

Thermodynamics of macromolecular systems

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Abstract - The difference between polymeric systems and small molecule mixtures appears mainly in miscibility behaviour. Polymer solutions, polymer blends and copolymer mixtures are considered on the basis of the still useful classic lattice model. Phase behaviour is sensitively governed by variations in chain length (distribution). Pressure and flow are important variables in polymer production and processing. The influence of pressure is treated on the basis of classical thermodynamic relations.

INTRODUCTION

The main difference between mixtures of small molecules and those containing polymers is the large disparity in numbers of molecules per unit volume. As a result, the combinatorial entropy per unit volume is drastically reduced when monomeric species in a mixture are polymerized, and the entropy-energy balance becomes very subtle. This feature shows up very sensitively in liquid-liquid phase relationships that may exhibit enormous changes upon seemingly small variations in macromolecular structure. Chain length (distribution) and copolymer composition present cases in point and are discussed below. When processed, polymer mixtures are subjected to elevated pressures and intensive flow fields, influences that have to be dealt with for obvious practical reasons.

THERMODYNAMIC STABILITY OF LIQUID MIXTURES

The influence of the chain length of the macromolecules in a binary liquid mixture can be illustrated with the aid of the rigid lattice treatment. For mixtures of small molecules we have the Van Laar/Bragg-Williams expression for ΔG , the Gibbs free energy of mixing (ref. 1)

$$\Delta G/NRT = x_1 \ln x_1 + x_2 \ln x_2 + g x_1 x_2 \quad (1)$$

where x_i is the mole fraction of component i , N the total amount of material in moles of lattice sites, g the Van Laar interaction parameter and RT has its usual meaning.

Polymer solutions can be treated on the same level of approximation by the Flory-Huggins-Staverman (FHS) equation (ref. 2 - 6)

$$\Delta G/NRT = \phi_1 \ln \phi_1 + (\phi_2/m_2) \ln \phi_2 + g \phi_1 \phi_2 \quad (2)$$

which expression replaces the mole fraction x_i in Eq. 1 by ϕ_i , the volume fraction,

and reduces the value of the second term significantly, dividing it by m_2 , the usually large number of lattice sites occupied by the macromolecules. The volume fractions are defined by

$$\phi_1 = n_1/N; \phi_2 = n_2m_2/N; N = n_1 + n_2m_2 \quad (3)$$

where n_i is the amount of component i in moles.

If the solvent molecules are also strung together in chain molecules occupying m_1 sites each, we have a similar reduction of the first term on the r.h.s. in Eq. 1. Binary polymer mixtures, or blends, can thus be characterized by

$$\Delta G/NRT = (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + g\phi_1\phi_2 \quad (4)$$

where ϕ_1 is now given by

$$\phi_1 = n_1m_1/N = x_1/(x_1 + x_2m_2/m_1) \quad (5)$$

The three cases, mixtures of small molecules, polymer solutions, and polymer blends share the same expression for the interaction parameter g , at least in a first approximation:

$$g = h/T; \quad h = z\Delta w_{12}/RT \quad (6)$$

where z is the coordination number of the lattice and Δw_{12} is the change in internal energy upon breaking one mole of 1-1 and 2-2 nearest neighbour contacts to create two moles of 1-2 contacts.

The parameter h can be related to ΔH , the enthalpy of mixing,

$$\Delta H/NR = h\phi_1\phi_2 \quad (7)$$

Contributions to the heat of mixing arise from the z nearest neighbour contacts per molecule or site. In macromolecular systems only two out of the z (= about 10) contacts do not contribute to ΔH and, hence, values of ΔH do not differ very much from those found in comparable small molecule systems. The contrast resides mainly in the combinatorial entropy of mixing per site, the drastic reduction by chain connectivity causing the entropy-energy balance to be very sensitive in polymeric systems. This effect can be recognized in the expression for the critical state of demixing where we have (ref. 1, 7, 8)

$$g_c = \frac{1}{2}(1/\sqrt{m_1} + 1/\sqrt{m_2})^2 \quad (8)$$

Comparing the three types of system at an arbitrary critical temperature of 400 K we note that the h values differ considerably (Table 1). As a result, a small molecule system can withstand considerable unfavourable interactions (large positive h) and remain homogeneous whereas a polymer mixture has hardly any resistance

TABLE 1. Typical values of interaction parameters

System	m_1	m_2	g_c	h/K
1. Small molecule system	1	1	2	800
2. Polymer solution	1	100	0.605	242
3. Polymer blend	100	100	0.02	8

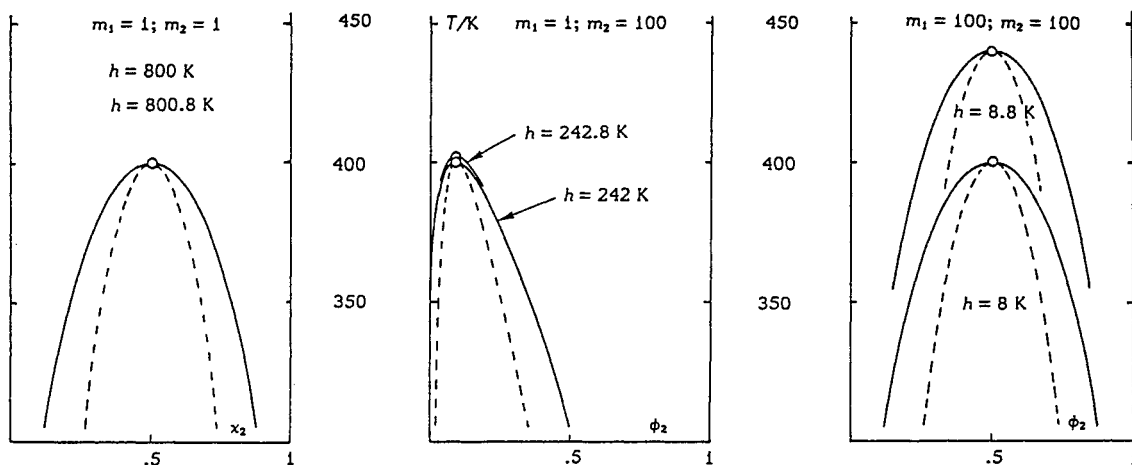


Fig. 1. Partial miscibility in Van Laar/Bragg-Willams and Flory/Huggins/Staverman systems. Left: mixture of small molecules; middle: polymer solution; right: polymer blend. Critical point: \circ , spinodal: - - -, binodal: —.

and readily becomes unstable. A variation of 0.1% in the heat of mixing, i.e., 0.8 K in h for system 1, hardly affects the location of the miscibility gap for that system, is noticeable in polymer solutions (shift of the critical temperature by 2 K), but is accompanied by a drastic change of miscibility behaviour in a polymer blend. Figure 1 illustrates these features, caused by chain connectivity. Polymer solutions are less resistant to demixing than comparable small molecule systems, polymer blends cannot remain homogeneous at the slightest positive ΔH . One-phase polymer blends do exist however, but are characterized by specific interactions leading to negative values of h .

Figure 1 also reveals that disparity in molecular size shifts the miscibility gap into the solvent-rich composition range (system 2). This feature has been amply illustrated by experiment and was already known and understood by Van der Waals, whose equation of state has molecular size as one of its parameters (ref. 9). Figure 2a shows this effect for an oligomeric system and also illustrates the great sensitivity to chain length. In Fig. 2b we have an example of an extremely asymmetrical miscibility gap.

The chain length distribution, typical for synthetic polymers, plays an important role and can be dealt with in a quantitative fashion. We refer the reader to the relevant literature (ref. 12, 13) and merely note here that the cloud point curve, a true binodal in a binary system, does not represent coexisting phases in the quasi-binary case where the polymeric constituent contains many homologous components. Such cloud point curves may assume a complicated shape (ref. 14), as is illustrated by Fig. 2a.

Figures 1 and 2 indicate the location of the spinodal curves (limit of stability) which obey the condition

$$[\partial(\Delta G/NRT)/\partial\phi_2]_{p,T} = 0 \quad (9)$$

Scattering techniques can be used to determine the location of spinodal points within the miscibility gap (ref. 15 - 17).

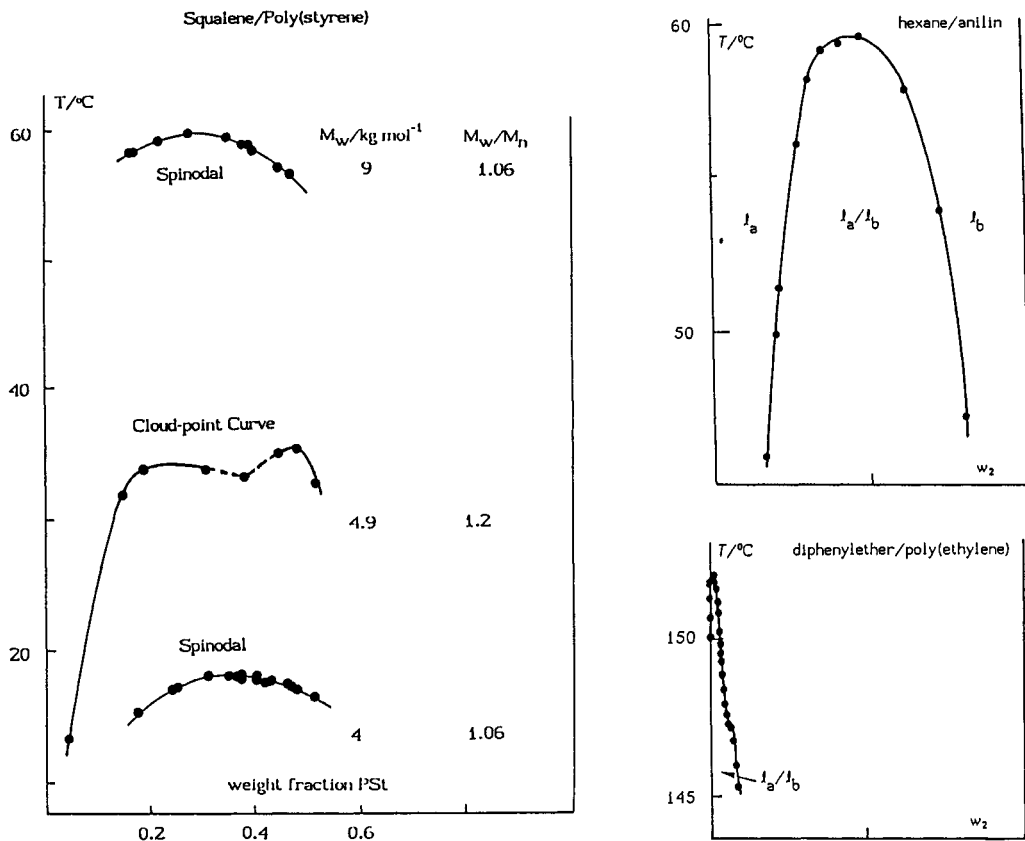


Fig. 2. (a, left): Spinodals and cloud point curve in the system squalene/poly(styrene) for indicated values of weight- and number-average molar mass, M_w and M_n . The ratio M_w/M_n is a measure for the width of the chain length distribution, the larger value indicating the wider distribution (ref. 10).

(b, right): Miscibility gap for a small-molecule system (top) and a poly(ethylene) solution (bottom) in which the molar masses of the constituents differ by a factor of about 10^3 (ref. 11).

MIXTURES OF STATISTICAL COPOLYMERS

Copolymerization is a powerful tool to overcome repulsive forces that would lead to extremely poor miscibility in mixtures of homopolymers. For instance, two homopolymers $P_{\alpha\alpha}$ and $P_{\beta\beta}$ with chain lengths $m_1 = 100$ and $m_2 = 100$ split into two phases at g values larger than 0.02 (Table 1). To obtain miscibility at $g = 2$ the two polymers would have to be depolymerized completely ($m_1 = 1$; $m_2 = 1$). A mixture of two copolymers, $P_{\alpha\beta_1}/P_{\alpha\beta_2}$, with chain lengths $m_1 = m_2 = 100$, each containing repeat units α and β , may still withstand demixing at $g_{\alpha\beta} = 2$, provided the α contents of the two polymers do not differ more than 10%. This seemingly illogical feature is explained by the fact that the α - β contacts, unfavourable for mixing, already exist in each of the two polymers before they are blended.

This remarkable behaviour was predicted by Scott who derived a ΔG expression for the systems in hand on the basis of the FHS model (ref. 18):

$$\Delta G/NRT = (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + g_{\alpha\beta}d_{12}^2\phi_1\phi_2 \quad (10)$$

where $g_{\alpha\beta}$ is the interaction parameter for α - β contacts and $d_{12} (= \phi_{\alpha_1} - \phi_{\alpha_2})$ is the difference in α content between the two copolymers. We note that ϕ_{α_1} and ϕ_{α_2} do not occur in the equation, it is only the difference d_{12} that matters on this level of approximation. Since $d_{12} < 0$, $g_{\alpha\beta}$ may assume relatively large values and still allow the system to remain miscible, d_{12}^2 attenuating its influence.

The stability limit is given by

$$1/m_1\phi_1 + 1/m_2\phi_2 - 2g_{\alpha\beta}d_{12}^2 = 0 \quad (11)$$

and defines the maximum tolerable composition difference $\Delta (= d_{12}$ on the spinodal) for the system to remain homogeneous. Scott's prediction was confirmed in later experiments (ref. 19, 20), albeit that Δ is usually not found to be independent of the individual ϕ_{α} 's.

Recently, Kambour *et al.* (ref. 21, 22) reported on the miscibility of poly(styrene) and poly(*p*-bromostyrene) and its dependence on chain length and bromine content. The material studied, anionically prepared poly(styrene), was partially brominated so that the chain lengths of original sample and its substitution products could be assumed to be identical, but for a contribution of the bromine atoms. Kambour *et al.* neglected the latter effect in their theoretical interpretation of the data.

In a first set of measurements poly(styrene) samples differing in chain length were mixed with their brominated derivatives and the maximum tolerable bromine content, Δ , was determined for a 50/50 (w/w) blend to remain homogeneous, *i.e.*, transparent. Δ was found to increase with decreasing chain length of the original poly(styrene). A second set concerned 50/50 mixtures of substituted poly(styrenes) of different bromine content. Kambour *et al.* found that the maximum tolerable difference in bromine content increased significantly with the average bromine content of the two constituents, at constant chain length.

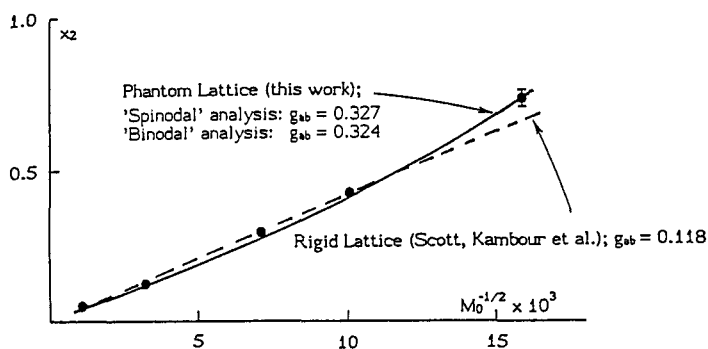


Fig. 3. Maximum tolerable bromine content, x_2 , for miscibility of 50/50 (w/w) mixtures of poly(styrene) and partially brominated poly(styrene) as a function of the molar mass of the primary homopolymer. Dashed curve: description by Scott's Eq. 12 with $g_{\alpha\beta} = 0.118$; drawn curve: description with either Eq. 16 with $g_{\alpha\beta} = 0.327$ or with binodal equations with $g_{\alpha\beta} = 0.324$. Data by Kambour *et al.* (ref. 21, 22).

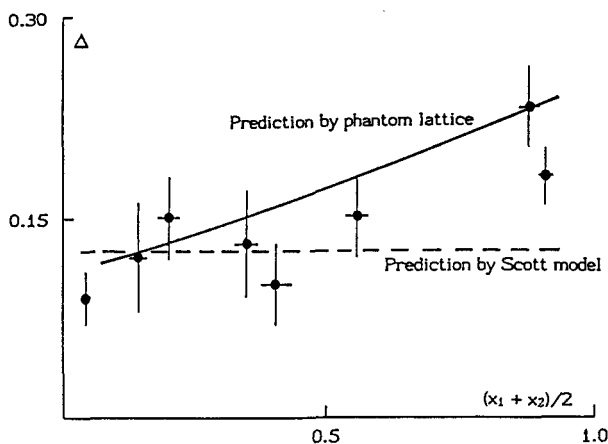


Fig. 4. Maximum tolerable composition difference, Δ , for miscibility of 50/50 (w/w) mixtures of partially brominated poly(styrenes). Dashed curve: prediction with Scott's Eq. 12 with $g_{\alpha\beta} = 0.118$; drawn curve: prediction with Eq. 16 ($g_{\alpha\beta} = 0.327$) or with binodal equations ($g_{\alpha\beta} = 0.324$). Data by Kambour *et al.* (ref. 21, 22).

The data were interpreted in terms of Scott's theory (ref. 18). For a system in which $m_1 = m_2 = m$, Eq. 11 changes into

$$\Delta = (2/mg_{\alpha\beta})^{\frac{1}{2}} \quad (12)$$

which relates Δ to the inverse square root of chain length m , in agreement with Kambour *et al.*'s findings for molar-mass values above 10^4 kg/mol. Lower chain lengths do not obey Scott's equation as is seen in Fig. 3. Eq. (11) predicts Δ to be independent of the composition of either of the two constituents but, again, this is not confirmed by the experiment (Fig. 4).

A simple extension of Scott's model already suffices to deal with the situation. The above treatment ignores the small change in molecular volume brought about by the bromination. Accounting for it proves to be an adequate remedy (ref. 23). We represent the partially brominated poly(styrene) (copolymer) molecules by chains, the beads of which are styrene units α , randomly carrying 'dangling' β groups, bromine atoms in the present case. The mole fraction of modified α units is x , the numbers of sites occupied by α units and β groups are 1 and b , respectively. If the primary chain contains m_0 units, the number of sites m , occupied by a modified chain is

$$m = m_0(1 + xb) = m_0p \quad (13)$$

Calculation of ΔH , the heat of mixing two samples differing in degree of modification (x_1 and x_2 , respectively), along the path defined by regular-solution rules (ref. 1) yields

$$\Delta H/NRT = (b\Delta/p_1p_2)^2 g_{\alpha\beta} \phi_1 \phi_2 = \Delta g_{\alpha\beta} \phi_1 \phi_2 \quad (14)$$

where $p_i = 1 + x_i b$. The free enthalpy of mixing now reads

$$\Delta G/NRT = (\phi_1/m_0p_1) \ln \phi_1 + (\phi_2/m_0p_2) \ln \phi_2 + \Delta g_{\alpha\beta} \phi_1 \phi_2 \quad (15)$$

In this first approximation we have introduced the factors p_i which deviate from unity because the bromination changes the numbers of occupied sites. Consequently, the 50/50 (v/v) composition is no longer a critical concentration, and the measured

Δ value does not refer to a spinodal situation. Ignoring this source of error we may use the spinodal equation to derive values for $g_{\alpha\beta}$. In the present approximation it reads

$$\Delta^2 = \{1 + b(x_1\phi_1 + x_2\phi_2)\}p_1p_2/2\phi_1\phi_2b^2g_{\alpha\beta}m_0 \quad (16)$$

Allowing for the fact that the 50/50 (w/w) composition is usually not a critical concentration complicates the analysis. The 50/50 cloud point may be considered to represent a binodal point (provided the samples have very narrow molar-mass distributions). The composition of the phase coexisting with that of the measured binodal point is unknown but we have an extra equation as well, two-phase equilibria being characterized by the equality of the chemical potential of each of the two components in the two phases.

The evaluation of the g values requires a convention with respect to the calculation of ϕ_i and m_i . The most convenient basic unit for the system is a mole of repeat units of one of the constituents. Then, ϕ_i equals the weight fraction and m_0 is the degree of polymerization of the primary chains. Further, $b = M_\beta/M_\alpha$, where M_α and M_β are the molar masses of α units and β groups, respectively.

Applying the, strictly speaking, irrelevant eq. (16) to the measured Δ values we may use the measured point for a particular primary molar mass to 'calibrate' $g_{\alpha\beta}$, and then use Eq. (16) to calculate Δ values for the other molar masses measured. If the data for the shortest primary chains among Kambour *et al.*'s data are used for the calibration, one finds $g_{\alpha\beta} = 0.327$. Since the other data were presumably taken at the same temperature, the same value of $g_{\alpha\beta}$ should apply. Figure 3 shows that the curve so calculated fits the data quite well, and includes the upturn at small m_0 , an effect not covered by Scott's equation (12). Next, Eq. (16) is used to predict the dependence of Δ on the average bromine content of blends of modified primary chains. Figure 4 demonstrates that the prediction follows the experimental trend, again in contrast to Scott's equation.

This result presents one more example of the extreme sensitivity of cloud points in polymer blends to variations in chain length (or sites occupied). However, the data should be treated as binodal points, even if this involves the assumption that the system may be described as a strictly-binary mixture. We accept this uncertainty because Kambour *et al.*'s primary samples were narrow-distribution poly(styrenes). Application of such a binodal treatment (ref. 23) leads to a value for $g_{\alpha\beta}$ of 0.324, again based on the sample with the shortest chains. The other Δ values can now be calculated and the curve so obtained is indistinguishable from that based on the spinodal analysis (Fig. 3). The predicted dependence of Δ on average composition shows the same feature (Fig. 4). In this particular example the two modes of evaluation are consistent, and include a high degree of agreement in the value of the interaction parameter $g_{\alpha\beta}$. This far from obvious result is obtained because the p_i values involved are small. Moreover, when samples with wide molar-mass distributions are used, such a fortuitous agreement will probably not be encountered (ref. 24). The example illustrates the necessity to specify the evaluation method when values for interaction parameters are reported. The present minor extension of Scott's model already shifts the g value by a factor of three.

EFFECT OF PRESSURE

Pressure plays a non-negligible role in polymer manufacture as well as processing. We may recall the low-density poly(ethylene) production in compressed ethylene at high pressure and temperature. Solution polymerization of ethylene in hydrocarbon solvents usually proceeds at elevated pressures. In both cases the actual working conditions include temperature and pressure ranges in which the system is unstable as a homogeneous one-phase liquid or fluid and knowledge of phase relations is essential for controlling the production.

Pressure also plays a not always recognized but subtle role in polymer blend processing. For instance, if the aim is the extrusion of a two-phase melt, the moderate pressures that build up during the process may be enough to turn the system into a homogeneous one-phase melt or *vice versa*.

While complete Bakhuis-Roozeboom $p(T, \phi_2)$ diagrams have largely to be surmised for macromolecular systems, the situation is not much better for small molecule systems. Some exceptions exist of which we show the comprehensive data by Schneider (ref. 25) on the liquid state of the system water/*n*-butyl glycol (Fig. 5). Miscibility increases with pressure which implies that the excess volume is negative. Maeda *et al.* (ref. 26) studied the pressure dependence of the lower critical cloud point of a blend of poly(phenylene oxide) and poly(*o*-fluoro *co p*-fluorostyrene) at the 50/50 (w/w) composition. Figure 6 represents their data and suggests a behaviour similar to that in Fig. 5. However, a saddle-type demixing behaviour, as sketched in Fig. 7, would also be conceivable and has been reported for solutions of poly(styrene) in *tert.* butylacetate (ref. 27). Figure 8, presenting the critical loci, shows that only the steep slopes of the saddle can be observed in this system, and also that variation of chain length affords a means of influencing phase relations in polymeric systems, a role not unlike that of pressure.

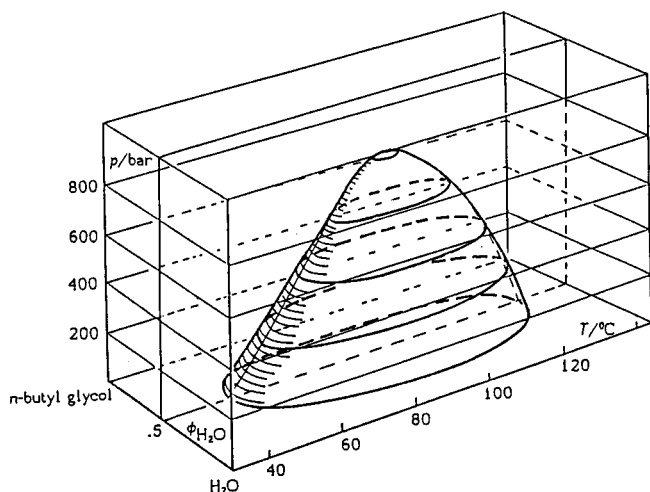


Fig. 5. Miscibility gap in the system water/*n*-butyl glycol. Data by Schneider (ref. 25).

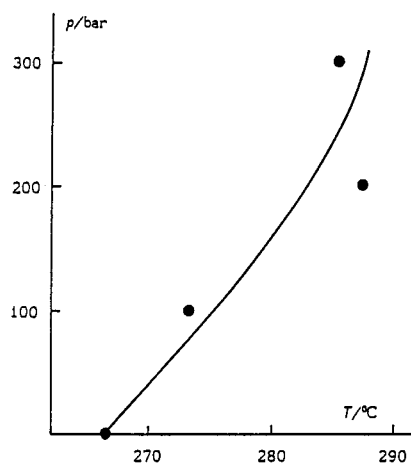


Fig. 6. 50/50 Isopleth for the system poly(phenylene oxide)/poly(*o*-fluorostyrene *co p*-fluorostyrene). Data by Maeda *et al.* (ref. 26).

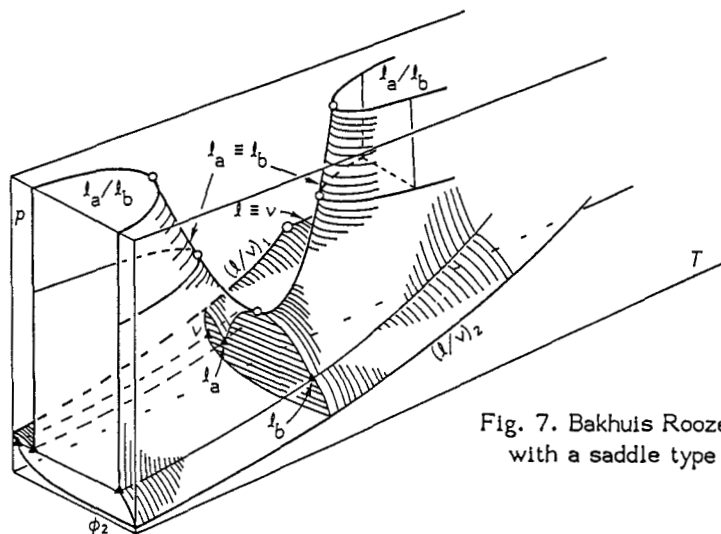


Fig. 7. Bakhuis Roozeboom diagram for a binary system with a saddle type miscibility gap in the liquid phase.

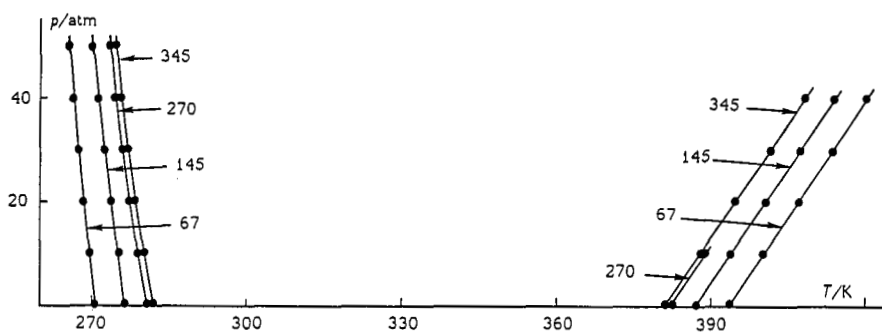


Fig. 8. Critical loci in the system *tert.*-butyl acetate/poly(styrene) for indicated values of the weight-average molar mass in kg/mol. Data by Saeki *et al.* (ref. 27.).

An extension of the cloud point determination beyond a single blend composition has revealed an interesting and unusual feature. Suzuki *et al.* (ref. 28) reported cloud point temperatures for the system poly(ethylacrylate)/poly(vinylidene fluoride) (PEA/PVDF) as a function of pressure and composition. Figure 9 summarizes the data in terms of $p(T)$ curves at constant composition (isopleths) and contains the far from obvious information that miscibility in the same system may either improve or be reduced by an increase of the pressure, depending on the composition of the blend. Important consequences for blend processing ensue, as can be seen in the constant pressure sections of Fig. 10, constructed from the isopleths. A planned two-phase extrusion may easily be jeopardized by the pressure building up in the extruder (situation A). Reversely, a homogeneous melt like B may be turned into a two-phase system when the pressure increases during extrusion.

Molecular treatments dealing with the influence of pressure exist but we rather draw the attention here to a semi-empirical approach. It is based on classical thermodynamic relationships and easily leads to a description of the unusual miscibility relations in PEA/PVDF. The treatment leaves the first two combinatorial terms in Eq. 4 unchanged and specifies the fashion in which the interaction parameter g must

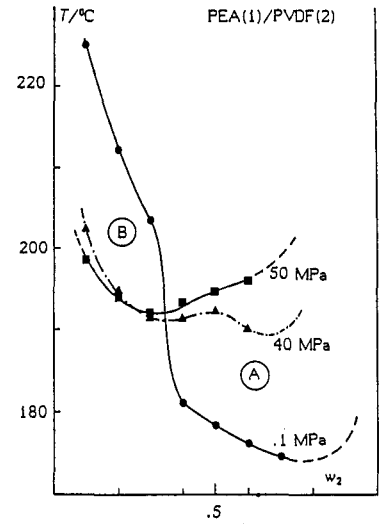
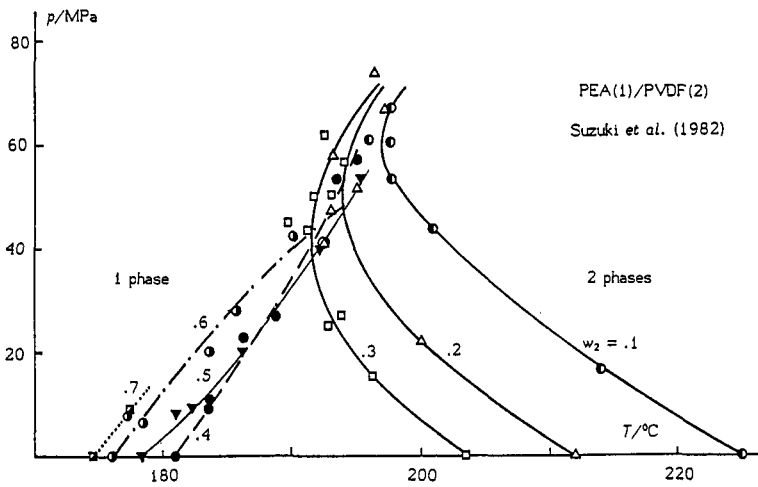


Fig. 9. Isoleths for the system poly(ethyl acrylate)/poly(vinylidene fluoride) (PEA/PVDF) for indicated mass fractions of PVDF. Data by Suzuki et al. (ref. 28.).

Fig. 10. Isobaric $T(w_2)$ sections based on Fig. 9 for indicated pressures.

be expected to depend on pressure and temperature. The general relationships

$$[\partial(\Delta G/NRT)/\partial p]_T = \Delta V^e/NRT \quad (17)$$

$$\kappa = - (1/V)(\partial V/\partial p)_T \quad (18)$$

$$\alpha = (1/V)(\partial V/\partial T)_p \quad (19)$$

serve to define $g(T, \phi_2, p)$ (ref. 29, 30). The excess volume is indicated by ΔV^e , the isothermal compressibility by κ and the thermal expansion coefficient by α .

Integration of Eqs 18 and 19 at constant κ and α , respectively, leads to exponential dependences of V on p and on T , usually representable in good approximation by linear functions of p and T . It stands to reason to assume that a difference of volumes, ΔV^e , will then also depend linearly on p and T . The left-hand side of Eq. 17 can be defined with Eq. 4 which yields

$$\phi_1\phi_2(\partial g/\partial p)_T = \Delta V^e/NRT \quad (20)$$

Eq. 20 shows the expediency of assuming the concentration dependence of ΔV^e to contain the multiplier $\phi_1\phi_2$. After integration, we find that g must at least be quadratic in p .

We use the data of Fig. 9 as an example and make some simplifying assumptions for for sake of clarity, sacrificing the intrinsically quantitative character of the procedure in favour of a qualitative treatment of the remarkable miscibility behaviour. We represent the system by a strictly-binary mixture in which the two polymers have identical relative chain lengths ($m_1 = m_2 = 100$) and ignore details of $g(\phi_2)$, writing

$$g = g_0 + g_1\phi_2 \quad (21)$$

Spinodal and critical conditions are obtained by standard procedures:

$$1/m_1\phi_1 + 1/m_2\phi_2 = 2g_0 - 2g_1(1 - 3\phi_2) \quad (\text{spinodal}) \quad (22)$$

$$1/m_1\phi_1^2 - 1/m_2\phi_2^2 = 6g_1 \quad (\text{critical point}) \quad (23)$$

Owing to the scatter of the data around the hand-drawn isopleths in Fig. 9, the $T(w_2)$ sections derived from them are not established very well. In addition, the location of the critical points is uncertain because of the unknown polydispersity of the two polymer samples. Nevertheless, the measured shift of the miscibility gap across the composition axis is significant enough to allow a rough estimation of the critical locus. The result is shown in Fig. 11 where we see that the $p(w_{2c})$ curve passes through a minimum w_{2c} value at the critical concentration w_{2c}^* , when the pressure is increased.

Limiting the temperature dependence of g to g_0 we conclude that the course of the critical locus requires g_1 to be at least a quadratic function of p (see Eq. (23)),

$$g_1 = g_{10} + g_{11}p + g_{12}p^2 \quad (24)$$

The minimum w_{2c} value at p^* supplies a relation between the coefficients, allowing g_1 to be written as

$$g_1 = g_{10} + g_{11}p(1 - p/p^*) \quad (25)$$

We select two critical points (indicated by the arrows in Fig. 11) to fix the values of g_{10} and g_{11} .

Spinodals pass through critical points and are located within the miscibility gap. Employing the usual first approximation for the temperature dependence of g_0 ,

$$g_0 = g_s + g_h/T, \quad (26)$$

we then note that g_h must depend on pressure because of the changes in shape the miscibility gap undergoes when the the pressure is varied (see Fig. 10). Writing a quadratic dependence we have

$$g_h = g_{h0} + g_{h1}p + g_{h2}p^2 \quad (27)$$

This manoeuvre adds four parameters (g_s and the three coefficients in Eq. 27), two of which can be fixed with the critical data mentioned above. To find values for the two remaining coefficients, one may either use another point on the estimated critical locus, or employ two cloud points. In the latter case we have two relations per cloud point, viz., the two equalities for the chemical potential of each component in the two phases, but increase the number of unknowns by the concentrations of the

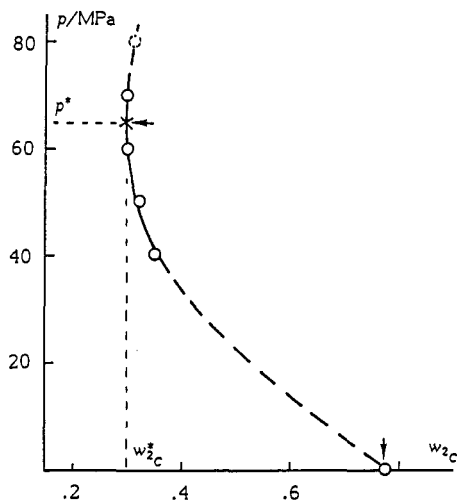


Fig. 11. Critical locus in the system PEA/PVDF estimated from the isopleths in Fig. 9. The two critical states used in the calculation of parameters are indicated by arrows.

phases coexisting with the selected cloud-point compositions. Hence, we need one cloud point per missing coefficient.

We can now calculate complete isopleths and see in Fig. 12 that the remarkable phase behaviour of the system PEA/PVDF can be reproduced in a qualitatively correct manner. Of course, the assumptions were severe but could easily be relaxed into a realistic picture if more information on the two polymer samples were available. In view of this situation we do not think specification of the parameter values used for Fig. 12 is worth while, the emphasis here being on the procedure.

One important aspect should be mentioned, however. The excess volume is defined by Eq. 17 and can be formulated as

$$\Delta V^e/NR = \phi_1\phi_2[g_{h_1} + 2g_{h_2}p + g_{11}\phi_2T(1 - p/p^*)] \quad (28)$$

The variation of mutual solubility with pressure is governed by the sign of the excess volume. Contraction upon mixing ($\Delta V^e < 0$) makes an increase of pressure improve miscibility, expansion ($\Delta V^e > 0$) has the reverse effect. The present system is peculiar in this respect since both phenomena occur. As a consequence, negative as well as positive values of ΔV^e should be contained in Eq. (28). Figure 13 shows that this is the case and we may conclude that the procedure is consistent.

The preceding remarks immediately lead to the question whether measurement of $\Delta V^e(T, \phi_2, p)$ might provide sufficient experimental information to model a molten polymer blend. Even if the difficulties met in performing such experiments with the high degree of accuracy required could be overcome, the results would only supply a part of the total number of parameters needed, as can be seen in Eq. (28). Obviously, it will remain necessary to measure spinodals and critical points, for which purpose experimental techniques exist and are being developed (ref. 15 - 17, 31).

It might be objected that this semi-classic treatment calls for an excessive number of parameters. However, the need for them is dictated by the course of the critical curve, estimated from direct experimental information, to which two equations apply per experimental point. The latter aspect effectively reduces the number of parameters.

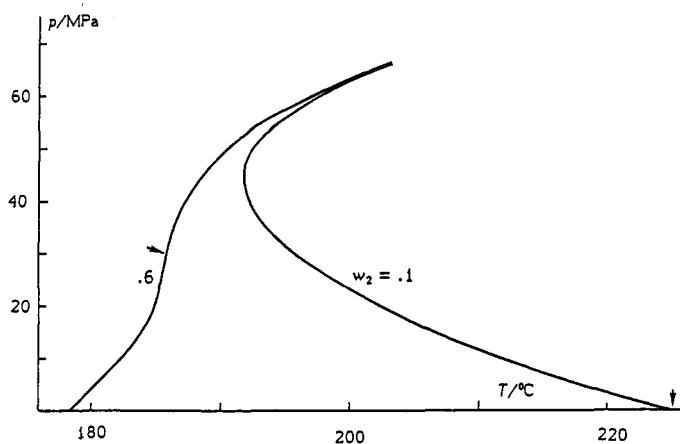


Fig. 12. Isopleths for the system PEA/PVDF, calculated for $w_2 = 0.6$ and $w_2 = 0.1$ with the semi-empirical procedure described in the text. The two cloud points used in the calculation of parameters are indicated by arrows.

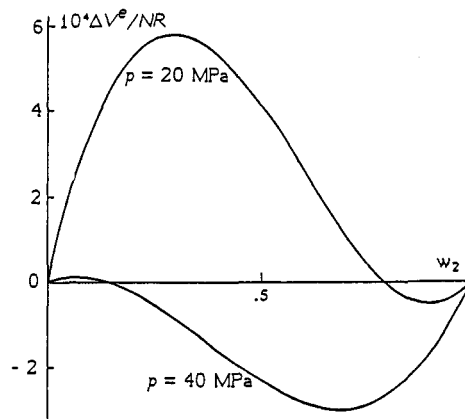


Fig. 13. Calculated excess volume for the system PEA/PVDF at 190°C for indicated pressures.

INFLUENCE OF FLOW

Recent experiments by Winter *et al.* on the system poly(vinyl methyl ether)/poly(styrene) (PVME/PS) have revealed that *elongational* flow may significantly affect miscibility. At one blend composition these authors found miscibility to be enhanced whereas the reverse effect was observed at another concentration (ref. 32). The situation resembles that in Fig. 10 where it is seen that pressure may tilt the two-phase area in a similar fashion. Mazich and Carr, who also worked with PVME/PS, found *shear* flow to lift the entire miscibility gap to higher temperatures (ref. 33). The practical implications of the effect are obvious, and various authors have tried to supply models that might be used to describe the phenomenon in an orderly manner (ref. 34 - 40). There are two types of approach: one leaves the thermodynamic parameters measured on the system at rest unchanged and adds terms for the energy stored in flow, another concentrates on changes the thermodynamic parameters undergo when the system is subjected to a flow field.

We mention an interesting example of the first type. Wolf used the free enthalpy expression so obtained to predict phase behaviour in shear (ref. 41). His treatment produced the peculiar prediction that a smooth one-peaked cloud-point curve should be expected to develop a second maximum upon the application of shear to the system. The quasi-static approach Wolf used may be open to criticism, but its viability was clearly demonstrated when he verified the predicted effect in the system decalin/poly(styrene) (ref. 42).

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