

A Novel Approach to Liquid-Liquid Equilibrium in Polymer Systems with application to Simplified PC-SAFT

Nicolas von Solms, Irene A. Kouskoumvekaki, Thomas Lindvig, Michael L. Michelsen
and Georgios M. Kontogeorgis*

*Centre for Phase Equilibria and Separation Processes (IVC-SEP), Department of
Chemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark*

* Corresponding Author, tel. +45 45 25 28 59, fax. +45 45 88 22 58, e-mail:
gk@kt.dtu.dk

Abstract

A recently developed equation of state (modified PC-SAFT) has been used to calculate binary liquid-liquid equilibria for polymer-solvent systems. A number of different polymers and solvents were examined as part of the study, including both non-associating and associating solvents. In general modified PC-SAFT is successful in modelling liquid-liquid equilibrium, successfully predicting the correct behaviour in many systems exhibiting upper, lower and both critical solution temperatures. Where predictions are not accurate, a small value of the binary interaction parameter is required to correlate experimental data. A novel method, which we call the method of alternating tangents, has been developed for finding liquid-liquid equilibrium in binary polymer-solvent systems. The algorithm is robust and traces the full temperature composition curve for both UCST and LCST type systems through the critical solution temperature. The algorithm has been successfully applied for all polymer molecular weights encountered in the experimental literature. The algorithm is applicable to any equation of state for which analytical fugacity coefficients and their derivatives are available, although application was restricted in this study to the modified PC-SAFT equation of state.

1. Introduction

Because of the negligible volatility of polymers, liquid-liquid phase equilibrium is generally more relevant in systems containing polymers, than are vapour-liquid and other types of phase equilibrium. Additionally, the presence of two liquid phases is far more common in systems containing polymers than in mixtures of smaller molecules. Consequently LLE in polymer systems has been studied quite extensively. A comprehensive review of models used in polymer thermodynamics has recently appeared [1]. Both activity coefficient and equation of state models have been used for calculating liquid-liquid equilibrium in polymer systems. Activity coefficient models that have found application in the area of polymer-solvent LLE include the Flory-Huggins model [2,3] and free-volume models such as UNIFAC-FV [4] and Entropic-FV [5,6]. Bogdanic and Vidal [7] used an Entropic-FV/UNIQUAC model to correlate LLE in the system PVAL-water. This system displays unusual “closed-loop” behaviour, where the UCST lies above the LCST. Equations of state that have been applied to polymer systems include the van der Waals [8,9] and Sako-Wu-Prausnitz [10] equation of state. The SAFT equation of state, developed in the early nineties, is a non-cubic, segment-based equation of state which was designed specifically to deal with systems containing polymers and associating fluids. A review of SAFT applications appeared recently [11]. A number of modifications of SAFT have also appeared in the last 12 years, including SAFT-VR [12] and PC-SAFT [13], a modification of which we employ in this work. Some applications to LLE have appeared [14,15]. Another successful approach is use the so-called EoS/ G^E (equation of state/excess Gibbs energy) method. This approach combines an equation of state (typically a cubic) with a mixing rule based on an activity coefficient model.

Unfortunately, phase equilibrium calculations in asymmetric mixtures such as those containing polymers can frequently cause computational difficulties. This is particularly true for liquid-liquid equilibrium, where two highly non-ideal liquid phases must be modelled with the same equation of state.

Here we investigate a method for finding liquid-liquid coexistence (binodal) compositions in binary polymer solvent mixtures. The method finds the spinodal compositions as a starting point for finding the binodals, as well as upper, or lower, or both critical solution temperatures. The equation of state employed in these calculations is a recently proposed modification of PC-SAFT [16,17] although it is applicable to any analytic equation of state capable of predicting phase equilibrium in polymer systems. A discussion of the method and its implementation follows, together with results for a variety of different polymers and solvents displaying different types of critical solution temperature behaviour.

2. Theory.

The equation of state used in these calculations is a simplified version of PC-SAFT developed in this group [16,17]. Specifically, all calculations were carried out using modification 2, in the terminology of von Solms et al. [16]. The original version of PC-SAFT was created by Gross and Sadowski and co-workers [13,14,18-20] and more details can be found in these works.

We call the proposed method the method of alternating tangents and it is best illustrated by reference to Figure 1. This figure shows the Gibbs energy of mixing for two binary systems as a function of the mole fraction of component 1. The method will be illustrated with reference to the system methanol(1)-cyclohexane(2), since this curve clearly shows the existence of two phases. The composition of methanol in each phase

is found by locating a single line which is a tangent to the curve in two places (the common tangent). In figure 1 these compositions are given by x_1^{eq1} and x_1^{eq2} . In fact the curve for the system PS(1)-acetone(2) also shows the existence of two phases, although this is not visible. The first step in the procedure is to determine whether a spinodal point exists (this is a necessary condition for phase separation). In the figure, the two spinodal points are given by the compositions x_1^{sp1} and x_1^{sp2} . The spinodal condition is given by $\frac{\partial^2 g^{RES} / RT}{\partial x^2} = 0$, i.e. an inflection point on the curve. Once a spinodal point has been found (using a Newton-Raphson method), the next step is to find the point of tangent of a line emanating from the spinodal point. In the figure this is the line connecting x_1^{sp1} and x_1 . This point is just to the left of x_1^{eq2} (i.e. we are not yet quite at the equilibrium concentration after one step). The equation whose solution gives this point of tangent is:

$$f(x_1) = \frac{g(x_1) - g(x_1^{sp1})}{x_1 - x_1^{sp1}} - \frac{dg}{dx}(x_1) = 0 \quad (1)$$

where $f(x_1)$ is our Newton target function to be solved and $g(x_1)$ is shorthand for

$\frac{g^{RES}}{RT}(x_1)$. The derivative is given simply by

$$\frac{dg}{dx}(x_1) = \ln x_1 + \ln \hat{\phi}_1 - \ln(1 - x_1) - \ln \hat{\phi}_2 \quad (2)$$

where $\hat{\phi}_i$ is the fugacity coefficient. In order to implement a Newton-Raphson routine, the first derivative of the Newton target function $f(x_1)$ is also required. This means that composition derivatives of the fugacity coefficients are required (from eq. 2). Both the fugacities and their composition derivatives have been calculated analytically for the modified PC-SAFT equation of state. Once the first tangent point has been found, the point of tangent opposite is then found in a similar way. This process is repeated

until the change in the composition at the tangent point is within a certain tolerance. At this point the equilibrium values have been calculated.

A major benefit of the method is that only one point needs to be found at a time, thereby avoiding simultaneous solution of the two equilibrium compositions. The criterion for the location of the critical solution temperatures (UCST or LCST) is that the two spinodal points (x_1^{sp1}, x_1^{sp2}) have equal values. Figure 2 shows the binodal and the spinodal curve in the system PS(1)-cyclohexane(2). At the UCST all four compositions converge. In the limit, as the critical temperature is approached, use can be made of a universal law which relates the binodal to the spinodal compositions.

Taking $x_1^{sp} = x_1^{eq1} + u(x_1^{eq2} - x_1^{eq1})$, the two spinodal points are found when u takes the two values obtained as solutions to the 2nd degree shifted Legendre polynomial

$$6u^2 - 6u + 1 = 0.$$

The search for the binodal points is aided by the fact $0 < x_1^{eq1} < x_1^{sp1}$ and $x_1^{sp2} < x_1^{eq2} < 1$ so the solution boundaries are well defined. Another feature which improves the robustness of the algorithm is to use logarithms of the compositions required in the algorithm. This is advantageous since the polymer is often present in the polymer-lean phase in minute amounts, particularly in systems which exhibit LCST behaviour. This problem is further exacerbated by the fact that mol fractions (rather than weight fractions) are used in the fugacity calculations. This may be problematic, especially when dealing with very high molecular weight polymers. However, no problems were encountered when using logarithms of compositions, even at the highest polymer molecular weight encountered in systems exhibiting LCST behaviour (the most difficult case).

3. Results and Discussion.

Polymer parameters for PC-SAFT were obtained from Gross and Sadowski [14]. Parameters for most of the solvents were obtained from Gross and Sadowski [13], with the exception of diisobutyl ketone (this work), *n*-alkanols [20] and acetone [17].

Figure 3 shows results for the system polystyrene-methylcyclohexane for different molecular weights of polystyrene. The experimental data are from the classic work of Dobashi et al. [21,22]. The lines are simplified PC-SAFT correlations with $k_{ij} = 0.0065$ for polystyrene molecular weights 10 200, 46 400 and 719 000 in order of increasing temperature. The data is reasonably well correlated over a very large range of molecular weight with a single value of the binary interaction parameter, k_{ij} . The binary interaction parameter was adjusted to give the correct upper critical solution temperature. However, the correct critical solution concentration is not obtained, although the experimental trends are correctly predicted by the model: The critical solution temperature increases and the polymer weight fraction at the critical solution temperature decreases with increasing molecular weight.

Figure 4 shows results for the system polyisobutylene-diisobutyl ketone at different polymer molecular weights. The experimental data is from Shultz and Flory [23]. The lines are simplified PC-SAFT correlations. Pure component parameters for diisobutyl ketone were obtained in this work. A single binary interaction parameter ($k_{ij} = 0.0053$) was used for all three systems, although it is evident that there is a weak dependence of molecular weight on k_{ij} . Incorporating a functional dependence of k_{ij} on molecular weight (for example a linear fit) would improve the correlation. It should also be noted that these three systems represent a very large range of molecular weights.

Figure 5 shows the results for HDPE-*n*-heptane, a system which displays lower critical solution temperature (LCST) behaviour. The experimental data are from Hamada et al. [24]. The same binary interaction parameter is used for all four molecular weights shown, although this could be fine-tuned. It is worth noting that the temperature range shown is extremely small (compared with for example figures 3 and 4), so this correlation can be considered to be good. An additional point is that generally LCST behaviour is rather insensitive to the binary interaction parameter. This is because LCST behaviour is usually observed at elevated temperatures, where the effect of the energy parameters are not as marked. Since k_{ij} is a correction to the cross energy parameter ε_{ij} , changing the k_{ij} value generally has only a marginal effect.

Figure 6 shows the results for a single molecular weight of HDPE in five different *n*-alkanol solvents from *n*-pentanol up to *n*-nonanol. The experimental data are from Nakajima et al. [25]. The results are well-correlated using simplified PC-SAFT using a small value of the binary interaction parameter k_{ij} . A k_{ij} value of around 0.003 gives a good correlation for all the systems, except HDPE-*n*-pentanol. In the figure, a small value ($k_{ij}=0.0006$) was used to correlate the data, although the data is also well predicted by simplified PC-SAFT ($k_{ij}=0$), giving an error in the upper critical solution temperature of 3 K.

Figure 7 shows the results for the system HDPE-butyl acetate. This system displays both UCST and LCST behaviour. The experimental data are from Kuwahara et al. [26]. A single binary interaction parameter ($k_{ij}=0.0156$) was used to correlate the data for both molecular weights shown. The binary interaction parameter was adjusted to give a good correlation for the UCST curve at the higher molecular weight

(64 000). As mentioned above, the LCST curve is rather insensitive to k_{ij} .

Nevertheless, the LCST curve is reasonably well correlated using this value. The prediction ($k_{ij}=0$) is almost as good for the LCST curve, although the UCST will then be substantially underpredicted.

Finally, figure 8 shows simplified PC-SAFT predictions ($k_{ij}=0$) in the system PP-diethyl ether. The experimental data are from Cowie and McEwen [27]. While the effect of molecular weight is captured by the model (decreasing LCST with increasing molecular weight), the magnitude of this effect is not accounted for. However the values of the LSCT, the concentration at the LCST and the shape of the curves are generally in good agreement with the experimental data.

4. Conclusions

We have developed a novel method, the method of alternating tangents, for finding liquid-liquid equilibrium in binary polymer-solvent systems. The algorithm is robust and traces the full temperature composition curve for both UCST and LCST type systems through the critical solution temperature. The algorithm worked successfully for all polymer molecular weights encountered in the experimental literature. The algorithm is applicable to any equation of state for which analytical fugacity coefficients and their derivatives are available.

We have tested the modified PC-SAFT equation of state developed in this group to predict and correlate LLE in systems containing a range of polymers and solvents, both associating and non-associating. In general modified PC-SAFT is successful in modelling LLE, successfully predicting the correct behaviour in many systems exhibiting upper, lower and both critical solution temperatures. Where predictions are

not accurate, a small value of the binary interaction parameter is required to correlate experimental data.

List of Symbols

FV	Free volume
HDPE	High density polyethylene
LCST	Lower critical solution temperature
LLE	Liquid-liquid equilibrium
PC	Perturbed chain
PP	Polypropylene
PS	Polystyrene
PVAL	Poly(vinyl alcohol)
SAFT	Statistical associating fluid theory
UCST	Upper critical solution temperature
VLE	Vapour-liquid equilibrium

References

- [1]. G.M. Kontogeorgis, "Thermodynamics of Polymer Solutions," in K.S. Birdi, *Handbook of Surface and Colloid Chemistry*, 2nd ed. CRC press, Boca Raton, 2003.
- [2]. P.J. Flory, *J. Chem. Phys.* 9, 660 (1941).
- [3]. M.L. Huggins, *J. Chem. Phys.* 15, 25 (1941).
- [4] T. Oishi and J.M. Prausnitz, "Estimation of solvent activities in polymer solutions using a group-contribution method," *Ind. Eng. Chem. Proc. Des. Dev.* 17, 333 (1978).
- [5]. H.S. Elbro, Aa. Fredenslund and P. Rasmussen, "Phase equilibria in aqueous polymer solutions," *Macromolecules* 23, 4707 (1990).
- [6]. G.M. Kontogeorgis, Aa. Fredenslund and D.P. Tassios, "Simple activity coefficient model for the prediction of solvent activities in polymer solutions," *Ind. Eng. Chem. Res.* 32, 362 (1993).
- [7]. G. Bogdanic and J. Vidal, "A segmental interaction model for liquid-liquid equilibrium calculations for polymer solutions," *Fluid Phase Equilib.* 173, 241 (2000).
- [8]. V.I. Harismiadis, G.M. Kontogeorgis, A. Saraiva, Aa. Fredenslund and D.P. Tassios, "Application of the van der Waals equation of state to polymers III. Correlation and prediction of upper critical solution temperatures for polymer solutions," *Fluid Phase Equilib.* 100, 63 (1994).
- [9]. A. Saraiva A, G.M. Kontogeorgis, V.I. Harismiadis, Aa. Fredenslund and D.P. Tassios, "Application of the van der Waals equation of state to polymers IV. Correlation and prediction of lower critical solution temperatures for polymer solutions," *Fluid Phase Equilib.* 115, 73 (1996).

- [10]. C. Browarzik and M. Kowalewski, "Calculation of the cloud point and the spinodal curve for the system methylcyclohexane/polystyrene at high pressure," *Fluid Phase Equilib.* 194, 451 (2002).
- [11]. E.A. Müller and K.E. Gubbins, "Molecular-based equations of state for associating fluids: a review of SAFT and related approaches," *Ind. Eng. Chem. Res.* 40, 2193 (2001).
- [12]. A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson and A.N. Burgess, "Statistical associating fluid theory for chain molecules with attractive potentials of variable range," *J. Chem. Phys.* 106, 4168 (1997).
- [13]. J. Gross and G. Sadowski, "Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules," *Ind. Eng. Chem. Res.* 40, 1244 (2001).
- [14]. J. Gross and G. Sadowski, "Modeling Polymer Systems Using the Perturbed-Chain Statistical Association Fluid Theory Equation of State," *Ind. Eng. Chem. Res.* 41, 1084 (2002).
- [15]. P.K. Jog, W.G. Chapman, S.K. Gupta and R.D. Swindoll, "Modeling of liquid-liquid-phase separation in linear low-density polyethylene-solvent system using the statistical associating fluid theory equation of state," *Ind. Eng. Chem. Res.* 41, 887 (2002).
- [16]. N. von Solms, M.L. Michelson and G.M. Kontogeorgis, "Computational and Physical Performance of a Modified PC-SAFT Equation of State for Highly Asymmetric and Associating Mixtures," *Ind. Eng. Chem. Res.* 42, 1098 (2003).
- [17]. I.A. Kouskoumvekaki, N. von Solms, M.L. Michelsen and G.M. Kontogeorgis, "Application of a Simplified Perturbed Chain SAFT Equation of State to Complex Polymer Systems" submitted to *Fluid Phase Equilib.*
- [18]. F. Tumakaka, J. Gross and G. Sadoski, "Modeling of polymer phase equilibria using Perturbed-Chain SAFT," *Fluid Phase Equilib.* 194-197, 541 (2002).
- [19]. J. Gross, O. Spuhl, F. Tumakaka and G. Sadowski, "Modeling Copolymer Systems Using the Perturbed-Chain SAFT Equation of State," *Ind. Eng. Chem. Res.* 42, 1266 (2003).
- [20]. J. Gross and G. Sadowski, "Application of the Perturbed-Chain SAFT Equation of State to Associating Systems," *Ind. Eng. Chem. Res.* 41, 5510 (2002).
- [21]. T. Dobashi, M. Nakata and M. Kaneko, "Coexistence Curve of Polystyrene in Methylcyclohexane. I. Range of Simple Scaling and Critical Exponents." *J. Chem. Phys.* 72, 6685 (1980).
- [22]. T. Dobashi, M. Nakata and M. Kaneko, "Coexistence Curve of Polystyrene in Methylcyclohexane. III. Asymptotic Behavior of Ternary System Near the Plait Point." *J. Chem. Phys.* 80, 948 (1984).

[23]. A.R. Shultz and P.J. Flory, "Phase Equilibria in Polymer-Solvent Systems." J. Amer. Chem. Soc. 74, 4760 (1952).

[24]. F. Hamada, K. Fujisawa and A. Nakajima, "Lower Critical Solution Temperature in Linear Polyethylene- n-Alkane Systems," Polym. J. 4, 316 (1973).

[25]. A. Nakajima, H. Fujiwara and F. Hamada, "Phase Relationships and Thermodynamic Interaction in Linear Polyethylene-Diluent Systems." J. Polym. Sci. Part A-2. 4, 507 (1966).

[26]. N. Kuwahara, S. Saeki, T. Chiba and M. Kaneko, "Upper and Lower Critical Solution Temperatures in Polyethylene Solutions." Polymer 15, 777 (1974).

[27]. J.M.G. Cowie and I.J. McEwen, "Lower Critical Solution Temperatures of Polypropylene Solutions." J. Polym. Sci., Polym. Phys. Ed. 12, 441 (1974).

Figure Captions

Figure 1. Illustration of the method of alternating tangents. The solid line is the system methanol(1)-cyclohexane(2). The dotted line is the system PS(1)-acetone. The two spinodal points are indicated by x_1^{sp1} and x_1^{sp2} . The equilibrium (binodal) points are indicated by x_1^{eq1} and x_1^{eq2} . Starting from a spinodal point, the equilibrium values can be calculated by solving for only one point.

Figure 2. Liquid-liquid equilibrium in the system polystyrene-cyclohexane for polystyrene molecular weight 1 270 000 showing both the spinodal and binodal (co-existence) curves. The two curves converge at the critical solution temperature.

Figure 3. Liquid-liquid equilibrium in the system polystyrene-methyl cyclohexane for different molecular weights of polystyrene. The experimental data are from Dobashi et al. [21,22]. The lines are simplified PC-SAFT correlations with $k_{ij} = 0.0065$ for polystyrene molecular weights 10 200, 46 400 and 719 000 in order of increasing temperature.

Figure 4. Liquid-liquid equilibrium in the system polyisobutylene-diisopropyl ketone. PC-SAFT parameters for diisopropyl ketone were obtained by fitting to experimental liquid density and vapour pressure data in the temperature range 260 – 600 K. The parameters were, $m = 4.6179$, $\varepsilon/k = 243.72$ K and $\sigma = 3.7032$ Å. Average percent deviations were 1.03 % for vapour pressure and 0.64 % for liquid density. Experimental data are from Shultz and Flory [23]. Lines are simplified PC-SAFT correlations with $k_{ij} = 0.0053$ at each of the three molecular weights.

Figure 5. Liquid-liquid equilibrium in the system HDPE-*n*-heptane. The experimental data are from Hamada et al. [24]. The lines are simplified PC-SAFT correlations with $k_{ij} = -0.006$ for the molecular weights shown. This system displays lower critical solution temperature (LSCT) behaviour.

Figure 6. Liquid-liquid equilibrium for HDPE with *n*-alkanols. The experimental data are from Nakajima et al. [25]. Lines are simplified PC-SAFT correlations for each of the five solvents (pentanol highest, nonanol lowest). Polymer molecular weight is 20 000. Binary interaction parameters are as follows: pentanol: 0.0006; hexanol: 0.003; heptanol: 0.0025; octanol: 0.0033; nonanol: 0.0029

Figure 7. Liquid-liquid equilibrium in the system HDPE-butyl acetate. The system displays both upper and lower critical solution behaviour. The experimental data are from Kuwahara et al. [26] for molecular weights 13 600 and 64 000. Lines are simplified PC-SAFT correlations with $k_{ij} = 0.0156$ for both molecular weights.

Figure 8. Liquid-liquid equilibrium in the system PP-diethyl ether. The system displays lower critical solution behaviour. The experimental data are from Cowie and McEwen [27]. The lines are PC-SAFT predictions ($k_{ij} = 0$) for the four molecular weight shown.

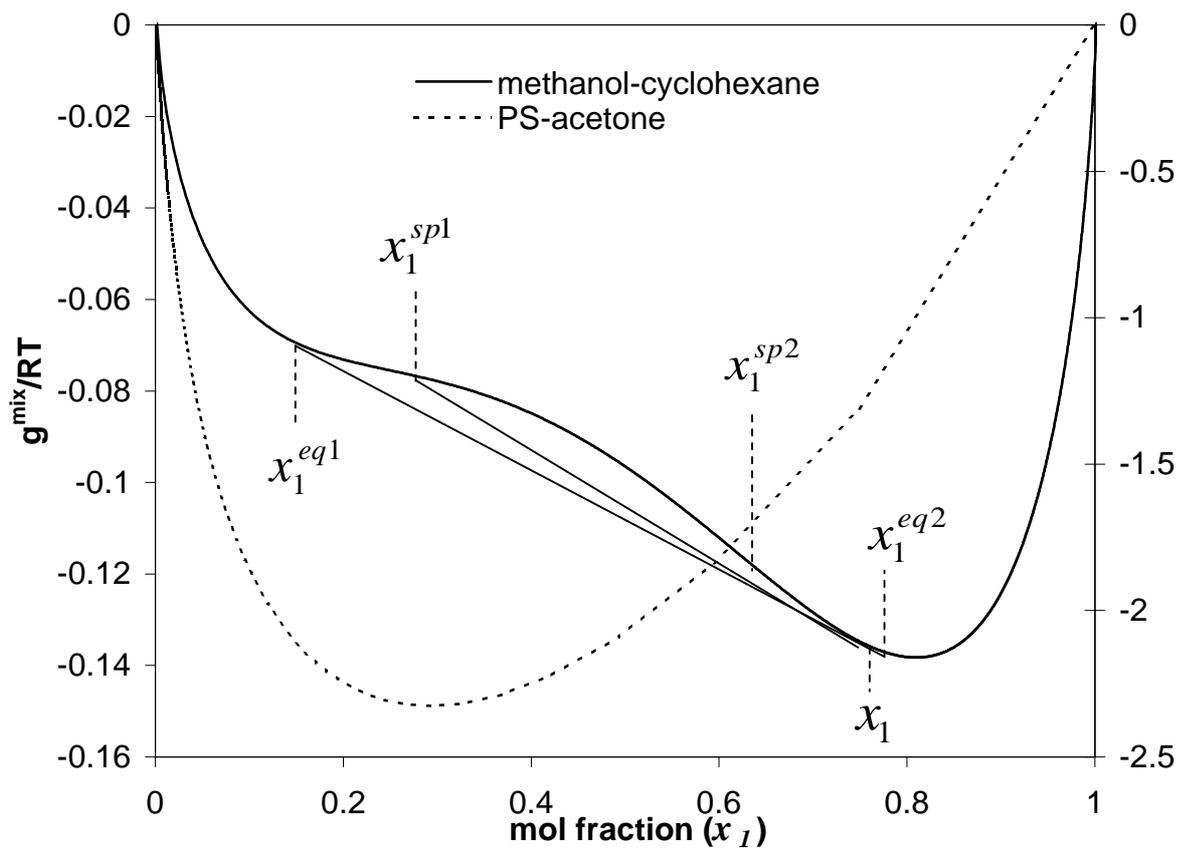


Figure 1 von Solms et al.

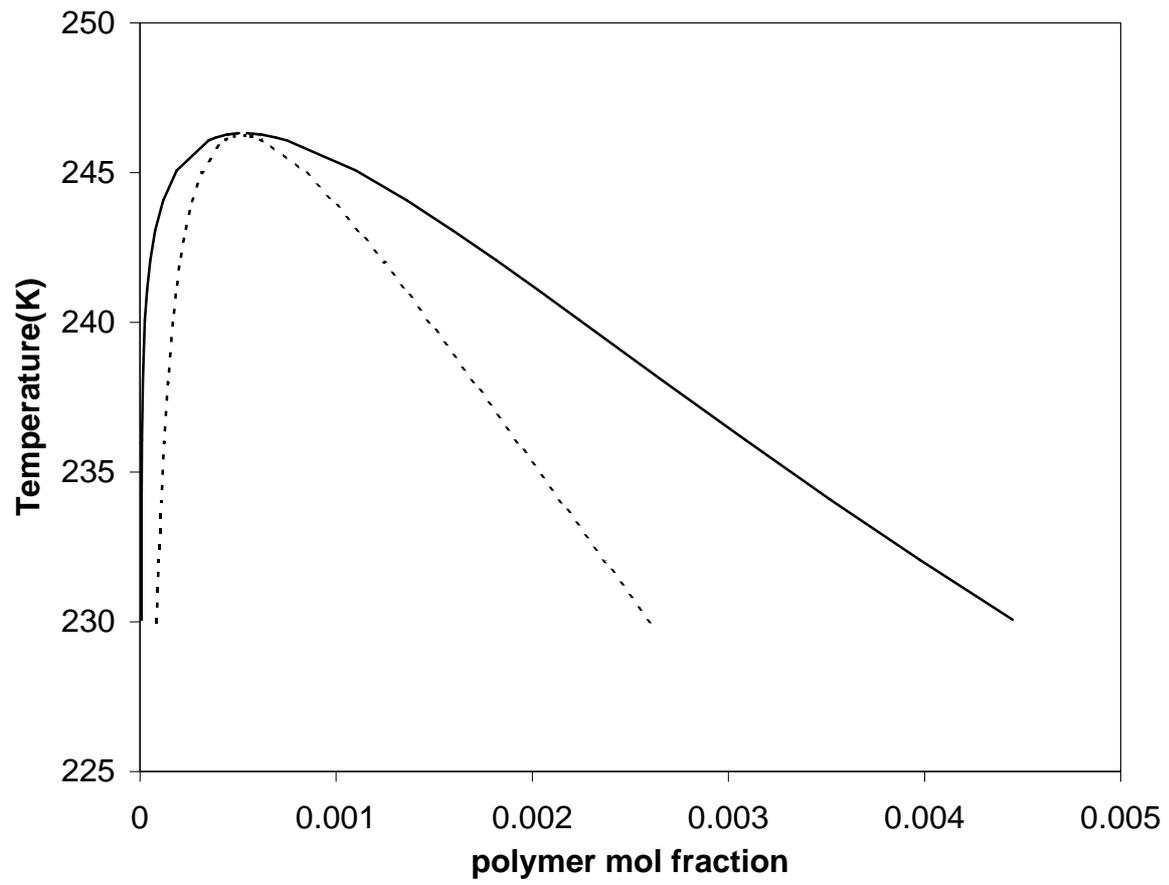


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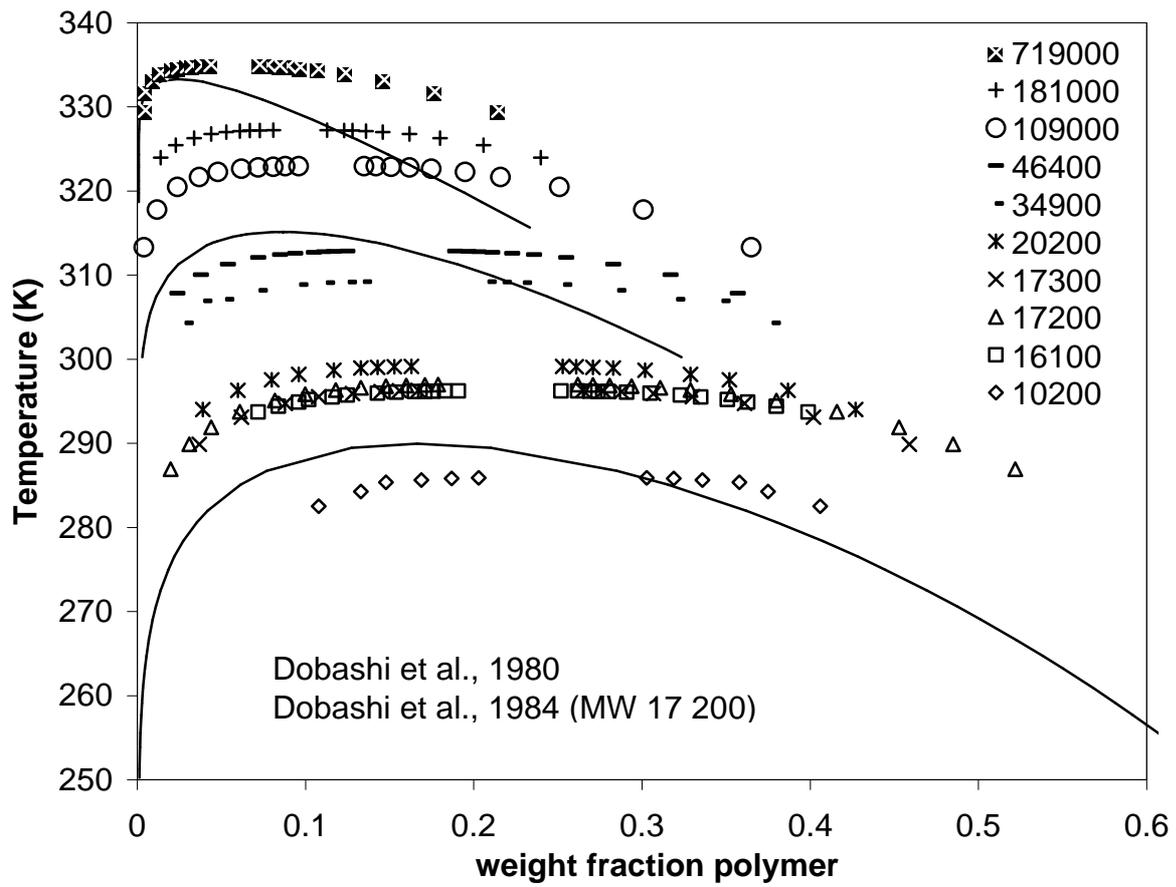


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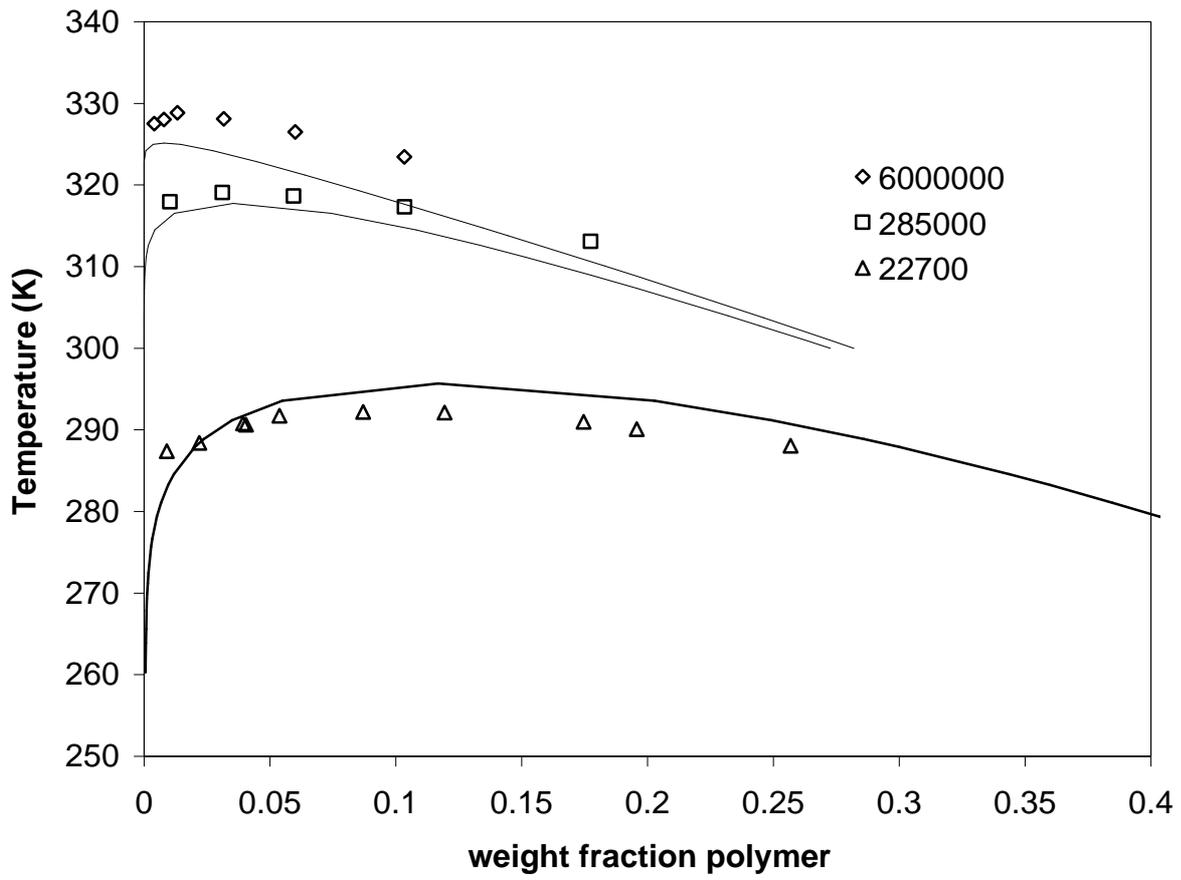


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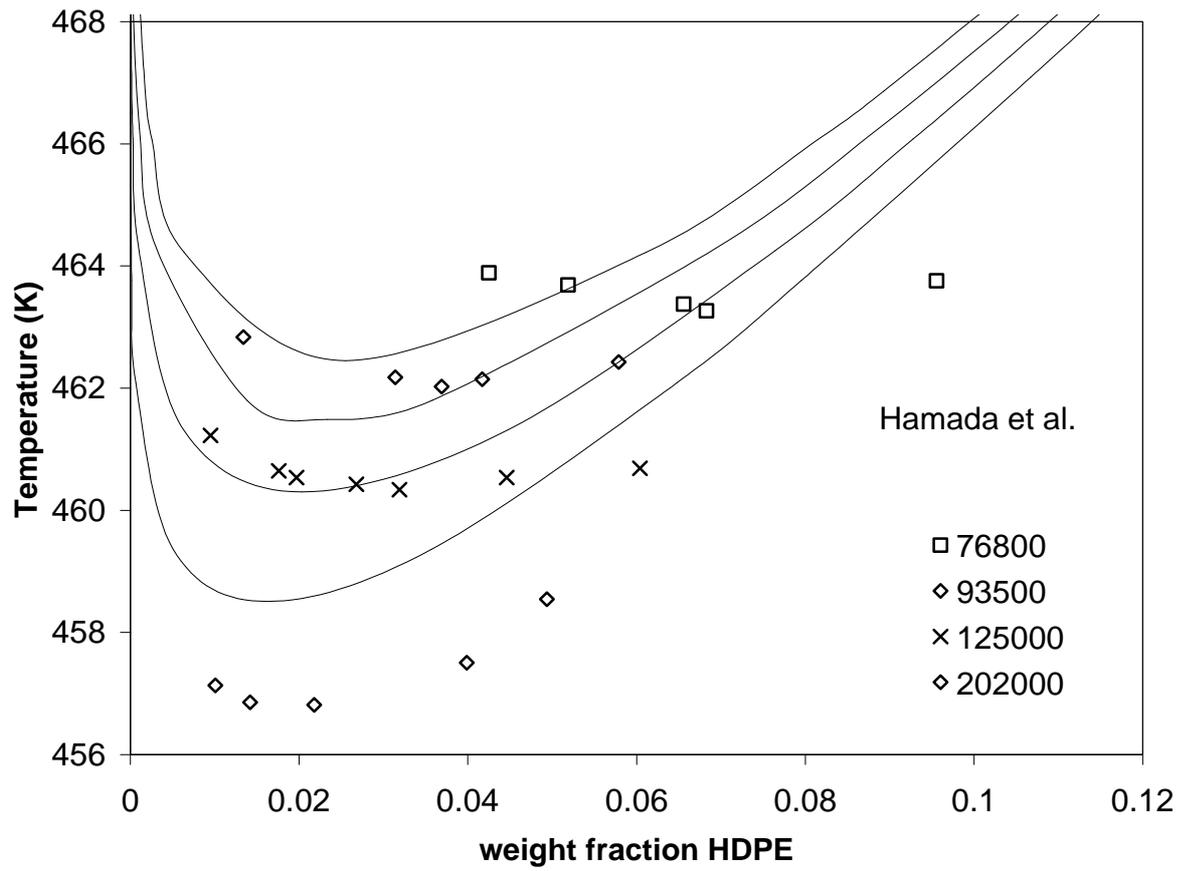


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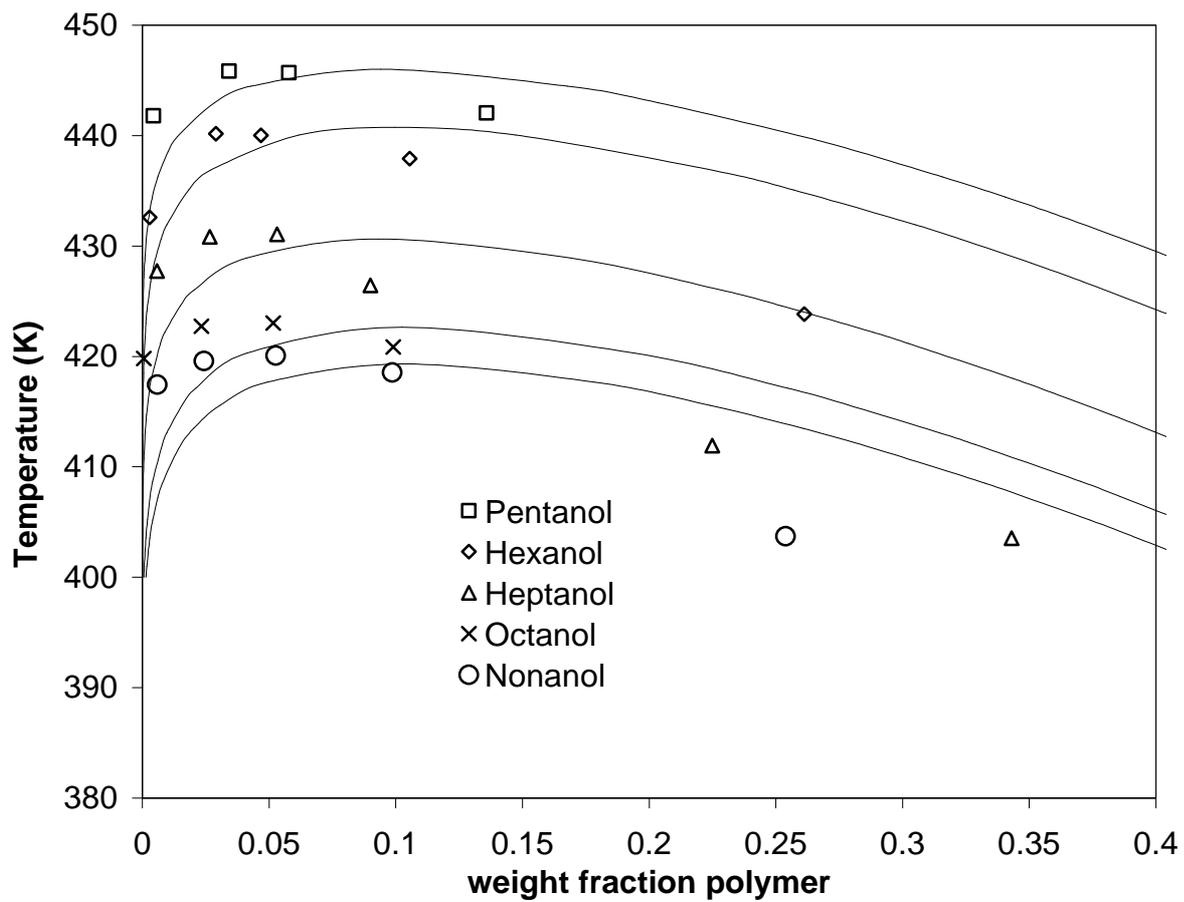


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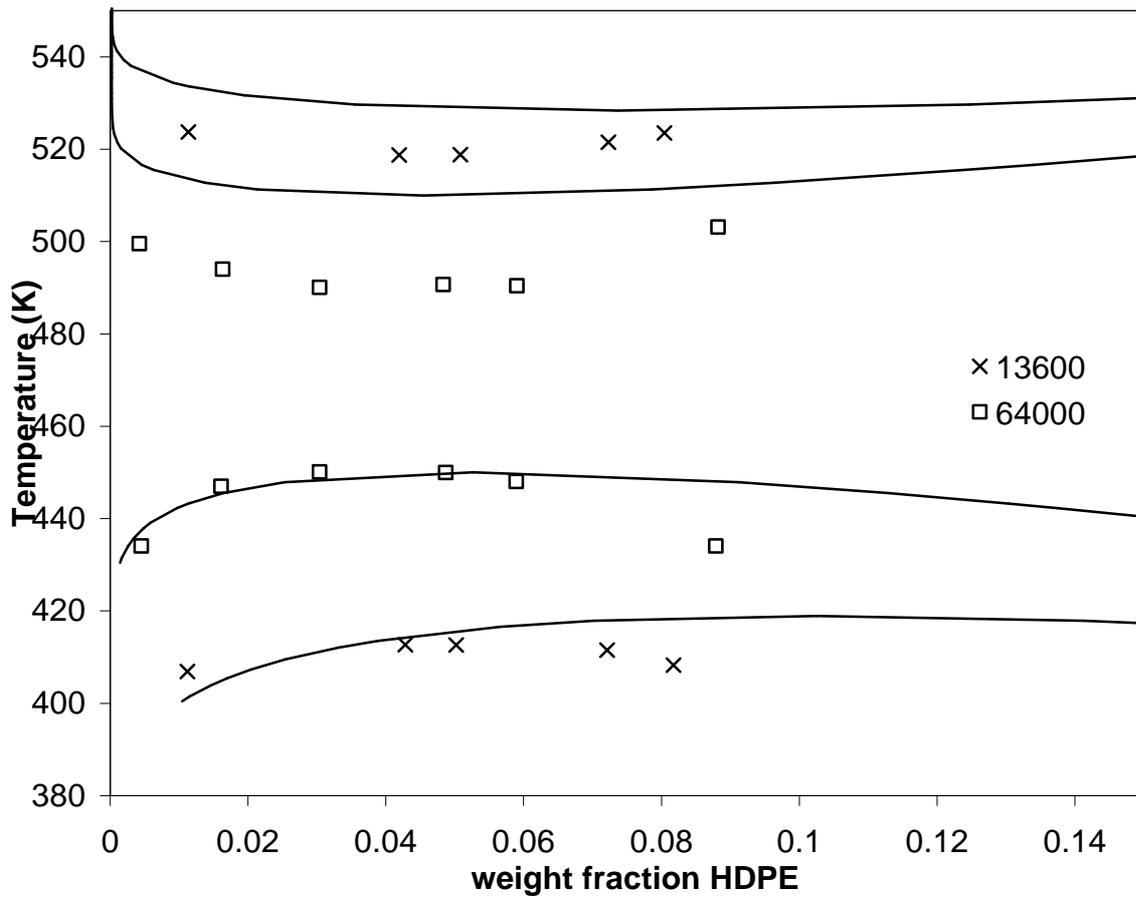


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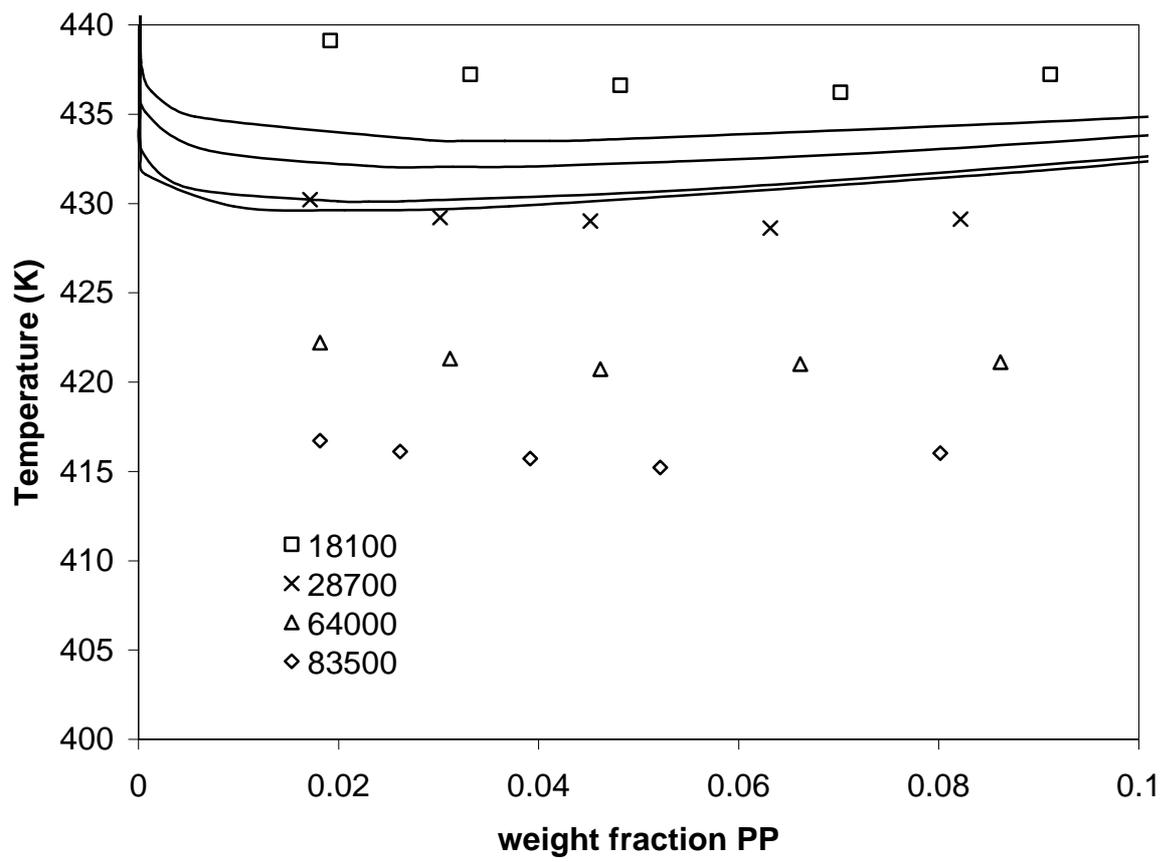


Figure 8 von Solms et al.