

PHASE EQUILIBRIA IN MIXTURES OF POLYMERS AND SUPERCRITICAL FLUIDS. EXPERIMENTAL SETUP AND INTRODUCTORY MEASUREMENTS.

J. Gregorowicz*, M. Łuszczuk, Z. Fraś

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224
Warszawa, Poland
gregor@ichf.edu.pl, fax: +48 22 631 16 19

An apparatus for measuring high-pressure phase equilibria at temperatures up to 473 K and pressures up to 2000 bar is presented. The applied method of the construction of a phase diagram for a fluid mixture requires the determination of families of P-T diagrams of constant composition (isopleths). The equipment consists of a variable volume view cell, temperature stabilizing system, pressure generation system and a system that make loading of the cell with a gas component possible. The equipment and the experimental procedure were tested by measuring phase equilibria for two mixtures ethylene – eicosane, and carbon dioxide – squalane. Phase equilibria in the system ethylene + linear low molecular weight polyethylene were also studied.

INTRODUCTION

Supercritical fluids are of continuing interests and importance as tunable solvents and reaction media in the chemical process industry. Their unique properties make them particularly attractive in polymer processing. In particular supercritical solvents have been regarded as prospective media for polymerization processes, polymer purification and fractionation, and as environmentally preferable solvents for powder formation. Understanding the phase behaviour in supercritical fluid – polymer solutions is a necessary condition to fully exploit the potential of supercritical fluid – based polymer processing. In this work a new apparatus for high pressure phase behaviour measurements is presented. Although we are going to focus in the future work on polymer solutions the equipment presented here has much wider application.

METHOD AND EQUIPMENT

The applied method of measurement is based on detection of phase transitions for constant composition mixtures as a function of pressure and temperature (isopleths). From the set of isopleths other sections (T-x and P-x) and full phase diagram can be deduced. The interpretation of the experimental data obtained requires a basic knowledge on theory of phase diagrams. A number of equipments based on this idea have been described in the literature. The construction presented in this work is based on ideas presented by Melichen et al.[1], Condo et al. [2] and Chan et al. [3].

A schematic diagram of the equipment for the high pressure phase equilibria measurements is depicted in Figure 1. The heart of the apparatus is a variable – volume high pressure view cell. It is constructed of titanium which ensures strength and at the same time comparatively low weight. The body of the cell is cylindrical in shape. Along its axis of symmetry a bore of 6 mm is drilled. The bore is closed off at one end by a sapphire window and an aluminum piston is placed inside. In the space between the window and the piston an investigated sample is placed. Through the other end of the cell's bore a working fluid enters

the cell to move the piston and pressurize the sample. Through the window the cell contents is illuminated by light from a boroscope bulb and reflected off the face of the piston. This makes it possible to detect phase transitions visually. Two pumps, one high-pressure hand pump and one high-pressure motorized pump, are used for charging the solvent and controlling the pressure of the cell respectively.

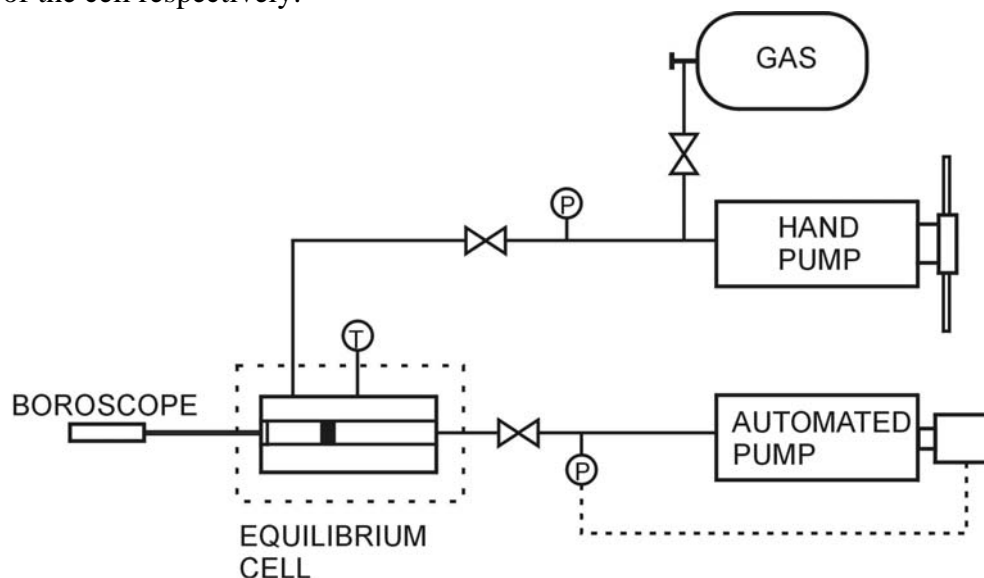


Figure 1. Schematic diagram of the high pressure equipment.

The first step of the experimental procedure is loading of the equilibrium cell with known amount of all components. The composition of the investigated mixture is established by weight. A stirring bar is also placed in the cell to ensure proper mixing during experiment. Then the mixture is pressurized, heated, and equilibrated by stirring to form a homogeneous solution. After equilibration, pressure is slowly decreased at constant temperature and phase transition is detected visually. In case of solid – fluid transition usually temperature is decreased at constant pressure.

MEASUREMENTS

The experimental setup and the procedure were tested by measuring phase equilibria for the binary systems composed of high molecular weight aliphatic hydrocarbons and ethylene or carbon dioxide. These mixtures can be regarded as models for polymer solutions. In this work phase equilibria for two systems: ethylene + eicosane and carbon dioxide + squalane were measured. The first system was chosen due to our interest in solid – liquid equilibria and the second one to check the performance of the equipment at high pressures. The results obtained agree with the literature data within experimental accuracy what proves correctness of the applied experimental procedure and proper construction of the apparatus. The phase equilibria for the system ethylene + linear low molecular weight polyethylene ($M_w = 600$ g/mol) were measured. The particular attention was paid to the solid liquid transition.

REFERENCES

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