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Solid Solubilities of Methoxyphenylacetic Acid Isomer Compounds in Supercritical Carbon Dioxide

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The solid solubilities of the isomers *o*-, *m*-, and *p*-methoxyphenylacetic acid were measured in supercritical carbon dioxide at 308.2 K over a pressure range of 11–34 MPa. The results were correlated by the Peng–Robinson equation of state and the augmented van der Waals–density-dependent local composition equation. The data showed that solubility increased in the order of *o*-, *p*-, and *m*-methoxyphenylacetic acid, and the latter equation of state gave a much better correlation than the Peng–Robinson equation.

Introduction

A potent application of supercritical fluid extraction is the isolation and purification of a mixture of isomers which have similar physical and chemical properties. Recently solubilities of isomers were measured in supercritical solvents (*1–3*).

In this study, the solid solubilities of the isomers *o*-, *m*-, and *p*-methoxyphenylacetic acid were measured in supercritical carbon dioxide at 308.2 K over a pressure range of 11–34 MPa by a flow-type method. The results were correlated by using the Peng–Robinson (PR) equation and the augmented van der Waals–density-dependent local composition (AVDW–DDLC) equation.

Experimental Section

Materials. *o*-Methoxyphenylacetic acid (purity 98%), *m*-methoxyphenylacetic acid (purity 99.5%), and *p*-methoxyphenylacetic acid (purity 99%) were supplied by Aldrich Chemical. *p*-Hydroxybenzaldehyde (minimum purity 99+%) was obtained from Tokyo Kasei Co. High-purity carbon dioxide (more than 99.9% pure) was supplied by Anjon Gas Co. All chemicals were used without further purification.

Procedure. The flow-type apparatus shown in Figure 1 was built to measure the solubilities of solid components in supercritical carbon dioxide.

The solids were charged into the stainless steel equilibrium cell (approximately 15 cm^3), which was installed in an air bath regulated at 308.2 ± 0.1 K.

Liquefied carbon dioxide, supplied from a gas cylinder with a dip tube, was transferred to a reservoir that acted as a surge tank to dampen any pressure fluctuations when using the metering pump (Milton Roy 920490). The high-pressure carbon dioxide then passed through a preheating coil, thus enabling the solvent to reach the desired temperature.

The solvent was introduced into an equilibrium cell which was packed with the solute to be extracted and alternate layers of glass wool to prevent solid compaction. Glass wool was also inserted at the top of the equilibrium cell to prevent entrainment of the solid.

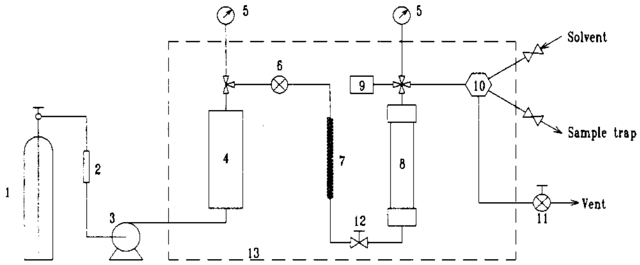

Figure 1. Schematic diagram of the experimental apparatus: (1) CO_2 cylinder, (2) line filter, (3) metering pump, (4) solvent reservoir, (5) Heise gauge, (6) pressure regulator, (7) preheater, (8) equilibrium cell, (9) thermocouple, (10) sampling valve, (11) micrometering valve, (12) valve, (13) air bath.

Table 1. Solubilities of *o*-, *m*-, and *p*-Methoxyphenylacetic Acid Isomers in Supercritical Carbon Dioxide at 308.2 K

o-methoxyphenylacetic acid		*m*-methoxyphenylacetic acid		*p*-methoxyphenylacetic acid	
p/MPa	$10^4 y_1$	p/MPa	$10^3 y_1$	p/MPa	$10^3 y_1$
12.2	0.76	11.7	0.73	12.1	0.19
18.1	1.42	18.0	1.68	18.0	0.40
24.0	2.58	23.9	2.60	24.0	0.81
30.0	3.33	30.0	3.72	30.3	1.18
33.7	3.67	33.9	3.98	33.9	1.44

The pressure of the system was controlled from 0 to 35 MPa with a pressure-reducing regulator (Tescom 26-1-21-24-008). The pressure in the equilibrium cell was measured by using a Heise gauge (0–40 MPa). The maximum error of this gauge is ±0.5% of the full scale reading. The gas flow rate was regulated by a metering valve (HIP 15-11AF2-V) and monitored with a flow meter. The measurement of the solubility of *o*-methoxyphenylacetic acid was carried out at several flow rates varying from 0.1 to 1.0 L/min at a given pressure. The solubilities obtained were independent of the flow rate.

After achievement of equilibrium, the fluid saturated with solid solute emerged from the cell and passed through a sampling valve (Reodyne 7010) equipped with a sample loop.

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Table 2. Physical Properties of Methoxyphenylacetic Acid Isomers

compound	T_m/K	T_b/K	T_c/K	P_c/MPa	ω	V_s/(cm^3/mol)	P^v/Pa	b^a/(cm^3/mol)
o-MPA	395.2–398.2	605.0	819.5	3.25	0.80	123.8	0.0232	64.91
m-MPA	344.2–346.2	579.1	788.9	3.25	0.73	123.8	0.0477	64.91
p-MPA	359.2–361.2	578.5	788.1	3.25	0.80	123.8	0.0527	64.91

[a] Molecular volume is 10% smaller than the Bondi volume.

Table 3. Interaction Parameters and AAD Values for the Methoxyphenylacetic Acid Isomer/CO$_2$ Systems in the PR Equation (308.2 K)

compound	k_{12}	AAD/%
o-methoxyphenylacetic acid	0.260	56.9
m-methoxyphenylacetic acid	0.191	43.8
p-methoxyphenylacetic acid	0.143	43.6

Table 4. Interaction Parameters and AAD Values for Methoxyphenylacetic Acid Isomer/CO$_2$ in the AVDW–DDLC Equation (308.2 K)

compound	k_{12}	AAD/%
o-methoxyphenylacetic acid	0.032	23.4
m-methoxyphenylacetic acid	−0.128	17.7
p-methoxyphenylacetic acid	0.074	32.7

The volume of the external sampling loop was calibrated to be 106.07 μL by a method previously described (*4*).

The sampling procedure using the microsampling valve was similar to the work of Dobbs (*5*).

The total amount of solute was analyzed using a gas chromatograph (HP 5890A) equipped with a capillary column (HP-1), an auto injector, and a flame ionization dectector. In this case *p*-hydroxybenzaldehyde was used as an internal standard. The detectable limit was about 10^{-6} in mole fraction. The accuracy of the solubility of *o*-methoxyphenylacetic acid is considered to be within 4% and 2% in the pressure ranges below 18 MPa and above 18 MPa, respectively. That of *m*- and *p*-methoxyphenylacetic acid is considered to be within 3% in all the pressure ranges.

Results and Discussion

Experimental solubilities of the isomers *o*-, *m*-, and *p*-methoxyphenylacetic acid in supercritical carbon dioxide at 308.2 K up to 34 MPa are given in Table 1. These results show that the compound with the lowest melting point, *m*-methoxyphenylacetic acid, exhibits the highest solubility, and the solubility decreases as the melting point increases.

In this study, the PR and AVDW–DDLC equations were used to correlate the experimental data.

In general, in order to use the local composition model, the chemical potential has to be expressed as a sum of related terms as follows (*6*):

$$RT \ln(\phi_i z) = \mu_i^{\mathrm{rep}} - \mu_i^{\mathrm{ig}} + \mu_i^{\mathrm{sr}} + \mu_i^{\mathrm{lr}} \tag{1}$$

where μ_i^{rep}, μ_i^{ig}, μ_i^{sr}, and μ_i^{lr} represent the effects of the repulsive, ideal gas, short-range, and long-range terms in the chemical potential, respectively.

The AVDW–DDLC model developed by Kim and Johnston (*7*) uses the mixed hard sphere equation for the repulsive chemical potential, and it contains long-range and short-range attractive contributions represented by AVDW (*8*) and DDLC, respectively.

Table 2 shows the properties of the methoxyphenylacetic acid isomers needed in thermodynamic calculations. The boiling point was estimated by using the Lydersen–Foreman–Thodos method in CHEMTRAN (*9*), and the critical temperature and pressure were estimated by using Lydersen's method (*10*). The acentric factor, molar volume, and vapor pressure were estimated by using the Lee–Kesler vapor pressure relation (*11*), the group contribution method (*12*), and the Wagner equation (*13*), respectively.

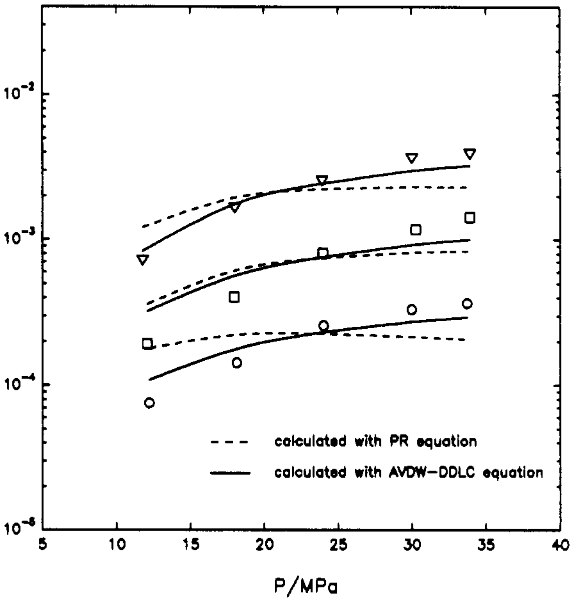

Figure 2. Experimental and calculated solubilities of (○) *o*-, (▽) *m*-, and (□) *p*-methoxyphenylacetic acid in supercritical CO$_2$ at 308.2 K.

The molecular volume required for the AVDW–DDLC model was obtained from the van der Waals volume (*14*).

The average absolute deviation (AAD) values calculated from the PR and AVDW–DDLC equations are tabulated in Tables 3 and 4, respectively.

The predictions by the PR and AVDW–DDLC equations are shown in Figure 2 for the solubilities of *o*-, *m*-, and *p*-methoxyphenylacetic acid in supercritical carbon dioxide at 308.2 K. The estimated value shows the underpredicting trend in the high-pressure range and the overpredicting trend in the low-pressure range.

The predicted values by the AVDW–DDLC equation show better results than those predicted by the PR equation because the AVDW–DDLC equation includes the clustering effect in the highly compressible region, and applies the nonrandomness to the system which has a large difference of polarity.

Glossary

b	molecular volume, cm^3/mol
k_{12}	binary interaction parameter
P^v	vapor pressure, Pa
R	gas constant, 83.14 (cm^3·bar)/(mol·K)
T	temperature, K
V_s	molar volume of the solid, cm^3/mol

Greek Letters

μ	chemical potential
ω	acentric factor

Subscripts

1	solvent
2	solute

b	boiling point
c	critical
m	melting point

Superscripts

calcd	calculated
exptl	experimental
ig	ideal gas
lr	long range
rep	repulsion
sr	short range

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