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# Solubilities and Diffusion Coefficients of Hydrogen, Carbon Monoxide, Ethylene, and Propylene in Liquid Triphenylphosphine

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**Henry's constants of hydrogen, carbon monoxide, ethylene, and propylene in liquid triphenylphosphine ($PPh_3$) were determined in the temperature range from 90 to 120 °C. Moreover, the diffusion coefficients of ethylene and propylene in liquid $PPh_3$ were measured at 90 °C and were found to be in satisfactory accordance with the values calculated from the Wilke–Chang correlation. The melting behavior of $PPh_3$ was briefly investigated. A marked supercooling was observed. All measurements were performed in a Cailletet tube.**

## Introduction

Lately, hydridocarbonyltris(triphenylphosphine)rhodium(I), dissolved in triphenylphosphine and capillary condensed into the pores of a support, has successfully been applied as a heterogeneous catalyst in the industrially important hydroformylation of propylene, i.e., the conversion of propylene, hydrogen, and carbon monoxide to *n*- and isobutyraldehyde (*1*, *2*).

In order to elucidate the possible role of diffusional retardation of the chemical reaction rate within this new catalyst, the solubilities and diffusion coefficients of hydrogen, carbon monoxide, and propylene in liquid $PPh_3$ had to be known. Since these solubilities could not be found in the literature, we decided to measure them.

Because the hydroformylation of ethylene was investigated as well, the solubility and the diffusion coefficient of ethylene in liquid $PPh_3$ were also measured. In this paper the results of this study are presented, together with some results concerning the melting behavior of $PPh_3$.

## Experimental Section

***Instrumental Section.*** The experiments were performed in a Pyrex glass capillary tube with an inner cross-sectional area of 12.6 mm$^2$, a total length of 0.50 m, and an external diameter of 13.0 mm (Cailletet tube), in which pressure can be created hydraulically by using mercury as a pressure intermediate. The tube was open on one end. A detailed description of the equipment is given by Aaldijk (*3*). Figure 1 shows a sketch of the Cailletet tube.

Ca. 0.5 g of solid $PPh_3$ was brought into the tube. Then a single gas of known pressure, temperature, and volume was added to the $PPh_3$ by means of a mercury displacement method. At the metering conditions the corrections for imperfect behavior of the gases were calculated to be negligible. The mass quantities of gas and $PPh_3$ were metered with an accuracy of 2% and 2.5%, respectively.

Pressures were measured by means of a calibrated pressure gauge with the appropriate range, the accuracy for the ranges 0–24.5, 0–9.8, and 0–0.98 MPa being 49, 9.8, and 0.98 kPa, respectively. The Cailletet tube was enclosed in a silicone oil thermostat bath, and the temperature was controlled to within 0.1 °C by using a proportional-integral-differential controller and measured to within 0.1 °C with a Pt-100 resistance thermometer. Mixing of the mixture was effected magnetically.

***Materials.*** Hydrogen (99.9 mol %) and carbon monoxide (99.5 mol %) were obtained from Union Carbide (USA); ethylene (99.98 mol %) and propylene (99.95 mol %) were obtained from Phillips (USA); and $PPh_3$ (99.5 wt %) was obtained from Fluka (Switzerland).

***Procedures. Bubble-Point Measurements.*** The solubilities of the four gases in liquid $PPh_3$ were measured for each gas separately. The Cailletet tube, filled with $PPh_3$, and the particular gas were brought to the desired constant temperature. Starting from the homogeneous liquid phase, the pressure was decreased step by step, always allowing sufficient time to attain equilibrium. During these measurements the liquid was well stirred. Bubble points were measured at 90, 105, and 120 °C. The reproducibility of the measurements, checked by duplication, was within 1%. The accuracy of the resulting Henry's constants was estimated to be 5%.

***Determination of the Diffusion Coefficients of Ethylene and Propylene in Liquid $PPh_3$ at 90 °C.*** The diffusion coefficients of ethylene and propylene in liquid $PPh_3$ were determined for each gas separately in the following way. The system was brought to a pressure $p_0$ in the two-phase region with continuous stirring of the liquid and the gas phase. Hereafter, the stirring was stopped and the pressure was suddenly raised to $p_1$ and kept at that value. Time was reckoned from that moment on. The volume decrease of the gas phase was determined as a function of time by using a kathetometer and a watch. From this volume decrease the time-averaged volume of gas transferred per unit time and per unit surface area of the gas–liquid phase boundary could be calculated and hence the diffusion coefficient (see Results and Discussion).

In this calculation the meniscus was assumed to be flat. In reality, however, the meniscus was curved. Judged by the naked eye, the contact angle of $PPh_3$ on the glass of which the Cailletet tube was made is ~30°. When this value for the contact angle was used, the relative error of the meniscus area, caused by the above assumption, was calculated to be 14%. The relative error of the volume decrease of the gas phase was 1%, whereas that of $t$ was negligible. The relative error of the resulting diffusion coefficients was 30%.

## Results and Discussion

***Bubble-Point Measurements.*** The experimental results and Henry's constants are given in Table I. Henry's constants of component i in liquid $PPh_3$ were calculated with eq 1.

$$f_i = \gamma_i x_i H_i \qquad (1)$$

It is assumed that $H_i$ is pressure independent. As $PPh_3$ is of extremely low volatility, it is furthermore assumed that the gas phase contains only component i and hence that $f_i$ is the fugacity of pure i in the gas phase. As $x_i$ was always low in our measurements, it is assumed that $\gamma_i$ is equal to unity. The validity of these assumptions was checked for propylene, which is the component with the highest solubility in $PPh_3$ (see Table I). At each of the three temperatures given in Table I, two additional bubble-point measurements were carried out, at $x_i$ values of 0.023 and 0.070. The same Henry's constants as given in Table I were obtained, which proves the validity of the above assumptions.

The fugacities of carbon monoxide, ethylene, and propylene were calculated according to the procedure described by Lee

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**Table I. Solubilities of Hydrogen, Carbon Monoxide, Ethylene, and Propylene in Liquid Triphenylphosphine**

| component i | bubble-point press., MPa | temp, °C | mole fraction of component i in liquid $PPh_3$, $x_i$, at the bubble point | fugacity coefficient $f_i/p_i$ | Henry's constant $H_i$, GPa |
|---|---|---|---|---|---|
| hydrogen | 11.62 | 90.0 | 0.043 | 1.06 | 0.29 |
| | 10.55 | 105.0 | 0.043 | 1.05 | 0.26 |
| | 9.57 | 120.0 | 0.043 | 1.05 | 0.23 |
| carbon monoxide | 5.79 | 90.0 | 0.032 | 1.01 | 0.18 |
| | 5.54 | 105.0 | 0.032 | 1.01 | 0.17 |
| | 5.25 | 120.0 | 0.032 | 1.01 | 0.17 |
| ethylene | 0.491 | 90.0 | 0.029 | 0.99 | 0.017 |
| | 0.546 | 105.0 | 0.029 | 0.99 | 0.019 |
| | 0.595 | 120.0 | 0.029 | 0.99 | 0.020 |
| propylene | 0.290 | 90.0 | 0.050 | 0.98 | 0.0057 |
| | 0.338 | 105.0 | 0.050 | 0.98 | 0.0066 |
| | 0.395 | 120.0 | 0.050 | 0.98 | 0.0077 |

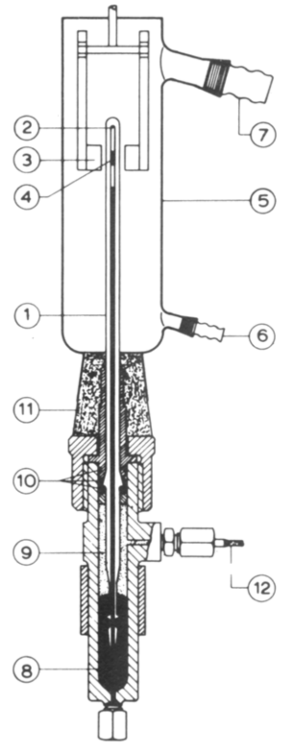

**Figure 1.** Cailletet tube assembly: (1) Cailletet tube; (2) sample; (3) magnets (with up-and-down motion); (4) glass-covered iron mixer; (5) glass thermostat; (6 and 7) silicone oil in and out; (8) mercury; (9) oil; (10) viton O-rings; (11) silicone rubber stopper; (12) line to dead-weight gauge.

**Table II. Diffusion Coefficients of Hydrogen, Carbon Monoxide, Ethylene, and Propylene in $PPh_3$ at 90 °C**

| | $10^9 D_i$, $m^2 s^{-1}$ | |
|---|---|---|
| component i | exptl | calcd |
| hydrogen | | 1.01 |
| carbon monoxide | | 0.89 |
| ethylene | 0.98 | 0.73 |
| propylene | 1.06 | 0.59 |

**Table III. Values of Properties and Parameters Used in Calculating the Diffusion Coefficients of Hydrogen, Carbon Monoxide, Ethylene, and Propylene in $PPh_3$ at 90 °C by the Wilke-Chang Equation**

| association parameter | temp, K | mol wt of $PPh_3$ | dynamic viscosity of liquid $PPh_3$ at 363.15 K, cP |
|---|---|---|---|
| 1 (*8*) | 363.15 | 262 (*9*) | 5.76 (*10, 11*) |

**Table IV. Molar Volumes of Hydrogen, Carbon Monoxide, Ethylene, and Propylene at Their Normal Boiling Points**

| component i | $V_i$, $cm^3 mol^{-1}$ |
|---|---|
| hydrogen | 28.37 (*12*) |
| carbon monoxide | 35.50 (*13*) |
| ethylene | 49.23 (*14*) |
| propylene | 69.14 (*15*) |

and Kesler (*4*), whereas that of hydrogen was calculated by the method outlined by Morgen and Childs (*5*).

The temperature dependence of Henry's constants is illustrated in Figure 2. According to thermodynamics, the logarithm of Henry's constant should as a first approximation be a linear function of the reciprocal temperature. Figure 2 shows that the expected behavior is indeed found.

***Diffusion Coefficients of Ethylene and Propylene in Liquid $PPh_3$ at 90 °C.*** If one assumes a flat meniscus of the $PPh_3$ in the Cailletet tube, the following equation holds (*6*):

$$\phi = 2(c_{i1} - c_{i0})[D_i/(\pi t)]^{1/2} \qquad (2)$$

Equation 2 is valid only if

$$D_i t/L^2 \ll 0.1$$

The values of $\phi$ (calculated from the gas volume decrease during time $t$), $c_{i1}$, and $c_{i0}$ (calculated with the aid of the Henry's constants mentioned in Table I) being known, the diffusion coefficients of ethylene and propylene are readily calculated from eq 2. For $t$ the values of 20 (ethylene) and 4.5 h (propylene) were used. For ethylene and propylene $L$ amounted to 0.08 and 0.04 m, respectively. The experimental values for the diffusion coefficients are given in Table II. Generally speaking, the difficulty in measuring diffusion coefficients is to ensure that there are no significant convection currents. From Table I it can be concluded that hydrogen, carbon monoxide, ethylene, and propylene exhibit a very slight solubility in $PPh_3$ under the given measuring conditions. This means that under these conditions the above-mentioned four gases are transported primarily by diffusion in $PPh_3$ (*7*).

When the appropriate values for $D_i$, $t$, and $L$ are used, it can be shown that the above inequality holds for both ethylene and propylene.

The diffusion coefficients of hydrogen and carbon monoxide could not be measured in this manner, because the solubilities of these gases in $PPh_3$ are too low. These, and the diffusion coefficients of ethylene and propylene as well, were calculated with the Wilke–Chang equation (*8*). The resulting values are also given in Table II. It is seen that the agreement between the experimental and calculated values is satisfactory. The values of properties and parameters used in calculating the diffusion coefficients by the Wilke–Chang equation are given in Tables III and IV.

***Melting Behavior of $PPh_3$.*** The melting point of $PPh_3$ was found to be 80.0 °C, in accordance with the literature (*9*). It was also found that liquid $PPh_3$ could be kept at a temperature of 54 °C (i.e., 26 °C below its melting point) for a period of 17

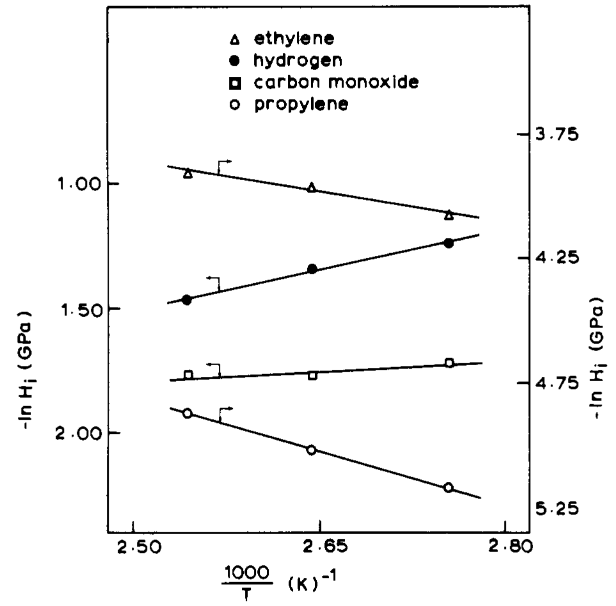

**Figure 2.** Henry's constants as a function of temperature.

h without showing any crystallization at all. This supercooling of $PPh_3$ was also observed by using differential scanning calorimetry.

## Acknowledgment

We gratefully acknowledge our indebtedness to Professor Dr. J. J. F. Scholten for his stimulating discussions.

## Glossary

| | |
|---|---|
| $c_{i0}$ | equilibrium concentration of component i in the liquid phase at the lower pressure $p_0$, mol m$^{-3}$ |
| $c_{i1}$ | equilibrium concentration of component i in the liquid phase at the higher pressure $p_1$, mol m$^{-3}$ |
| $D_i$ | diffusion coefficient of component i in liquid $PPh_3$, m$^2$ s$^{-1}$ |
| $f_i$ | fugacity of component i in the gas phase, Pa |
| $H_i$ | Henry's constant of component i in liquid $PPh_3$, Pa |
| $L$ | twice the height of the liquid-phase column in the Cailletet tube, m |
| $T$ | absolute temperature, K |
| $t$ | time elapsed since the pressure was suddenly raised from $p_0$ to $p_1$, s |
| $V_i$ | liquid molar volume of solute i at its normal boiling point, cm$^3$ mol$^{-1}$ |
| $x_i$ | mole fraction of component i in the liquid phase |
| $\gamma_i$ | activity coefficient of component i in the liquid phase; $\gamma_i$ approaches unity when $x_i$ approaches zero |
| $\phi$ | time-averaged mole flux of component i, mol m$^{-2}$ s$^{-1}$ |

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# Volumetric Properties of Molten Hydrated Salts. 5. $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ System

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A manometric method is used to measure the densities of molten $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ (M = Li, Na, K, $NH_4$, Ag, and Tl) mixtures from 285 to 365 K. Equations representing the densities and equivalent volumes as a function of temperature are given. Composition dependence of equivalent volumes obeyed the principle of additivity of volumes except for the $LiNO_3$-containing system; small negative deviations in the latter have been explained in terms of the greater electrostriction which the $H_2O$ molecules undergo.

## Introduction

Recently an increasing interest in molten hydrated salt systems has developed because of their theoretical (*1-17*) and applied (*18-25*) importance. Molten salt models are generally used to understand the behavior of these systems because their structure is predominantly an ionic distribution perturbed by water molecules. The densities and equivalent volumes of molten mixtures of hydrated nitrates and some monovalent nitrates (*13-16*) have indicated that $Li^+$ ions strongly compete for water of hydration with divalent hydrated cations. In this paper, the densities of $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ (M = Li, Na, K, $NH_4$, Ag, and Tl) have been reported to study the effect of different ions on the volumetric properties of trivalent hydrated nitrates.

## Experimental Section

The purities and the grades of the chemicals used in this study were as follows: $Fe(NO_3)_3 \cdot 9H_2O$, 98%, LR (SM); $LiNO_3$,

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