SOLUBILITY OF GASES AT 25°C AND HIGH PRESSURES: THE SYSTEMS CO$_2$ + C$_4$ ALCOHOLS

I. Găinar*, Daniela Bala

Abstract: At 25°C and pressures between 5 and 45 bar, the solubilities of carbon dioxide in C$_4$ alcohol (n-butanol, sec-butanol, iso-butanol and tert-butanol) were determined. The experimental data were compared with calculated values using the principle of the corresponding state as well with those obtained from a method based on the dependence of activity coefficient on the solubility parameter of gas. In all cases, greater experimental values in comparison with calculated one were observed.

Introduction

This study represents a continuation of a program started over 20 years ago concerning the solubility of gases in liquids at high pressures. For this purpose an original device was constructed that allows to obtain pertinent data in a wide range of temperature (-10 °C to 50°C) and pressures up to 100 bar.

Constructive details of experimental device were presented in an earlier publication [1].

A large variety of organic solvents was studied: alifatic and aromatic hydrocarbons [2], ethers [3], esters [4], ketones [5] and alcohols [6].

The solubility of a singular gases (CO$_2$, H$_2$, N$_2$, He) as well as gas mixtures (CO$_2$ + H$_2$ + N$_2$) were determined. For some of these systems, simple and more elaborated methods were used for theoretical calculation [7, 8].

Materials and method

Principle of experimental method as well as working procedure and analysis of obtained data were previous presented [1].

The four studied alcohols were Merck high purity compounds (for chromatography), and carbon dioxide was a pure Linde gas (99.9%).

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Analele Universității din București – Chimie, Anul XIV (serie nouă), vol. I-II, pg. 271-278

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Experimental parameters were measured with high precision (working pressure ± 0.01 bar, working temperature ± 0.02°C, pressure of desorbed gas ± 0.05 mm Hg, and mass of solvent with analytical balance).

Experimental data

The experimental results are presented in table 1, where P is working pressure and \( x^l \) is the solubility of CO\(_2\) in alcohols at 25°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>n-butanol</th>
<th>iso-butanol</th>
<th>sec-butanol</th>
<th>tert-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (°C)</td>
<td>P [bar]</td>
<td>( x^l )</td>
<td>P [bar]</td>
<td>( x^l )</td>
</tr>
<tr>
<td>25</td>
<td>42.76</td>
<td>0.282</td>
<td>34.81</td>
<td>0.268</td>
</tr>
<tr>
<td></td>
<td>35.30</td>
<td>0.252</td>
<td>29.22</td>
<td>0.237</td>
</tr>
<tr>
<td></td>
<td>25.00</td>
<td>0.179</td>
<td>24.12</td>
<td>0.184</td>
</tr>
<tr>
<td></td>
<td>14.31</td>
<td>0.135</td>
<td>19.41</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>10.19</td>
<td>0.118</td>
<td>14.61</td>
<td>0.113</td>
</tr>
<tr>
<td></td>
<td>5.39</td>
<td>0.090</td>
<td>10.29</td>
<td>0.088</td>
</tr>
</tbody>
</table>

Isothermal values of gas solubilities function of working pressures are plotted in figures 1 - 4.

**Fig. 1.** The system CO\(_2\) + n-butanol

**Fig. 2.** The system CO\(_2\) + iso-butanol

**Fig. 3.** The system CO\(_2\) + sec-butanol

**Fig. 4.** The system CO\(_2\) + tert-butanol
Because tert-butanol is in solid state at 25°C the experimental solubility of CO₂ in this solvent were determined at 27°C. For all these systems one observe linear dependence of gas solubility versus pressure.

**Theoretical considerations**

In order to apply the principle of the corresponding states to calculate the solubility of gases in liquids we consider that the fugacity of the solvate as a hypothetical liquid at P = 1.013 bar depends only on temperature and its properties. As a consequence, it is possible to apply the theory of the corresponding states and to establish the conditions in which the reduced fugacity of hypothetical liquid solvate is a universal function of reduced temperature.

Consider a gaseous component at fugacity \( f_2 \) dissolved isothermally in a liquid not near its critical temperature. The solution process is accompanied by a change in enthalpy and in entropy, as occurs when two liquids are mixed. However, in addition, the solution process for the gas is accompanied by a large volume because the partial molar volume of the solute in the condensed phase is much smaller than that in the gas phase. This large decrease in volume distinguishes solution of a gas in a liquid from solution of another liquid or of a solid. Therefore, to apply regular solution theory (that assumes no volume change), it is necessary first to “condense” the gas to a volume close to the partial molar volume that it has as a solute in a liquid solvent. The isothermal solution process of the gaseous solute is then considered in two steps, I and II [9]:

\[
\Delta G = \Delta G_I + \Delta G_{II} \tag{1}
\]

\[
\Delta G_I = RT \ln \frac{f_2^{(\text{pure})}}{f_2^R} \tag{2}
\]

\[
\Delta G_{II} = RT \ln \gamma_2^I \cdot x_2^I \tag{3}
\]

where \( f_2^{(\text{pure})} \) is the fugacity of (hypothetical) pure liquid solute and \( \gamma_2^I \) is the symmetrically normalized activity coefficient of the solute referred to the (hypothetical) pure liquid (\( \gamma_2^I \to 1 \) as \( x_2^I \to 1 \)).

In the first step, the gas isothermally “condenses” to a hypothetical state having a liquid-like volume. In the second step, the hypothetical liquid-like fluid dissolves in the solvent. Since the solute in the liquid solution is in equilibrium with the gas that is at fugacity \( f_2^R \), the equation of equilibrium is:

\[
\Delta G = 0 \tag{4}
\]
We assume that the activity coefficient for the gaseous solute is given by the regular-solution equation:

\[ RT \ln \gamma_2^f = v_2^l (\delta_1 - \delta_2)^2 \theta_1^2 \]  

(5)

where \( \delta_1 \) is the solubility parameter of the solvent, \( \delta_2 \) is the solubility parameter of solute, \( v_2^l \) is the molar “liquid” volume of solute, and \( \theta_1 \) is the volume fraction of solvent.

By combining of these five equations we finally obtain:

\[
\frac{1}{x_2^l} = \frac{f_2^{\text{pure}}}{f_2^{\text{g}}} \exp \left[ \frac{v_2^l (\delta_1 - \delta_2)^2 \theta_1^2}{RT} \right]
\]

(6)

Equation (6) allows calculating the solubility of gases in liquids. It requires three parameters for the gaseous component as a hypothetical liquid: the pure liquid fugacity, the liquid volume, and the solubility parameter. These parameters are all temperature dependent; however, the theory of regular solutions assumes that at constant composition:

\[ T \ln v_2^l \sim \gamma \]  

(7)

and therefore, the quantity \( v_2^l (\delta_1 - \delta_2)^2 \theta_1^2 \) is not temperature-dependent. As a result, any convenient temperature may be used for \( v_2^l \) and \( \delta_2 \) provided that the same temperature is also used for \( \delta_1 \) and \( v_1^l \) [10].

The fugacity of the hypothetical pure liquid has been correlated in a corresponding-state plot shown in figure 5 (for a total pressure of 1.013 bar); the fugacity of the solute divided by its critical pressure is shown as a function as a ratio of the solution temperature to the solute’s critical temperature.

For reduced temperatures domain 0.7 ÷ 0.8, the vapor pressures of liquefied gases (as CO\(_2\)) was used, for obtaining the plot of \( \frac{f_2^l}{P_{cr}} \) as function of \( \frac{T}{T_{cr}} \). For reduced temperatures greater than 0.8, the solubility gases data were used.

As we expected, the curvature rises with increasing the reduced temperature, but presents a maximum in the vicinity of Boyle point [11, 12].

Literature data indicate [13, 14] that equation of regular solutions is valid only for non-polar systems, therefore it can’t be directly used for correlation solubilities of gases in polar solvents. Nevertheless this approach presented above concerning the correlation of solubilities of gases in non-polar solvents suggests an empirical method useful for polar solvents.
For a certain polar solvent and a given temperature, a representation of gas-solubility versus of a certain property of the gas (for example the force constant or critical temperature) don’t lead to a curve with a regular aspect. This aspect is given by the fact that the solubility of gas depends not only of solvit-solvent interaction but on the fugacity of pure solvit in condense state; consequently, one parameter of gas is not sufficient for obtaining a good correlation. Instead of realising a direct correlation of solubilities is much useful to correlate the activity coefficient, which refers to a hypothetical liquid solvent. The fugacities presented in figure 5 depend only on solvit properties, therefore are independent on solvent, so that it is possible to use it for calculation of activity coefficients of solvits both in polar and non-polar solvents.

The solubility at partial pressure of 1.013 bar is correlated with activity coefficient by relation:
For a non-polar gas in a polar solvent the activity coefficient of the gas should depend on its volume and solubility parameter according to a function as:

\[
\ln \gamma'_2 = v'_2 \cdot f(T, \delta_2, \text{solvent properties})
\]  

(9)

The parameters \( v'_2 \) and \( \delta_2 \) depend only on solvitation properties, therefore their values and fugacity \( f'_2 \) can be used with polar solvents. Equation (9) suggests that the solubility data in polar solvents can be correlated by using of isothermal representation of \( \left( \frac{\ln \gamma'_2}{v'_2} \right) \) versus \( \delta_2 \).

Results and Discussions

We have applied these theoretical considerations in order to calculate solubilities of carbon dioxide in \( \text{C}_4 \) alcohols (n-butanol, iso-butanol, sec-butanol and tert-butanol), at 298.15K and 1.013 bar. We have used the following values of characteristic constants [10, 15, 16]:

\[ v'_2 = 55 \text{ cm}^3\text{ mol}^{-1} \]
\[ \delta_2 = 6.0 \left( \frac{\text{cal} \cdot \text{cm}^{-3}}{\text{mol}} \right)^{1/2} \]
\[ f'_2 = 40.7 \text{ bar} \]

In the following table are presented the calculated values of gas-solubilities together with experimental values obtained by extrapolation of experimental curves at \( P = 1.013 \text{ bar} \).

<table>
<thead>
<tr>
<th>substance</th>
<th>( \Delta^v H ) (kcal mole(^{-1}))</th>
<th>( \Delta^v E ) (kcal mole(^{-1}))</th>
<th>( \delta_1 ) (cal cm(^3)mol(^{-1})) ( ^{1/2} )</th>
<th>( x_2^{\text{calc}} )</th>
<th>( x_2^{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butanol</td>
<td>10.344</td>
<td>9.751</td>
<td>10.32</td>
<td>0.0044</td>
<td>0.0657</td>
</tr>
<tr>
<td>sec-butanol</td>
<td>9.737</td>
<td>9.144</td>
<td>9.99</td>
<td>0.0056</td>
<td>0.0291</td>
</tr>
<tr>
<td>iso-butanol</td>
<td>9.992</td>
<td>9.400</td>
<td>10.07</td>
<td>0.0053</td>
<td>0.0382</td>
</tr>
<tr>
<td>tert-butanol</td>
<td>9.335</td>
<td>8.741</td>
<td>9.63</td>
<td>0.0073</td>
<td>0.0723</td>
</tr>
</tbody>
</table>
One observes a great discrepancy between calculated and experimental values of gas-solubilities. Similar observations are cited in literature in a lot of other cases of gas-solubilities correlations – generally, experimental values are greater as calculated one.

One reason of this discrepancy is a fact that the application of the principle of the corresponding state (PCS) to calculate gas-solubility is limited to non-polar systems, and on the other side, the great quadrupole moment of carbon dioxide has a substantial influence on calculated values.

The values of $x_2^{calc}$ depend also on the choice of values for $\nu_2^l$, $\delta_2$, and $f_2^l$. For example values of $\nu_2^l$ vary between 35 and 55 cm$^3$ mole$^{-1}$, and $\delta_2$ vary between 5.20 and 6 (cal cm$^{-3}$)$^{1/2}$. On the other hand specific chemical interactions can lead to a intensification of the gas solubility much more as this is predicted by physical correlations (dipole – quadrupole interaction).

In the figure 6 is presented the dependence of $\frac{\log \gamma^l}{\nu_2^l}$ versus $\delta_2$ for C$_4$ alcohols.

From this figure we obtain by extrapolation at $\delta_2 = 6.0 \left(\text{cal} \cdot \text{cm}^{-3}\right)^{1/2}$ a value for $\gamma^l_2 = 2.75$. By using of this value and the equation (8) we obtain $x_2^{calc} = 0.0090$, much smaller as experimental values. An interesting fact is that the ideal solubility for CO$_2$ equal to 0.0160 is much closer to experimental values.
REFERENCES