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Thermodynamics of Polymer Systems

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Summary: This work gives an introduction into the thermodynamic modeling of polymer systems. After a short overview about the different basics of thermodynamic models, results obtained with the recently proposed PC-SAFT equation of state are discussed exemplarily for systems containing polymers as well as copolymers.

Keywords: copolymers; equation of state; modeling; polymers; solubility; sorption; thermodynamics

Introduction

Mutual solubility of polymers and volatile organic substances are of importance for many applications in polymer chemistry and polymer engineering. Polymerizations, which should be performed in homogeneous phase, require the complete miscibility of monomer, polymer, solvent (liquid or supercritical) and other additives. Subsequently, the extraction of the polymer product from the reaction mixture requires a phase split (into two liquid phases or into a vapor and a liquid phase) to obtain a polymer product of high purity at one side as well as the unreacted monomer at the other-hand side. In this context the devolatilization of polymers is of particular interest. Another example is the use of polymer membranes for the separation of two volatile organic compounds. Here, besides the knowledge of diffusivity, also the solubility (sorption) of the different components in the polymer membrane is an important prerequisite for an efficient process.

However, experimental data of polymer solubility is often scarce. Considerable experimental effort is generally required for determining these properties of polymer systems. Here, thermodynamics can provide powerful and robust tools for modelling of experimental data and even prediction of the thermodynamic behavior.

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Phase Equilibria in Polymer Systems

Polymer Solubility (Liquid-Liquid Equilibria)

Polymers very often show only limited miscibility with liquid solvents. Moreover, miscibility is not only a function of temperature, pressure and polymer concentration, but also of molecular weight as well as of molecular-weight distribution of the polymer.

A typical phase behavior of a polymer/solvent system is shown in Figure 1 for the solubility of polystyrene in methylcyclohexane. At low temperatures this system shows a region of demixing into two liquid phases (LL).

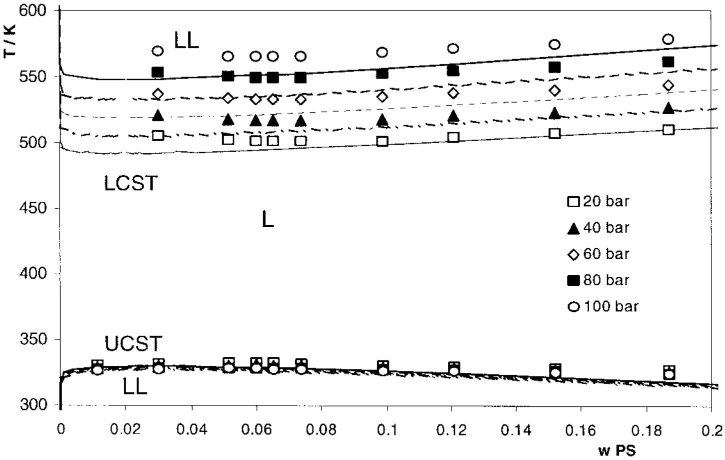

Figure 1: Phase behavior in the system methylcyclohexane (1)-polystyrene (2) (M_w=405 kg/mol) for different pressures. Symbols are experimental data (Enders and de Loos 1997). Lines are calculations with the PC-SAFT equation of state (Gross and Sadowski 2002)

In this region an increasing temperature leads to an improved miscibility. Above the critical temperature (Upper Critical Solution Temperature; UCST) the system is at first completely miscible and forms a homogeneous liquid solution (L). However, for polymer/solvent systems typically also a liquid-liquid demixing at high temperatures is observed. The reason is the so-called free-volume effect: solvent and polymer show at high temperatures, esp. when approaching the critical temperature of the solvent, large differences in thermal expansion Thus, the density (reverse of "free volume") of the solvent decreases much more than that of the polymer. This causes a separation of polymer and solvent and therewith a demixing. With further increasing temperature this effect becomes even more pronounced. Therefore, this demixing is increasing with increasing temperature and shows a Lower Critical Solution Temperature (LCST).

The experimental demixing data in Figure 1 are shown for different pressures. As to be seen, the UCST-demixing is only slightly influenced by pressure, as it is typically the case for incompressible liquids. However, the LCST demixing shows a pronounced pressure dependence because of the free-volume difference at high temperatures that is directly determined by system pressure. As shown in Figure 1, in most cases an increasing pressure improves the miscibility.

Moreover, polymer solubility is a strong function of polymer molecular weight. Figure 2 shows as an example the solubility of polyethylene (LDPE) in ethylene for the indicated molecular weights of the polymers. For a given polymer concentration the cloud-point data indicate which pressure has to be applied for obtaining a homogeneous solution. It becomes obvious that smaller polymers are better soluble and thus need a smaller pressure to be dissolved than large polymers.

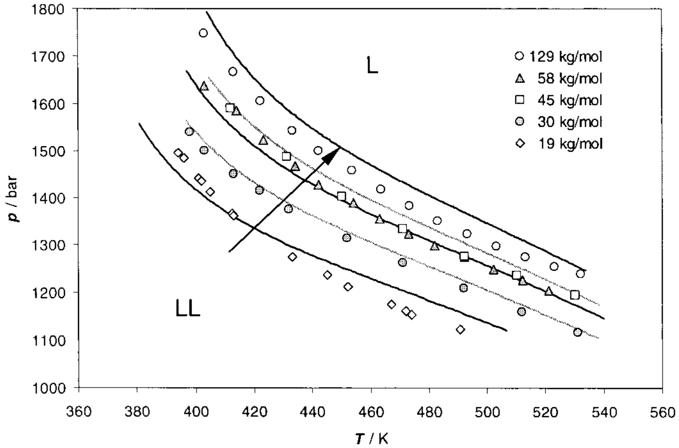

Figure 2: Solubility of poly(ethylene) (LDPE) in ethylene for increasing molecular weights of the polymer. Symbols are experimental cloud-point data (Latz and Buback 2003), lines are predicted with the PC-SAFT model (Tumakaka 2003)

Therefore, for polydisperse polymers the molecular-weight distribution of the polymer has also to be considered in the modeling (e.g. Behme et al. 2003).

Solvent Sorption in Polymers (Vapor-Liquid Equilibria)

At low pressures (below the vapor pressure of the pure solvent), the solvent starts to evaporate from the polymer solution. On the other hand (e.g. for membrane applications), solvent vapor of a given partial pressure may dissolve in the polymer. In these cases a liquid polymer/solvent mixture is in equilibrium with pure solvent vapor. This is exemplarily shown in Figure 3 for the system chlorobenzene/polystyrene.

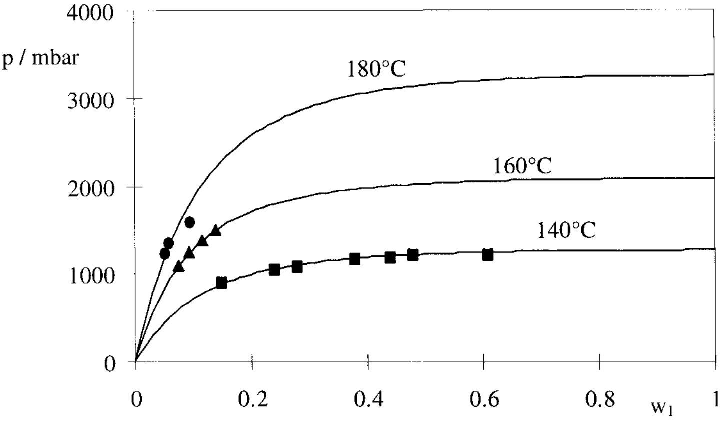

Figure 3: Sorption curves of chlorobenzene (1) in polystyrene(2) at different temperatures. Symbols are experimental data (Sadowski et al. 1997). w_1 is the weight fraction of the solvent.

As it can be seen, the amount of solvent sorbed in the liquid polymer solution is a strong function of solvent partial pressure and temperature.

There are several data collections available for the vapor-liquid equilibria of polymer/solvent systems (e.g. Danner and High 1993, Wohlfarth 1994) as well as of copolymer/solvent systems (e.g. Wohlfarth 2001).

Modeling

g^E-Models

The sorption of a solvent vapor in a polymer can be described using Eq.(1):

$$p = x_1 \gamma_1 p_{01}^{LV} \qquad (1)$$

where p is the pressure, x_1 is the mole fraction and γ_1 the activity of the solvent, respectively. p_{01}^{LV} is the pure-component vapor pressure of the solvent at system temperature.

Very often, instead of mole fraction x_1, the weight fraction w_1 is used. Eq. (1) than becomes:

$$p = w_1\,\Omega_1\,p_{01}^{LV} \qquad (2)$$

where Ω_1 is the weight-fraction activitiy coefficient.

For the description of liquid-liquid demixing, the thermodynamic phase-equilibrium conditions can be formulated based on mole fractions or weight fractions, respectively, as:

$$x_i^I\gamma_i^I = x_i^{II}\gamma_i^{II} \qquad (3)$$

or

$$w_i^I\Omega_i^I = w_i^{II}\Omega_i^{II} \qquad (4)$$

The activity coefficients γ_1 and Ω_1 in Eq.s (1) to (4) are calculated from g^E-models using classical thermodynamic relations.

The first g^E-model developed for polymer solutions is the well-known expression from Flory 1942 and Huggins 1941, which was developed based on a lattice theory:

$$\frac{g^E}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \Phi_1\Phi_2\chi\bar{r} \qquad (5)$$

Here, Φ_i is the volume fraction of the solvent and of the polymer, respectively, $\bar{r}$ is the average segment number and χ is a binary parameter. This parameter has to be fitted to binary experimental data and does depend on temperature and very often also on concentration. Especially due to the last reason, a lot of efforts were done by different authors to find reasonable expressions for the concentration dependence of the χ–parameter (Kleintjens 1979, Qian et al. 1991, Hu et al. 1991, Bae et al. 1993).

Besides this, solvent activity coefficients can also be calculated using group-contribution methods. Some of them are based on the well-known UNIFAC model, which was originally proposed for low-molecular-weight substances (Fredenslund et al. 1977). It was found that an application of this model to polymer solutions always leads to values of solvent activity coefficients, which are too small. Therefore, Oishi and Prausnitz 1978 proposed to add a free-volume contribution, which takes into account the above-discussed free-volume effect. Using this

UNIVAC-FV version, the results of the predictions could be improved remarkably (Figure 4).

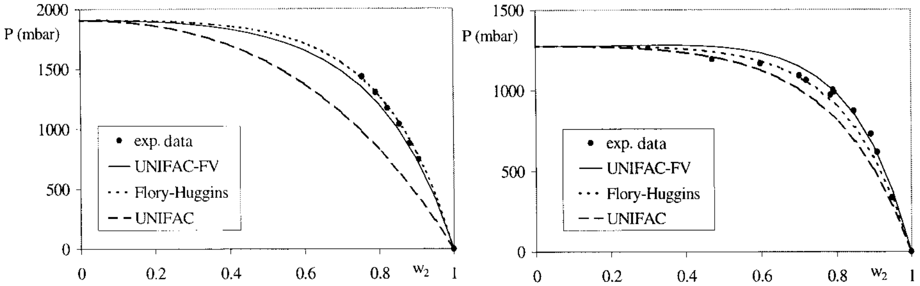

Figure 4: Vapor-liquid equilibrium in polymer solutions using UNIFAC, UNIFAC-FV and Flory-Huggins. a) polybutadiene/hexane at 23.5°C (exp. Data: Saeki et al. 1992). b) polystyrene/methyl ethyl ketone at 25°C (exp. data: Bawn et al. 1950)

Later, other models were also developed which consider free-volume contributions (e.g. Entropic-FV from Elbro et al. 1990 and Kontogeorgis et al. 1993).

g^E models in general can only be used to describe the activity coefficients of incompressible fluids. They do not take into account density changes of a system and thus they cannot be applied to describe non-idealities of the vapor phase at elevated and high pressures. Moreover, they cannot predict LCST demixing of a polymer - solvent system.

These drawbacks can be avoided by using an equation of state. This type of model consequently considers the relation between temperature, pressure, concentration and density of a system and can be applied to calculate fugacity coefficients. These later quantities allow formulating the phase-equilibrium conditions for polymer and solvent as:

$$x_i^I \varphi_i^I = x_i^{II} \varphi_i^{II} \qquad (6)$$

Equations of state

There are different approaches for the development of an equation of state described in literature. One early-considered possibility is to extend a lattice theory by introducing holes. Therewith, the number of holes in the lattice is a measure for the density of the system. Density changes in the system are realized via a variation of the hole number. Equations of state based on this idea are for example the Lattice-Fluid Theory (Sanchez and Lacombe 1976) and the Mean-Field Lattice-Gas theory from Kleintjens and Koningsveld 1980.

Another approach to obtain an equation of state is based on the partition function of a system derived from statistical mechanics. One of these models is the Perturbed-Hard-Chain Theory (PHCT) proposed by Beret and Prausnitz 1975. It was subsequently extended and modified by Cotterman et al. 1986 and Morris et al. 1987 (Perturbed-Soft-Chain Theory PSCT).

However, to derive an analytical equation of state directly from the partition function it needs several assumptions, which are of severe nature, esp. for polymer systems.

An alternative way is the application of so-called perturbation theories (e.g. Barker and Henderson 1967; Weeks et al. 1971). The main assumption here is that the residual (difference to ideal-gas state) part of the Helmholtz energy of a system A^{res} (and therewith also the system pressure) can be written as sum of different terms whereas the main contribution is described by the Helmholtz energy of a chosen reference system A^{ref}. Contributions to the Helmholtz energy which are not covered by the reference system are considered as perturbations and are described by A^{pert}.

$$A^{res} = A - A^{id} = A^{ref} + A^{pert} \tag{7}$$

$$p = p^{ref} + p^{pert} \tag{8}$$

An appropriate reference system (at least for solvent molecules) is the hard-sphere (hs) system. Here, the molecules are assumed to be spheres of a fixed diameter and do not have any attractive interactions. Such a reference system covers the repulsive interactions of the molecules, which are considered to mainly contribute to the thermodynamic properties of the system. Moreover, for hard-sphere systems analytical expressions for $A^{ref} = A^{hs}$ and $p^{ref} = p^{hs}$ are available (e.g. Carnahan and Starling 1969).

Deviations of real molecules from the reference system may occur e.g. due to attractive interactions (dispersion), formation of hydrogen bondings (association), non-spherical shape of the molecules (chain formation). These contributions can be accounted for by using different perturbation terms. Depending on what kinds of perturbation are considered and which expressions are used for their description, different models based on perturbation theories were developed in literature.

The first model in this category that was widely used also for industrial applications is the

Statistical Associated Fluid Theory (SAFT) (Chapman et al. 1989, 1990; Huang and Radosz 1990,1991).

Here, a chain-like molecule (solvent molecule or polymer) is assumed to be a chain of m identical spherical segments. Starting from a reference system of m hard spheres (A^{hs}) this model considers three perturbative contributions, which are assumed to act independently: attractive interactions of the (non-bonded) segments (A^{disp}), hard-sphere chain formation (A^{chain}) and association (A^{assoc}):

$$A^{res} = m\,A^{hs} + m\,A^{disp} + A^{chain} + A^{assoc} \qquad (9)$$

The Carnahan-Starling formulation is used for A^{hs}, the segment-segment dispersion A^{disp} is described using a fourth-order perturbation term (Chen and Kreglewski 1977); contribution of chain formation as well as the association term is based on the work of Wertheim 1987. Subsequently, various perturbation theories were developed which are also based on Eq. (9) but differ in the use of specific expressions for the different types of perturbations. Examples are the Perturbed Hard-Sphere-Chain Theory (PHSC) from Song et al. 1994, as well as the models proposed by Chang and Sandler 1994, Gil-Villegas et al. 1997, and Hino and Prausnitz 1997.

The recently proposed Perturbed-Chain SAFT (PC-SAFT) model (Gross 2001; Gross and Sadowski 2001, 2002) is a modification of SAFT which was developed especially to improve the description of polymer systems. Here the reference system of hard chains is used instead of the hard-sphere system. Therefore, the dispersion term now considers the attraction of chain-molecules instead of unbonded spheres and is a function of chain length m:

$$A^{res} = A^{hard\,chain} + A^{disp}(m) + A^{assoc} \qquad (10)$$

Most of the perturbation theories require three pure-component parameters, which have a physical meaning: the number of segments (which is proportional to the molecular weight for polymers), the size of the segments, and the energy related to the interaction of two segments. To describe a binary system, in most cases an additional binary parameter (k_{ij}) is required.

In the following, some results for the modeling of polymer/solvent systems are discussed to illustrate the ability of today's equations of state to model and to predict (extrapolate) the phase equilibria in those systems.

Description of Polymer Phase Equilibria – Results

Homopolymer Systems

Equations of state can be used to describe vapor-liquid as well as liquid-liquid equilibria.

Figure 5 gives first an example for the prediction of the vapor-liquid equilibrium in the polyethylene/toluene system. The figure shows experimental data for different (relatively low) molecular weights of the polymer, which are compared with predictions using the SAFT and PC-SAFT model, respectively. The binary parameter k_{ij} is zero in both cases. Thus, the lines are not fitted to the shown binary data but were calculated using pure-component information only. This clearly shows that SAFT as well as PC-SAFT are able to predict the vapor-liquid equilibrium in this system and even correctly consider the molecular-weight dependence. Moreover it can be seen that PC-SAFT is slightly superior.

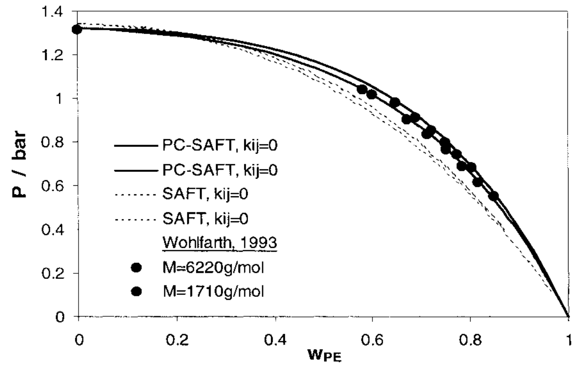

Figure 5: Vapor-liquid equilibrium of toluene(1)/polyethylene(2) for different molecular weights of the polymer. Symbols are experimental data. Lines are predictions with SAFT and PC-SAFT, respectively (Gross and Sadowski 2002)

For the solubility of polymers in liquids the molecular-weight dependence of phase equilibria is even more pronounced. This was already exemplarily shown in Figure 2, which also contains modeling results with the PC-SAFT model. It is obvious that the model can even predict the influence of molecular weight qualitatively (there were no parameters fitted to the experimental data shown in Figure 2).

Figure 6 exemplarily illustrates the ability of an equation of state to model the solubility of LDPE in a variety of solvents. The amount of polymer is about 5 wt.% in all cases. Using PC-SAFT the experimental cloud points can be described with high accuracy. Although for each system only one binary temperature-independent parameter was used, the model could even describe the changing slope of the cloud-point curves from negative for ethylene and ethane to positive for C_3 and C_4 solvents.

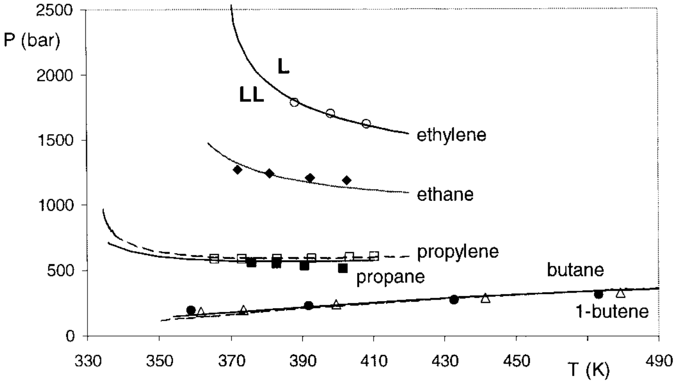

Figure 6: Cloud-point data of different polyethylene (LDPE)/solvent systems. Symbols are experimental data from Hasch 1996. Lines are PC-SAFT calculations (Tumakaka et al. 2002)

The addition of a gas to a polymer/solvent system usually decreases the polymer solubility. The compressed gas acts as an anti solvent (e.g. Bungert et al. 1998) and shifts the LCST-demixing gap to lower temperatures and higher pressures (because of the added gas, higher pressures are required to keep the system homogeneous). Using only pure-component and binary parameters for the three subsystems (all of them temperature independent) this behavior can be described qualitatively and even nearly quantitatively using the PC-SAFT model (Figure 7).

Copolymer-Systems

The original versions of the above-mentioned perturbation theories consider a molecule as chain of identical segments. Recently, several models were extended to allow for taking into account also different types of segments and therewith to describe copolymer systems (e.g. Song et al. 1996, Banaszak et al. 1996, Shukla and Chapman 1997).

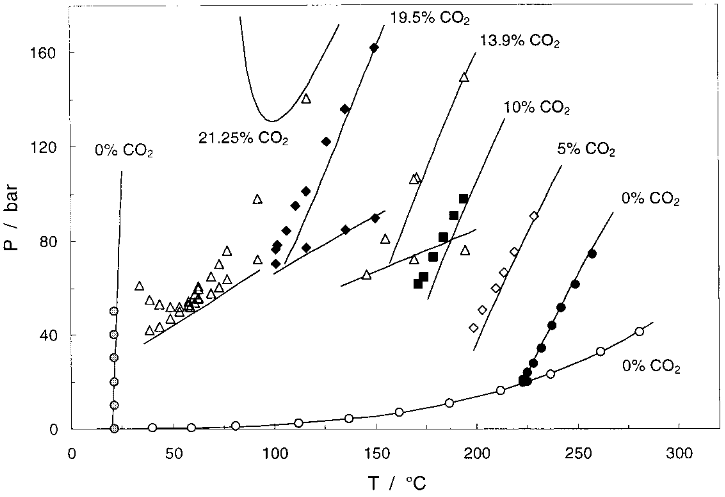

Figure 7: Cloud-point data in the system polystyrene/cyclohexane/CO_2. Molecular weight of the polymer is M_w = 101 kg/mol. Amount of polymer is 10 wt% on CO_2-free basis. Symbols are experimental VLE and LLE data (Saeki et al. 1973, de Loos 1994, Bungert 1998). Lines are PC-SAFT calculations (Gross and Sadowski 2002)

In the copolymer version of the PC-SAFT model, the required segment parameters for a copolymer are taken from the corresponding homopolymers. To describe a copolymer/solvent system three binary parameters are required. The two of them, which describe the copolymer segment1/solvent and the copolymer segment2/solvent interactions, respectively, are determined from the two homopolymer/solvent systems. Thus, the only parameter that has to be determined from copolymer/solvent data is the binary parameter which accounts for the interaction of the unlike segments in the copolymer.

Figure 8 shows the result of this approach for the modeling of the solubility of poly(ethylene-1-butene) in propane. Using pure-component and binary homopolymer information and only one constant parameter for the ethylene segment/butylene segment interaction, the solubility of the copolymers could be described nearly quantitatively over the whole range of copolymer compositions.

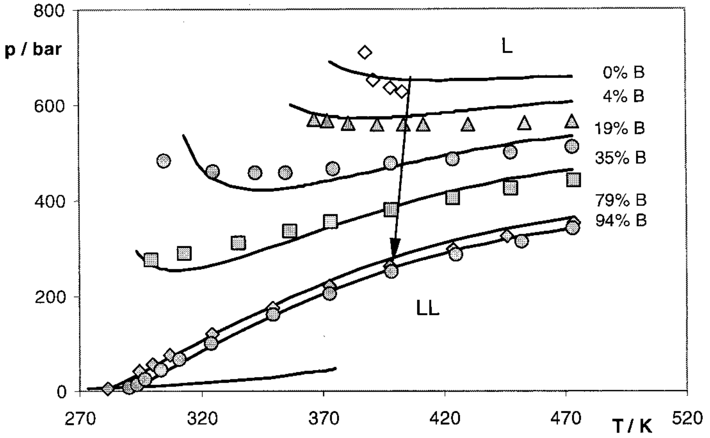

Figure 8: Cloud-point pressures in the system poly(ethylene-co-1-butene)/propane for different copolymer compositions (mole percent butene in the backbone is indicated; 0% B = LDPE). Polymer weight fraction is about 0.05. Symbols are experimental data (Chen et al. 1995). Lines are PC-SAFT calculations (Gross et al. 2003)

Results of similar quality could also be obtained for the solubility of ethylene-co-alkylacrylate copolymers in ethene (Figure 9). For the poly(ethylene-co-propylacrylate) copolymer the solubility is increasing with increasing amount of propylacrylate-monomers in the copolymer backbone. In contrast, for the poly(ethylene-co-methylacrylate) the solubility first increases (cloud-point pressure decreases) due to favorable methylacrylate/ethene interactions but after reaching a maximum (pressure minimum) solubility again decreases because of the strong interactions among the methylacrylate monomers. The homopolymer poly(methylacrylate) could even not be dissolved in ethene at pressures below 3000 bar. Although the two systems show this qualitatively different behavior, the copolymer version of PC-SAFT could model the experimental data in both cases with good accuracy.

Conclusions

Thermodynamics can provide a powerful tool to model and even to predict polymer phase equilibria. Whereas g^E-models can be used to model sorption phenomena and liquid solubility at low temperatures (UCST demixing), equations of state are applicable to all kinds of fluid phase equilibria. Especially the well-founded equations of state which were developed based on perturbation theories are able to model polymer phase equilibria using a minimum amount of parameters and with high accuracy. Because of their strong physical basis these models allow safe extrapolations and to a certain extend even predictions of thermodynamic behavior.

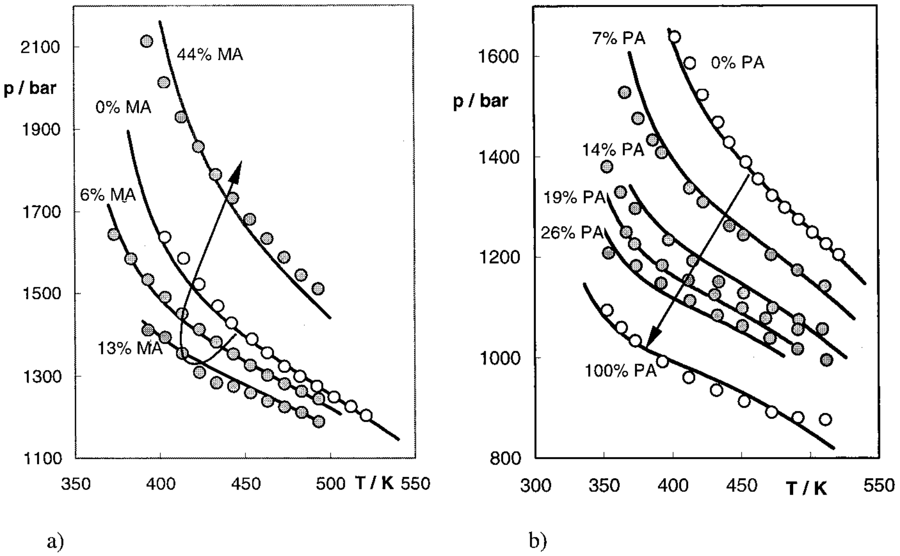

Figure 9: Cloud-point pressures for poly(ethylene-co-alkylacrylate)/ethylene systems at different copolymer compositions (mole percent of acrylate monomer in the backbone is indicated). a) Solubility of poly(ethylene-co-methylacrylate) (0% MA = LDPE). b) Solubility of poly(ethylene-co-propylacrylate) (0% PA = LDPE; 100% PA = poly(propylacrylate)). Polymer content is about 5 wt%. Symbols are experimental data. Lines are PC-SAFT calculations (Becker et al. 2003)

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