

Miscibility behavior of polymer systems: equation of state contributions

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MISCIBILITY BEHAVIOR OF POLYMER SYSTEMS:
EQUATION OF STATE CONTRIBUTIONS

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1. Introduction

A proper understanding of the phase behavior of polymer solutions and mixtures is of interest scientifically and technologically. Classical thermodynamic theories have been reasonably successful in rationalizing phase behavior. With the pioneering work of Flory (1), Huggins (2), Staverman (3) a.o. a theoretical understanding of upper critical (UCM) phase behavior, i.e. demixing with decreasing temperature, was obtained. For non-polar systems UCM phase behavior results due to combinatorial entropy contributions, which at high temperatures lead to miscibility, and unfavorable energetic interactions which at low temperatures cause the system to demix. The understanding of lower critical (LCM) phase behavior, i.e. demixing with increasing temperature, emerged 30 years later with the advent of equation of state theories (4-7). Despite the theoretical understanding often only a qualitative agreement between experiment and theory is obtained. This is especially true if one is interested in the influence of pressure on the miscibility behavior. With the statistical thermodynamic theory developed in the previous paper (8) it is shown that also for the latter quantitative predictions can be obtained.

2. Phase behavior: spinodal and critical conditions

The phase stability of mixtures at given pressure P and temperature T is governed by the Gibbs free energy G related to the Helmholtz free energy F and the equation of state

$$G = F + PV \quad (1)$$

where V is the volume of the mixture.

In the P-V-T-composition diagram of a binary mixture of components A and B spinodal and critical conditions can be defined and are related to the second and third compositional derivatives of the Gibbs free energy respectively (9). The spinodal is defined by

$$J_{sp} = \partial^2 G / \partial \phi_b^2 = 0 \quad (2)$$

where ϕ_b is the segment fraction of component B in the mixture. The critical condition, which is also a spinodal point, is given by

$$J_{sp} = 0 \text{ and } J_{cr} = \partial^3 G / \partial \phi_b^3 = 0 \quad (3)$$

3. Critical temperature: influence of pressure

The change of the critical temperature with pressure $(\partial T / \partial P)_c$ can be related to the compositional curvature of volume and enthalpy of the mixture (10)

$$(\partial T / \partial P)_c = (\partial^2 V / \partial \phi_b^2)_c / (\partial^2 H / \partial \phi_b^2)_c \quad (4)$$

where the subscript c indicates that the derivatives have to be evaluated at the critical temperature and composition for a given pressure.

The curvature of the enthalpy of mixing is directly related to the type of phase behavior. For LCM and UCM phase behavior one finds (10)

$$\text{LCM: } (\partial^2 H / \partial \phi_b^2) > 0 \quad (5a)$$

$$\text{UCM: } (\partial^2 H / \partial \phi_b^2) < 0 \quad (5b)$$

Consequently, according to Eqs. (4) and (5) the slope of the critical temperature with pressure is directly related

to the curvature of the volume of mixing as a function of composition.

4. Comparison of theoretical predictions with experimental data

The molecular parameter values used in the comparison with experiment are summarized elsewhere (11). The pure component parameters are obtained from the equation of state behavior of the constituents. The cross interactional parameters ϵ^*_{ab} and v^*_{ab} are calculated from the critical point (T_c and w_{2c}) for the system CH/PS3 (see Table 1) (12). With the molecular parameters fixed all configurational thermodynamic properties, e.g. critical conditions, can be predicted for different polymer samples in cyclohexane. In Table 1 it can be observed that the chain length dependence of the critical coordinates is not predicted accurately. The agreement between experiment and theory can be improved if allowance is made for a small change in the cross interactional parameters with chain length (13). However it is believed that the discrepancies are a direct consequence of the mean field approximation adopted in the statistical theory. For the present purpose the discrepancies are accepted and we focus on the predictions concerning LCM phase behavior and the influence of pressure on miscibility. It has been shown previously that the predicted LCM demixing is in reasonable agreement with experimental data. Therefore with the present hole theory a semi-quantitative prediction of the entropy driven LCM demixing is obtained, using parameter values extracted from the enthalpy driven UCMT phase behavior.

In Figure 1a the influence of pressure on the critical temperature of the system PS4/CH is shown (14). Initially the slope of the critical temperature with pressure $(\partial T / \partial P)_c$ is negative but at sufficiently high pressure the slope becomes zero and finally positive. Furthermore Saeki et. al. measured the pressure dependence of the critical temperature for different molar masses in a pressure range where changes in slope with pressure, as shown in figure 1a, are not observed (15). In Figure 1b the initial slope $(\partial T / \partial P)_c$ is negative for high molar masses in agreement with the data of Wolf and Geerisen. However if the molar mass is decreased sufficiently a positive slope $(\partial T / \partial P)_c$ is observed. In Figure 1 the solid line is the predicted pressure dependence according to the hole theory. Although the agreement with experiment is not quantitative, especially in Figure 1b, the observed agreement with experiment is very gratifying, remembering that no adjustable parameters are involved since they have already been determined as stated previously. According to Eqs. 4 and 5 the change in slope with molar mass and pressure is directly related to the compositional curvature of the volume of mixing. In Figure 2 the predicted excess volume ΔV is plotted as a function of pressure at constant molar mass. As a function of molar mass at atmospheric pressure a similar composition dependence is observed. For sufficiently high molar masses and at moderate pressures the excess volume is positively curved for all polymer concentrations. Consequently a negative slope $(\partial T / \partial P)_c$ is predicted. Upon applying pressure or decreasing the molar mass of the polymer, locally at low polymer concentrations a negative curvature of the excess volume ensues. For high pressures and small molar masses the region extends over a larger polymer concentration range. Depending on the location of the critical composition in a region of positive, zero or negative curvature, the slope $(\partial T / \partial P)_c$ is negative, zero or positive respectively. Unpublished results of Wolf et. al. show that the experimental and theoretical composition dependencies of the excess volume for different molar masses are in qualitative agreement (16). In view of the agreement observed in Figure 1b only a qualitative agreement can be expected. However the main features of the dependence of the excess volume on composition and chain length are reproduced. Thus a consistent thermodynamic prediction of the complicated pressure dependence is obtained.

5. Cell and free site volumes

In the hole theory the excess volume can be viewed as the result of two volume changes upon mixing, i.e. a volume change ΔY due to a change in the fraction of free lattice sites and a volume change $\Delta\Omega$ due to the change of the volume per lattice site (the cell volume)

$$\Delta V = \Delta Y + \Delta\Omega \quad (6)$$

In Figure 3 the different contributions to the total volume change ΔV are shown for three different pressures. The volume change due to the change in the fraction of free lattice sites is very sensitive to pressure. The changes in excess cell volume $\Delta\Omega$ however are practically pressure independent. Upon pressurizing the densification of the liquid related to ΔY is reduced. Consequently, for sufficiently high pressures the excess cell volume becomes relatively more important and cause a local change in curvature of the total excess volume ΔV , also shown in Figure 2. Furthermore the excess cell volume $\Delta\Omega$ is practically independent of the molar mass. Only the occupied fraction of segments ΔY is sensitive to changes in molar mass. Consequently for sufficiently low polymer molar masses the cell volume changes $\Delta\Omega$, relative to ΔY , become more important and cause the total excess volume ΔV to change curvature.

6. Influence of cell and free lattice site volumes on LCMT phase behavior.

In polymer solutions showing LCM phase behavior differences in lattice free site volume are large compared to the changes in cell volume. Therefore, the contribution of the excess cell volume is not able to manifest itself. Consequently in polymer solutions the LCM miscibility gap will be raised with pressure. For polymer mixtures however volume changes due to change in the fraction of free lattice sites are much smaller compared to those in polymer solutions. In this case cell volume effects can become noticeable and, eventually, the LCM miscibility gap may lower in temperature with pressure. Furthermore the two different contributions to the excess volume may cause a complicated pressure dependence of the spinodal condition in the temperature-composition diagram. It is worth mentioning that a complicated pressure dependence on cloud-point curves has been observed experimentally (17).

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Tables

Table 1. Critical coordinates for different PS sample in CH.

sample code	M_w kg/mol	T_c K	w_{2c} mass frac.	T_c K	w_{2c} mass frac.
PS1	51	288.85	0.146	292.10	0.121
PS2	166	296.60	0.099	297.88	0.081
PS3	520	301.15	0.064	301.15	0.064
PS4	600	301.34	--	--	--

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