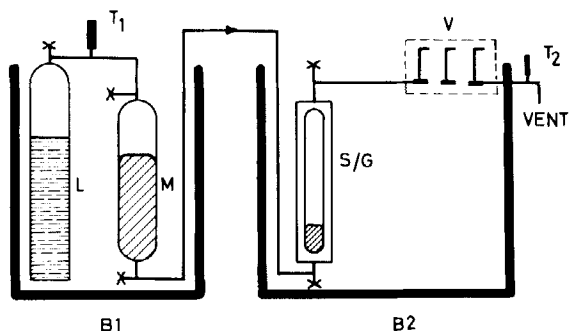


Figure 1: Schematic Diagram of Sampling Apparatus.

this modified technique. A small cylinder (L) containing two-phase carbon dioxide was immersed in a thermostatted water bath ( $B_1$ ). The vapour stream was connected to the upper valve of a Whitey double-ended sample cylinder (M), which was filled with clean mercury. The lower valve of this sample cylinder was connected to the lower valve of a Jerguson liquid level gauge (S/G) which contained a quantity of liquid carbon dioxide saturated with an organic solid (naphthalene) in equilibrium with carbon dioxide vapour. The liquid level gauge outlet was coupled to three series-connected Valco internal volume sample injection valves (V), which, together with the solution containment vessel, were immersed in a second thermostatted water bath ( $B_2$ ). The temperature of the first bath ( $B_1$ ) was maintained slightly above that of the second bath ( $B_2$ ). Vapour-phase carbon dioxide was vented to atmosphere by means of a micrometering valve located downstream of the sample injection valves. The venting of vapour allowed the admission of mercury into the liquid level gauge. When all traces of vapour had been removed, the micrometering valve was closed so that thermal equilibrium could be re-established. This was verified by noting the constancy of the pressure in both the mercury reservoir and the liquid level gauge by means of two strain gauge pressure transducers ( $T_1, T_2$ ). If

necessary, the temperature of bath  $B_1$  was adjusted to ensure that a small but positive pressure difference existed between the mercury reservoir and the liquid level gauge.

When equilibrium was established, the micrometering valve was cracked and a slow stream of solution was withdrawn through the sample injection valves. The flowrate of solution was monitored by passing the vaporized solvent exiting the micrometering valve through a precision wet gas meter.

This revised sampling system ensured that the sample stream was homogeneous and that the composition of the bulk solution remained constant during the sampling and analytical procedures.

#### Absolute Calibration of Carbon Dioxide

In most instrumental methods of analysis, quantitation is effected by comparing the detector response resulting from sample processing to that obtained from processing a number of mixtures whose accurate compositions are known. Unfortunately, because of vapour-liquid equilibrium, it is extremely difficult to prepare a standard solution of substrate dissolved in liquid carbon dioxide. Therefore, in this study, a different approach was taken. It involved the construction of a calibration curve for carbon dioxide and noting the chromatographic response.

Following the procedure of Ogan and Katz (16), the actual volumes of three Valco internal-volume sample injection valves (nominally  $0.5 \text{ mm}^3$ ,  $2 \text{ mm}^3$  and  $5 \text{ mm}^3$ ) were determined using a solution of recrystallized naphthalene in methanol as the ultra-violet-absorbing compound. The design of the Waters Associates absorbance detector greatly facilitated this procedure since this detector is equipped with both a digital absorbance meter and a direct absorbance output. Both are scaled such that 1.0 Absorbance Unit is equal to 1.0 volt output.

With a knowledge of the actual volumes of liquid carbon dioxide injected, the number of moles of carbon dioxide could therefore be computed from the literature value (17) of the liquid density at the temperature of the experiment. In this and

subsequent experiments, the temperature of the solution was maintained at  $25.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ . A plot of moles of carbon dioxide against the peak area was prepared and is shown as Figure 2. Clearly, the response of the differential refractometer was non-linear. However, we were able to demonstrate that a sample of liquid carbon dioxide as large as  $5\text{ mm}^3$  in fact "saturated" the detector. That is, the signal from the detector was diminished. However, the use of another valve of nominal volume of  $2\text{ mm}^3$  and a delivery volume different to the other valve of the same nominal volume enabled the injection of three different volumes of liquid  $\text{CO}_2$  within the linear range of the refractive index detector. The actual volumes delivered by the valves are presented in Table 1.

The calibration curve for carbon dioxide at  $25.0^{\circ}\text{C}$  using these valves is shown as Figure 3, demonstrating that the differ-

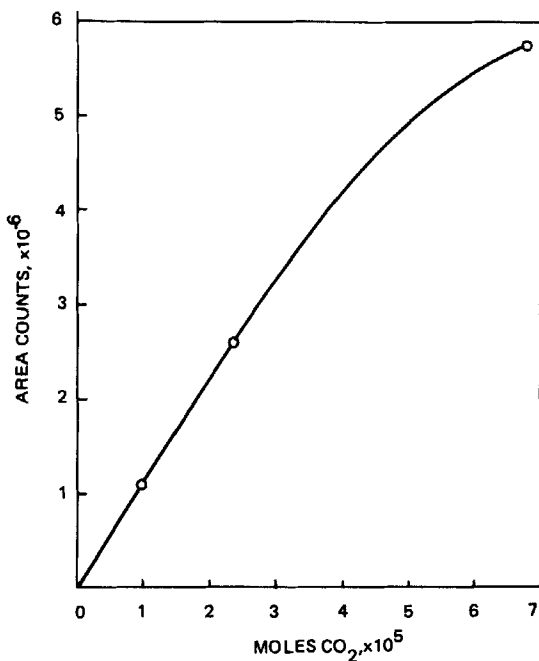


Figure 2: Calibration Curve for Carbon Dioxide. Nominal Valve Volumes are  $0.5\text{ mm}^3$ ,  $2\text{ mm}^3$  and  $5\text{ mm}^3$ .

TABLE 1

Actual Delivery Volume of Each Valco Valve ( $\text{mm}^3$ )

Nominal Volume	Delivered (mean)	Volume (std. dev.)
0.5	0.552	0.006
2	1.43	0.02
2	1.59	0.02

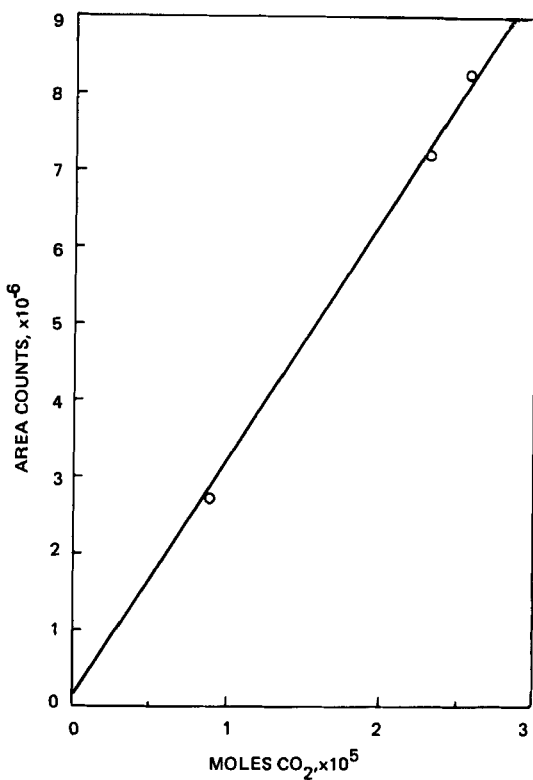


Figure 3: Plot of Area Counts Against Moles for Carbon Dioxide.



ential refractometer's response is indeed linear for the range of injected volumes used.

### Solubility of Naphthalene in Liquid Carbon Dioxide

Although we were confident that a procedure such as has been described above was a valid method for quantifying the amount of liquid carbon dioxide present in a solution, it was necessary to verify the accuracy of the technique by comparing solubility data obtained from this method with published values. Only two systems of organic compounds in liquid carbon dioxide have been described with sufficient precision to enable a valid comparison of data; the systems referred to are: naphthalene-CO<sub>2</sub> and iodine-CO<sub>2</sub> (10). Since iodine could not be detected by the UV absorbance detector ( $\lambda = 254 \text{ nm}$ ), we attempted to determine the solubility of naphthalene in liquid carbon dioxide at 25°C.

### Procedure

Preliminary experimentation resulted in the selection of an eluent composed of 80 v% acetonitrile/20v% water as suitable for the separation of naphthalene and carbon dioxide. A calibration curve for carbon dioxide was prepared using "ANAEROBIC" grade liquid carbon dioxide (99.95% minimum purity) obtained from the Commonwealth Industrial Gases Limited (Sydney, Australia). The liquid level gauge was then emptied of mercury and carbon dioxide and recrystallized naphthalene (Eastman Organic Chemicals), sufficient to produce a saturated solution, was introduced to the vessel. Liquid carbon dioxide was then admitted, the vessel connected to the mercury reservoir and then the vapour-phase carbon dioxide was vented. After attaining thermal equilibrium, the liquid level gauge was removed to a purpose-designed, end-over-end rotation apparatus to ensure that the system was thoroughly mixed and indeed saturated. The vessel was then replaced in the water bath, mercury and solution withdrawal lines connected and the system allowed to come to thermal equilibrium once more. Meanwhile, a series of solutions of naphthalene dissolved in the

mobile phase were prepared and a calibration curve for naphthalene obtained. The curve was a straight line passing through the origin.

When the saturated solution had equilibrated, the micro-metering valve was cracked and a stream of solution withdrawn and several injections into the liquid chromatograph were made. The resulting peak areas for naphthalene and carbon dioxide were averaged and the respective number of moles computed from the calibration curves. Then a single estimate of the mole fraction of naphthalene in solution was computed. The entire procedure of calibration, equilibration and analysis was repeated twice yielding a total of three estimates of the solubility of naphthalene in liquid carbon dioxide.

### RESULTS

Solubilities are expressed in a variety of ways: wt %, wt/vol, and mole fraction. In view of the significant volume contraction which may occur when liquid carbon dioxide and organic substrates are mixed (11), wt % and mole fraction are to be preferred.

Quinn (10) has reported that the solubility of naphthalene in liquid  $\text{CO}_2$  at  $25^\circ\text{C}$ , when expressed as mole fraction, is  $0.00698 \pm 0.00002$ . This result compares favourably with that determined by this laboratory:  $0.0069 \pm 0.0001$ .

### CONCLUSION

We have described a technique whereby accurate solubility data for systems comprising an organic substrate dissolved in liquefied carbon dioxide may be obtained. For injected volumes, of up to  $1.6 \text{ mm}^3$ , we have calculated that the calibration curve should be linear for liquid carbon dioxide at temperatures in the

range of  $-5^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ . Therefore this technique may be applied to many systems of practical importance. One such application is the extraction of natural products from biological materials, where data on the solubility of a complex substrate may be required at a variety of process temperatures.

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