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Volume of mixing and solubility of water in Athabasca bitumen at high temperature and pressure

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ABSTRACT

With the merging of operating conditions for proposed high-temperature production and refining processes for heavy oil and bitumen, there is a growing interest in the phase behavior, thermophysical properties and reaction outcomes for water + heavy hydrocarbon resource mixtures at elevated temperatures and pressures. Athabasca bitumen, from Canada, is a commercially exploited hydrocarbon resource where 50 wt.% of the material possesses a nominal boiling point exceeding 797 K. In a prior publication, the phase behavior type of the Athabasca bitumen + water binary was identified experimentally as Type IIIb, according to the vanKonynenburg and Scott naming scheme. The present contribution focuses on the volume of mixing and the solubility of water in the Athabasca bitumen-rich liquid phase over the temperature interval 523–644 K and over the pressure interval 3.9–26.2 MPa. The measurements were obtained using a high-pressure variable-volume beryllium-walled view-cell, equipped with non-intrusive X-ray transmission tomography. X-ray tomography permits visual observation of the number of coexisting phases, and their corresponding volumes. Phase volume and density measurements were validated by reproducing published values for 1-methyl naphthalene up to 573.8 K. Water solubility values were validated by reproducing data for the 1-methyl naphthalene + water and toluene + water binaries up to 573.2 K and 553.2 K, respectively. Measured solubility and excess volume values are also placed in a broader context by comparison with pertinent literature data.

1. Introduction

Phase behavior [1] mutual solubility and other physical property data for water + hydrocarbon mixtures are necessary for the development, design and optimization of a variety of high temperature industrial processes such as bitumen production and upgrading. The properties of mixtures of water + Athabasca bitumen and other heavy hydrocarbons are of growing interest because water, at high temperature, provides a reaction medium for upgrading heavy hydrocarbons [2–10] that may prove to be preferred over conventional hydrocarbon based ones. In addition to upgrading applications, the solubility and volume of mixing of water in heavy hydrocarbon resources are essential to the development of production models for oil and bitumen production processes such as the Steam Assisted Gravity Drainage (SAGD) method where net water consumption, and water recycling present both environmental and economic challenges [11]. This study was also motivated by the potential to reduce the overall cost of production of finished products in the future by merging aspects of fluid composition and operating conditions for in situ production and upgrading processes. For example, water is already used in production and the solvent properties and solubility of water in the near-critical region make it an efficient medium for carrying out chemical reactions, and the changes of water solubility with temperature and pressure may facilitate subsequent water–hydrocarbon separation and water reuse.

The thermophysical properties and phase behavior of water–hydrocarbon mixtures at high-temperature have received limited attention and there are few benchmark data sets available to underpin industrial process design, development or optimization. Data are available for a limited number of pure hydrocarbon + water and hydrocarbon mixture + water cases. Maczynski et al. [12–23] reviewed and critically compiled the published data for mutual solubilities of C5–C36 hydrocarbons + water/seawater mixtures. Their compilation provides a comprehensive collection of mutual binary solubility data over a broad range of temperatures. Brown et al. [24] provide solubility data for binary mixtures of water with acetophenone, anisole, 1-octanol and toluene in the temperature range of 370 K to 550 K. Tsonopoulos et al. [25–30] measured and correlated mutual solubility data for hydrocarbon + water binaries under three phase liquid–liquid–vapor equilibrium conditions up to

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their upper critical end points (UCEP) where for example, the phase compositions of both liquid phases for homologous series of alkanes, alkyl cyclohexanes, 1-alkenes, and alkyl benzenes at high temperatures are reported [30]. Chandler [31] reported the mutual solubilities of toluene + water and benzene + water up to 473 K along the LLV three-phase curve up to a pressure of 17.2 MPa. Anderson et al. [32] investigated the mutual solubilities and vapor pressures for four binary and one ternary aqueous mixture. Leet et al. [33] studied the mutual solubilities of water and six polycyclic aromatic hydrocarbons including N-, O-, and S-containing polycyclic aromatics at high temperatures. Neely et al. [34] measured the mutual hydrocarbon–water liquid–liquid equilibrium data for mixtures comprising the benzene, toluene, and 3-methylpentane in a temperature range from ambient temperature up to 500 K. Brunner [35,36] studied the phase behavior and critical phenomena of water + n-alkanes binary mixtures (up to n-eicosane) and water + aromatic compounds at pressures and temperatures exceeding the critical point of water. Phase equilibrium measurements for water + tetralin and 1-methylnaphthalene, up to 673.2 K, are also available [37]. Phase equilibrium data for reservoir fluids, including water, are very scarce. De Hemptinne et al. [38] investigated the phase equilibria of petroleum fractions + water mixtures and Pedersen [39] reported equilibrium compositions, three-phase equilibrium pressure and temperatures for water + petroleum reservoir fluids up to 473 K.

High-temperature experimental phase density and excess volume data for hydrocarbon + water mixtures are limited to a few studies. Abdulagatov et al. [40–45] conducted measurements for water + n-pentane to n-octane, and water + benzene at temperatures near the critical point of water and report liquid phase thermodynamic properties and partial molar volumes. Furutaka et al. [46–50] measured compositions and densities of hydrocarbon-rich phases at equilibrium for water + benzene, toluene, ethylbenzene, n-hexane and n-decane mixtures in the vicinity of the upper end critical point of these mixtures using infrared spectroscopy. Their work focused on unsaturated hydrocarbon-rich phases at pressures above the LLV three-phase curve. They report large and positive volumes of mixing for hydrocarbon-rich liquids. Hnedkovsky et al. [51,52] present phase density and partial molar volume data of hydrocarbons at infinite dilution for water-rich liquid phases where the hydrocarbons include benzene, toluene, and cresols over the temperature interval 298.15–573.15 K.

In our prior work we showed that the Athabasca bitumen + water pseudo binary mixture exhibits Type IIIb phase behavior [1] according to the naming scheme of vanKonynenburg and Scott [53]. Type IIIb phase behavior occurs because for this hydrocarbon + water mixture the hydrocarbon critical temperature is much higher than the critical temperature of water [35,36]. The key characteristics of Type IIIb phase behavior are illustrated in Fig. 1. The LLV three-phase equilibrium curve extends from low temperature up to the vicinity of the critical point of water where it is intersected by the liquid–vapor critical locus extending from the critical point of water. This intersection, the upper critical point (UCEP), is where the water-rich liquid and vapor phases become critically identical. Above the UCEP temperature a maximum of two phases arise in the phase diagram. This phase behavior contrasts with the behavior of typical hydrocarbon + water mixtures, available in the literature, which exhibit Type II or Type IIIa phase behavior as discussed previously [1]. For Type IIIa phase behavior, the hydrocarbon-rich phase becomes critically identical to the vapor phase at the upper critical end point. At low temperatures, the properties of Type IIIa and Type IIIb binary mixtures differ little but they are expected to diverge at high temperatures. The high temperature properties of the hydrocarbon-rich liquid phase are the focus of the current study where phase compositions, and excess volumes for model hydrocarbon + water mixtures are used to benchmark measurements for water + Athabasca bitumen mixtures and to place them in a broader context.

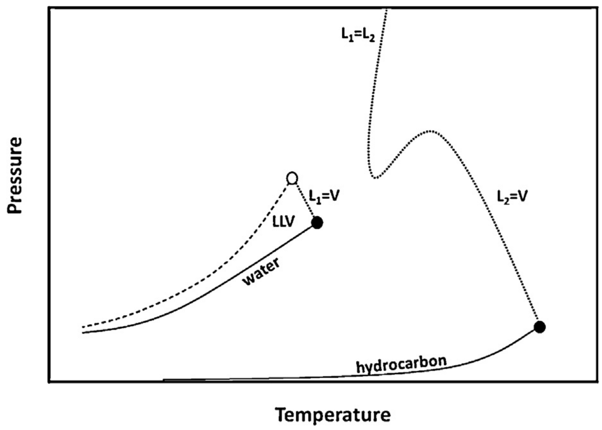

Fig. 1. Type IIIb pressure-temperature projection for water + hydrocarbon binary mixtures. (●) Critical points for the water and the hydrocarbon, and (○) the UCEP for the mixture. (⋯⋯) and (- - -) are the critical locus and LLV three-phase curve respectively and (—) denotes vapor/bubble pressure curves [1].

Table 1
Properties for Athabasca bitumen [21].

	wt.%
Elemental composition	
Carbon	83.2 ± 0.9
Hydrogen	9.7 ± 0.4
Nitrogen	0.4 ± 0.2
Sulphur	5.3 ± 0.2
Oxygen	1.7 ± 0.3
SARA analysis	
Saturates	16.1 ± 2.1
Aromatics	48.5 ± 2.3
Resins	16.8 ± 1.2
Asphaltene (C_5)	18.6 ± 1.8

2. Experiments and methodology

Athabasca bitumen, provided by Syncrude Canada Ltd., Alberta, Canada, was produced by a commercial froth treatment process. SARA analysis for Athabasca bitumen is presented in Table 1 [54]. Water (99.99 wt.%, HPLC grade supplied by Sigma–Aldrich), toluene (99.9 wt.% supplied by Fischer Scientific), and 1-methyl naphthalene (99.0 wt.% supplied by Acros Organics) were used without further purification.

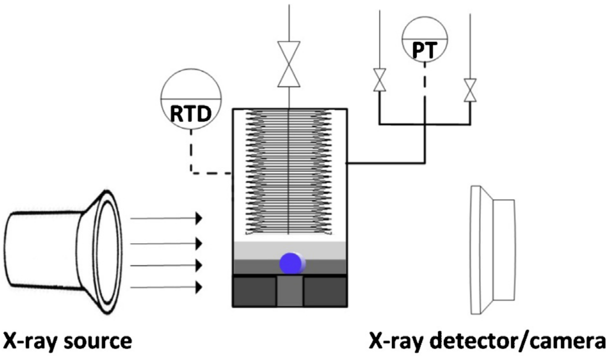

Fig. 2. The X-ray view cell schematic. The view-cell is equipped with a variable volume bellows and a magnetic stirrer.