J. of Supercritical Fluids 79 (2013) 11–18

Contents lists available at SciVerse ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Phase behavior measurement for poly(isobornyl acrylate) + cosolvent systems in supercritical solvents at high pressure

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ARTICLE INFO

Article history:
Received 28 June 2012
Received in revised form
31 December 2012
Accepted 2 January 2013

Keywords:
High pressure phase behavior
CO_2
Poly(isobornyl acrylate)
Isobornyl acrylate
Supercritical solvents

ABSTRACT

We have conducted experiments to obtain cloud-point data of binary and ternary mixtures for poly(isobornyl acrylate) [P(IBnA)] (Mw = 100,000) + isobornyl acrylate(IBnA) in supercritical carbon dioxide (CO_2), P(IBnA) (Mw = 100,000) + dimethyl ether (DME) in CO_2, P(IBnA) (Mw = 100,000) in propane and butane, and P(IBnA) (Mw = 1,000,000) in propane, propylene, butane and 1-butene at high pressure conditions. Phase behaviors for these systems were measured at a temperature range from 323.4 K to 474.1 K and pressure up to 296.7 MPa. The cloud-point curves of P(IBnA) (Mw = 100,000) + IBnA and DME in CO_2 change from upper critical solution temperature (UCST) behavior to lower critical solution temperature (LCST) behavior as IBnA and DME concentration increases, and liquid–liquid–vapor phase behavior appears for the P(IBnA) (Mw = 100,000) + CO_2 + 80.3 wt.% IBnA system. Phase behaviors of P(IBnA) and 50 wt.% IBnA in CO_2 and P(IBnA) in propane and butane show the pressure difference in accordance with Mw = 1,000,000 and Mw = 100,000 of P(IBnA). Also, the solubility curves for IBnA in supercritical CO_2 were measured at a temperature range of (313.2–393.2) K and pressure up to 22.86 MPa. The experimental results were modeled with the Peng–Robinson equation of state (PR-EOS) using a mixing rule including two adjustable parameters. The critical property of IBnA is estimated with the Joback–Lyderson method.

1. Introduction

Poly(isobornyl acrylate) [P(IBnA)] is characterized by having high hardness, good flexibility, adhesion, alcohol resistance, and heat resistance. Therefore, it has been widely used in applications as such active diluents of radiation curing coating, gloss varnish for metal, engineering plastics, and optical fiber coating [1].

The phase behavior of binary mixtures consisting of hydrocarbons with supercritical CO_2 play an important role in chemical separations, supercritical fluid (SCF) extraction, polymerizations, and industrial applications [2–5]. Among representative SCF solvents, CO_2 has received attention from a variety of application fields such as polymer material synthesis, particle generation, foaming, coating, and extraction [6–10]. Also, supercritical CO_2 is widely used as an environmentally friendly solvent (possible to reuse cyclically in process) owing to its inexpensiveness, nonflammability, and nontoxicity [11]. Particularly, it is a good solvent with low molecular weight in nonpolar molecules [12].

The process using properties of supercritical CO_2 has been in the spotlight as a new innovation technology. The studies have been actively done not only for efficiency improvement to produce product of high quality, but also for environmental conservation and energy conservation and so on, which are considered as a social problem in the field of the food industry, chemical industry, pharmaceutical industry, material industry, environmental industry and energy-guzzling industry, which have led to a wide range of applications.

Byun et al. [13–15] have reported studies about phase behavior for the poly(isobutyl acrylate) + CO_2 + isobutyl acrylate system with cosolvents, the effect of cosolvent concentration on phase behavior for poly(isodecyl acrylate) in supercritical CO_2, propane, propylene, butane, 1-butene and dimethyl ether (DME), phase behavior on the binary and ternary mixtures of poly(isooctyl acrylate) + SCF solvents + isooctyl acrylate and CO_2 + isooctyl acrylate systems, and phase behavior of poly(isopropyl acrylate) and poly(isopropyl methacrylate) in SCF solvents and SCF solvent + cosolvent mixtures.

Table 1 lists the critical temperature (T_c), critical pressure (p_c), acentric factor (ω), polarizability (α), dipole moment (μ), and quadrupole moment (Q) of each solvent and cosolvent used in this study [16–19]. C_3 (propane and propylene) hydrocarbons (or C_4 hydrocarbons) are similar in critical properties and polarizabilities. CO_2 has a quadrupole moment, no dipole moment, low critical temperature and pressure (304.3 K and 7.38 MPa), about 100 times higher diffusion constant than water and a low dielectric constant. DME is a Brønsted base (proton acceptor) which can form strong hydrogen bonds with acrylic acid repeat units in the P(IBnA)

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0896-8446/$ – see front matter
http://dx.doi.org/10.1016/j.supflu.2013.01.001

Table 1
Critical temperatures, critical pressures, critical densities, polarizabilities, dipole moments, and quadrupole moments of solvents used in this study [16–19,21].

Solvents	T_c (K)	p_c (MPa)	ρ_c (kg m^{-3})	ω	$\alpha \times 10^{30}$ (m^3)	$\mu \times 10^{30}$ (C m)	$Q \times 10^{40}$ (C m^2)
CO_2	304.3	7.38	469	0.225	2.65	0.00	−14.34
Propane	342.9	4.25	217	0.152	6.29	0.27	4.00
Propylene	365.1	4.62	236	0.148	6.26	1.23	8.34
Butane	425.3	3.80	228	0.193	8.14	0.00	0.00
1-Butene	419.6	3.97	234	0.187	8.24	1.13	8.34
Dimethyl ether	400.0	5.30	258	0.192	5.22	4.34	4.00
Isobornyl acrylate	694.0	2.09		0.666			

polymer. DME has a polarizability of 5.22×10^{-30} m^3 smaller than the values for C_3 and C_4 hydrocarbons, and it possesses a dipole moment and quadrupole moment which is substantially larger than the dipole moment of any of the hydrocarbon solvents investigated.

The purpose of this study was to obtain high-pressure experimental values for the P(IBnA) + solvents + cosolvent systems and the CO_2 + IBnA system. Cloud-point curves were obtained at pressures up to 296.7 MPa and temperatures up to 474.1 K in order to determine the effect of solvent equality, cosolvent composition, and hydrogen bonding on the phase behavior of P(IBnA) + solvent and P(IBnA) + solvent + cosolvent mixtures. The cloud-point curves of P(IBnA) + IBnA (or DME) in supercritical CO_2 change from upper critical solution temperature (UCST) behavior to lower critical solution temperature (LCST) behavior as IBnA and DME concentration increases.

The results of experiments for the CO_2 + IBnA system were correlated with the Peng–Robinson equation of state (PR-EOS) [20] using a van der Waals one-fluid mixing rule that includes two adjustable parameters. The critical pressure, critical temperature and acentric factor of IBnA were estimated by the Joback method with group-contributions, while the vapor pressure was estimated by the Lee–Kesler method [21].

2. Experimental

2.1. Materials

P(IBnA) [CAS RN 69175-26-4, Mw = 1,000,000 and 100,000 (GPC)] and poly(isobornyl methacrylate) [P(IBnMA)] [CAS RN 64114-51-8, Mw = 100,000 (GPC)] and isobornyl acrylate (IBnA) (>96.0% purity; CAS RN 5888-33-5) used in this work were obtained from Scientific Polymer Products, Inc. and used as received. The chemical structure of isobornyl acrylate is shown in Fig. 1. CO_2 (99.8% minimum purity) was obtained from Daesung Industrial Co. and propane (98.0% purity) was obtained from LG Gas (E1). Propylene (99.6% purity), butane (97.0% purity), and 1-butene (99.5% purity) were obtained from Yeochun NCC Co., and dimethyl ether (99.5% purity) was obtained from LG VCM and used as received.

2.2. Apparatus and procedure

Fig. 2 shows the schematic diagram of typical variable volume view cell apparatus used for phase behavior measurement for ternary and binary mixture systems, which has already been described [22]. The binary mixture measurement method has also been described in detail elsewhere [22,23]. Cloud-points are measured for the polymer solutions at a fixed P(IBnA) concentration of 5.0 ± 0.5 wt.%, which is typical of the concentrations used for the polymer + SCF solvents or polymer + SCF solvent + cosolvent mixture. Polymer was loaded into the inside of the cell to within ±0.002 g, and then the cell was purged with nitrogen several times followed by SCF fluid solvent to ensure that all of the air and organic matter had been removed. Liquid IBnA was injected into the cell to within ±0.002 g using a syringe, and supercritical solvent and cosolvent were transferred into the cell gravimetrically to within ±0.004 g using a high-pressure bomb. The mixture was compressed to the desired pressure using an internal piston with water by operating a high pressure generator (HIP Inc., model 37-5.75.60), and the pressure of the mixture was measured with a Heise gauge [Dresser Ind., model CM-108952 (0–345.0) MPa, accurate to within ±0.35 MPa]. The temperature in the cell was measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Yokogawa, model 7563, accurate to within ±0.005%). The system temperature was typically maintained to within ±0.2 K below 473.0 K and ±0.4 K above 473.0 K. The inside of the cell was viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. Light was transmitted into the cell with a fiber optic cable connected at one end to a high density illuminator (Olympus Optical Co., model ILK-5) and at the other end to a borescope. Cloud points for polymer + solvent + cosolvent mixtures were measured at a fixed P(IBnA) concentration of ~5 wt.%. The solution in the cell was well mixed using a magnetic stir bar activated by an external magnet beneath the cell. The binary and ternary mixtures in the cell were heated to the desired temperature and pressurized until a single phase was achieved, and they were maintained in the one-phase region at fixed temperature for 30–40 min at least to reach thermal equilibrium conditions. At the one-phase condition, pressure was slowly decreased until the solution became cloudy. The cloud-point pressure and temperature are defined as a point at which the mixture becomes so opaque that it is no longer possible to

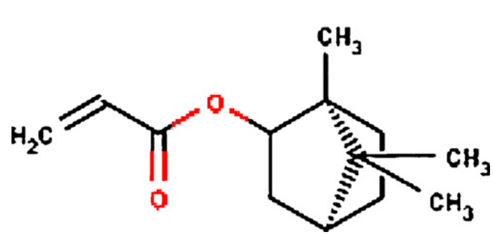

Fig. 1. Chemical structure of isobornyl acrylate (IBnA).

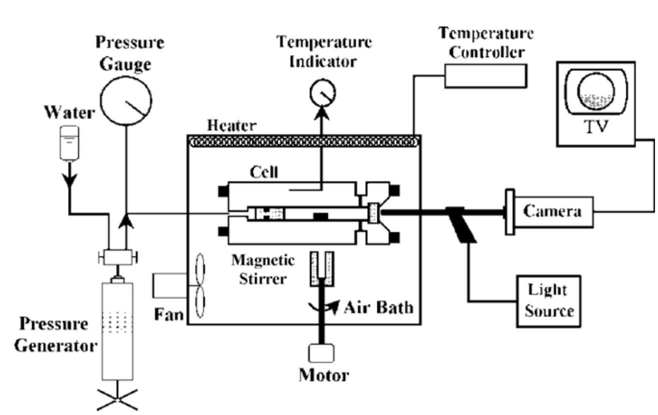

Fig. 2. Schematic diagram of the experimental apparatus.