



SOLUBILITY DATA IN BINARY SYSTEMS: CO₂ + BUTAN-2-OL AND CO₂ + 2-METHYL-2-PROPANOL AT HIGH PRESSURES

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abstract The solubility of carbon dioxide in butan-2-ol and 2-methyl-2-propanol at high pressures (up to 4.5 MPa) and in the temperature range (268.15 to 313.15) K were measured. At lower temperatures and high pressures large deviations from Henry's Law were observed. The data for these two systems were compared with those obtained for systems CO₂ + butan-1-ol and CO₂ + 2-methyl-1-propanol.

Introduction

Knowledge of the solubility of gases in liquids is of active interest for fundamental research as well as for practical applications, especially to the design and implementation of many processes. Data for *carbon dioxide - alcohols* systems are of great interest in supercritical fluid extraction in the oil and natural gas, and in the pharmaceutical, surfactants and food industries [1-4]. Determination of the solubility of gases at high pressures presents greater difficulties than in an apparatus that operates at atmospheric pressure. These difficulties come from problems due to adequate mixing of the gaseous and liquid phases to ensure equilibrium saturation, to pressure and temperature control, to sampling and to measurements at high pressures, in general. In order to overcome all these problems an original device was constructed in our laboratory. Details of experimental device were presented in an earlier publication [5].

In this work we have investigated the isomeric effects of various solvents on the gas solubility (carbon dioxide) at high pressures and we compared the present results with those obtained for the other two C4 alcohols (butan-1-ol, 2-methyl-1-propanol) [6,7]. There are several papers concerning the systems CO₂ + butan-2-ol [8-12] and CO₂ + 2-methyl-2-propanol [13-15].

Experimental

Materials. Carbon dioxide (mass fraction purity > 0.997) was provided by Linde Gaz Romania, Bucharest, Romania. The two alcohols studied were Merck compounds: butan-2-ol,

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$\geq 98.0\%$, 2-methyl-2-propanol, $\geq 99.0\%$. The chemicals were used as supplied, without further purification.

Method. The equipment contains the following components: controlled supply system for purified gas, equilibrium gas-liquid cell provided with thermostating system, sampling and analysis system for measuring the amount of dissolved gas and pressure measuring system. Principle of experimental method as well as working procedure and analysis of obtained data were presented in previous paper [5]. Experimental parameters (working pressure up to 4.5 MPa and working temperature in the range (268.15 to 313.15) K were measured with uncertainties: pressure $\pm 10^{-2}$ MPa, temperature $\pm 0.02^0$, pressure of desorbed gas ± 6.66 Pa. The volume of solvent was estimated (max. error: $\pm 10^{-3}$ cm³) knowing the solvent density and the mass of ampoule. The mass of solvent sample is determined by using of an analytical balance with an accuracy of ± 0.0001 g.

Results and Discussions

The experimental results for the solubility of carbon dioxide in butan-2-ol, 2-methyl-2-propanol at temperatures 273.15K, 283.15 K, 293.15 K, 298.15 K, 303.15 K, 313.15 K and pressures up to 4.7 MPa are given in Table 1. In this table the solubility of CO₂ is expressed by mole fractions, x_2 . Because the melting point of 2-methyl-2-propanol is 298.15 K we started our experimental measurements for this solvent from 300.15 K.

The pressure dependence of carbon dioxide solubility in organic solvents (butan-2-ol, 2-methyl-2-propanol) is plotted in the following two figures (Figs 1 and 2).

Table 1 Mole fraction, x_2 , of carbon dioxide in various solvents at different temperatures and pressures

T/K = 273.15		T/K = 283.15		T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 313.15	
x_2	p/MPa	x_2	p/MPa	x_2	p/MPa	x_2	p/MPa	x_2	p/MPa	x_2	p/MPa
Butan-2-ol											
0.913	4.71	0.573	4.25			0.331	4.14	0.298	3.55	0.224	3.43
0.655	3.53	0.418	3.66	0.303	3.58	0.265	3.34	0.256	2.96	0.201	2.97
0.483	3.00	0.279	3.04	0.244	2.97	0.220	2.50	0.210	2.45	0.165	2.45
0.346	2.45	0.245	2.53	0.177	2.24	0.178	1.96	0.187	1.96	0.141	1.96
0.263	2.11	0.200	2.01	0.139	1.62	0.135	1.52	0.152	1.47	0.120	1.47
0.213	1.47	0.164	1.55	0.108	1.05	0.103	1.02	0.109	1.03	0.090	0.94
0.164	0.93	0.125	1.10	0.066	0.59	0.080	0.54	0.059	0.52	0.060	0.49
0.131	0.49	0.080	0.59								
			T/K = 300.15		T/K = 303.15		T/K = 308.15		T/K = 313.15		

Table 1. continued

T/K = 273.15		T/K = 283.15		T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 313.15	
x_2	p /MPa	x_2	p /MPa	x_2	p /MPa	x_2	p /MPa	x_2	p /MPa	x_2	p /MPa
2-Methyl-2-propanol											
-	-	-	-	0.404	3.54	0.387	4.04	0.402	4.08	0.382	4.12
-	-	-	-	0.338	2.99	0.360	3.46	0.335	3.48	0.323	3.48
-	-	-	-	0.310	2.50	0.291	2.78	0.309	2.99	0.299	3.00
-	-	-	-	0.265	2.02	0.285	2.46	0.284	2.45	0.241	2.48
-	-	-	-	0.222	1.52	0.254	1.96	0.253	1.96	0.198	1.96
-	-	-	-	0.149	1.01	0.210	1.47	0.213	1.58	0.157	1.49
-	-	-	-	0.116	0.56	0.165	1.03	0.174	1.03	0.143	1.03
-	-	-	-	-	-	0.132	0.59	0.125	0.62	0.089	0.54

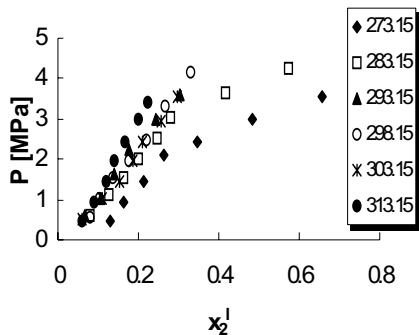


Fig. 1 Variation of gas solubility with pressure at different temperatures for butanol-2-ol

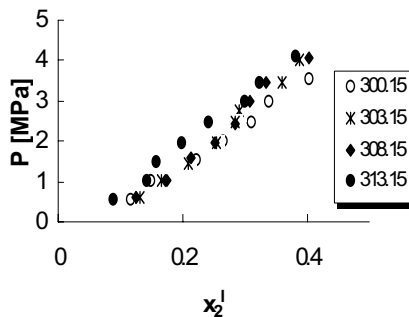


Fig. 2 Variation of gas solubility with pressure at different temperatures for 2-methyl-2-propanol

One can observe that solubility of carbon dioxide in butan-2-ol at lower temperature (273.15 and 283.15 K) is greater than 0.5, it means that a new equilibrium is established: the solubility of liquid in the condensed gas. From the analysis of figure 1 we observed that at high pressure and low temperature, the pressure dependence of solubility is not linear, so binary system did not obey to Henry's Law. The same behaviour was observed also in the case of systems CO₂ + butan-1-ol and CO₂ +2-methyl-1-propanol [6]. The most pregnant deviations from Henry's Law are observed at high pressures and the lowest temperatures (273.15, 283.15) K. For the alcohols the deviations decrease in order: butan-2-ol, 2-methyl-2-propanol, butan-1-ol.

Henry's Law is an accurate description of ideal dilute solutions, gases dissolving in liquids, when concentration and partial pressures are reasonably low. As concentration and partial pressure increase, deviation from Henry's Law become noticeable. For polar molecules the deviations can be important even at small pressures. In this work and previous one [6], used alcohols are polar liquids and even though carbon dioxide has no dipole moment, its quadrupole moment can lead to strong interactions with solvent molecules which explained high values of carbon dioxide solubility in all C4 alcohols and also deviations from Henry's

Law. In studying isomeric effects on gas solubility in liquids, molecular symmetry have an important contribution.

A possible explanation for understanding of the mechanism for the dissolution process of the gas in liquids is the following: in the first step of the process, a cavity with a certain geometry has to be formed in the solvent in order to allow the introduction of a gas molecule; in the second step the gas molecule interacts with surrounding solvent (Scaled Particle Theory) [16]. The first step implies work necessary to create the cavity. The amount of this work depends on the molecular symmetry. The solubility of gas increased in solvents with higher symmetry. In the case of 2-methyl-2-propanol the values of the surface tension coefficients (STEN) [17] as well as the molecular polarizability have the lowest values as a consequence of nearly spherical symmetry (Table 2).

Table 2 Some structural properties of investigated organic solvents at $T = 298.15$ K

Solvent	<i>EPS</i>	<i>STEN</i> / (dyne/cm)
Butan-1-ol	17.320	24.93
Butan-2-ol	15.936	22.54
2-Methyl-1-propanol	16.788	23.23
2-Methyl-2-propanol	12.470	19.96

At lower temperatures (273.15, 283.15) K and the highest pressures, we have observed a spectacular phenomenon for all systems investigated: the solvent saturated with carbon dioxide suddenly expands in the gaseous phase to form a unique phase.

Conclusions

The solubility of carbon dioxide in butan-2-ol is greater than 0.5 at lower temperatures (273.15 and 283.15 K) and high pressure (greater than 3.5 MPa), having same behaviour as butan-1-ol and 2-methyl-1-propanol. In these conditions a new equilibrium is established; the pressure dependence of solubility is not linear, so binary system did not obey to Henry's Law. At higher temperatures (greater than 283.15), the pressure dependence of solubility becomes linear. Isomeric effects on gas solubility in C4 alcohols were explained by taking into account the molecular symmetry of partners.

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