

PHASE CHANGES AND THERMODYNAMIC COEFFICIENTS IN THE CONTEXT OF HIGH PRESSURE POLYMERIZATION

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ABSTRACT

High pressures of more than 100 bar and high temperatures of 150 – 300 °C are neither a curiosity nor exclusively a matter of fundamental research. In fact, quite the opposite is true, as there are a couple of large-scale operations dealing with such extreme conditions. In this context the high pressure synthesis of low-density polyethylene (LDPE) deserves special mention. Due to the high production of this polyolefine, which amounts to more than 39 billion pounds in a year, a thorough optimization of the production process is extremely important in terms of competitiveness.¹ Considerable improvements can be achieved by systematic, simulation-aided reaction engineering. However, this approach requires the knowledge of the full kinetic scheme and the values of many physical properties.

Whereas the basic reaction network of the radical polymerization together with the rate coefficients as for example described by Busch is now generally accepted, the correlations assumed for the thermodynamic coefficients such as the heat capacity need to be revisited.² The latter partly date back to the beginning of the last century and are often incomplete in the sense that they only cover pure component properties.³ All potential excess effects, resulting either from an asymmetric solution of a polymer in a supercritical fluid or from non-ideal mixtures of low-molecular mass substances as present the case of copolymerizations, have been neglected in the experimental studies. Furthermore, a re-evaluation of phase equilibrium data at high pressure, which are of interest for the product separation, could be beneficial because they are typically determined by visually and the results might hence depend on the observer.

The scanning transitionometer provides a promising tool for both aims. It is designed in analogy to a twin calorimeter and can record differential heat fluxes. Unlike a standard DSC however, it can be used up to 4000 bar and 300°C. The instrument's sensitivity, which is especially important for the assessment of heat capacities, is unprecedented and reached with the use of three-dimensional thermopiles. Different ways of applying pressure should enable the experimenter to differentiate between mere physical impacts of pressure and the interaction of the pressurizing fluid with a chosen sample.

Because of its technological advantages in comparison with other high-pressure techniques, scanning transitionometry is tested as a method to close the gap in terms of thermodynamic coefficients of more component systems at high pressure. Specifically its applicability for the measurement of heat capacities will be discussed and the results will be juxtaposed against the early examinations of pure component compounds. Also the advantages of the calorimetric over the visual determination of phase changes will be shown.

References

¹T.E. Nowlin, *Business and Technology of the Global Polyethylene Industry: An In-depth Look at the History, Technology, Catalysts, and Modern Commercial Manufacture of Polyethylene and Its Products*, Wiley **2014**.

²M. Busch, *Macromol. Theor. Simul.* **2001**, *10*, 408.

³K. Zentel, Master-Thesis, Darmstadt **2015**.