

HIGH PRESSURE SOLUBILITY OF CARBON DIOXIDE IN SOME C4 ESTERS

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Experimental results concerning the solubility of carbon dioxide in some C4 esters are presented. We have used the following four acetic esters: n-butyl acetate, iso-butyl acetate, sec-butyl acetate and tert-butyl acetate. The experimental data were performed at high pressures (up to 4.5 MPa) and in the temperature range 268.15 ÷ 313.15 K. For all investigated esters, especially at low temperatures, one observe deviations from Henry's Law. A theoretical interpretation of the dissolution process in term of enthalpy of solvation is presented.

INTRODUCTION

Measurements of gas solubilities in liquids are of considerable interest not only from a practical point of view, due to their usefulness in industrial processes and other fields (design of absorption equipment, purification of gases, etc.), but also for contributing to the theoretical comprehension of intermolecular forces. This latter aspect offers the possibility of testing the theoretical and semiempirical models developed for both solution and solvent effects on chemical equilibria and the rate of reactions.

The increasing industrial and academic interest in high and low pressure data of the carbon dioxide + alcohol systems have been indicated in the large number of publications for the last few years. Solubility of carbon dioxide in C4 alcohols were reported in a great number of papers.¹⁻³⁰

In comparison with the case of systems CO₂ + C4 alcohols, data concerning solubility of carbon dioxide in acetic esters of C4 alcohols are very poor.^{6,16}

In this work we have investigated the isomeric effects of various solvents on the gas solubility (carbon dioxide) at high pressures. We have selected four solvents: the four C4 acetic esters (n-butyl acetate, iso-butyl acetate, sec-butyl acetate and tert-butyl acetate). Experimental parameters (working pressure up to 4.5 MPa and working temperature in the range 268.15 ÷ 313.15 K) were measured with high precision: pressure ± 10⁻² MPa,

temperature ± 0.02⁰, pressure of desorbed gas ± 0.05 mm Hg and mass of solvent with analytical balance.

EXPERIMENTAL

The corresponding four esters were Lancaster solvents for synthesis (England).

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; pressure measuring system; cathetometer.

The equilibrium cell (stainless steel made) with an inner volume of 170 cm³ is suspended in a thermostat bath (model Lauda K4R) and by means of an electromechanical device the two phases (solvent and CO₂) are intensively mixed. The phase equilibrium is achieved in few hours. After the establishment of phase equilibrium, a sample of about 1 cm³ of solvent saturated with gas is collected in an ampoule. The dissolved gas is desorbed in a thermostated glass vessel with known volume and its pressure is measured by using of a mercury manometer and a high precision cathetometer. The pressure measurements system works in two steps: the first one for the gas supply is controlled by a Bourdon manometer (precision class 0.6) and the second one for phase equilibrium achievement using a deadweight gauge (precision class 0.05, effective active area of rotative piston is of 0.50502 cm²). The precision of pressure measurements is determined by using of a differential capacitive pressure transducer. The volume of solvent is estimated (max. error: ± 10⁻³ cm³) knowing the solvent density and the mass of ampoule. The mass of solvent sample is weighted by using of an analytical balance. A detailed description of the experimental set-up and method can be found in a previous paper.³¹

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RESULTS AND DISCUSSION

The experimental results for the solubility of carbon dioxide in n-butyl acetate, iso-butyl acetate, sec-butyl acetate and tert-butyl acetate 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 Tables 1 to 4. In these tables the solubility of CO₂ is expressed by mole fraction x_2^l .

Table 1

Solubility of CO₂ in n-Butyl acetate

273.15		283.15		293.15		298.15		303.15		313.15	
x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]
				0.770	4.07	0.660	3.97	0.588	3.85	0.530	3.93
0.857	3.01	0.745	3.29	0.637	3.48	0.596	3.45	0.555	3.45	0.497	3.44
0.744	2.45	0.691	2.99	0.598	2.95	0.525	2.98	0.491	3.00	0.432	2.94
0.576	1.77	0.599	2.46	0.518	2.42	0.457	2.47	0.428	2.46	0.384	2.48
0.473	1.43	0.502	1.96	0.419	1.97	0.389	1.97	0.349	1.97	0.308	1.99
0.402	1.06	0.403	1.52	0.338	1.51	0.310	1.47	0.281	1.50	0.245	1.48
0.232	0.59	0.283	1.02	0.240	1.01	0.238	1.05	0.211	1.02	0.164	1.00
		0.166	0.59	0.142	0.55	0.143	0.59	0.123	0.52	0.112	0.60

Table 2

Solubility of CO₂ in iso-Butyl acetate

273.15		283.15		293.15		298.15		303.15		313.15	
x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]
		0.869	3.84	0.649	3.27	0.662	3.82	0.622	3.80	0.528	3.58
0.826	2.84	0.825	3.40	0.615	2.94	0.618	3.41	0.582	3.43	0.450	2.86
0.783	2.49	0.741	2.92	0.533	2.45	0.552	2.94	0.533	2.95	0.400	2.47
0.664	2.01	0.634	2.44	0.455	1.98	0.484	2.45	0.448	2.42	0.340	2.00
0.525	1.50	0.526	1.91	0.377	1.52	0.400	1.96	0.387	1.96	0.260	1.48
0.405	0.98	0.429	1.51	0.232	0.86	0.329	1.47	0.305	1.49	0.198	0.98
0.229	0.52	0.312	1.03	0.164	0.51	0.242	0.98	0.229	1.00	0.123	0.50
		0.185	0.53			0.132	0.49	0.144	0.48		

Table 3

Solubility of CO₂ in sec-Butyl acetate

273.15		283.15		293.15		298.15		303.15		313.15	
x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]
0.879	3.11	0.883	3.92	0.780	4.14	0.735	4.17	0.720	4.03	0.608	4.22
0.870	2.94	0.820	3.48	0.703	3.57	0.636	3.51	0.638	3.29	0.548	3.50
0.759	2.45	0.731	2.84	0.626	3.01	0.576	3.00	0.558	2.94	0.474	3.00
0.651	1.99	0.650	2.49	0.545	2.47	0.492	2.50	0.494	2.45	0.417	2.51
0.532	1.47	0.543	1.96	0.446	1.94	0.435	1.97	0.407	1.99	0.345	2.01
0.383	1.01	0.435	1.47	0.364	1.47	0.343	1.52	0.334	1.49	0.284	1.52
0.267	0.51	0.322	1.03	0.278	0.99	0.256	1.02	0.237	0.96	0.229	1.03
		0.205	0.51	0.200	0.59	0.160	0.55	0.157	0.56	0.132	0.53

Table 4

Solubility of CO₂ in tert-Butyl acetate

273.15		283.15		293.15		298.15		303.15		313.15	
x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]	x_2^l	P[MPa]
		0.936	4.12	0.780	4.02	0.750	4.17	0.750	4.10	0.630	3.90
0.939	3.05	0.881	3.55	0.727	3.53	0.695	3.58	0.679	3.52	0.567	3.43
0.843	2.56	0.768	3.10	0.658	3.02	0.636	3.04	0.578	2.99	0.524	2.96
0.712	2.09	0.666	2.43	0.605	2.55	0.555	2.55	0.510	2.43	0.426	2.38
0.595	1.54	0.590	2.07	0.520	1.99	0.447	2.01	0.420	2.01	0.375	1.99
0.429	1.06	0.460	1.42	0.442	1.55	0.391	1.59	0.348	1.53	0.300	1.52
0.307	0.60	0.358	1.07	0.348	1.02	0.314	0.98	0.260	1.08	0.231	1.03
		0.264	0.58	0.263	0.59	0.237	0.55	0.192	0.54	0.165	0.59

The pressure dependence of carbon dioxide solubility in the four organic solvents is plotted in

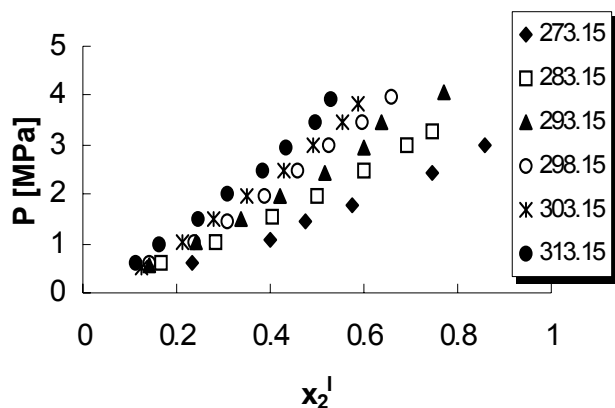


Fig. 1 – Variation of gas solubility with pressure at different temperatures for n-butyl acetate.

the following four figures (figure 1 – figure 4).

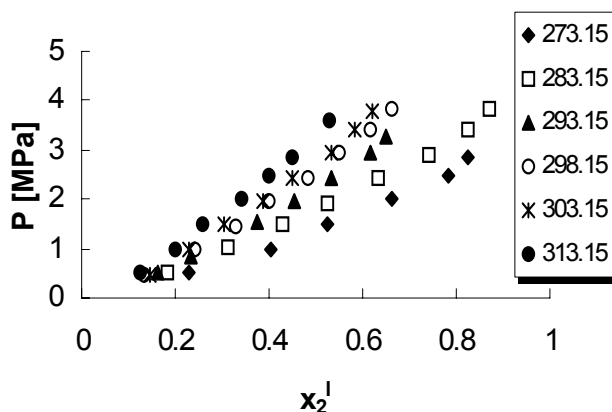


Fig. 2 – Variation of gas solubility with pressure at different temperatures for iso-butyl acetate.

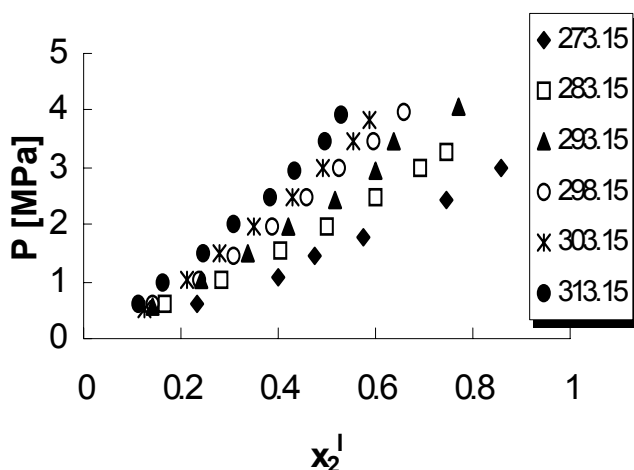


Fig. 3 – Variation of gas solubility with pressure at different temperatures for sec-butyl acetate.

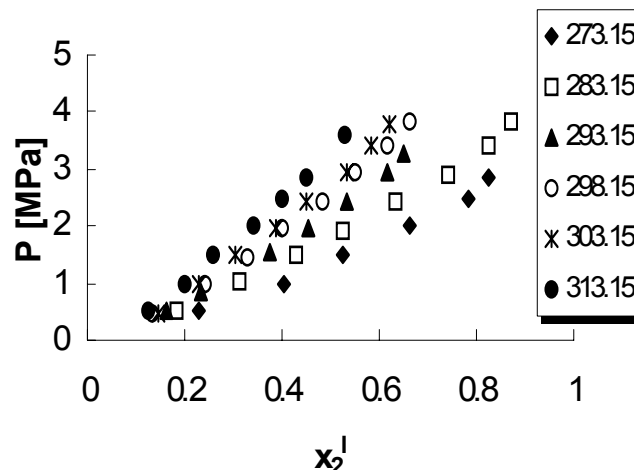


Fig. 4 – Variation of gas solubility with pressure at different temperatures for tert-butyl acetate.

From the analysis of the above figures the isomeric effects on the carbon dioxide solubility in the four solvents investigated are obvious. The most pregnant deviations from Henry's Law are observed at high pressures and the lowest temperatures (273.15 K, 283.15 K). For these four esters the deviations decrease in order: sec-butyl acetate, tert-butyl acetate, iso-butyl acetate, n-butyl acetate).

Some theoretical considerations concerning the liquid-gas solubility process

The particular behaviour of the different gas-liquid solutions investigated can indubitably be attributed to the differences in the intermolecular

interactions between the CO₂ molecules and the solvent molecules. A good measure for these interactions is the solvation energy of the CO₂ molecule to be immersed in the liquid phase.

The solvation energy can be estimated using molecular modeling, where CO₂ is considered in a solvent simulated by a continuous medium having certain characteristics (dielectric constant (EPS), surface tension coefficient (STEN), molecular volume (VMOL) and Solvent Radius (RSOLV)).

We have used in the following such a model known as PCM (Polarizability Continuous Model), where the interaction energies are imagined as a reaction of the molecule to that field having the mentioned characteristics.³²⁻³⁶

The solvation energy has been estimated using the quantum molecular ab initio program GAMESS (RHF, N31-6G, PCM), by means of which the quantum states of the CO₂ molecule

were calculated considering the other component in the mixture as a solvent simulated in PCM approximation.³⁷ The parameters used for such calculations are given in Table 5.

Table 5

The PCM parameters

Solvent	EPS	RSOLV (Å)	VMOL (Å ³)	STEN (dyne/cm)	Molecular Refraction (cm ³)	Solvation Energy (kcal/mol)
n-butyl acetate	5.07	2.877	131.00	24.88	31.62	-2.67
iso-butyl acetate	5.068	2.876	131.40	23.06	31.57	-2.67
sec-butyl acetate	5.135	2.876	131.40	24.11	31.57	-2.68
tert-butyl acetate	5.672	2.876	131.10	22.14	31.58	-2.80

The EPS (dielectric constant) values are found in the literature³⁸ as well as STEN (surface tension coefficient).³⁹

As far as the other quantities are concerned they were calculated using the chemical simulator ChemSketch 5.12 (Advanced Chemistry Development Inc., trial version).

The Molecular Volume (VMOL) found are given in column 4.

The radius of the solvent (RSOLV) has been estimated using an empirical formula:

RSOLV (in Å) = 0.053294 + 0.893127 (Molecular Refraction)^{1/3}, found from linear regression for twelve solvents contained in the database of the GAMESS code.³⁷

Column 7 of Table 5 summarizes the solvation energy values calculated with the PCM approximation as the difference between the total energy in solution and in the initial gas phase.

The solvation energies can be useful to understand the behavior of investigated systems.

CONCLUSIONS

At lower temperatures (273.15 K, 283.15 K) and the highest pressures, for all investigated systems, we have observed deviations from Henry's Law.

The solubility of carbon dioxide in some solvents depends on the molecular symmetry of these compounds. From the table 5 one observe that some physical constants of tert-butyl acetate differ from the other three esters: dielectric constant is greater and the surface tension coefficient is lower. For a higher symmetry configuration is necessary a lower work to create a convenient cavity in the solvent that allows to introduce a carbon dioxide molecule. From some configurations correspond a greater solvation energy. For the

others three esters that possess very close physical constants, the solvation energies are identical.

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