The effect of pressure on the determination of the Flory–Huggins χ parameter by vapour pressure measurements

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The pressure experienced by polymer solutions during vapour pressure measurements varies with the composition of the solution at fixed temperature. The effect of this pressure variation upon the determination of the Flory–Huggins χ parameter through vapour pressure or vapour sorption measurements is examined. It is found that the effect is negligibly small at room temperature, but that it may become worth considering near lower critical solution temperature (*LCST*) conditions. Thus, for the system polystyrene–toluene, which exhibits a *LCST* at 277°C, consideration of the pressure variation effect during dissolution leads, when the weight fraction of polymer exceeds 0.9, to an estimated decrease in the value of χ of the order of 10%. The equivalent effect on light scattering determinations of the χ parameter is also briefly discussed.

(Keywords: pressure; Flory–Huggins χ parameter; vapour pressure measurements)

General remarks

Quite generally, in a constant temperature mixing process, the Helmholtz free energy change ΔF_{mix} is the sum of two contributions:

$$\Delta F_{\mathrm{mix}} = [\Delta F_{\mathrm{mix}}]_{\mathrm{V}} + \int_{V_{\mathrm{I}}}^{V_{\mathrm{I}}+V^{\mathrm{E}}} P(V)\,\mathrm{d}V \qquad (1)$$

Here $[\Delta F_{\mathrm{mix}}]_{\mathrm{V}}$ is the free energy change when mixing occurs at constant volume, V_{I} is the initial volume of the unmixed species and V^{E} is the excess volume of mixing. If $V^{\mathrm{E}} > 0$ at atmospheric pressure, a constant volume mixing may be obtained by applying an adequate external pressure, so that in this case:

$$\Delta F_{\mathrm{mix}} = [\Delta F_{\mathrm{mix}}]_{\mathrm{V}} \qquad (2)$$

In a similar manner, in a constant temperature mixing process, the Gibbs free energy (free enthalpy) change ΔG_{mix} is again the sum of two contributions:

$$\Delta G_{\mathrm{mix}} = [\Delta G_{\mathrm{mix}}]_{\mathrm{P}} + \int_{P_{\mathrm{I}}}^{P_{\mathrm{I}}+\Delta P} V_{\mathrm{sol}}(P)\,\mathrm{d}P \qquad (3)$$

Here $[\Delta G_{\mathrm{mix}}]_{\mathrm{P}}$ is the constant pressure free enthalpy change, V_{sol} the pressure dependent volume of the solution, P_{I} the initial pressure applied on the unmixed species and $P_{\mathrm{I}} + \Delta P$ the final pressure acting upon the solution. If $\Delta P = 0$ (constant pressure process), then:

$$\Delta G_{\mathrm{mix}} = [\Delta G_{\mathrm{mix}}]_{\mathrm{P}} \qquad (4)$$

Now $[\Delta F_{\mathrm{mix}}]_{\mathrm{V}}$ and $[\Delta G_{\mathrm{mix}}]_{\mathrm{P}}$ are essentially the same, and the chemical potential change of the solvent (species 1) upon mixing is given by

$$\Delta\mu_1 = \left[\frac{\partial}{\partial n_1}\Delta F_{\mathrm{mix}}\right]_{\mathrm{T,V},n_i} = \left[\frac{\partial}{\partial n_1}\Delta G_{\mathrm{mix}}\right]_{\mathrm{T,P},n_i} \qquad (5)$$

where n_i is the number of moles of species i.

The above remarks, at first sight trivial, are in fact of primary importance in polymer solution thermodynamics because they permit an unambiguous determination of the constant volume theoretical parameter χ (or g, see below) from constant pressure experiments in which V^{E} is not necessarily zero. In other words, the χ parameter in the constant volume original Flory–Huggins equation may be correctly determined by applying constant pressure thermodynamic data to that equation.

The Flory–Huggins interaction parameter χ

Consider the Flory–Huggins equation for the constant volume Helmholtz free energy change upon mixing polymer and solvent; in its weight fraction version this equation reads[1,2]:

$$[\Delta F_{\mathrm{mix}}]_{\mathrm{V}} = [\Delta G_{\mathrm{mix}}]_{\mathrm{P}} = RT[n_1 \ln w_1 + n_2 \ln w_2 + g_{\mathrm{w}} n_1 w_2] \qquad (6)$$

Here n_1 and n_2 are moles and w_1 and w_2 weight fractions of solvent and polymer, respectively, g_{w} is the Flory–Huggins parameter, the subscript indicating that the equation is written on a weight fraction basis. The term g_{w} differs somewhat from g, the Flory–Huggins parameter, when equation (6) is written on a volume fraction basis. Differentiating equation (6) with respect to n_1 keeping n_2, T and P constant, one obtains for the chemical potential change of the solvent, with the assumption that g_{w} depends on composition:

$$\Delta\mu_1 = RT\left[\ln(1 - w_2) + \left(1 - \frac{M_1}{M_2}\right)w_2 + \chi_{\mathrm{w}} w_2^2\right] \qquad (7a)$$

$$\chi_{\mathrm{w}} = \frac{\mathrm{d}}{\mathrm{d}w_1}(w_1 g_{\mathrm{w}}) \qquad (7b)$$

where M_1 and M_2 are the molecular weights of, respectively, solvent and polymer. If g_{w} (or, conversely, χ_{w}) is constant with composition, then $g_{\mathrm{w}} = \chi_{\mathrm{w}}$, a mostly unjustified assumption of the early Flory–Huggins theory[3]. If equation (7) is written on the more usual volume fraction basis, then one would have $\chi = \mathrm{d}[(\varphi_1 g)/\mathrm{d}\varphi_1]$, with again χ differing[4] from χ_{w}.

The advantage of writing equation (7) on a weight fraction basis lies in the fact that all the parameters on the right-hand side of the equation except g_{w} are pressure

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and temperature independent. In the following we assume that χ_w is constant with composition, so that $g_w = \chi_w$. This is sufficient for present purposes. It should be noted that g_w or χ_w will not be considered to be exclusively related to the free energy change accompanying the formation in solution of solvent–polymer pairs from solvent–solvent and polymer–polymer pairs, as assumed in the original Flory–Huggins theory, rather g_w and χ_w will be considered to be parameters of more general significance, in which the pair interchange energy is but one component of these parameters. This complies with the more recent theories of polymer solutions, developed during the 1960s and early 1970s by Flory *et al.*[5], Delmas *et al.*[6] and others[7,8], which are based on the Prigogine cell model theory of solutions[9]. (Those unfamiliar with these newer theories may simply consider g or χ as being just adjustable parameters able to fit experimental data.)

Effect of pressure on the vapour pressure determination of the χ parameter

Among the various techniques allowing the determination of solvent activity, solvent chemical potential and the χ parameter, some common techniques are vapour pressure, vapour sorption, osmotic pressure and light scattering measurements. Except perhaps osmometry, which by definition is the search for a pressure effect, all other techniques are sensitive to the fact that there is a variation in the pressure applied on the solution, as the vapour pressure of the solvent changes with composition. To ascertain that this pressure effect does exist, it suffices to observe that when a polymer is introduced in a solvent to be dissolved, it first experiences a pressure equal to the vapour pressure of the solvent. (Hydrostatic pressure effects are not considered here and are assumed to be absent or negligible.) As the polymer dissolves, the vapour pressure is lowered, until the equilibrium vapour pressure of the solution is reached. Therefore, during the dissolution process, besides the dominant term in the free enthalpy change due to mixing, there is a correction term due to pressure variation. Equivalent considerations apply if solvent vapour is distilled on the polymer, to obtain concentrated solutions. Due to special apparatus or the experimental procedure, the pressure variation might be circumvented, in which case measurements are made with the solution not being in equilibrium with its vapour. Such cases should be examined separately. Here we shall exclusively be concerned with the usual case, where, before dissolution, the solvent–polymer system experiences the vapour pressure of the pure solvent, and after dissolution, that of the solution.

Pressure variation effects under usual temperature conditions are so small that they are completely negligible and experimentally undetectable (see below). However, in the vicinity of lower critical solution temperature (*LCST*) conditions, the effect is no longer negligible, and may account for an up to 10% correction (in absolute value) to the calculated χ value.

To illustrate this point we replace, according to equation (3) (where we neglect the effect of pressure on the volume of the solution), equations (6) and (7) by the following two equations:

$$\Delta G = [\Delta G_{\mathrm{mix}}]_{\mathrm{P}} + V_{\mathrm{sol}}\Delta P$$
$$= RT[n_1 \ln w_1 + n_2 \ln w_2 + \chi_w n_1 w_2] + V_{\mathrm{sol}}\Delta P \qquad (6')$$

$$\Delta\mu_1 = RT[\ln(1 - w_2) + w_2 + \chi_w w_2^2] + V_1\Delta P \qquad (7a')$$

In equation (7a′), V_1 is the partial molar volume of the solvent. We neglect, in the same equation, the term $(M_1/M_2)w_2$. We now focus on vapour pressure measurements, but the conclusions reached also apply to vapour sorption measurements. We choose to apply equation (7a′) to the polystyrene–toluene system, which has been studied by Bawn *et al.*[10] and Scholte[2]. This system displays at room temperature a χ parameter which is close to 0.4 and nearly independent of composition*, so that, at least near such temperature conditions, it is legitimate to confuse g_w and χ_w. We shall consider two temperatures: 80 and 277°C. The first of these temperatures is the highest one used by Bawn *et al.*, where the pressure variation effect is bound to be the most important; the second one is that of the *LCST* of the polystyrene–toluene system[11]. To be able to compute the second term in equation (7a′), we first need the absolute value of the pressure of toluene vapour at 80 and 277°C. These pressures were estimated using the Antoine equation[12], with values of the constants A, B and C given by Boublik *et al.*[13]. Using these values the Antoine equation yielded to better than 1% the vapour pressure of toluene at its boiling and critical temperatures (1×10^5 and 41.45×10^5 Pa, respectively[14]). At 80 and 227°C the corresponding pressures are found to be 0.396×10^5 and 22.4×10^5 Pa, respectively. We then need the ratio of the vapour pressure of the solution over that of the pure solvent at specified compositions. At 80°C the ratio may be estimated from reference 10. At 277°C we assume, in the absence of experimental data and as a rough estimate, the same value for the ratio. We further need the partial molar volumes of toluene. These are not known at either 80 or at 277°C, but an approximate value of 100 ml mol^{-1} at all compositions should be sufficient for present purposes. Finally, we assume a constant value for χ_w equal to 0.5 at both temperatures and at all compositions. The results of the calculations are given in *Tables 1* and *2*.

Table 1 shows that at 80°C the correction to χ_w is at most 0.25% and therefore negligible. It should be

Table 1 Effect of pressure on the determination of the χ_w parameter: polystyrene–toluene at 80°C

w_2	$[\Delta\mu_1]_{\mathrm{P}}$ (J mol^{-1})	$[RT\chi_w w_2^2]_{\mathrm{P}}$ (J mol^{-1})	$V_1\Delta P$ (J mol^{-1})	$\Delta\chi_w/\chi_w$ ($\times 10^{-2}$)
0.6	−401	528	−0.47	−0.089
0.8	−1437	939	−1.46	−0.155
0.9	−2929	1189	−2.45	−0.206
0.95	−6007	1325	−3.17	−0.240

Table 2 Effect of pressure on the determination of the χ_w parameter: polystyrene–toluene at 277°C

w_2	$[\Delta\mu_1]_{\mathrm{P}}$ (J mol^{-1})	$[RT\chi_w w_2^2]_{\mathrm{P}}$ (J mol^{-1})	$V_1\Delta P$ (J mol^{-1})	$\Delta\chi_w/\chi_w$ ($\times 10^{-2}$)
0.6	−623	823	−29	−3.52
0.8	−2237	1463	−90	−6.15
0.9	−4562	1851	−151	−8.15
0.95	−7291	2063	−195	−9.45

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* See reference 3. The Scholte values of χ_w for the polystyrene–toluene system as reproduced in this review article do not correspond to those in the original article[2]

considerably smaller at room temperature. However, as shown in *Table 2*, the effect is no longer negligible near *LCST* conditions and may amount to a 10% negative correction to χ (i.e. a decrease of 10% in the value of χ_w).

Discussion

In the absence of experimental determinations of the partial molar volume of the solvent and of solvent activities near *LCST* conditions, equation (7a′) cannot be used for the precise determination of the χ_w parameter and the effect of pressure on the evaluation of this parameter. The rough estimates in *Table 2* show however that the effect may not be negligible near *LCST* conditions. The effect is larger at high polymer concentrations and is enhanced by high solvent critical pressure and low critical temperature. These considerations apply to both vapour pressure and vapour sorption measurements. The light scattering technique should also be sensitive to the pressure variation effect. Application of light scattering theory of polymer solutions[15] to χ_w determinations was performed in particular by Scholte, who studied the polystyrene–cyclohexane system[16]. Light scattering data provide the quantity $\partial\Delta\mu_1/\partial w_1$. If pressure effects are not negligible, then one should write $\Delta\mu_1 = [\Delta\mu_1]_P + V_1\Delta P$ and equate the right-hand side of equation (8) in reference 16 to the derivative with respect to w_1 of the latter quantity. Thus, χ_w here also becomes pressure dependent. A detailed analysis (beyond the scope of this communication) will undoubtedly show equivalent effects of pressure on χ_w as before. However, as light scattering measurements are usually restricted to relatively low concentrations, the interest of considering pressure effects for this technique might be only academic. In any case, this point should be carefully investigated. Finally, at high temperatures, the Flory–Huggins combinatorial entropy $-R[n_1 \ln w_1 + n_2 \ln w_2]$ cannot be considered to be adequate, as the free volume in the solution becomes very important. To extend the above expression to, say, *LCST* conditions, one may for example consider ‘holes’ in the solution and derive the combinatorial entropy of mixing of a binary polymer–solvent system on the basis of three ‘components’: polymer, solvent and holes. Several investigators, in particular Sanchez and Lacombe[8], have used holes in the past as a distinct species in polymer solution theory.

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