

Experimental pressure versus temperature isochoric - isoplethic curves for systems related to the supercritical hydrogenation of polybutadiene

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INTRODUCTION

Linear low density polyethylene of low polydispersity index could be obtained by hydrogenating low polydispersity index polybutadienes (PBs). In conventional hydrogenation processes, the system always presents, at least, two fluid phases during the reaction progress. The presence of an interphase implies lower mass transfer rates. This could be overcome by using a supercritical fluid as reaction medium, so that the hydrogenation process occurs, in principle, under single fluid phase conditions. To hydrogenate the PB under supercritical conditions, the solvent (or solvent mixture) should be able to simultaneously dissolve the PB, the hydrogen and the reaction products. The high asymmetry of the reactive mixture, which is in part due to the large difference in size between the H₂ and PB molecules, implies a high immiscibility level in the absence of the supercritical solvent or solvent mixture. In particular, the 'PB + solvent mixture' system should be homogeneous at the conditions of temperature, pressure and PB concentration range at which the PB hydrogenation is to be carried out. The purpose of this work is to experimentally find the conditions under which a number of 'PB + solvent mixture' systems, and related subsystems, are homogeneous. In a typical experiment, an in-house constant volume cell is loaded with a known amount of a known composition mixture. Next, the pressure is measured at set temperature, covering the temperature range of interest. Clearly, the measured and recorded pressure versus temperature curve is an isopleth (constant overall composition) and it is also an isochor (constant overall density). Slope changes in the curve imply changes in the phase condition, i.e., this experimental technique also provides saturation conditions. At high enough temperature, the system becomes homogeneous, and it remains so at higher temperatures. Pressure vs Temperature isochoric-isoplethic trajectories were measured in this work for a number of pure solvents, solvent mixtures, and systems made of PB and a solvent mixture. The experiments were performed at varying overall density and varying overall mixture composition.

MATERIALS & METHODS

We synthesized the PB by anionic polymerization under a high vacuum inert atmosphere. The obtained PB number average molecular weight (M_n) is 1588 g/mol and the weight-average molecular weight (M_w) is 1764 g/mol. The PB molecular weight is significantly less than those of our previous studies, [2-3]. This implies homogeneity conditions less severe than those for higher molecular weight PBs. The other materials are the following: Diethyl ether (DEE), purity 99.8% w/w, Dorwill (Grand Bourg, Argentina), and n-propane (C3), purity 99% w/w, Transportadora de Gas del Sur (Bahía Blanca, Argentina). The in-house apparatus is made of a cylindrical constant volume (12.23 cm³) cell (stainless steel, OD: ½", wall thickness: 2.5 mm). It has a valve for loading/discharging the solvents. The cell temperature and pressure are respectively measured using a "K" type thermocouple (± 0.5 °C) and a manometer (± 2.5 bar). The atmospheric pressure is measured by using a digital barometer (paroscientific, Inc. model 735). The readings of both

pressure sensors are added to obtain the absolute pressure. The reactor temperature is kept constant by a Novus N480D PID controller which acts on a couple of heating resistances (250 W each). An aluminum cylindrical shell is placed in between the resistances and the cell wall. The cell, shell, resistances and valve, are all placed within a thermally insulated chamber. The experimental procedure is as follows: [a] PB is loaded into the cell having it open to the atmosphere. [b] the cell is purged with the gaseous component of the system to be studied. [c] liquid solvent is loaded by using a regular syringe. [d] the cell is closed. [e] the gaseous component is loaded using an auxiliary cell. The amounts of PB, liquid solvent and gaseous component fed into the cell are all gravimetrically known. Once the cell is loaded, it is placed in the chamber. Next, the desired temperature is set. The temperature and pressure are measured after equilibrium is reached. This is repeated for the temperature range of interest.

RESULTS & DISCUSSION

To validate the experimental technique, isochoric isopleths were measured for the pure substances propane, diethyl ether, n-pentane and dimethyl ether, at temperature ranges covering two-phase and single-phase conditions; and compared with data from the NIST Chemistry Webbook [6]. The same was done for the propane + n-pentane system. In this case our data were compared to those of Sage et al [9]. As an illustrative example of the obtained experimental results, Fig. 1 depicts the evolution of pressure as a function of temperature for the system C3+DEE+ PB, at two different conditions. The observed changes in slope indicate phase transitions which are here interpreted as bubble points. The high temperature segments show a characteristic linear behavior of an isochoric-isoplethic homogeneous system.

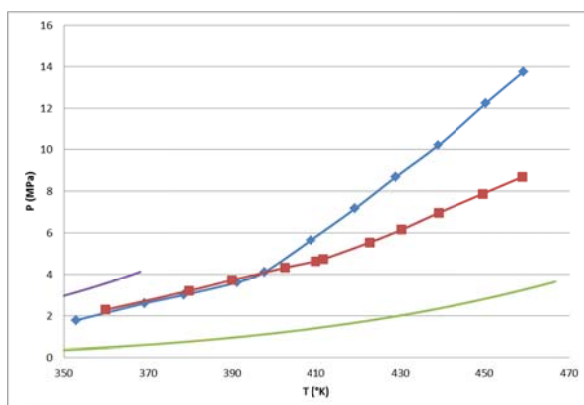


Figure 1. Pressure vs Temperature at constant overall composition and constant overall density (ρ), for the system C3+DEE+ PB. Lines and markers: Blue: $\rho=0.40$ gr/ml; XC3=0.64; %PB=3.2%; Red: $\rho=0.31$ gr/ml; XC3=0.63; %PB=3.9%. XC3: propane mole fraction. %PB: polybutadiene weight percent. Pure compound vapor-liquid equilibrium curves: Green: DEE [6]. Violet: C3 [7]. Consecutive markers are connected with straight lines, for a better visualization.

CONCLUSIONS

The simple and robust isochoric-isoplethic method is useful for detecting potential homogeneity conditions to carry out PB hydrogenation reactions. The experimental results obtained in this work will be useful to guide future hydrogenation experiments that will be conducted in batch mode.

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