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Phase equilibria and diffusion coefficients in the poly(dimethylsiloxane) + n-pentane system

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Abstract

This work presents a comparison of vapor–liquid equilibria (VLE) data and diffusion coefficients of the system poly(dimethylsiloxane) + n-pentane measured using three experimental methods: gravimetric sorption, pressure decay and inverse gas chromatography. These methods differ in the underlying experimental principles as well as in the complexity of data analysis. Despite of these differences, the agreement of the measured VLE data is excellent. Diffusion coefficients were measured with satisfactory accuracy using the gravimetric sorption as well as the pressure decay method. The VLE data are modeled using the PC-SAFT equation of state.

Keywords: Vapor–liquid equilibria; Diffusion coefficients; Experimental methods; Poly(dimethylsiloxane); n-Pentane; PC-SAFT

1. Introduction

Without doubt John Prausnitz and his work had and still have a tremendous influence on the way many processes are run in industry, e.g. in the chemical and petrochemical industry, in the polymer industry, and in life-science oriented areas. His development of molecular-thermodynamic models and his experimental findings have not only lead to a better understanding of physico-chemical effects that are important in industry, but to a better design of many industrial processes, leading to considerable savings of energy and other resources and to products of higher quality. As John Prausnitz likes to point out “Chemical engineers exist because society wants chemical products that will satisfy human needs. Chemical Engineering is driven by society’s wish for a better life.” [1].

In this work, where we present a comparison of vapor–liquid equilibria (VLE) data and diffusion coefficients of a polymer–solvent system, we would like to remind of the influence of John Prausnitz on the development of modern polymer thermodynamics, on its development in Germany, and on its application in industry.

The inspiration of John Prausnitz not only comes through his famous books and a countless number of scientific papers, but through lectures and through personal encounters. He has been a visitor of many places and research groups all over the world. Very often we have seen him in Germany. Some of us (R.D. and O.P.) even had the privilege to work with him and to learn from him in Berkeley. His profound knowledge of the German thermodynamics community has made him an important referee and has thus directly influenced our careers (G.S. and R.D.). John Prausnitz always wants to go beyond thermodynamics and chemical engineering, to broader our view to new developments in science and to important things beyond science. His writing is unique, his letters often are like poetry, quality and quantity of his letter writing is beyond comparison.

Many years ago, John Prausnitz raised our interest in molecular thermodynamics of polymer systems, either in academia (G.S. and K.K.) or in industry (R.D. and O.P.). Nowadays, Bayer Material Science is one of the leading producers of high-quality polymers, and polymer thermodynamics has become the major field of activity of the Thermophysical Property Group of Bayer Technology Services. The precise knowledge of thermophysical properties of polymer systems can have a strong influence on the design of polymer production processes, covering many unit operations from the purification of the educts, the polymerization and different separation steps for product purification

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[2]. In general, polymer systems show strong deviations from ideal behavior. The insufficient availability of reliable predictive methods for these systems coupled with the required high quality of the thermodynamic properties often lead to the necessity of experiments.

Permanently increasing demands for higher polymer quality, e.g. optical grade quality polycarbonate for high-density optical storage systems, lead to the development of new techniques for polymer finish processing. Some major goals of polymer finish processing are the efficient removal of undesired impurities from the polymerization process like catalyst, monomer, oligomer, and solvent molecules as well as (mostly) white color, homogeneity, and constant quality. Some of these issues are directly connected with the phase equilibria and diffusion coefficients of the involved systems.

In order to be able to use standardized equipment for testing the applicability of new techniques and to get the basic understanding of the process, e.g. two-phase flow in highly viscous fluids, very often model systems are used. The industrial polymer + solvent system is substituted by a polymer + solvent model system, which has been chosen that it exhibits very similar relevant properties at ambient conditions like the industrial polymer + solvent system at process conditions (up to 700 K). Several of these model systems are based on poly(dimethylsiloxane) (PDMS), because the major thermophysical properties of PDMS have been investigated well and PDMS is available with very different average molecular weights covering a wide range of viscosities.

Additionally, in polymer thermodynamics the comparability of experimental data is often difficult to estimate. This is caused by the fact that polymers differ not only in chemical structure (like solvent molecules) but also in branching, molecular weight, molecular-weight distribution, etc.

In this study, we present vapor–liquid equilibria (VLE) data and diffusion coefficients of the system PDMS + *n*-pentane measured using three different methods: gravimetric sorption, pressure decay, and inverse gas chromatography. Since exactly the same polymer sample has been used for all different measurements, this allows for a sound comparison of the considered methods and therewith provides a realistic impression of the data reliability.

2. Experimental

In the past, many different methods have been developed to determine vapor–liquid equilibria and diffusion coefficients in polymer–solvent systems. Pressure decay [3] and sorption measurements, either gravimetric [4,5] or piezoelectric [6], are widely used to determine both properties simultaneously. Inverse gas chromatography (IGC) is mostly used to determine the activity coefficients at infinite dilution [7], but was also extended for measurements at finite concentration [8]. Diffusion coefficients can be measured as well, but are not easy to determine accurately because of the difficulties to ensure a constant coating thickness within the IGC column.

Other methods to determine both properties at the same time are permeation methods [9], where primarily the permeability and the diffusivity are determined whereas the solubility is calculated in a subsequent step.

Differential vapor-pressure measurements as well as ultracentrifuge or light-scattering measurements can be used to determine VLE data [10], the first two applicable to concentrated solutions the latter only to dilute solutions. Spectroscopic methods like UV-, IR- or Raman-spectroscopy can be applied to determine concentrations in the two phases. A detailed review of experimental methods to determine VLE data in polymer solutions was written by Wohlfarth [11].

Methods for the determination of mutual diffusion coefficients, other than the ones mentioned above, are interferrometric methods [12], FTIR–ATR spectroscopy [13], Rayleigh scattering [14], and NMR imaging [15].

In the following three sections the different experimental methods used in this work (gravimetric sorption, pressure decay, and IGC) are briefly described.

2.1. Gravimetric sorption measurements

The principle of the gravimetric sorption method is to measure the weight increase of a solid or non-evaporating liquid sample in a solvent–vapor or gas atmosphere due to absorption of the vapor or gas in the sample. The equipment, the experimental procedure and the data analysis have been previously described [4] and are therefore only briefly discussed here.

2.1.1. Apparatus

The equipment consists of a magnetic suspension balance (Rubotherm) [16] which measures the weight with a reproducibility of ±0.03 mg (Fig. 1). The weight can be between 0.01 and 30 g. The solvent vapor is fed into the measuring cell from an independently thermostated solvent vaporizer by means of an inlet valve establishing a constant solvent vapor flow through the cell. This ensures proper removal of all leakages into the cell and thus a pure solvent atmosphere even for long experimental times. Pressure and temperature in the cell are kept constant by means of an outlet valve at the lower end of the cell and an air thermostat, respectively. The accuracy of the pressure transducer is ±0.5% of the reading and the pressure constancy is better than ±0.01 kPa in the range of 0.01 and 133 kPa. The temperature is measured with an accuracy of ±0.05 K and is kept constant within ±0.05 K.

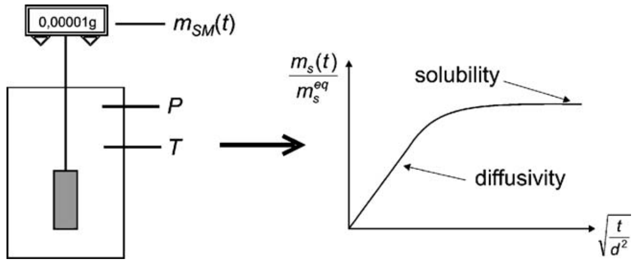

Fig. 1. Schematic representation of the gravimetric sorption principle and the data analysis with respect to solubility and diffusivity.