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High-pressure phase behavior of ternary systems (carbon dioxide + alkanol + hydrophobic ionic liquid)

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ABSTRACT

Some homogeneous liquid mixtures of an ionic liquid and a lower alkanol (e.g., methanol) can be forced to undergo a liquid–liquid phase split (resulting in a three-phase liquid–liquid–vapor (L_1L_2V) equilibrium) by pressurization with a gas. Such systems exhibit the phenomenon of “salting out by a nearcritical gas”. That phenomenon is often observed at temperatures around the critical temperature of the gas in liquid mixtures where at least one of the liquid components is a good solvent for that gas. New experimental results for both the L_1L_2V equilibrium and the corresponding critical endpoint lines of the two ternary systems (carbon dioxide + methanol + 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6]) and (carbon dioxide + 1-butanol + 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [hmim][Tf_2N]) at temperatures between 293 and 333 K are reported. The experiments were performed with an “analytical method”. The liquid–liquid phase split exists only at pressures between a lower critical endpoint line (where both liquid phases become critical and coexist with a vapor phase) and an upper critical endpoint line (where one of the phases becomes critical with the vapor phase while the critical phases coexist with another liquid phase). The compositions of the coexisting three phases L_1, L_2, and V differ considerably; a high-density, ionic liquid-rich liquid phase (L_1) coexists with an alkanol-rich liquid phase (L_2) of lower density and a vapor phase (V) that is virtually ionic liquid-free. For both systems, it was observed that, at constant temperature, increasing pressure shifts the L_1 phase towards higher contents of ionic liquid and gas and less alkanol, whereas in the L_2 phase the mole fractions of ionic liquid and alkanol decrease. Higher temperatures result in a smaller difference between the pressures of both critical endpoint lines. Experimental results for both critical endpoint lines and for the compositions of the coexisting liquid phases are reported.

1. Introduction

Experimental and theoretical work on gas solubility in ionic liquids is often initiated by a process engineering point of view. Consequently, the adherent miscibility and immiscibility phenomena were already considered in some of the earliest studies in that field. For example, in 2001, Brennecke et al. reported that mixtures of CO_2 and [bmim][PF_6] – at that time the most commonly investigated room-temperature ionic liquid – turned out to remain biphasic (liquid–vapor) up to extremely high pressures (3.1 kbar [1]), while CO_2 significantly dissolves into an ionic liquid-rich liquid phase, the coexisting vapor phase remains virtually ionic liquid-free [2].

Therefore, the idea to employ CO_2 to extract components from an ionic liquid solvent medium without cross-contamination emerged. One of the most discussed topics is the question “Can the unique characteristics of ionic liquids be exploited for applications where conventional solvents, like, e.g., volatile organic compounds (VOCs), fail?” That question arises as most ionic liquids have very low (nearly negligible) vapor pressures and as they are considered to be environmentally benign. Supercritical fluids, particularly supercritical CO_2, are forming the other major alternative solvent group. Most important from the practical point of view, however, is the fact that both ionic liquids and supercritical fluids commonly share an outstanding versatility. Supercritical fluids (which can be described as compressed gases) have tunable thermodynamic properties (via the variables pressure and temperature). Ionic liquids (being salts) can be molecularly tailored to feature specific thermodynamic as well chemical properties by a subtle selection of cations and anions. The capability of CO_2 to induce a phase split in homogeneous liquid mixtures at relatively moderate pressures (in other words, a salting-out effect) has been known for some decades [3,4]. Typical candidates for such liquid mixtures

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are aqueous solutions of hydrophilic organic solvents, e.g., an alkanol, pressurized by a so-called "nearcritical" gas, e.g., CO_2, when the operational temperature does not deviate drastically from the critical temperature of the gas. The phenomenon "salting out with a nearcritical gas" manifests in a three-phase liquid–liquid–vapor (L_1L_2V) equilibrium confined to a certain defined pressure, temperature, and composition region. The phase split results from the influence of the dissolved gas on the intermolecular interactions between the components of the liquid phase, as, for example, CO_2 has a higher solubility in methanol than in water, and, consequently, a water-rich phase (L_1) coexists with a methanol-rich phase (L_2). Ionic liquids, in turn, were observed to display a somehow similar behavior during respective experiments. The binary system ([bmim][PF_6] + methanol) is completely miscible at ambient conditions, and, as already mentioned, a significant amount of CO_2 can be dissolved in both solvent components [2].

The next step was bringing these two conceptions together, triggered by those apparent similarities, and the expected salting-out effect was first reported by Scurto et al. for the ternary system (CO_2 + methanol + [bmim][PF_6]) in 2002 [5]. This phenomenon is particularly appealing for extraction. Control of number of phases and composition of coexisting phases can be done via pressure, and, referring to a statement by Nunes da Ponte and Rebelo [6], a cascade of phase changes gives a tool for integrated reaction and separation. An opportunity is given to administer the number of phases in a way where the formation of a second liquid phase (L_2, CO_2-rich) can be used to separate reaction products that originate from an ionic liquid reaction medium and to regenerate the ionic liquid phase. Scurto et al. observed in their investigation of the system (CO_2 + methanol + [bmim][PF_6]) [5] that, at a constant temperature, starting from a liquid–vapor equilibrium at low pressures, an increase of CO_2 pressure leads to an uptake of CO_2 in the liquid phase and, at a certain pressure, a second liquid phase (L_2) is generated. Further increase of CO_2 pressure squeezes the ionic liquid out from the upper liquid phase L_2 into the bottom liquid phase L_1. When the upper liquid phase L_2 and the vapor phase V merge at the upper critical endpoint, that phase is practically free of any ionic liquid.

Today, various applications that employ ionic liquids have been described and the interest in further applications is serious and vibrant [7]. Nunes da Ponte and Rebelo [6] also emphasized that a direct analysis of the coexisting phases is desirable if not mandatory to assess their potential for becoming implemented in reaction and/or extraction techniques. But even in 2008, Kühne et al. [8] came to say, "However, one of the challenges to apply this concept to existing processes is the lack of information on the phase behavior of different systems".

Thus, the intention of our present work is to extend the knowledge on the particular phase behavior of such ternary systems with providing new experimental data. Our group has a long-running experience in investigations of the salting-out phenomenon with nearcritical gases (cf., [9–11]). An analytical method was developed that allows the visual determination of critical endpoints as well direct sampling from the coexisting liquid phases with subsequent analysis of composition and density. Prior to this work, the equipment was also used for investigations on the high-pressure multiphase behavior of aqueous solutions of an alcohol (1-propanol as well as 2-propanol) which were pressurized by ethene [10]. Here, experimental data are reported for two ternary systems, where the "gaseous" component is carbon dioxide, one of the solvent components is a room-temperature ionic liquid ([bmim][PF_6] or [hmim][Tf_2N]) and the other solvent component is an alkanol (methanol or 1-butanol) at temperatures between 293 and 333 K and pressures between about 4 and 12 MPa, respectively. The experiments comprised the determination of the corresponding critical endpoint lines including the binary critical line for the vapor–liquid equilibrium of one binary subsystem (CO_2 + methanol) as well as the composition of the coexisting liquid phases L_1 and L_2 in the three-phase L_1L_2V equilibrium for both ternary systems.

2. Experimental section

2.1. Materials and sample pretreatment

Carbon dioxide (3.5, volume fraction ≥ 0.9995) was supplied by TV Kohlensäure Technik und Vertrieb GmbH, Ludwigshafen, Germany. Acetonitrile (p.a., mass fraction > 0.995 (GC)), methanol (p.a., mass fraction > 0.998 (GC)), and 1-butanol (p.a., mass fraction > 0.998 (GC)) were all from Merck KGaA, Darmstadt, Germany. CO_2 and the organic solvents were used without further purification. Both ionic liquids, [bmim][PF_6] ($C_8H_{15}F_6N_2P$, high purity, mass fraction > 0.99; $M = 284.18$) and [hmim][Tf_2N] ($C_{12}H_{19}N_3F_6O_4S_2$, high purity, mass fraction > 0.99, $M = 447.42$) were supplied by IoLiTec GmbH, Denzlingen, Germany. The ionic liquids were degassed and dried under vacuum over a period of about 24 h to remove traces of water and other volatile impurities. These procedures were identical to those applied in previous investigations on gas solubility in pure ionic liquids (cf., e.g., Kumełan et al. [12] and the references cited therein). Karl Fischer titration analysis yielded a water mass fraction of 0.00019 for [bmim][PF_6] and 0.00025 for [hmim][Tf_2N], respectively.

2.2. Apparatus

The high-pressure equipment operates according to a static-analytical method. It is designed for working temperatures between about 263 and 353 K and up to a maximum pressure of 30 MPa. The setup basically originates from studies on high-pressure phase equilibria in ternary systems (nearcritical gas + water + organic solvent [10]) as well as the partitioning of biomolecules to the coexisting liquid phases in such systems [13,14]. Originally, the apparatus was adapted to investigate multi-component systems, where the entire phase-forming compounds (i.e., water, an alkanol, and a nearcritical gas) display high volatility and thus can be analyzed by gas chromatography (cf., Ref. [10] and the corresponding references cited therein). Later, the analysis of low-volatile and high-molecular biomolecules required the addition of a HPLC device (for the time being equipped with a UV/vis detector) [13].

In the present work, the analytical parts had to be adapted for ionic liquids, and an additional refractive-index (RI) detector was assembled to the equipment. Fig. 1 illustrates the entire experimental arrangement.

The cylindrical, pivot-mounted high-pressure cell (C) is made of non-magnetic stainless steel. It has an internal volume of about 30 cm^3 and is equipped with sapphire windows (W; diameter = 16 mm, Badische Industrie-Edelstein GmbH, Elzach, Germany) at both sides to allow for visual observation of the cell content. Further, the cell is surrounded by an insulating heating jacket made of the same material. Homogenization of the cell content is accomplished by a small magnetic stirring rod which is driven from outside. Two sample loops are connected to the cell, and, due to the pivotal construction, the whole cell can be rotated, so that the coexisting phases can be sampled and analyzed individually. The operational temperature is monitored by two calibrated platinum resistance thermometers (PT; Heraeus Sensor Technology GmbH, Kleinostheim, Germany) coupled with a high-precision resistance bridge (F26, Automatic Systems Laboratories, New Addington, United Kingdom), and electronic pressure sensors (DA; suitable for pressures of 0–20 MPa and 0–40 MPa, respectively; WIKA GmbH,