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Equilibrium thermodynamics of the ternary membrane-forming system nylon, formic acid and water

A. M. W. Bulte*, E. M. Naafs, F. van Eeten, M. H. V. Mulder, C. A. Smolders and H. Strathmann
Faculty of Chemical Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
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The binary Flory–Huggins interaction parameters for the ternary membrane-forming system nylon, formic acid and water have been obtained from literature data, swelling values and melting point depression. Nylon 4,6 nylon 6 and a copolymer of nylon 4,6 and 6 were examined. The isothermal crystallization boundaries were determined experimentally and the binodal miscibility gap was calculated for these ternary systems. It was found that the crystalline state is the thermodynamically favourable state for each system. Experimental data and calculated phase diagrams are discussed in relation to membrane formation. Although the thermodynamic properties of the system dictate the phase separation that can take place, the kinetic parameters are of equal significance with respect to membrane formation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ternary systems; melting point depression; crystallization)

INTRODUCTION

Membrane preparation by means of phase inversion is widely used today both on a laboratory scale and in industry[1]. The concept of phase inversion covers a range of different techniques, of which immersion precipitation is the most important. Here, a thin film of a concentrated solution, consistent of a polymer and a solvent, is cast on a support. The film is immersed in a non-solvent, which is miscible with the solvent. As a result the non-solvent diffuses into the film and the solvent diffuses out of the film; i.e. a diffusion-induced phase separation (DIPS) process takes place. Phase separation may take place if thermodynamic conditions allow a homogeneous film to demix into two or more phases. Knowledge of the thermodynamic properties of such a ternary system is very important for understanding and predicting membrane formation.

Nylon 4,6 is a semicrystalline polymer that has been used as a polymer for membrane preparation. It has been shown[2] that two different phase separation processes are competitive during membrane formation: solid–liquid (S–L) demixing and liquid–liquid (L–L) demixing[2]. Solid–liquid demixing or crystallization leads to membranes with a spherulitic or axialitic morphology. The typical cellular morphology has been observed for liquid–liquid demixing. Other aliphatic polyamides, such as nylon 6, nylon 6,6, nylon 6,10 and nylon 11, are used as membrane materials as well. The preparation and use of these membranes have been described in a number of patents[3–5].

Solid–liquid demixing or crystallization of the polymer in a ternary system can take place because the melting temperature of the pure polymer is depressed by the presence of the two low-molecular-weight components. Melting point depression of the polymer can lead to isothermal crystallization. Crystallization or solid–liquid demixing results in two separated phases in equilibrium; one phase is the pure crystalline polymer and the other is a more diluted polymer solution. Flory[6] has worked out phase diagrams with experimental data of the melting point depression or dissolution curves (liquidus) for a number of binary systems, deriving the binary Flory–Huggins (F–H) polymer–diluent interaction parameters. It has been shown that the binary melting point depression curve becomes more asymmetric with increasing difference between the molar volumes of the low- and the high-molecular-weight component[7–9]. With knowledge of the F–H interaction parameters in a system in which melting point depression occurs, a crystallization line can be calculated.

For understanding the basis of phase separation processes taking place during membrane formation, knowledge of the equilibrium thermodynamics is essential. This paper is focused on the experimental determination of melting point depression data for the system under study. For this ternary system, nylon 4,6, formic acid and water, in which high mutual interaction forces exist, the use of the Flory–Huggins theory would be less suitable. This theory, however, is widely applied in membrane science[10–15]. Therefore the experimental data will be linked with the F–H theory in order to compare

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* To whom correspondence should be addressed

this system with others and to calculate mass transfer during membrane formation with available computer models using F–H theory[14].

Altena *et al.*[10] and Burghardt *et al.*[11] have attempted to obtain data for calculation of the equilibrium boundary between the homogeneous phase and the region showing solid–liquid phase separation for (ternary) membrane-forming systems. Binary and ternary crystallization curves can be derived if Flory–Huggins interaction parameters for all the components are available. In liquid–liquid phase separation an equilibrium between two liquid phases exists. In membrane-forming systems, in which one polymer is present, the two phases are a polymer-rich and a polymer-lean phase. The homogeneous region and the miscibility gap are defined by a binodal curve. Knowledge of the binary Flory–Huggins interaction parameters allows one to calculate this binodal as shown by Flory[6] and Tompa[16], and later by various authors[12–15] from our laboratory. Both solid–liquid and liquid–liquid phase separation can occur in binary and ternary systems. This has clearly been shown by Burghardt[17] for a binary situation.

From phenomenological data on membrane formation it has been concluded that for the ternary system nylon 4,6, formic acid and water, both solid–liquid demixing and liquid–liquid demixing occurs[2]. A hypothesis was formulated suggesting crystallization to be the thermodynamically favourable process. Detailed knowledge about the location of the crystallization line, however, is necessary to obtain further insight into the membrane formation of aliphatic polyamides. In order to obtain a better understanding of the influence of the location of the crystallization line on membrane formation, the thermodynamics of nylon 4,6 will be compared with that of other nylon types. The aim of this paper is to find a thermodynamic description for three membrane-forming systems: nylon 4,6, nylon 6 and a copolymer of the two with 5% of nylon 6 units incorporated, with formic acid as a solvent and water as a non-solvent.

THEORY

Construction of a phase diagram with solid–liquid and liquid–liquid demixing

For a binary system, phase diagrams can be derived by plotting the free enthalpy as a function of the volume fraction (see *Figure 1*)[6,17]. In the plots on the left-hand side of this figure the free enthalpy of the mixture is given as a function of the polymer volume fraction. Polymer solutions with a polymer volume fraction between ϕ_α and ϕ_β can lower their free enthalpy at a temperature T_1 by phase separation into the liquid phases ϕ_α and ϕ_β; the corresponding miscibility gap (liquid–liquid phase separation) is located as is indicated in *Figure 1b*, where the L–L region and the homogeneous region are given as a function of temperature. At lower temperatures ϕ_β shifts to larger polymer fractions and the miscibility gap becomes larger.

The chemical potential of the crystalline phase is represented by a point on the polymer ordinate (μ_C). The location of this point depends on the choice of polymer and the temperature. When this point is located beneath the molar free enthalpy of the pure liquid polymer [$\mu_B^o(P, T)$], solutions with a polymer concentration larger than ϕ_γ can lower their free enthalpy by phase separation into a pure crystalline phase and a phase with composition ϕ_γ. The phase diagram can be constructed as shown in *Figure 1d.* When a homogeneous polymer solution is cooled to a temperature T_1 two types of phase separation processes can occur (see *Figure 1d*). At higher polymer concentrations crystallization or S–L demixing is responsible for phase separation and at lower concentrations phase separation is controlled by the location of the binodal curve leading to L–L demixing.

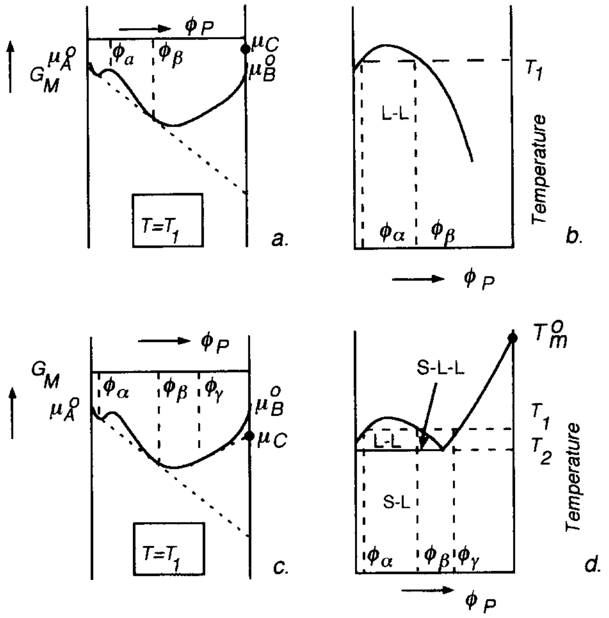

Figure 1 (a) and (c) Free enthalpy of the mixture (G_M in J mol^{-1}) as a function of the polymer volume fraction ϕ_P. The binary phase diagrams are schematically given for two different situations: (b) liquid–liquid (L–L) demixing (no crystallization occurs); and (d) liquid–liquid (L–L) demixing and solid–liquid (S–L) demixing. μ_A^o and μ_B^o are the chemical potentials of the pure state at constant pressure and temperature of the low-molecular-weight component (A) and the polymer (B), respectively. μ_C is the chemical potential of the crystalline state at a temperature below the melting temperature of the pure polymer. At the melting temperature of the pure polymer (T_m^o), $\mu_C = \mu_B^o$

At one specific temperature (T_2 in *Figure 1d*) the chemical potential of the crystal state lies on the tangent line of the compositions ϕ_α and ϕ_β. At this temperature the three phases—the polymer-lean phase, the polymer-rich phase and the crystalline state—are at equilibrium with each other. Thus in binary systems at a certain temperature a three-phase equilibrium (L–L–S) exists.

A liquid solution and a solid crystal (S–L) are the phases present at still lower temperatures ($T < T_2$) if only crystallization of the polymer phase is taken into account.

A ternary system with a crystallizable polymer

An isothermal three-component phase diagram for a polymer (subscript 3), solvent (subscript 2) and a non-solvent (subscript 1) is given in *Figure 2.* At lower polymer concentrations phase separation is controlled by liquid–liquid demixing, whereas at higher concentrations solid–liquid phase separation is involved. The three-phase region (S–L–L) is a plane in a ternary isothermal phase diagram, because there is one additional degree of freedom compared with the binary case. The area on the right-hand side near the polymer–non-solvent axis is thermodynamically controlled by solid–liquid phase separation.

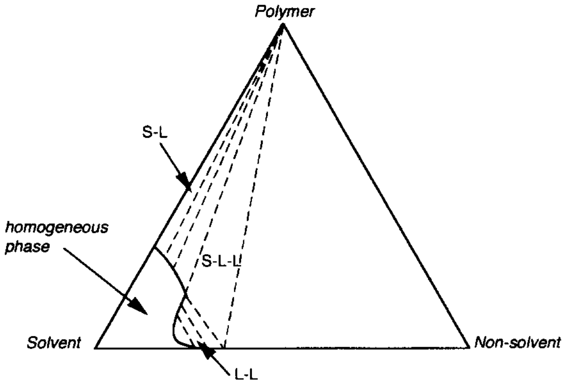

Figure 2 A ternary phase diagram with liquid–liquid demixing and solid–liquid demixing (crystallization of the polymer phase)

Theoretical background of the calculations

The crystallization line. The crystallization line in a phase diagram can be calculated according to the theory of melting point depression[6]. At equilibrium between the liquid solution and crystalline polymer, the chemical potentials of the polymer repeating units (μ_u) in both phases must be equal:

$$\mu_u = \mu_u^c \tag{1}$$

in which μ^c represents the chemical potential of the polymer repeating unit in the crystalline state. The temperature at which this condition is satisfied can be referred to as the melting point T_m, which will depend on the composition of the liquid phase.

The condition of equilibrium between crystalline polymer and the polymer in solution can be restated as follows:

$$\mu_u - \mu_u^o = \mu_u^c - \mu_u^o \tag{2}$$

In other words, the difference between the chemical potential of the crystalline repeating unit and the unit in the standard state, i.e. the pure liquid polymer at the same temperature and pressure, must be equal to the decrease in chemical potential of the polymer unit in the solution relative to the same standard state.

The right-hand term is the negative of the free enthalpy of fusion per polymer repeating unit, ΔG_u (the indices u and o stand for the quantities per mole of repeating unit in the polymer and the pure state, respectively); with $\Delta H_u/\Delta S_u$ equal to T_m^o the following relation can be obtained:

$$\begin{aligned}\mu_u^c - \mu_u^o &= -\Delta G_u = -(\Delta H_u - T\Delta S_u) \\ &= -\Delta H_u\left(1 - \frac{T}{T_m^o}\right)\end{aligned} \tag{3}$$

where ΔH and ΔS represent the heat and entropy of fusion, respectively.

The left-hand term of equation (2) can be obtained from the first derivative of the free enthalpy of mixing with respect to the number of moles of component 3, n_3:

$$\Delta\mu_3 \equiv \left(\frac{\partial \Delta G_m}{\partial n_3}\right)_{P,T,n_j} \tag{4}$$

with $\Delta\mu_3$ expressed in J mol^{-1} of polymer and $\Delta\mu_u$ in J mol^{-1} of repeating unit of the polymer.

The free enthalpy of mixing, ΔG_m, for a ternary system can be expressed according to the Flory–Huggins theory:

$$\begin{aligned}\frac{\Delta G_m}{RT} &= n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12} n_1 \phi_2 \\ &\quad + g_{13} n_1 \phi_3 + g_{23} n_2 \phi_3\end{aligned} \tag{5}$$

The binary interaction parameters g_{ij} are assumed to be dependent on concentration.

Rewriting the equations with the ratios of the molar volumes (η) $s = \eta_1/\eta_2$ and $r = \eta_1/\eta_3$ with the subscript 1 for non-solvent, 2 for solvent and 3 for polymer and assuming that $r \rightarrow 0$, then according to Altena *et al.*[10] the following equation can be derived for the melting point depression:

$$\begin{aligned}\frac{-R}{\Delta H_u}\frac{\eta_u}{\eta_1}\Big\{&-\phi_1 - s\phi_2 + (g_{13}\phi_1 + s g_{23}\phi_2)(\phi_1 + \phi_2) \\ &-g_{12}\phi_1\phi_2 - s\phi_2 v_2(1 - v_2)\frac{\delta g_{23}}{\delta v_2}\Big\} - \left(\frac{1}{T_m} - \frac{1}{T_m^o}\right) = 0\end{aligned} \tag{6}$$

in which η_u is the molar volume per repeating unit in the polymer. It is *assumed* that the binary Flory–Huggins parameters g_{ij} are truly binary in ternary and quaternary situations, i.e. that they are only dependent on the components i and j and not on the third component k [$g_{ij} \neq g_{ij}(\phi_k)$]; g_{13} is assumed to be constant, since no information about a concentration dependence of a polymer in a non-solvent can be obtained. The interaction parameters are now dependent on the following composition variables, with ϕ_2 and ϕ_3 in the limiting binary cases with components 1–2 and 2–3 only being replaced by u_2 and v_2 respectively, for the ternary case:

$$\begin{aligned} g_{12} &= g_{12}(u_2) \qquad u_2 = \frac{\phi_2}{(\phi_1 + \phi_2)} \\ g_{23} &= g_{23}(v_2) \qquad v_2 = \frac{\phi_2}{(\phi_2 + \phi_3)}\end{aligned} \tag{7}$$

in which u_2 and v_2 reflect the ratios of volume fractions of solvent–non-solvent and solvent–polymer, respectively.

The isothermal crystallization line at a chosen temperature T_m can be calculated if appropriate parameters are selected for ΔH_u and the various interaction parameters g_{ij}, and if T_m^o and the molar volumes (η) are known.

The binodal. The approach of Altena and Smolders[12], Reuvers and Smolders[14] and Boom *et al.*[15] will be followed to calculate the liquid–liquid miscibility gap in a ternary system. The chemical potentials for the three components are found by differentiation of equation (5) with respect to n_1, n_2 and n_3, respectively. Liquid–liquid demixing results in phase separation into two liquid phases: a polymer-lean phase with $\Delta\mu_i$ of the first phase ($\Delta\mu_i^{\text{1st phase}}$) and a polymer-rich phase with $\Delta\mu_i$ of the second phase ($\Delta\mu_i^{\text{2nd phase}}$). At equilibrium the chemical potentials of component i in both phases are equal, their difference being zero. This is approached numerically by minimizing the function F:

$$F = \sum_{i=1}^{3}\left[\frac{\Delta\mu_i^{\text{1st phase}}}{RT} - \frac{\Delta\mu_i^{\text{2nd phase}}}{RT}\right]^2 \tag{8}$$

Evaluation of the interaction parameters

Solvent–non-solvent interaction parameter (g_{12}). The concentration-dependent parameter $g_{12}(\phi_2)$ represents the interaction between solvent and non-solvent, for this system water (1) and formic acid (2). The excess free enthalpy of mixing (G^E) equation (9):

$$g_{12}(\phi_2) = \frac{1}{x_1\phi_2}\left[x_1 \ln\left(\frac{x_1}{\phi_1}\right) + x_2 \ln\left(\frac{x_2}{\phi_2}\right) + \frac{G^E}{RT}\right] \qquad (9)$$

$$G^E = RT\sum_i x_i \ln \gamma_i$$

in which x_1 and x_2 are the mole fractions, ϕ_1 and ϕ_2 the volume fractions, G^E the excess free enthalpy of mixing and γ_i the activity coefficient of component i. The g_{12} parameter can be calculated by using data from the literature[18].

In *Figure 3* the G^E values are given as a function of the mole fraction of water (1). Strong negative values are obtained over the whole concentration range, indicating that strong interaction forces exist between solvent and non-solvent. Strongly negative values for interaction parameters are not very common. To check the validity of the negative values for G^E, excess values were calculated from activity coefficients derived from the Van Laar equation[19], for which appropriate parameters are available[20]. *Figure 3* shows data for both the experimental[18] and theoretical[20] excess free enthalpy of mixing. The experimental data were taken from Krasovskii and Makurina[18] whereas the theoretical data were calculated from the Van Laar equation with parameters taken from Campbell and Campbell[20]. The calculated excess free enthalpy of mixing is negative over the whole concentration range, but values are less negative compared with the experimental values. The coefficients used for the calculation of activity coefficient with the Van Laar equation[19] are derived from experimental data for vapour–liquid equilibria. Dimer formation of formic acid molecules in the vapour phase is not taken into account, resulting in a less negative theoretical G^E value.

For our system we use the interaction parameter derived from the experimental values for G^E. In *Figure 4* the g_{12} interaction parameter derived from these data is given as a function of the volume fraction of water (ϕ_1).

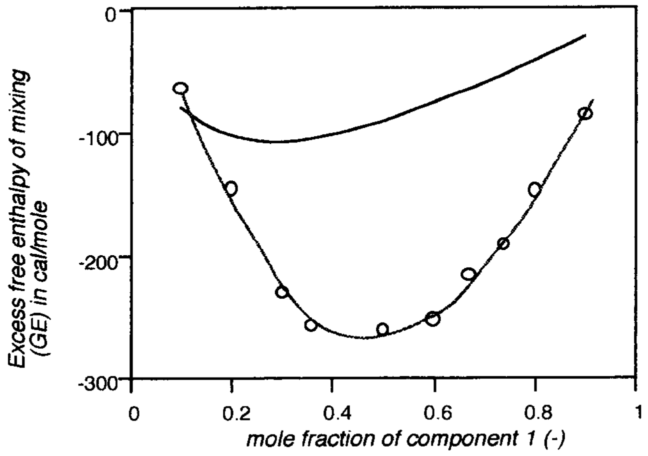

Figure 3 Experimental[18] (points) and theoretical[20] (curve) data for the excess free enthalpy of mixing of formic acid/water mixtures

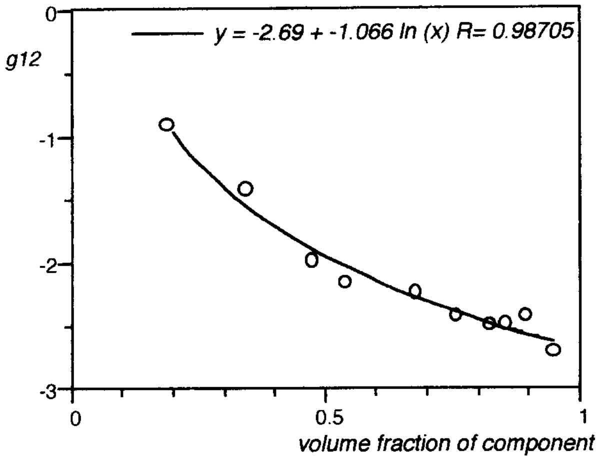

Figure 4 The water–formic acid interaction parameter (g_{12}) as a function of the volume fraction of water

The concentration dependence can be described by equation (10) (see also *Figure 4*):

$$g_{12} = -2.69 - 1.066\ln(\phi_1) \qquad 0.2 < \phi_1 < 0.95 \qquad (10)$$

To use a binary interaction parameter in a ternary system a composition variable u_2 has been defined [see equation (7)]; ϕ_1 (or $1 - \phi_2$) in equation (10) must then be replaced by $(1 - u_2)$.

Non-solvent–polymer interaction parameter (g_{13}). The interaction parameter between non-solvent and polymer can be obtained from the swelling value of the polymer in the non-solvent. At equilibrium swelling conditions the derivative of the free enthalpy of mixing (ΔG_m) with respect to component 3 (n_3) equals zero and g_{13} can be calculated. Since it is not possible to determine this parameter as a function of concentration, it is usually taken to be constant (then also written in the literature as χ_{13}). The mass uptake of water in nylon 4,6 films has been determined to be 15 wt%. Since swelling only takes place in the amorphous regions[21], the mass uptake has been corrected for the 50% crystallinity of the polymer samples[22]. An interaction parameter of 1.8 is then calculated. The mass uptake of nylon 6 is 11 wt% at 30% crystallinity. The crystal units in the polymer film can be considered as physical crosslinks that will hinder the swelling of the amorphous polymer matrix. Without this hindrance a somewhat higher mass uptake can be expected, resulting in lower values for the interaction parameter. For all three nylons the following will be used:

$$g_{13} = 1.5 \qquad (11)$$

Solvent–polymer interaction parameter (g_{23}). Literature data for the solvent–polymer interaction parameter g_{23} for the system nylon, formic acid and water are not available. Experimental melting point depression data for the ternary system will be used to fit a g_{23} with equation (6).

The molar volumes (η) of the components are found by taking the ratio of the molecular weight (M) and the density (ρ). The values for the three components are listed in *Table 1*. T_m° and ΔH_u were taken from the literature[20,22]. Isothermal crystallization is calculated at a temperature of 30°C (303 K).

Table 1 Physical constants for the studied components

	M (g mol^{-1})	ρ (g cm^{-3})	T_m° (K)	ΔH_u (J mol^{-1})	η_u (cm^3 mol^{-1})
Nylon 4,6	25 000^a	1.18	623	46 000	171
Nylon 4,6-*co*-6	25 000^a	1.18	623	46 000	171
Nylon 6	25 000^a	1.14	533	28 700	99
Water	18	1.00	–	–	–
Formic acid	46	1.22	–	–	–

^{a} The number-average molecular weight, M_n, as reported by the supplier

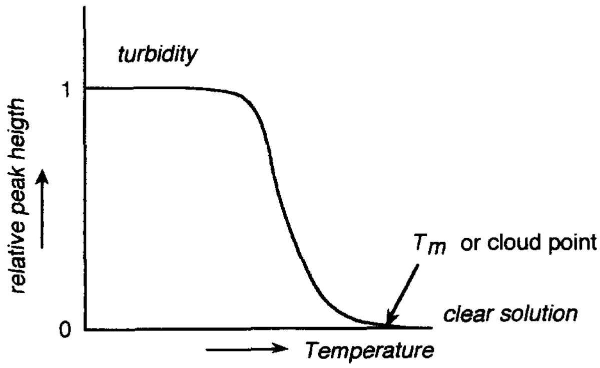

Figure 5 A typical laser light transmission profile

EXPERIMENTAL

Sample preparation

Nylon 4,6 (Stanyl KS 400), nylon 6 (Ultramid B3) and nylon 4,6-*co*-6 (Stanyl KS 611), kindly supplied by DSM, The Netherlands, were dried *in vacuo* for at least 24 h at 70°C for nylon 4,6 and the copolymer and at 30°C for nylon 6. Solutions, with a concentration of 3 to 20 wt% polymer, were prepared by dissolving the appropriate amount of polymer in formic acid (Merck, analytical grade 98%) in Erlenmeyer flasks closed with septa. Under continuous stirring demineralized water was added very slowly to the solution at room temperature until the pre-calculated ratio of solvent and non-solvent was reached. Samples were taken from these ternary compositions with a syringe through a septum into glass capillaries, which were frozen in liquid nitrogen, evacuated and sealed. The samples were kept at 8°C until complete demixing occurred (their appearance then was white or opaque). The demixing time varied from several hours to several weeks.

Laser light transmission

Cloud points were measured by using a light transmission technique. Tubes containing a demixed solution of a certain composition (ϕ_1, ϕ_2 and ϕ_3) were positioned in a rotating wheel placed in a thermostated bath at 25°C. The temperature of the bath was increased by 2°C h^{-1}, controlled by a temperature control unit. At the same time the rotating wheel was driven by a small motor at a velocity of 2 rotations per h. Laser light (He-Ne, 633 nm, 10 mV) was passed through the glass capillaries and the transmittance was detected and continuously monitored by a recorder. A typical plot obtained from these experiments is given in *Figure 5*. Here a relative peak height of one indicates that there is minimal light transmission through the turbid sample and a relative height of zero indicates that the transmission is maximum, i.e. the solution is completely transparent. The melting temperature is located at the point where the measured line intersects the baseline (offset temperature).

RESULTS

Cloud point data

The melting temperatures of various solutions with varying compositions of the three nylons (from 2 to 20 vol% polymer) were determined from cloud point measurements. The measurements were carried out in duplicate with an accuracy of about 2°C.

It was observed visually that the samples did not demix instantaneously during sample preparation. Water could be added to the polymer solution in such a quantity that the composition of the sample entered the inhomogeneous region, while turbidity was still not observed. For the samples with the highest cloud point temperature, turbidity only occurred after several hours.

A ternary system with an amorphous polymer, solvent and non-solvent is usually determined easily by a titration method. Upon addition of non-solvent to a polymer solution a clear, distinct cloud point can be determined in such cases. The system under study, however, did not show such behaviour. Turbidity was usually only observed after several hours. It can therefore be concluded that turbidity of the solutions here must be caused by solid–liquid demixing and not by liquid–liquid phase separation or even spinodal decomposition.

Figure 6 shows the measured melting temperatures as a function of the volume fraction of water (ϕ_1). It can be observed that the melting temperatures increase with increasing polymer or water fraction at a constant content of the other component. In other words, in these directions the solid–liquid demixing area is entered more deeply. In addition, a linear relationship exists between T_m and ϕ_1 within the range of the experimental data (40–80°C). This dependence of the melting temperature in a ternary system has not been reported previously in the literature. A melting temperature of 30°C or lower was not measured. Apparently the degree of undercooling of ~20°C is not large enough to induce crystallization for these nylons. This phenomenon has also been observed with crystallization from the melt. A degree of undercooling of at least 30°C or more is necessary to induce crystallization within a reasonable time.

Since the aim of these measurements (among others) is to determine the isothermal crystallization line at $T = 30$°C, it is necessary to extrapolate the experimental data to the axis of $T = 30$°C. This can be achieved by deriving a phenomenological relationship between the melting temperature and the composition of the solution. To obtain the most suitable form of such a relationship, the K value [equation (12)] of various relations was calculated in a minimization procedure:

$$K = \sum_{\text{all}} (T_{m,m} - T_{m,c})^2 \qquad (12)$$

In this equation $T_{m,m}$ is the measured melting temperature and $T_{m,c}$ is the calculated melting temperature. It

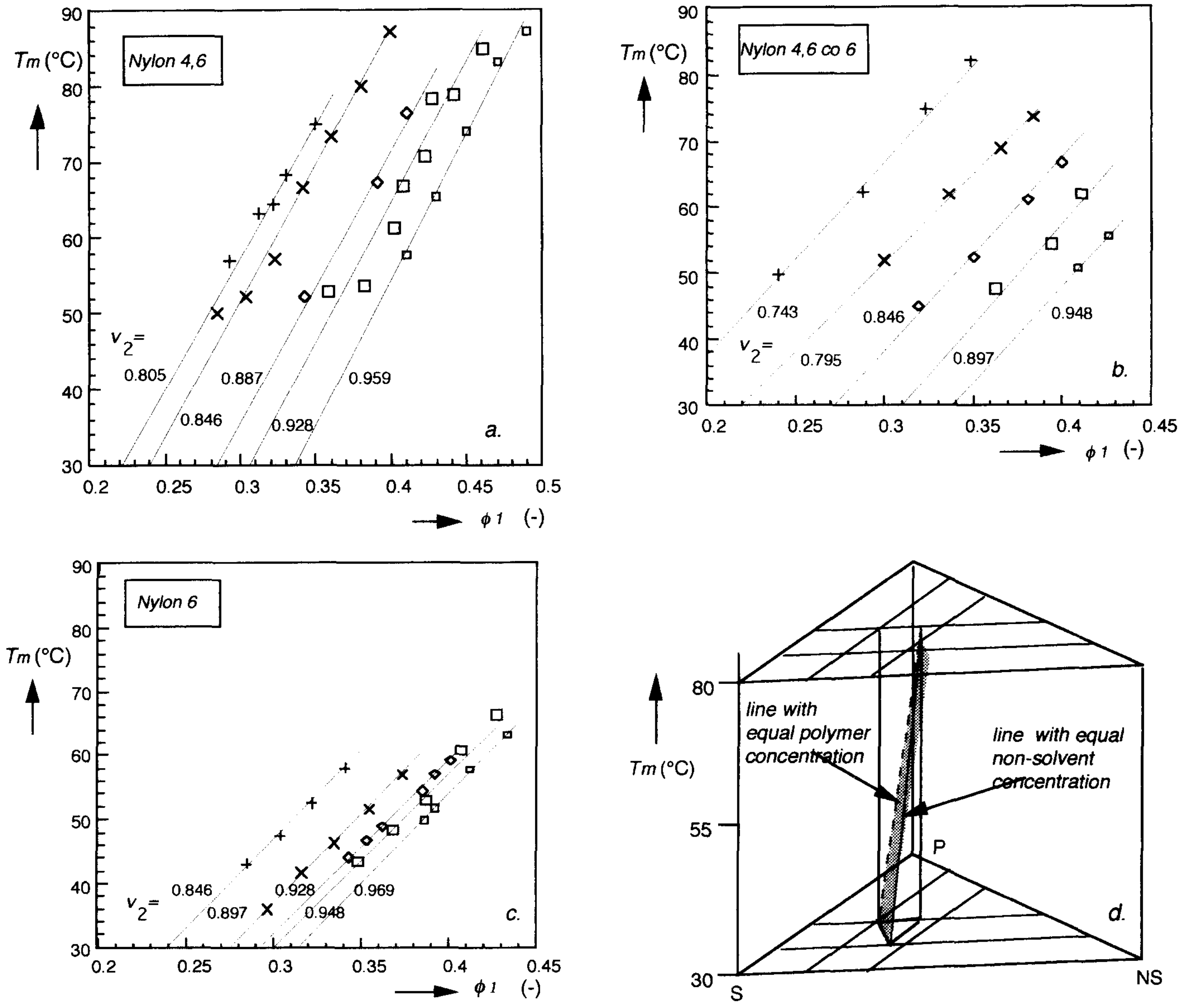

Figure 6 Measured melting temperatures as a function of the volume fraction of water for three different nylons: (a) nylon 4,6; (b) nylon 4,6-*co*-6; (c) nylon 6. The lines connect points with the indicated v_2 value. Not all the experimental data are shown in these figures. In (d) the schematical phase diagram as a function of composition and temperature is given for nylon 4,6

appeared that the following relationships with no more than three fitting constants gave the lowest K values and thus the best fits.

Nylon 4,6:

$$T_{m,c} = -98.65 - 332.9\ln(v_2) + 367.6\ \phi_1 v_2(°C) \quad (13a)$$

Nylon 4,6-*co*-6:

$$T_{m,c} = -100.4 - 301.3\ln(v_2) + 348.0\ \phi_1 v_2(°C) \quad (13b)$$

Nylon 6:

$$T_{m,c} = -67.31 - 235.3\ln(v_2) + 294.3\ \phi_1 v_2(°C) \quad (13c)$$

These are mathematical relations without any physical meaning and they cannot be applied for other ternary systems. To give an indication of the quality of these fits, the average absolute values of $T_{m,m} - T_{m,c}$ (ΔT_{av}) and the percentage of points with $T_{m,m} - T_{m,c} < 2°C$ and $T_{m,m} - T_{m,c} < 5°C$ are given in *Table 2*.

Table 2 Parameters indicating the quality of fit of equations (13a) to (13c)

	$T_{m,m} - T_{m,c}$		
	ΔT_{av} (°C)	< 2°C (%)	< 5°C (%)
Nylon 4,6	2.3	54	92
Nylon 4,6-*co*-6	1.0	91	100
Nylon 6	0.6	96	100

Since an empirical relationship has been derived, the melting temperature of a mixture can now be calculated accurately as a function of the composition (*Figure 7*). It can be observed that the location of the crystallization line for the different polymers does not differ very much. Moreover, it is clear that the copolymer has the largest homogeneous area. This can be understood, considering the fact that the copolymer is no more than 'poisoned' nylon 4,6 and the polymer chains will thus have more difficulty in rearranging into their specific crystalline order[21].

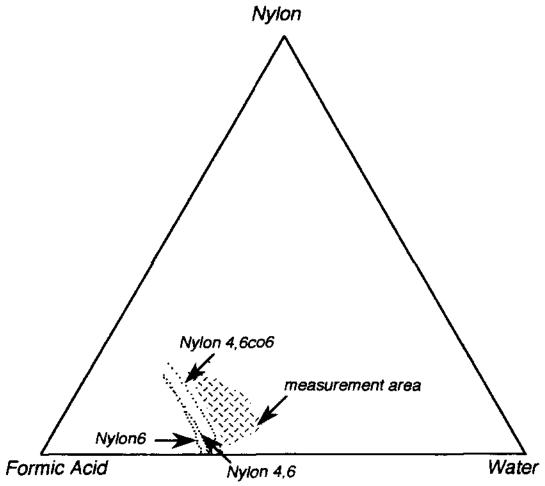

Figure 7 The isothermal crystallization lines at $T = 30°C$ of the three different polyamides in the system polyamide/formic acid/water. The measurement area gives the location of the measured melting points at higher temperatures of the ternary samples (*Figure 6*)

Interaction parameters

The values obtained for the melting temperatures were used for the calculation of the concentration-dependent interaction parameter g_{23} of the nylons and formic acid. A spreadsheet program (MS Excel 4.0) with a Newton minimizing procedure was used and the best fit was obtained with the following logarithmic functions.

Nylon 4,6:

$$g_{23} = -3.95 - 1.46 \ln v_2 \tag{14a}$$

Nylon 4,6-*co*-6:

$$g_{23} = -4.32 - 1.32 \ln v_2 \tag{14b}$$

Nylon 6:

$$g_{23} = -3.91 - 1.59 \ln v_2 \tag{14c}$$

It is remarkable that the values of the polymer–solvent interaction parameter are highly negative. Such low values are very unusual; the lowest value reported previously was −4.1 for cellulose nitrate with n-propyl acetate as solvent[23]. The negative interaction parameters can partly be explained by the high interaction forces between the nylons and formic acid due to hydrogen bonding. Evaluating the values for g_{23}, it should be realized that the Flory–Huggins theory was originally developed for mixtures where the components do not show high mutual interaction forces such as hydrogen bonding and acid–base interactions. It is clear that this condition is not met for the systems studied here. An additional problem is that the value of the enthalpy of fusion for the polymer repeating unit is taken as a constant, which might not quite be the case; lower values for ΔH_u give less negative values for g_{23}.

However, it should be realized that equations (14) are partly based on experimental data, from which g_{23} is determined indirectly. Since the range of v_2 values in these data is limited (from about 0.70 to 0.98), care should be taken when using these equations outside this area.

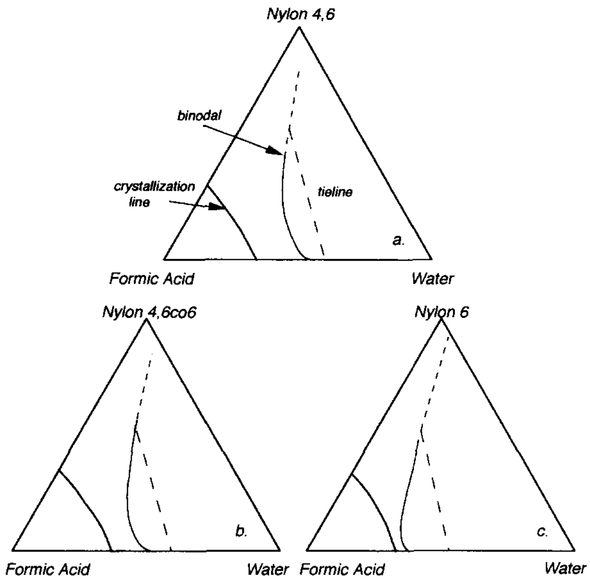

Figure 8 (Phase) diagrams of the three membrane forming systems: (a) nylon 4,6; (b) nylon 4,6-*co*-6; (c) nylon 6. The crystallization line is derived from the experimentally determined melting temperatures. The binodal is calculated with the derived Flory–Huggins parameters. It should be noted that for a strict thermodynamic phase diagram the binodals can only be drawn as 'virtual' binodals. The location of the hidden binodals, however, is important for membrane formation

Calculation of the ternary phase diagrams

So far, only the isothermal crystallization lines for the different membrane-forming systems have been determined. In order to complete the phase diagrams, the binodals must be determined as well. For such calculations, the algorithm described by Altena and Smolders[12] was used. The values for the interaction parameters were taken from equations (10), (11) and (14); the values for the physical constants are given in *Table 1*.

The results of the calculations are shown in *Figure 8*, which gives the complete (phase) diagrams for the three membrane-forming systems. It should be realized that the exact location of the binodal drawn in *Figure 8* becomes less certain as the value of v_2 decreases. In the case of nylon 6 the crystallization line and the binodal almost cross each other, while in the case of nylon 4,6 and the copolymer there is quite a gap between those lines. This means that, for all unstable compositions, crystallization is the thermodynamically most favourable demixing process. In other words, for these systems the binodal only has thermodynamic significance as a *virtual* (hidden) binodal. In membrane formation, however, kinetics plays a very important role as well and the location of the binodal is quite essential for the ultimate membrane morphology, which can be related to mass transfer calculations of solvent and non-solvent fluxes during the first moments of immersion precipitation using the local temporary equilibrium between the coagulation bath and the polymer film. This local equilibrium is given by a point on the binodal as has been described by Reuvers and Smolders[14].

DISCUSSION

The hypothesis that the crystallization line is positioned more closely to the solvent corner than the binodal curve, following from the phenomenological experiments described recently[2], is confirmed by the calculations and experiments in this paper.

Strong interaction between solvent and non-solvent can be expected because of a large contribution of hydrogen bonding and partial dissociation of formic acid in water. A relatively large exothermic heat of mixing, which occurs with water and formic acid, contributes to a negative excess free enthalpy of mixing and consequently to negative interaction parameters, g_{12}. Solvent and polymer show a strong intermolecular interaction that is also based on hydrogen bonding. From earlier work on membrane formation with Nomex[24], an aromatic polyamide, it is known that dissolution of the polymer in formic acid leads to an increase in temperature, i.e. an exothermic heat of mixing is found.

Cloud points are very often determined from turbidity measurements upon cooling. However, for systems in which it is expected that crystallization is involved, cloud points should be detected by heating turbid mixtures instead of cooling clear solutions. Similar to the determination of melting points in pure polymers, the melting temperature and the crystallization temperature may differ by 30 to 50°C depending on the cooling rate and the crystallization kinetics of the polymer. The experiments confirmed that crystallization is highly influenced by kinetics; solutions with a melting temperature of around 30°C or lower did not crystallize within 6 weeks during storage at 8°C. This problem was circumvented by the determination of melting or dissolution temperatures by heating turbid systems, and reproducible melting points were obtained. Real equilibrium melting points should be determined by taking the lamella thickness into account and extrapolating the data to infinite lamellae thicknesses. The aspect is not considered in our measurements. The determination of T_m according to our method, however, will be sufficient for understanding phase separation during membrane formation.

The shape of the crystallization curves is in agreement with experimentally observed crystallization lines for poly(phenylene oxide)[25] and poly(L-lactide)[26]. The crystallization line will not cross the solvent–non-solvent axis, which is an asymptote for the crystallization line, just as it is for the binodal curve. The calculations carried out by Burghardt *et al.*[11], which resulted in a crystallization curve with a 'maximum', can be valid only if at intermediate non-solvent concentration a mixture of solvent and non-solvent is a better solving agent for the polymer.

Implications for membrane formation

From both calculations and experiments it can be concluded that crystallization or solid–liquid demixing is thermodynamically the most favourable phase separation process for this ternary system. It has been shown, however, that in some cases a membrane morphology has been obtained from these ternary systems that is typical for liquid–liquid demixing[2,11]. Membranes prepared from immersion precipitation are a result of a diffusion-induced phase separation process. During the diffusion process the composition in the cast film changes continuously and thermodynamic equilibrium is never reached during the different stages of the membrane-forming process. Both thermodynamic and kinetic parameters thus play a role in the final membrane morphology. In crystallization several kinetic parameters are involved: the (reptation) diffusion of polymer molecules to a growing crystal and the surface reaction of a chain onto the surface. Primary nucleation is dictated by both thermodynamic and kinetic effects. Before crystallization can take place a certain degree of supersaturation or undercooling is necessary. This means, that especially for membrane-forming systems in which crystallization is involved, dynamic phase separation cannot be described by equilibrium thermodynamics alone.

For many membrane-forming systems crystallization is a 'slow' process so that it is not involved in membrane formation. Even in turbidity or cloud point measurements a true crystallization point will not be observed. Phenomena that are not understood are ascribed to a gelation boundary that in reality very well may be a crystallization line for semicrystalline polymers. For the semicrystalline polymers poly(phenylene oxide), cellulose acetate and poly(L-lactide) effects of crystallization should not be excluded.

CONCLUSIONS

The melting temperature, measured by cloud point experiments in mixtures of nylons in formic acid and water, is linearly related to the volume fraction of water at constant v_2 values. These experimental data were used to develop a phenomenological relationship between the melting temperature of the mixture and its composition. It was shown that these relationships provide a satisfactory description of the experimental data; the melting temperature of a ternary mixture of the components mentioned (with $0.75 < v_2 < 0.96$) can be predicted within a range of 1–2°C.

To model the equilibrium thermodynamic conditions of the three components of the membrane-forming systems nylon 4,6, nylon 6 and nylon 4,6-*co*-6, formic acid and water, the three binary Flory–Huggins interaction parameters were determined. The concentration-dependent water–formic acid interaction parameter, g_{12}, was taken from the literature; while g_{13}, which was considered to be a constant, was calculated from sorption experiments. These relationships were combined with melting point depression phenomena described with the Flory–Huggins theory, making it possible to derive the polymer–solvent interaction parameter g_{23} as a function of v_2. The data needed to calculate the other interaction parameters were acquired from the literature. The values found for the polymer–solvent interaction parameter, g_{23}, are highly negative.

The complete isothermal phase diagrams of the three different membrane-forming systems at $T = 30$°C could be derived. The isothermal crystallization lines could be calculated directly from the phenomenological relationships. The location of the binodals was calculated, using the interaction parameters derived earlier. Equilibrium crystallization lines and binodal curves can be calculated. For this system the crystallization line is positioned more closely to the solvent corner than the binodal, which is in agreement with the hypothesis stated earlier[2]. Although crystallization is the thermodynamically more favourable process, liquid–liquid demixing may not be excluded because kinetic parameters play an important role in membrane formation.

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NOTATION

g_{ij}	Flory–Huggins interaction parameter between the components i and j
G_{M}	Free enthalpy of the mixture (J mol^{-1})
ΔG_{m}	Free enthalpy of mixing (J)
G^{E}	Excess free enthalpy of mixing (J mol^{-1})
ΔH	Enthalpy change (J mol^{-1})
M	Molecular weight (g mol^{-1})
n	Number of moles
R	Gas constant (J mol^{-1} K^{-1})
ΔS	Entropy change (J mol^{-1} K^{-1})
r	Ratio of the molar volumes of the non-solvent and the polymer (η_1/η_3)
s	Ratio of the molar volumes of the non-solvent and the solvent (η_1/η_2)
T	Temperature (K)
T_{m}	Melting temperature (K)
u_2	$= \phi_2/(\phi_1 + \phi_2)$
v_2	$= \phi_2/(\phi_2 + \phi_3)$
x_i	Mole fraction of component i
γ_i	Activity coefficient of component i
η	Molar volume (cm^3 mol^{-1})
μ	Chemical potential (J mol^{-1})
ρ	Density (g cm^{-3})
ϕ	Volume fraction
χ	Flory–Huggins interaction parameter

Indices

c	Crystalline state
o	Pure (amorphous) state
1	Non-solvent
2	Solvent
3	Polymer
u	Repeating unit in the polymer
α	Polymer-lean phase
β	Polymer-rich phase
γ	Polymer solution in equilibrium with the crystalline state