Mathematical calculation of binodal curves of a polymer/solvent/ nonsolvent system in the phase inversion process

Yong-Ming Wei[a], Zhen-Liang Xu[a,b], Xiao-Tian Yang[a], Hong-Lai Liu[c]

[a]*Chemical Engineering Research Center, [b]Key Laboratory for Ultrafine Materials, [c]Department of Chemistry, East China University of Science and Technology (ECUST), 130 Meilong Road, Shanghai 200237, P.R. China Tel. +86 (21) 6425-2989; Fax: +86 (21) 6425-2989; email: chemxuzl@ecust.edu.cn*

Abstract

Four methods of calculating Flory–Huggins interaction parameters from solubility parameters were examined by comparing calculated binodal curves with experimental data. This is a promising method to calculate interaction parameters from solubility parameters because of the wide use of solubility parameters. The fitting results were satisfactory after the optimization of the correction constant according to the membrane casting systems mentioned. The optimized correction constants were 0.09 and 1.01 for the polymer/solvent and polymer/nonsolvent, respectively. The constants were obtained from PES/solvent and PSF/solvent systems and checked with PSF/DMAc/nonsolvent systems. Calculation was carried out, based on Flory–Huggins solution theory, to analyze the behavior of the polymer/solvent/nonsolvent system phase diagram with the influence of parameter sets in a wide range. It was found that with the increment of solvent/polymer interaction parameters or nonsolvent/polymer interaction parameters the miscibility gaps decreased. However, the miscibility gaps increased with the increment of nonsolvent/solvent interaction parameters.

Keywords: Binodal curve; Flory–Huggins; Interaction parameter; Solubility parameter; Ternary phase diagram; Miscibility gap

1. Introduction

The phase separation process is one of the main methods for the preparation of asymmetric polymer membranes. A ternary phase diagram is very useful in the description of the thermodynamic properties of a three-component system of polymer/solvent/nonsolvent which is usually used to make asymmetric membranes by immer-

*Corresponding author.

sion precipitation [1,2], the essential means to prepare the membrane with phase separation induced by changing the concentration of the solution. Different ternary systems result in different membranes with different structures.

Altena et al. [2] proposed the following explanation: (1) the equilibrium thermodynamic properties of a three-component system of polymer/solvent/nonsolvent, such as a liquid–liquid phase separation and gelation; (2) the exchange of solvent and nonsolvent during membrane formation and the effect on the kinetics of the above-mentioned demixing phenomena. A proper model for the formation process of asymmetric membranes should, of course, include both sets of factors. Koenhen et al. [3] and Broens et al. [4] suggested that the porosity of the sublayer was ascribed to liquid–liquid phase separation and the pores were formed most probably by nucleation and growth of the dilute polymer phase. Cohen et al. [5] proposed a different model for the formation of porous structures in the coagulation step during membrane formation. Their model was based on diffusion-induced phase separation at the spinodal in the ternary system.

The thermodynamic properties of the casting solution and coagulation pairs play a very important role on the structure and performance of a membrane prepared by immersion precipitation. Altena et al. [2] calculated the binodal curves of two membrane-forming systems: cellulose acetate/solvent/water and polysulfone/solvent/water. During their calculation, the interaction parameter (g_{12}) of nonsolvent and solvent was taken to be concentration-dependent, and the other interaction parameters of polymer with solvent (g_{23}) and with nonsolvent (g_{13}) were kept constant. Based on the Flory–Huggins theory, the relation between the behavior of the ternary phase diagram for the typical membrane-forming systems and various parameters was analyzed by Yilmaz et al. [1]. The importance of various parameters in controlling the phase-diagram behavior was demonstrated. It was concluded that

g_{23} should also be considered as concentration-dependent. And the concentration dependency of the solvent/polymer interaction parameter (g_{23}) played a critical role in affecting the nature of the miscibility gap. Also the effect of the chain length distribution on the phase behavior of polymer solutions in a single solvent was described qualitatively [6]. The influences of molecular weight and molecular weight distribution appear to be strongest in the region of low m_n [7], but unfortunately, the data for the concentration dependency and molecular weight distribution dependence of g_{23} is quite limited, which holds back the application.

In this paper the Flory–Huggins interaction parameter from solubility parameters [8–11] was calculated, and the correction constant was optimized on the basis of polyethersulfone (PES)/solvent/water systems, polysulfone (PSF)/solvent/water systems and was checked by PSF/solvent/nonsolvent systems. The involved nonsolvents were water, ethanol, butanol and pentanol; the involved solvents were N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1-methyl-2-pyrrolindone (NMP). In addition, the behavior of the polymer/solvent/nonsolvent system phase diagram with the effects of parameter sets in a wide range was analyzed.

2. Calculation of binodal curves of the polymer/solvent/nonsolvent system in the phase inversion process

2.1. Thermodynamics of polymer/solvent/nonsolvent system

The Flory–Huggins theory [12] for polymer solutions was extended to a three-component system by Tompa [13] and was widely used to describe the ternary phase diagram of the membrane casting system: polymer/solvent/nonsolvent [1,2].

The Gibbs free energy (ΔG_m) of the mixing of the membrane casting system is as follows:

$$\frac{\Delta G_m}{RT} = n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_3 \ln \varphi_3 \qquad (1)$$
$$+ g_{12}(u_2)n_1 \varphi_2 + g_{13} n_1 \varphi_3 + g_{23} n_2 \varphi_3$$

where subscripts 1, 2 and 3 refer to nonsolvent, solvent and polymer, respectively, while n_1 and φ_1 are the amount and volume fraction of component i (nonsolvent, solvent and polymer) respectively; R and T are the gas constant and temperature, respectively; g_{13} is the solvent/nonsolvent parameter, which is assumed to be a function of u_2 with $u_2 = \varphi_2/(\varphi_1 + \varphi_2)$; g_{13} is the nonsolvent/polymer interaction parameter, which is assumed to be constant; g_{23} is the solvent/polymer interaction parameter, which is assumed to be constant.

The conditions for liquid–liquid equilibrium are:

$$\Delta \mu_i^{\alpha} = \Delta \mu_i^{\beta} \qquad i = 1, 2, 3 \qquad (2)$$

where i represents different components; α and β denote polymer-rich and polymer-lean phases (also dilute phase) respectively.

From Eq. (1), Eqs. (3)–(5) for the chemical potentials of the components in the mixture are derived:

$$\frac{\Delta \mu_1}{RT} = \ln \varphi_1 + 1 - \varphi_1 - \frac{V_1}{V_2} \varphi_2 - \frac{V_1}{V_3} \varphi_3$$
$$+ \left[g_{12}(u_2) \varphi_2 + g_{13} \varphi_3 \right] (\varphi_2 + \varphi_3) \qquad (3)$$
$$- \frac{V_1}{V_2} g_{23} \varphi_2 \varphi_3 - \varphi_2 u_1 u_2 \frac{dg_{12}(u_2)}{du_2}$$

$$\frac{\Delta \mu_2}{RT} = \ln \varphi_2 + 1 - \frac{V_2}{V_1} \varphi_1 - \varphi_2 - \frac{V_2}{V_3} \varphi_3$$
$$+ \left[\frac{V_2}{V_1} g_{12}(u_2) \varphi_1 + g_{23} \varphi_3 \right] (\varphi_1 + \varphi_3) \qquad (4)$$
$$- \frac{V_2}{V_1} g_{13} \varphi_1 \varphi_3 + \frac{V_2}{V_1} \varphi_1 u_1 u_2 \frac{dg_{12}(u_2)}{du_2}$$

$$\frac{\Delta \mu_3}{RT} = \ln \varphi_3 + 1 - \frac{V_3}{V_1} \varphi_1 - \frac{V_3}{V_2} \varphi_2 - \varphi_3$$
$$+ \left(\frac{V_3}{V_1} g_{13} \varphi_1 + \frac{V_3}{V_2} g_{23} \varphi_2 \right) (\varphi_1 + \varphi_2) \qquad (5)$$
$$- \frac{V_3}{V_1} g_{12}(u_2) \varphi_1 \varphi_2$$

In Eqs. (3)–(5), V_i represents the pure molar volume of species i. In these equations, only binary interaction parameters are used. These values either were taken from the literature or were determined by independent experiments, but there is an obvious difference in the resources. The effects of changing these interaction parameters on the location of the binodal curves in ternary phase diagrams were investigated, and the reliability of interaction parameters were considered.

2.2. Method for calculating binodal curves

2.2.1. Calculation procedure

The procedure to calculate the binodal curves used by Altena et al. [2] was adopted here. Two material balance equations given as following are used in addition to the above-mentioned chemical potential balance equations.

$$\sum \varphi_i = 1 \qquad (6)$$

One of the compositions was chosen as an independent variable with substituting the material balance equations into Eqs. (3)–(5). Three non-linear algebraic equations are left. In this case, φ_3^{β} was also chosen as an independent variable because of the easier convergence [1]. φ_2^{α}, φ_3^{α} and φ_2^{β} were chosen as dependent variables. The objective function is

$$F = \sum f_i^2 \qquad (7)$$

with

$$f_1 = \Delta\mu_1^\alpha - \Delta m_1^\beta$$

$$f_2 = s\left(\Delta\mu_2^\alpha - \Delta\mu_2^\beta\right) \qquad (8)$$

$$f_3 = r\left(\Delta\mu_3^\alpha - \Delta\mu_3^\beta\right)$$

where r and s are the ratios of the molar volumes V_1/V_2 and V_3/V_3, respectively.

2.2.2. Evaluation of solvent/nonsolvent interaction parameter (g_{12})

The binary interaction parameter between nonsolvent (1) and solvent (2), g_{12}, can be calculated from the excess Gibbs free energy (G^E) which is generally obtained from vapor–liquid equilibrium experiments [1,2,14]. There is a relationship between G^E and G_m as follows:

$$\begin{aligned} G^E &= \Delta G_m - RT\left(x_1 \ln x_1 + x_2\right) \\ &= -x_1 \ln\left(x_1 + \Lambda_{12}x_2\right) - x_2 \ln\left(x_2 + \Lambda_{21}x_1\right) \end{aligned} \qquad (9)$$

where x_i stands for the mole fractions of component i and R is the ideal gas constant. Λ_{ij} is the Wilson parameter.

For the binary system

$$\Delta G_m/RT = x_1 \ln\varphi_1 + x_2 \ln\varphi_2 + g_{12}x_1\varphi_2 \qquad (10)$$

From Eqs. (9) and (10), the following equation can be obtained:

$$\begin{aligned} g_{12} = &\left[-x_1 \ln\left(x_1 + \Lambda_{12}x_2\right) - x_2 \ln\left(\Lambda_{21}x_1 + x_2\right) \right. \\ &\left. + x_1 \ln x_1 + x_2 \ln x_2 - x_1 \ln\varphi_1 - x_2 \ln\varphi_2\right]/x_1\varphi_2 \end{aligned} \qquad (11)$$

It is generally accepted that g_{12} is concentration dependent and so is g_{23} There are two forms to fit g vs φ. The polynomial form was suggested by Tompa [13] and used by Altena et al. [2]:

$$g\left(\varphi_2\right) = a_0 + a_1\varphi_2 + a_2\varphi_2^2 + \dots \qquad (12)$$

In addition, Eq. (13) was suggested by Koningsveld et al. [15] and has been adopted by many authors [1,16]:

$$g(\varphi_2) = \alpha + \frac{\beta}{1 - \gamma\varphi_2} \qquad (13)$$

For a ternary system, g_{12} is assumed to be a function only of $\varphi_2/\left(\varphi_1 + \varphi_2\right)$. Thus, g_{12} is obtained by replacing φ_2 with $u_2 = \varphi_2/\left(\varphi_1 + \varphi_2\right)$ in the above two equations.

2.2.3. Evaluation of the solvent/polymer interaction parameter (g_{23})

There are many experimental methods to determine the solvent/polymer interaction parameter (g_{23}), listed in Table 1 [17]. It can be seen that there is a scope of the application for every method. The most commonly used methods are osmosis (OS) [18,19], vapor pressure (VP) [12] and inverse gas chromatography (IGC) [20,21]. Those methods cover the whole range of the concentration. (See the above-mentioned references for detailed information.) In this paper the solvent/polymer interaction parameters were calculated from solubility parameters of solvents and polymers as shown below.

2.2.4. Evaluation of the nonsolvent/polymer interaction parameter (g_{13})

The nonsolvent/polymer interaction parameter was usually determined by the swelling equilibrium method [1,22] using data from equilibrium sorption experiments. The following equation was used:

$$\ln\frac{p}{p^0} = \ln\varphi_1 + \left(1 - \frac{2}{x_n}\right)\varphi_3 + g_{13}\varphi_3^2 \qquad (14)$$

Different methods in Table 1 were used for the determination of the nonsolvent/polymer interaction parameter. Sometimes there is an obvious

Table 1
Different methods for the determination of solvent/polymer interaction parameters

Typical range of concentration	Methods	Abbreviation
$\varphi_3 \to 0$	Scattering methods	LS
	Osmosis	OS
$0 < \varphi_3 < 0.3$	Light scattering	LS
	Differential vapor-pressure methods	ΔVP
$0.3 < \varphi_3 < 0.8$	Vapor-pressure methods	VP
$\varphi_3 \to 1$	Inverse gas chromatograph	IGC
$0 < \varphi_3 < 0.3$ (only for poor solvent)	Critical miscibility	CM

difference between interaction parameters measured by different methods for the same system. For example, Zeman et al. [23] investigated the interaction parameter of water–PES in a wide concentration range by light scattering measurements and obtained the value of g_{13}, which was 1.6. But the value of g_{13} at high concentration with the volume fraction of PES being 0.97 was 2.73, which was obtained from the swelling measurements. It is shown below that such a difference has a great effect on the phase diagram. Also the solvent/polymer interaction parameters were calculated from solubility parameters of solvents and polymers as shown below.

2.2.5. Calculation of binary interaction parameters from solubility parameters

All the above-mentioned methods evaluate experimentally the interaction parameter. A promising method to calculate the interaction parameter from the Hansen solubility parameter was used for the polymer/solvent/nonsolvent system. Hansen solubility parameters can be easily obtained from standard thermodynamic tables [10,24] because of their wide application, or at least they can be calculated from a group

contribution method as suggested by Meder [25]. It is promising to calculate the Flory–Huggins parameters from the solubility parameter, and there have been some attempts as summarized below.

Method A: Based on the regular solution theory, the relationship between the Flory–Huggins interaction parameter and the solubility parameters is [8]:

$$\chi_{12} = \frac{V_1}{RT}\left(\delta_1 - \delta_2\right)^2 \tag{15}$$

Method B: Peppas et al. [9] calculated Flory interaction parameters on the basis of the following procedure [12] utilizing the corresponding solubility parameters of two components. In general, the interaction parameters, χ_{12} is defined as

$$\chi_{12} = \frac{zX_1\Delta w_{12}}{kT} = \chi_H + \chi_s \tag{16}$$

where z is the lattice coordination number, X_1 is the number of polymer segments relative to solvent, Δw is the interaction energy. The term χ_s is the entropic contribution of approximately 0.34. The term χ_H is the enthalpy contribution and can be calculated from solubility parameters as shown by Mikos et al. [26]:

$$\chi_H = \frac{V_1}{RT}\left[\left(\delta_1 - \delta_2\right)^2 + 2I_{12}\,\delta_1\,\delta_2\right] \tag{17}$$

where I_{12} is a binary interaction parameter. For the system consisting of two components with a similar chemical structure, $I_{12} = 0$. The following equation is obtained:

$$\chi_{12} = 0.34 + \frac{V_1}{RT}\left(\delta_1 - \delta\right)^2 \tag{18}$$

Method C: Hansen [10] suggested using the following equation with $\alpha = 1$ for the estimation

of Flory–Huggins interaction parameters from the Hansen parameter:

$$x_{12} = \alpha \frac{V_1}{RT} \left[\left(\delta_{1,d} - \delta_{2,d}\right)^2 + 0.25 \left(\delta_{1,p} - \delta_{2,p}\right)^2 + 0.25 \left(\delta_{1,h} - \delta_{2,h}\right) \right] \quad (19)$$

Method D: Lindving et al. [11] estimated Flory–Huggins interaction parameters from the Hansen parameter with an optimum value of the correction constant $\alpha = 0.6$. As mentioned [11], the correction constant was different for different species pairs.

In this work the above-mentioned relationships between the Flory–Huggins interaction parameter and the solubility parameters were checked. The correction constant α was optimized according to the membrane casting system.

3. Results and discussion

3.1. Comparison of calculated binodal curves with experimental data

Six commonly used polymer/solvent/non-solvent casting membrane systems, i.e., PES/DMAc/water, PES/DMF/water, PES/DMSO/water, PES/NMP/water, PSF/DMAc/water, and PSF/NMP/water were used to investigate the

validity of the above-mentioned methods. The concentration-dependent water/solvent interaction parameters were calculated by Eq. (11). Wilson parameters of water/solvent systems are listed in Table 2. The data of $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{11})$ can be obtained directly from Gmehling and Onken [27]. Λ_{12} and Λ_{21} can be converted from $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ by the following equation:

$$\Lambda_{ij} = \frac{V_{mj}}{V_{mi}} \; e^{-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}} \quad (20)$$

where V_m is molar volume, and $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ stand for constants in the reference. Λ_{12} and Λ_{21} stand for Wilson parameters. The UNIFAC method [28] was employed because there were no vapor–liquid equilibrium data available.

Then the interaction parameters were fitted by Eqs. (12) and (13). The fitting coefficients are listed in Table 3 in polynomial form and in Table 4 in rational form.

The solvent/polymer and nonsolvent/polymer interaction parameters were calculated by the above-mentioned methods. Solubility parameters listed in Table 5 were taken from Grulke [29]. The calculated value of solvent/polymer and non-solvent/polymer interaction parameters are listed in Table 6.

The binodal curves were calculated using different interaction parameters in Tables 3 and 6

Table 2
Wilson parameters involved

1	2	V_{m1}	V_{m2}	$(\lambda_{12} - \lambda_{11})$	$(\lambda_{21} - \lambda_{22})$	Λ_{12}	Λ_{21}
Water	DMAc	18	92.5	383.1849	− 27.5258	2.6915	0.2038
Water	DMF	18	77.0	814.3194	− 575.2156	1.5304	0.4832
Water	DMSO	18	71.3	− 241.5231	− 1665.9792	5.9546	0.0152
Water	NMP	18	96.5	1489.0589	− 1202.5857	0.4343	1.4199
Ethanol	DMAc	58.5	92.5			3.0199	0.1906
Butanol	DMAc	91.5	92.5			0.8351	0.7442
Pentanol	DMAc	106.9	92.5			0.5779	0.6341

Table 3
Coefficients of solvent/nonsolvent interaction parameters for $g(\varphi_2) = a_0 + a_1\varphi_2 + a_2\varphi_2^2 + a_3\varphi_2^3 + a_4\varphi_2^4$

System	a_0	a_1	a_2	a_3	a_4
Water-DMAc	0.4672	0.1126	0.0404	0.0012	0.0159
Water-DMF	0.4727	0.1496	0.1245	−0.0936	0.1248
Water-DMSO	0.1899	−1.9256	4.6527	−5.1585	2.0797
Water-NMP	0.5483	−0.0920	2.0522	−3.9428	2.6792
Ethanol-DMAc	−0.1518	−0.2713	0.5063	−0.4394	0.1513
Butanol-DMAc	0.4554	−0.0292	0.0127	−0.0050	0.0022
Pentanol-DMAc	1.0260	−0.2006	0.1375	−0.0517	0.0143

Table 4
Coefficients of solvent/nonsolvent interaction parameters for $g(\varphi_2) = \alpha + \beta / (1 - \gamma\varphi_2)$

System	α	β	γ
DMAc-water	0.1407	−0.3266	−0.3432
DMF-water	0.1695	−0.3034	−0.5010
DMSO-water	−0.2285	−0.4335	6.5804
NMP-water	0.3497	−0.1981	0.7797
DMAc-ethanol	−0.2174	0.0691	−6.9939
DMAc-butanol	0.4024	0.0531	−0.5830
DMAc-Pentanol	0.8430	0.1840	1.2816

Table 5
Solubility parameters involved

Name	V_m	δ_d	δ_p	δ_h
PES		17.60	10.40	7.80
PSF		18.38	16.48	7.49
DMAc	92.5	16.80	11.50	10.20
DMF	77.0	17.40	13.70	11.30
DMSO	71.3	18.40	16.40	10.20
NMP	96.5	18.00	12.30	7.20
Water	18.0	15.50	16.00	42.40

Table 6
Calculated values of polymer/solvent and polymer/nonsolvent interaction parameters using different methods

| Polymer	Solvent/nonsolvent	Method A	Method B	Method C	Method D
PES	DMAc	0.02	0.36	0.09	0.05
PES	DMF	0.26	0.60	0.18	0.11
PES	DMSO	0.64	0.98	0.32	0.19
PES	NMP	0.04	0.38	0.04	0.03
PSF	DMAc	0.36	0.70	0.39	0.24
PSF	NMP	0.33	0.67	0.18	0.11
PES	Water	4.91	5.25	2.26	1.36
PSF	Water	3.55	3.89	2.27	1.36

and are shown in Fig. 1. From our experience Methods A and B overestimate the PES/water interaction parameter, which led to the high value of this parameter, as shown in Table 6. Thus, the high interaction parameter could not be used to calculate the binodal curves. Only the binodal
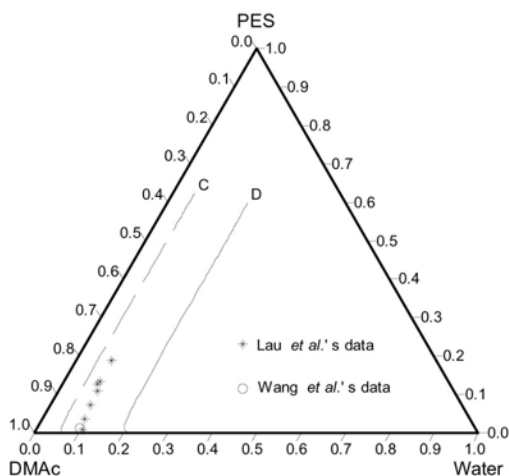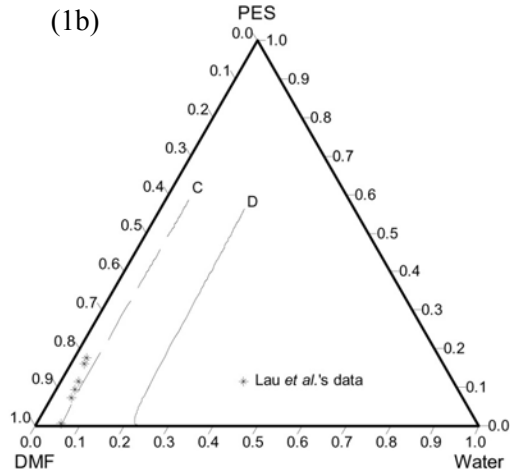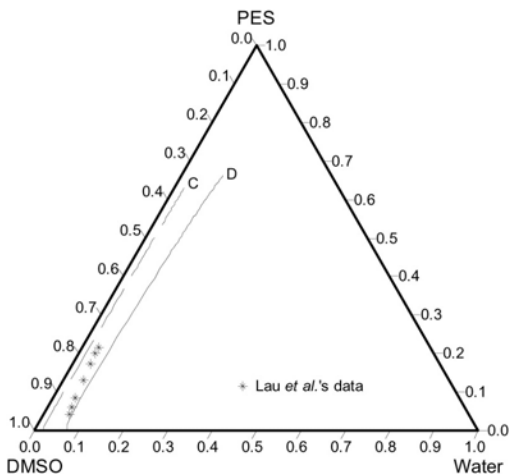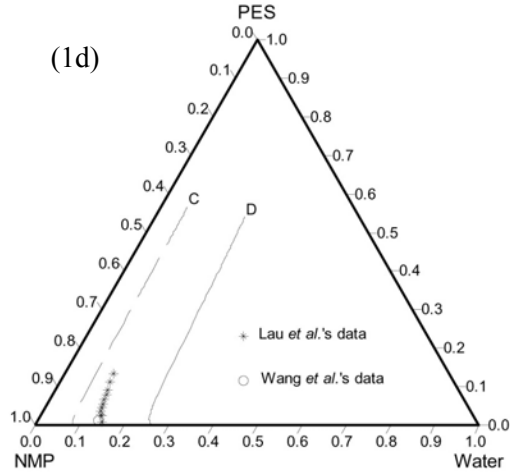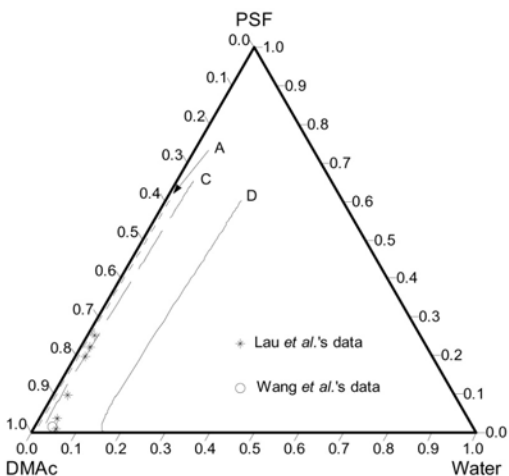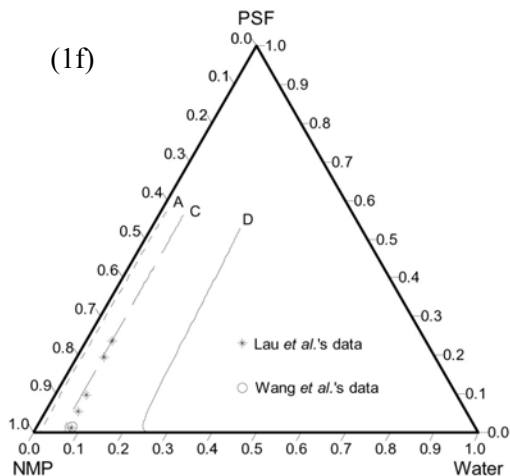
Fig. 1. Comparison of different methods to calculate the interaction parameter.

Table 7
Optimized interaction parameters for PES/solvent/water and PSF/solvent/water systems[a]

Interaction parameter	χ_{23}	χ_{13}
PES/DMAc/water	0.01	1.88
PES/DMF /water	0.02	2.79
PES/DMSO/water	0.03	1.86
PES/NMP/water	0.00	1.86
PSF/DMAc/water	0.04	2.74
PSF/NMP/water	0.02	2.33
PSF/DMAc/water[a]	0.04	2.67

[a]From Qin et al.'s data [32].

Table 8
Optimized correction constants for PES/solvent/water and PSF/solvent/water systems[a]

Correction constant	α_{23}	α_{13}
PES/DMAc/water	0.08	0.83
PES/DMF/water	0.09	1.23
PES/DMSO/water	0.08	0.82
PES/NMP/water	0.08	0.82
PSF/DMAc/water	0.09	1.21
PSF/NMP/water	0.09	1.03
PSF/DMAc/water[a]	0.09	1.16
Average	0.09	1.01

[a]From Qin et al.'s data [32].
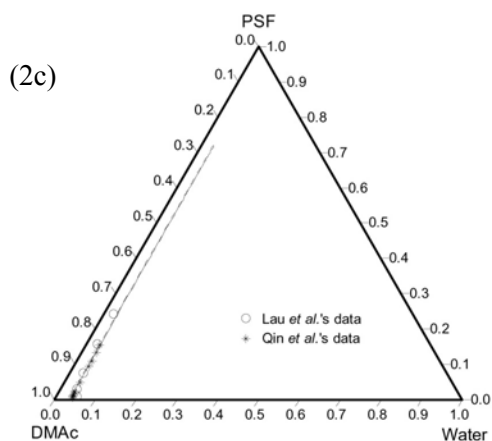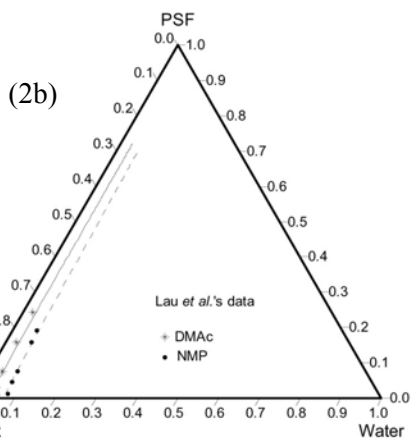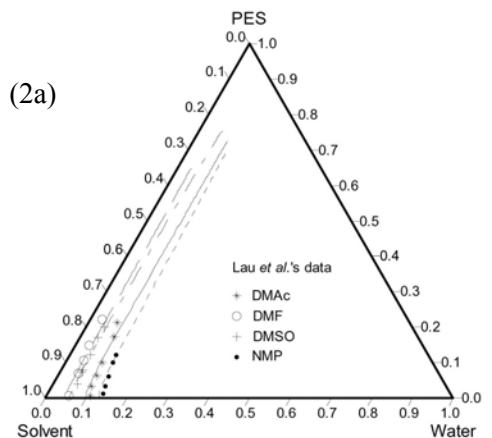
Fig. 2. Binodal curves fitted to the experimental data of PES/solvent/water and PSF/ solvent/water systems.

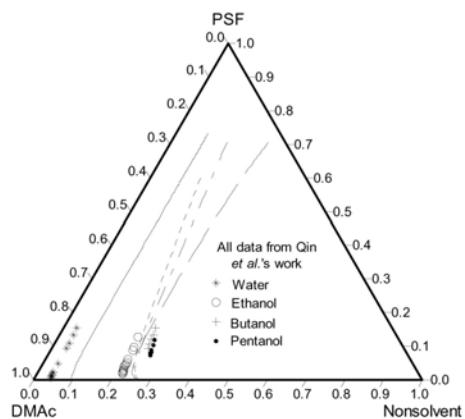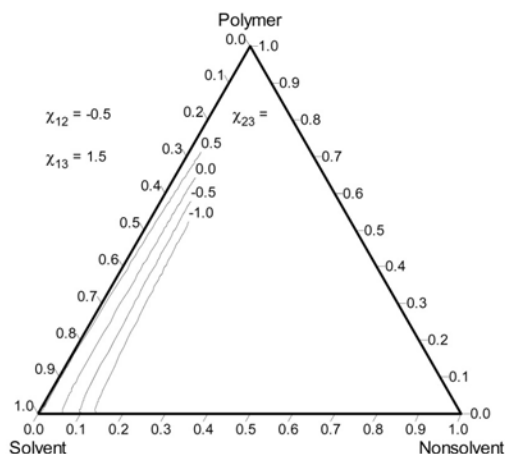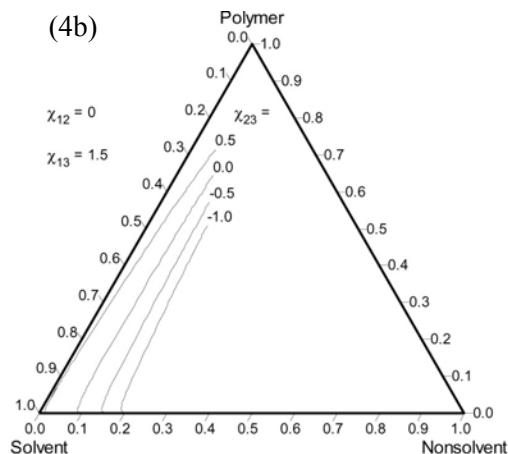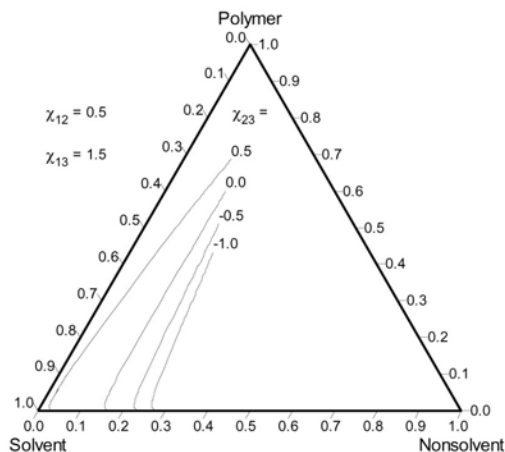Fig. 3. Binodal curves fitted to the experimental data of PSF/DMAc/nonsolvent systems.
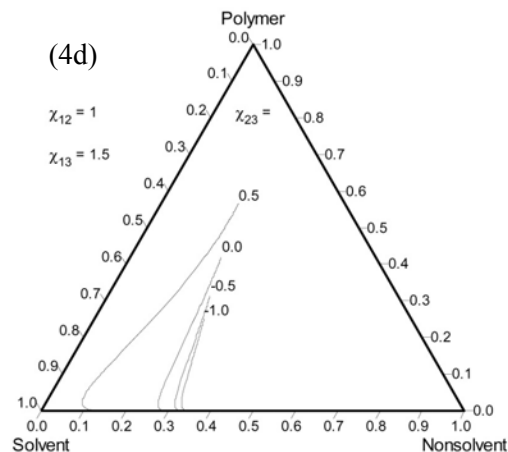
(4a)

(4b)

(4c)

(4d)

curves calculated from Methods C and D are shown in Fig. 1 for the PES/water systems. Method B was unsuitable for PSF/water systems for the same reason.

The star marked points were taken from Lau et al.'s experimental data [30] and circle marked points were taken from Wang et al.'s experimental data [31]. It can be seen from Fig. 1 that the solid and dash lines are close to the experimental data, which means that Method C is promising to calculate the interaction parameters from solubility parameters; and Method C is flexible because of the correction constant (α) of Eq. (19). The following section discusses the correction constant in detail.

3.2. Optimizing correction constant according to PES/solvent/water systems and PSF/solvent/water systems

It can be seen that Eq. (19) is promising to calculate the interaction parameters from solubility parameters as mentioned above. But there was obvious deviation of some polymer/solvent/nonsolvent systems such as PES/NMP/water, which means that there should be a different optimized correction constant for different pair systems. For example, the optimized correction constant of nonsolvent/polymer systems should be different from that of solvent/polymer systems. Thus, the correction constant of Eq. (19) should be optimized according to ternary casting mem-
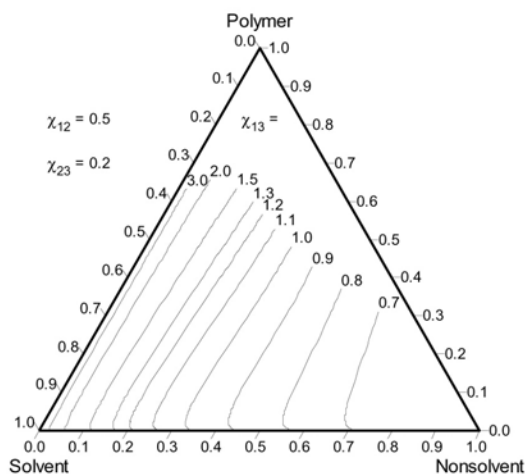
(4e)
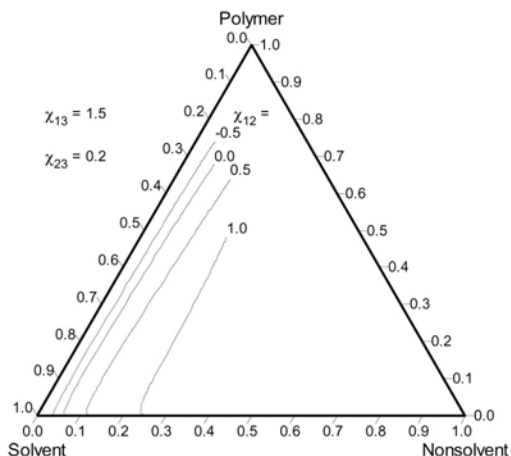
(4f)
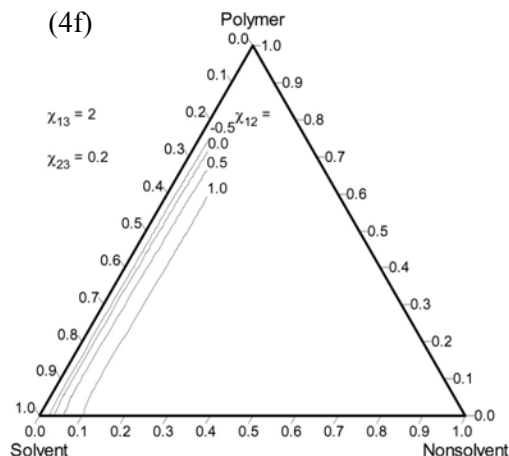
(4g)

Fig. 4. Binodal curves for a wide range of parameter sets.

brane systems. Such an attempt was made in this work according to membrane casting systems.

The nonsolvent used was water. The solvents were DMAc, DMF, DMSO and NMP. The polymers were PES and PSF. The nonsolvent/solvent interaction parameters in Table 3 were used. Solvent/polymer and nonsolvent/polymer interaction parameters were calculated using Eq. (19) with the correction constants being optimized according to the precipitation curves taken from Qin et al. [32] and Lau et al.'s [30] experiment. Lau et al.'s [30] data were used hereafter converting the unit from weight percent to volume percent. The optimized interaction parameters for

the PES/solvent/water systems and PSF/solvent/ water systems are listed in Table 7. Fig. 2 shows the binodal curves fitted to the experimental data. It can be seen from Fig. 2 that after the correction constant was optimized, Eq. (19) was more suitable to calculate the interaction parameters. The binodal curves calculated from the interaction parameters can fit the experimental data better.

The optimized correction constants (α_{23} and α_{13}) for each ternary system are listed in Table 8, which are suitable for the PES/solvent/water systems and at least the PSF/solvent/water systems. From Table 8 it can be concluded that the correction constant α_{23} for the polymer/solvent inter-

action parameters was around 0.09. The approximate correction constant α_{13} for the PES/water and PSF/water was 1.01.

3.3. Checking the correction constant by PSF/ DMAc/nonsolvent systems

The above-mentioned ternary systems have the same nonsolvent — water. More ternary systems with different nonsolvents such as ethanol, butanol and pentanol, which were usually added to the polymer solution as additives, were investigated here to check the validity of the correction constant in common membrane casting solutions. The solvent and polymer in these systems were DMAc and PSF. The experimental data were taken from Qin et al. [32].

The nonsolvent/solvent interaction parameters were obtained in the same way as mentioned above, but the Wilson parameters were estimated through the UNIFAC method due to a lack of vapor–liquid equilibrium data. From Fig. 3 it can be concluded that the correction constants obtained above were acceptable in the case of a lack of experimental binodal data.

3.4. Binodal curves for a wide range of parameter sets

Calculations were carried out, based on the Flory–Huggins solution theory, to analyze the behavior of the ternary polymer/solvent/non-solvent phase diagram for typical membrane-forming systems by Yilmaz et al. [1]. The consideration was given especially to the behavior related to the concentration dependency of the interaction parameters. Here the influence of parameter sets in a wide range was seen. All the parameters were assumed to be concentration independent in a reasonable range.

The polymer/solvent interaction parameters are reasonable in the range of less than 0.5 and the polymer/nonsolvent interaction parameters are reasonable in the range of greater than 0.5

according to the Flory–Huggins theory. But the solvent/nonsolvent interaction parameters are reasonable in a more flexible range without specific maximum and minimum values. The wide range of investigation of interaction parameters sets is shown in Fig. 4(a–d). Each part shows the tendency that the miscibility gaps decrease with the increment of the polymer/solvent interaction parameters, which means the solvent changes from a good one to a poor one for the polymer. Together with Fig. 4(e) and (f), the tendency is seen where the miscibility gaps increase with the increment of the nonsolvent/solvent interaction parameters, which means the difference between nonsolvent and solvent increased. Fig. 4(g) shows the tendency for the miscibility gaps to decrease rapidly with the increment of polymer/nonsolvent interaction parameters, especially in the range of 0.7–1.5.

4. Conclusions

Four methods of calculating Flory–Huggins interaction parameters from solubility parameters were examined by comparing calculated binodal curves with experimental data. It was seen from the result that Method C is a promising method because of the good fitting results and the flexibility to change the correction constant according to different systems. It was also promising because the Hansen solubility parameters can be easily obtained from standard thermodynamic tables for their wide application, or at least they can be calculated from group contribution theory. The fitting results were more satisfactory after the optimization of the correction constant according to the membrane casting systems mentioned herein. The optimized correction constant for polymer/solvent was 0.09 and the optimized correction parameter for polymer/nonsolvent was about 1.01. These correction constants were examined by the PSF/DMAc/nonsolvent systems and acceptable results were obtained.

Calculation was carried out, based on the Flory–Huggins solution theory, to analyze the behavior of the polymer/solvent/nonsolvent system phase diagram with the influence of parameter sets in a wide range. It was found that with an increment of solvent/polymer interaction parameters or nonsolvent-polymer interaction parameters, the miscibility gaps decreased. However, the miscibility gaps increased with the increment of nonsolvent/solvent interaction parameters.

Acknowledgments

References

[1] L. Yilmaz and A.J. McHugh, Analysis of nonsolvent-solvent-polymer phase diagrams and their relevance to membrane formation modeling, J. Appl. Polym. Sci., 31 (1986) 997–1018.

[2] F.W. Altena and C.A. Smolders, Calculation of liquid-liquid phase separation in a ternary system of a polymer in mixture of solvent and nonsolvent, Macromolecules, 15 (1982) 1491–1497.

[3] D.M. Koenhen, M.H.V. Mulder and C.A. Smolders, Phase separation phenomena during the formation of asymmetric membranes, J. Appl. Polym. Sci., 21 (1977) 199–215.

[4] L. Broens, F.W. Altena, C.A. Smolders and D.M. Koenhen, Asymmetric membrane structures as a result of phase separation phenomena, Desalination, 32 (1980) 33–45.

[5] C. Cohen, G.B. Tanny and S. Prager, Diffusion-controlled formation of porous structures in ternary polymer systems, J. Polym. Sci., Polym. Phys. Ed., 17 (1979) 477–489.

[6] R. Koningsveld and A.J. Staverman, Liquid-liquid phase separation in multicomponent polymer solutions. I. Statement of the problem and description of

methods of calculation, J. Polym. Sci. Part A-2: Polym. Physics, 6 (1968) 305–323.

[7] R. Koningsveld and A.J. Staverman, Polymer fractionation. I. The preparative problem, J. Polym. Sci. Part A-2: Polym, Physics, 6 (1968) 367–381.

[8] T. Lindvig, M.L. Michelsen and G.M. Kontogeorgis, Thermodynamics of paint related systems with engineering models, AIChE J., 47 (2001) 2573–2584.

[9] N.A. Peppas and L. Brannon-Peppas, Controlled release of fragrances from polymers I. Thermodynamic analysis, J. Controlled Release, 40 (1996) 245–250.

[10] C.M. Hansen, Hansen Solubility Parameters, CRC Press, Boca Raton, FL, 2000.

[11] T. Lindvig, M.L. Michelsen and G.M. Kontogeorgis, A Flory-Huggins model based on the Hansen solubility parameters, Fluid Phase Equilibria, 203 (2002) 247–260.

[12] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

[13] H. Tompa, Polymer Solutions, Butterworths, London, 1956.

[14] L.P. Cheng, A.W. Dwan and C.C. Gryte, Isothermal phase behavior of Nylon-6, -66 and -610 polyamides in formic acid-water systems, J. Polym. Sci. Part B: Polymer Physics, 32 (1994) 1183–1190.

[15] R. Koningsveld and L.A. Kleintjens, Liquid-liquid phase separation in multicomponent polymer systems. X. Concentration dependence of the pair-interaction parameter in the system cyclohexane-polystyrene, Macromolecules, 4 (1971) 637–641.

[16] T.-H. Young and W.-Y. Chuang, Thermodynamic analysis on the cononsolvency of poly(vinyl alcohol) in water-DMSO mixtures through the ternary interaction parameter, J. Membr. Sci., 210 (2002) 349–359.

[17] N. Schuld and B.A. Wolf, Polymer-solvent interaction parameters, in: J. Brandrup, E.H. Immergut and E.A. Grulke, eds., Polymer Handbook, Wiley, New York, 1999.

[18] P.J. Flory, Molecular weights and intrinsic viscosities of polyisobutylenes, J. Amer. Chem. Soc., 65 (1943) 372–382.

[19] R.M. Fuoss and D.J. Mead, Osmotic pressures of polyvinyl chloride solutions by a dynamic method, J. Phys. Chem., 47 (1943) 59–70.

[20] D. Patterson, Y.B. Tewari, H.P. Schreiber and J.E.

Guillet, Application of gas-liquid chromatography to the thermodynamics of polymer solutions, Macromolecules, 4 (1971) 356–359.

[21] N.F. Brockmeier, R.W. McCoy and J.A. Meyer, Gas chromatographic determination of thermodynamic properties of polymer solutions. I. Amorphous polymer systems, Macromolecules, 5 (1972) 464–470.

[22] D. Bonner, Vapour-liquid equilibria in concentrated polymer solutions, J. Macromol. Sci. Revs. Macromol. Chem., C13 (1975) 263–319.

[23] L. Zeman and G. Tkacik, Thermodynamic analysis of a membrane-forming system water/N-methyl-2-pyrrolidone/polyethersulfone, J. Membr. Sci., 36 (1988) 119–140.

[24] K.L. Hoy, New values of the solubility parameters from vapor pressure data, J. Paint Technol., 42 (1970) 76–118.

[25] M. Meder, A primer on perfuming polymers, Perfumer Flaverist, 11 (1986) 37–45.

[26] A.G. Mikos and N.A. Peppas, The Flory interaction parameter for hydrophilic copolymers with water, Biomat., 9 (1988) 419–423.

[27] J. Gmehling and U. Onken, Vapor-liquid equilibrium data collection I. Aqueous-organic systems, in: D. Behrens and R. Eckermann, eds., Chemistry Data Series, Vol. 1, Dechema, Frankfurt, 1977.

[28] A. Fredenslund, J. Gmehling and P. Rasmussen, Vapor-liquid equilibria using UNIFAC, Elsevier North-Holland, Amsterdam, 1977.

[29] E.A. Grulke, Solubility parameter values, in: J. Brandrup, E.H. Immergut and E.A. Grulke, eds., Polymer Handbook, Wiley, New York, 1999.

[30] W.W.Y. Lau, M.D. Guiver and T. Matsuura, Phase separation in polysulfone/solvent/water and polyethersulfone/solvent/water systems, J. Membr. Sci., 59 (1991) 219–227.

[31] D. Wang, K. Li, S. Sourirajian and W.K. Teo, Phase separation phenomena of polysulfone/solvent/organic nonsolvent and polyethersulfone/solvent/organic nonsolvent systems, J. Appl. Polym. Sci., 50 (1993) 1693–1700.

[32] J. Qin and C. Jiang, Study on phase diagrams of polysulfone membrane forming system, Mo Kexue Yu Jishu, 10 (1990) 13–18.