

# THE SOLUBILITY OF CO<sub>2</sub> IN SOME C<sub>4</sub> ALCOHOLS AT HIGH PRESSURES

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**abstract:** The aim of this work is to present the results concerning the solubility of CO<sub>2</sub> in some C<sub>4</sub> alcohols, namely *n*-butanole and *iso*-butanole by pressures up to 4 MPa and in temperature range 0 ÷ 40 °C. For both systems we observed remarkable values of gas solubility at all values of pressures and temperatures. Molecular structures of the alcohols have a small influence and therefore the obtained data are comparable. A different behaviour was observed at the lowest temperature and highest pressures for both alcohols. In these conditions the gas solubility exceeds the value 0.5, it means that a new equilibrium is established: the solubility of liquid in the condensed gas.

## Introduction

The solubility of gases in liquids is an area of active interest from both the theoretical and practical standpoints. Both the dilute solutions resulting from the low solubility of many gases in liquids, and the large variety of sizes, shapes, and polarities of gases molecules to act as “probes” have made the solubility of gases in liquids an excellent tool to investigate the test theories of liquid properties and liquid structure. A knowledge of the solubility of gases is of practical importance in various industrial processes, in the study of artificial atmospheres for divers and astronauts, in the interaction of gases with our environment (as in the biological oxygen demand in natural waters), in processes for saline water demineralization, and in the study of various biological fluids and tissues.

Determination of the solubility of gases in liquids at high pressure has become of increasing importance. The problems of adequate mixing of the gas and liquid phases to ensure saturation, pressure and temperature control, and sampling and measurement of the gas dissolved at high-pressure present greater difficulties than in apparatuses that operate at atmospheric pressure.

The solubility of gases in liquids has been expressed in terms of many different units, depending on the particular application. The principal methods of expressing gas solubility are: the Bunsen coefficient –  $\alpha$ , the Kunsen coefficient –  $S$ , the Ostwald coefficient –  $L$ , the mole fraction –  $x_2$ , the absorption coefficient –  $\beta$ , the Henry’s Law constant –  $K_H$ , the weight solubility  $C_w$  [1, 2].

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In our determinations we used mole fraction solubility  $x_2$ , which is given by:

$$x_g = x_2 = \frac{n_g}{n_g + n_s} \quad (1)$$

for two components, where  $n$  is the number of moles (of gas and of solvent). The difficulty with this equation is that the gas solubility is directly proportional to the gas partial pressure via Henry's law. To be unambiguous then, both the partial pressure of the gas and the temperature of measurement must be specified to fix the mole fraction.

In this experiment we shall determine the solubility of CO<sub>2</sub> in *n*-butanole and *iso*-butanole at pressures up to 4 MPa and in temperature range 0 ÷ 40 °C.

This work is a continuation of a programme initiated for some years ago concerning the solubility of gases in a wide category of organic solvents: hydrocarbons, alcohols, ketones at high pressure and a wide domain of temperatures [3÷5].

## Materials and Methods

The experimental device and the detailed description of working method is presented in a separate research [6]. By using of this experimental method we have performed a study concerning the influence of temperature and pressure on gas solubility. In this purpose we have selected two alcohols namely *n*-butanole and *iso*-butanole. The used alcohols were Merck products and carbon dioxide was Linde gas one with high purity.

The measured experimental parameters were:

- working pressure (measured with a precision of 10<sup>-2</sup> MPa);
- working temperature (measured with a precision of 0.02<sup>0</sup>C);
- mass of alcohol (weighted with analytical balance);
- pressure of the desorbed gas (measured with a precision ± 0.005 mm Hg).

## Results and Discussion

Using the measured experimental parameters we calculate the moles number of the desorbed gas which represents the value of the carbon dioxide solubility in the given conditions of pressure and temperature. For the calculations the ideal gas equation was used, because the values of measured pressure did not exceed the values of working pressure. Other equations, as virial state equations were tested, but without any significant differences concerning the obtained values. The experimental data are presented in Table 1.

The pressure dependence of carbon dioxide solubility in *n*-butanole and *iso*-butanole is comparatively presented in Figs. 1÷6.

**Table 1.** The solubility of carbon dioxide in *n*-butanole and *iso*-butanole at various temperatures

<i>t</i> (°C)	<i>n</i> -butanole				<i>iso</i> -butanole			
	<i>P</i> <sub>working</sub> (MPa)	<i>m</i> <sub>alcohol</sub> (g)	<i>P</i> <sub>CO<sub>2</sub></sub> (mm Hg)	<i>x</i> <sub>CO<sub>2</sub></sub>	<i>P</i> <sub>working</sub> (MPa)	<i>m</i> <sub>alcohol</sub> (g)	<i>P</i> <sub>CO<sub>2</sub></sub> (mm Hg)	<i>x</i> <sub>CO<sub>2</sub></sub>
0	3.89	0.1881	67.85	0.731	3.60	0.2224	94.70	0.762
	3.19	0.3427	56.55	0.554	3.09	0.5732	57.36	0.429
	2.50	0.8068	45.63	0.298	2.47	0.8886	48.81	0.292
	2.01	1.1403	44.75	0.228	2.06	1.0420	44.75	0.244
	1.37	1.1319	32.73	0.179	1.53	1.1726	36.60	0.190
	0.78	1.0623	23.55	0.143	1.08	1.4629	30.70	0.136
	0.64				0.64	1.4079	16.70	0.082
10	4.49	0.2880	43.90	0.534	3.53	0.4661	36.24	0.369
	3.48	0.5291	38.66	0.355	3.02	0.6632	37.16	0.296
	2.35	1.0701	41.64	0.226	2.59	0.8808	37.75	0.244
	1.83	1.0013	30.98	0.189	1.93	1.1120	35.50	0.194
	1.25	1.1841	24.81	0.136	1.47	1.4807	30.95	0.136
	0.71	1.8088	20.55	0.079	0.99	1.3469	19.30	0.097
	0.61				0.61	1.6989	13.67	0.057
20	4.53	0.4976	34.70	0.344	4.31	0.7054	51.01	0.352
	4.13.04	0.7436	45.01	0.313	3.48	0.7715	40.27	0.282
	3.44	0.6039	33.40	0.294	3.02	0.8282	35.70	0.245
	2.52	0.9372	31.95	0.204	2.51	0.9417	32.25	0.205
	1.98	0.9842	28.31	0.178	1.98	0.9361	24.47	0.164
	0.73	1.3697	14.41	0.073	1.44	1.3774	25.83	0.124
	0.51				0.94	1.3229	19.46	0.100
25	4.28	0.7591	39.62	0.282	0.51	1.7541	14.29	0.058
	3.53	0.8513	38.10	0.252	3.48	0.7300	35.50	0.268
	2.50	1.2887	37.31	0.179	2.92	0.7015	29.00	0.237
	1.43	1.5147	31.33	0.135	2.41	1.2836	38.50	0.184
	1.02	1.6042	28.50	0.118	1.94	1.5712	36.20	0.148
	0.54	1.2789	16.18	0.090	1.46	1.4869	25.08	0.113
	0.57				1.03	1.2581	16.05	0.088
30	4.27	0.8738	42.83	0.269	0.57	1.5429	13.05	0.060
	4.10	0.7489	33.71	0.253	3.54	0.5798	28.50	0.270
	3.35	1.1284	41.27	0.216	2.98	0.7647	29.12	0.223
	2.45	1.6610	42.05	0.160	2.62	0.6351	22.45	0.200
	1.78	1.7915	32.07	0.119	1.99	1.1885	28.68	0.154
	1.16	1.4820	19.82	0.091	1.55	1.3065	23.62	0.120
	0.67	2.0241	16.35	0.057	1.03	1.6634	21.20	0.087
40	4.45	0.9527	39.37	0.237	0.53	1.6975	12.30	0.052
	3.45	1.1118	36.77	0.199	3.22	0.8361	28.43	0.204
	2.43	1.6702	37.09	0.143	2.65	0.9634	27.72	0.178
	1.51	1.2146	15.98	0.090	2.14	1.1823	25.10	0.138
	0.74	1.3803	11.53	0.059	1.67	1.7799	32.32	0.120
					1.08	1.2458	15.18	0.084
				0.54	1.9400	12.00	0.044	

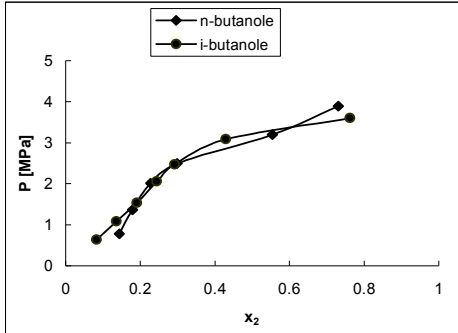


Fig. 1. The pressure dependence of  $\text{CO}_2$  solubility in *n*-butanol and *i*-butanol at  $0^\circ\text{C}$

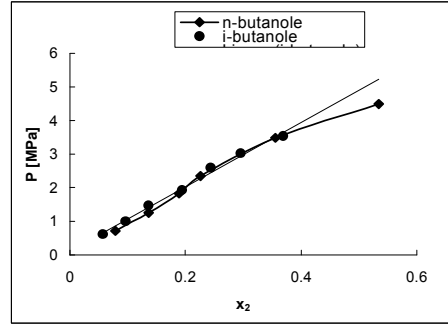


Fig. 2. The pressure dependence of  $\text{CO}_2$  solubility in *n*-butanol and *i*-butanol at  $10^\circ\text{C}$

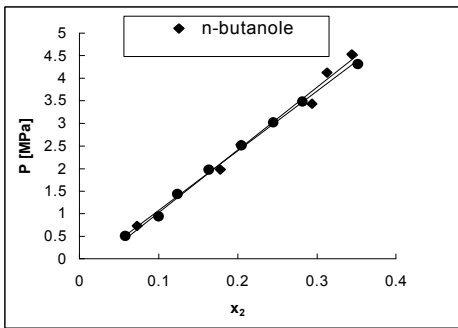


Fig. 3. The pressure dependence of  $\text{CO}_2$  solubility in *n*-butanol and *i*-butanol at  $20^\circ\text{C}$

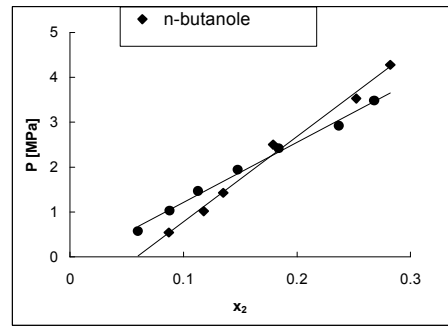


Fig. 4. The pressure dependence of  $\text{CO}_2$  solubility in *n*-butanol and *i*-butanol at  $25^\circ\text{C}$

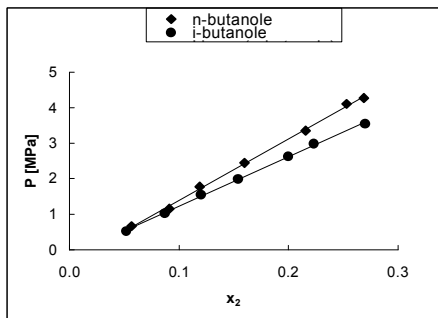


Fig. 5. The pressure dependence of  $\text{CO}_2$  solubility in *n*-butanol and *i*-butanol at  $30^\circ\text{C}$

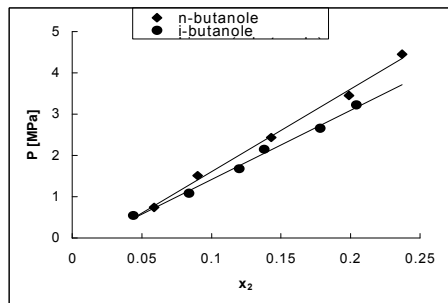


Fig. 6. The pressure dependence of  $\text{CO}_2$  solubility in *n*-butanol and *i*-butanol at  $40^\circ\text{C}$

## Conclusions

Analyzing the above results we obtained the following conclusions:

- at high pressures (greater than 3-4 MPa) and low temperature, 0<sup>0</sup> and 10<sup>0</sup>C respectively, the solubility have great values. In these conditions the gas solubility exceeds the value 0.5 (as we can see from Table 1) and a new equilibrium is established: the solubility of liquid in the condensed gas. The liquid phase disappeared and in the working cell we have one phase with fog aspect;
- decreasing the pressure, the equilibrium curves change their slopes and at molar fractions smaller than 0.3 the pressure dependence of solubility becomes linear, it means that Henry's Law can be applied (see Fig. 1). At 10<sup>0</sup>C the phenomenon is less visible, but still we can remark the slope changing in *n*-butanole (see Fig. 2);
- increasing the temperature, the pressure dependence of solubility becomes linear on the entire range of values, it means that the Henry's Law is respected (Fig. 3 – Fig. 6).

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