

Effect of cosolvent on the phase behavior of binary and ternary mixture for the poly(2-dimethylaminoethyl methacrylate) in supercritical solvents



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ABSTRACT

Cloud-point behaviors at pressure up to 230 MPa and temperatures up to 463 K were measured for poly(2-dimethylaminoethyl methacrylate) [P(2-DMAEMA)] in CO₂ (carbon dioxide), C₃H₈ (propane), C₃H₆ (propylene), C₄H₁₀ (butane), C₄H₈ (1-butene), and CH₃OCH₃ [dimethyl ether (DME)], as well as for the P(2-DMAEMA) + 2-dimethylaminoethyl methacrylate (2-DMAEMA) (or DME) in supercritical CO₂. The phase behavior for the P(2-DMAEMA) + CO₂ + 2-DMAEMA mixture was measured in changes of the pressure–temperature (*p*, *T*) slope and with 2-DMAEMA mass fraction of 0.0 wt%, 5.5 wt%, 11.6 wt%, 21.2 wt% and 48.1 wt%. With 51.4 wt% and 60.4 wt% 2-DMAEMA to the P(2-DMAEMA) + CO₂ solution, the cloud point curves take on the appearance of a typical lower critical solution temperature (LCST) boundary, liquid + liquid transition and liquid + vapor transition. The cloud point curves for the P(2-DMAEMA) + CO₂ + (0.0–95.0) wt% DME systems change the (*p*, *T*) curve from upper critical solution temperature region to lower critical solution temperature region as the DME mass fraction increases. The phase behavior curves for P(2-DMAEMA) in alkane hydrocarbons were about 50–60 K higher than P(2-DMAEMA) + alkene hydrocarbons curves, at a fixed pressure of about 70.0 MPa. Also, the impact by 2-DMAEMA and DME mass fraction for the P(2-DMAEMA) + propane + 2-DMAEMA + DME system was measured at temperatures to about 453 K and a pressure range of 4.3–192.9 MPa.

The experimental data was presented for the CO₂ + 2-DMAEMA system at temperatures ranging from 313.2 to 393.2 K and pressures up to 19.07 MPa. The CO₂ + 2-DMAEMA system exhibits type-I phase behavior with a continuous critical mixture curve and was correlated with Peng–Robinson equation of state using a van der Waals one-fluid mixing rule including two adjustable parameters. The property of 2-DMAEMA was obtained by Constantinou–Gani group contribution method.

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1. Introduction

Phase behavior for the binary and ternary mixtures of polymers + supercritical solvents and polymer + supercritical solvent + cosolvent systems at relevant conditions of pressure, temperature and composition are extremely valuable for engineers in the design and operation of various polymer industrial processes [1–3]. Also, high-pressure phase equilibria of binary mixtures for the carbon dioxide + hydrocarbon systems are of interest in a wide range of numerous chemical processes such as separation processes [4,5], supercritical fluid (SCF) extraction [6,7], polymerization processes condition [8] and fine chemical industry.

Recently modern plastic engineering technology is applying methacrylate-based polymers for a variety of uses. Along with methacrylate monomers, methacrylate polymers are used mainly in prostheses, contact lenses, coatings and adhesives [9,10]. Particularly, research into the experimental data of methacrylate monomers in SCF solvents has been valuable for the chemical plant design by providing information on polymer processes and polymerization conditions [11,12]. Poly(2-dimethylaminoethyl methacrylate) [P(2-DMAEMA)] has numerous potential uses, including a nonviral gene delivery vector [13] in water purification [14] and in drug delivery [15], as well as a coating for soil-resistant surfaces [16] and for wettability of surfaces [17], and an ion exchange media for protein separation [18]. In addition, 2-dimethylaminoethyl methacrylate (2-DMAEMA) is used as a component of copolymers in the polymer industry, in coatings and in paper agents [19].

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Previous work has demonstrated that phase boundary for binary and ternary mixtures consisting of polymer and cosolvent in SCF solvent shifted to lower pressures upon addition of cosolvent in the solution [20–24]. Gregg et al. [20] has reported the phase behavior of telechelic polyisobutylene (PIB) in subcritical and supercritical fluids (ethane, propane, dimethyl ether, carbon dioxide and chlorodifluoromethane) at temperature up to 473 K and at pressure up to 200 MPa. Xiong and Kiran [21] have studied solubility of polyethylene molecular weight standards ($M_w = 2150, 16,400, 108,000$ and $420,000$) in near- and supercritical *n*-butane and *n*-butane/CO₂ mixtures at pressures up to 70 MPa. Lora and McHugh [22] determined experimental cloud-point and vapor-liquid data for poly(methyl methacrylate) + CO₂ + methyl methacrylate in the temperature range of 299–443 K, to pressures as high as 250 MPa, and with cosolvent concentrations of 10.4, 28.9, and 48.4 wt%, and CO₂ + methyl methacrylate mixtures at temperatures of 313.2 K, 353.2 K and 378.7 K. Experimental cloud-point data up to 478 K and 248.0 MPa for binary and ternary mixtures of poly(2-ethylhexyl methacrylate) + CO₂ + 2-ethylhexyl methacrylate system was reported by Liu et al. [23]. In addition, the phase equilibria of CO₂ + alkyl methacrylate systems have been revealed by several researchers. McHugh and Byun [24] studied the phase equilibria of ethyl methacrylate and butyl methacrylate in supercritical carbon dioxide in the temperature range from 318.2 K to 383.2 K and at pressures up to about 16 MPa. These systems show the phase behavior of type-I of the six types of simple pressure–temperature diagrams. A detailed description of type-I phase behavior along with its characteristics can be found in the reports by Scott and van Konynenburg [25] and McHugh and Krukoniis [26]. To provide phase behavior information for the design of high pressure processes, measured bubble and dew-point data of binary systems are modeled using the Peng–Robinson equation of state (P–R EOS) [27]. These results can give valuable information for the rational design and operation of the supercritical region.

The goal of this work is to determine the impact of 2-dimethylaminoethyl methacrylate (2-DMAEMA) cosolvent on the phase behavior of P(2-DMAEMA) + supercritical CO₂. Cloud-point data are obtained regarding the effect of DME cosolvent on the P(2-DMAEMA) + supercritical CO₂ binary system. Binary cloud-point curves are also obtained for P(2-DMAEMA) in supercritical propane, propylene, butane, 1-butene and DME. These data show the effect of solvent polarity on the location of cloud-point curves.

The critical properties (T_c, p_c), acentric factor (ω), polarizability (α), dipole moment (μ), and quadrupole moment (Q) of each solvent and cosolvent used in this study are listed in Table 1 [28–32]. C₃H₈ and C₃H₆ hydrocarbons (or C₄H₁₀ and C₄H₈) have similar critical properties and polarizabilities. In addition, C=C (a double bond) within C₃H₆ and C₄H₈ hydrocarbons generates a significant quadrupole moments that favor interaction with weak polar 2-DMAEMA groups in the polymer. The same comparisons are evident with C₄H₁₀ and C₄H₈. Hence, it is possible to determine the impact of quadrupole interactions, which are essentially independent of dispersion interactions. This impact can be evaluated by comparing cloud-point curves from each pair of alkane and alkene solvents. DME has a significant dipole moment that allows the effect of dipole interactions to be compared with that of quadrupole interactions found with alkenes and CO₂. Monomer 2-DMAEMA and DME are used as cosolvents with CO₂. The experimental data for the CO₂ + DME binary system previously is reported by Tsang and Streett [33], which has a critical-mixture curve and a highest pressure of 7.9 MPa at about 335 K. The vapor–liquid equilibria data for the CO₂ + 2-DMAEMA binary mixture were obtained to complement the P(2-DMAEMA) + CO₂ + 2-DMAEMA data presented here. The experimental data for the CO₂ + 2-DMAEMA system has not been found in the literature. These data complement the P(2-DMAEMA) + CO₂ + DME data obtained in the present study.

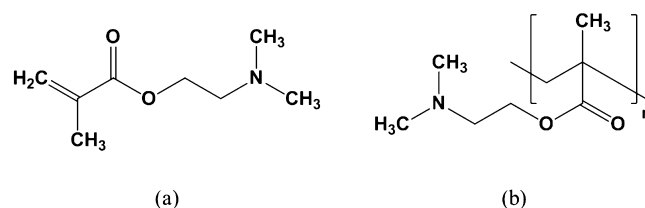


Fig. 1. Chemical structure of 2-dimethylaminoethyl methacrylate (a) and poly(2-dimethylaminoethyl methacrylate) (b).

Therefore, the binary phase behavior data for CO₂ with 2-DMAEMA or DME show if any of the binary mixtures form multiple phases in the (p, T, x) regions in which the cosolvents are used. The CO₂ + 2-DMAEMA experimental data were fit to the P–R EOS [27] in order to calculate phase boundary curves at elevated operating temperatures and pressures.

2. Experimental

2.1. Materials

CO₂ (mass fraction purity > 0.999) was obtained from Daesung Industrial Gases Co., propane (mass fraction purity > 0.980) from LG Gas (E1), and propylene (mass fraction purity > 0.996), butane (mass fraction purity > 0.970), 1-butene (mass fraction purity > 0.995) and dimethyl ether (DME) (mass fraction purity > 0.995) from LG Chemical Co. These materials were used with no further purification. Poly(2-dimethylaminoethyl methacrylate) [P(2-DMAEMA)] ($M_w = 44,000$; M_w/M_n : 1.6; $T_g = 291$ K) and 2-dimethylaminoethyl methacrylate (2-DMAEMA) (mass fraction purity > 0.990) were obtained from Scientific Polymer Product, Inc. The chemical structure of [P(2-DMAEMA)] and 2-DMAEMA are shown in Fig. 1. The P(2-DMAEMA) was in a toluene solution, the polymer solution was placed under vacuum pump (ULVAC KIKO Inc., model GVD-050A, Japan) for at least 10 hrs in the Rotavapor R-205 (Büchi, including bath B-490) to remove toluene. The specifications of all chemicals used are summarized in Table 2.

2.2. Apparatus and procedure

Vapor–liquid equilibrium and cloud-point curves were obtained using a high-pressure experimental apparatus, variable-volume view cell described in detail elsewhere [34,35]. The experimental apparatus was used to construct the (p, x) isotherms for the 2-DMAEMA + CO₂ binary mixtures [34] and the cloud-point curves for the polymer + SCF solvent + cosolvent mixtures [35]. The mixture in the view cell was compressed to the desired pressure by an internal piston displaced with water in a high-pressure generator (Model: HIP 37-5.75-60). The mixture pressure in the view cell was measured with a Heise gauge (Model: Dresser CM-108952, 0–345.0 MPa, accurate to ± 0.35 MPa; Model: Dresser CM-53920, 0–34.0 MPa, accurate to ± 0.034 MPa).

Bubble point, dew point and critical point were measured for the CO₂ + 2-DMAEMA system. The solution in the cell is compressed to the one phase at a fixed temperature. The inside of solution is maintained in the one phase region for at least 30–40 min to reach phase equilibrium. The pressure is then slowly decreased until two phases appear. A bubble point is obtained when small vapor bubbles appear first in the cell, while a dew point is obtained if a fine mist appears in the cell. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volume upon the formation of the two phases. Bubble point, critical point and dew point data for the CO₂ + 2-DMAEMA mixtures were measured and reproduced at least twice to within ± 0.02 MPa and ± 0.2 K. The

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