Thermodynamic Consistency Test for Equilibria Involving Cross-Linked Polymers

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The implications of the peculiarities of equilibria involving a cross-linked polymer network and a solvent were examined in the derivation of a thermodynamic consistency test. While strict application to a binary system achieves no tangible result, it is shown that a simple expression can be obtained from the Gibbs-Duhem equation, if several sets of data, including both binary and ternary, are combined. The expression derived was applied to previously reported multicomponent data. The results and further developments of the newly proposed test are discussed.

Introduction

Phase equilibria of systems involving polymers have received increased attention during the past years, but for the most part a quantitative understanding of their properties has not been reached. Besides the classic situation of polymers in a solution exhibiting phase-partitioning behavior, a large number of situations concern three-dimensional cross-linked polymer networks, subject to swelling phenomena, but incapable of migrating to the surrounding solvent phase upon contact. This type of system plays an important and expanding role in many fields, such as medicine, biology, separations technology, and the pharmaceutical industry (Prausnitz, 1995). From a practical point of view, the cross-linked polymer is brought in contact with several components in most cases; from the thermodynamic point of view this leads to multicomponent systems, which are more complex to study and have received little attention. An evaluation tool of the thermodynamic consistency of the experimental data would be of crucial interest for these systems, and is developed from the knowledge of the amount of solvent sorbed in the polymer phase at thermodynamic equilibrium.

The objective of this work is to use a thermodynamic consistency test to investigate the possibilities and the limits of the assessment of the validity of experimental equilibrium data involving a cross-linked polymer network. Interest in these types of tests has already been shown for vapor–liquid equilibria (Bertucco et al., 1997; Jackson and Wilsak, 1995; Null, 1970) as well as for adsorption on solids (Rao and Sircar, 1996). To our knowledge, no research on the thermodynamic consistency of cross-linked polymer–solvent equilibria has been reported. This is probably because, as is well known, it is impossible to test single-solvent–polymer swelling data for thermodynamic consistency because the polymer cannot enter the solvent phase.

In this article, a test has been derived from the Gibbs–Duhem equation. This test is used to check the reliability of the experimental data.

Equilibrium Conditions

Classic vapor – liquid equilibrium

The conditions for equilibrium between two phases (I and II) in direct contact (Table 1, case I) are

$$T^{I} = T^{II}; \qquad P^{I} = P^{II} \qquad \text{and} \qquad \mu_i^{I} = \mu_i^{II} \qquad \text{(for each component } i\text{)}, \quad (1)$$

where μ_i is the chemical potential for component i.

The validity of experimental vapor–liquid equilibria can be judged by a consistency test derived from the well-known Gibbs–Duhem equation (other thermodynamic expressions can also be used such as in the calculation of the fugacity coefficient):

$$-SdT + VdP - n_1 d\mu_1 - n_2 d\mu_2 = 0.$$

Different procedures can be obtained by different manipulations of the initial Gibbs–Duhem equation (Jackson and Wilsak, 1995), such as the Van Ness–Byer–Gibbs test, the integral or differential test, and the infinite dilution test.

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For instance, assuming the pressure term to be negligibly small, the final integrated form of the integral test applied to a binary mixture at constant temperature is

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0,$$

where γ_1 and γ_2 are the activity coefficients of each component, and x_1 corresponds to the molar fraction of component 1 in a binary mixture. The application of the test only implies the calculation of values of γ_1 and γ_2 for each of the data points.

Phase equilibrium for a binary system containing a cross-linked polymer

The case of a cross-linked polymer in contact with the fluid phase cannot be treated like a classic two-phase system because of the arguments discussed below.

1. The polymers studied consist of long-chain molecules, cross-linked to create a three-dimensional tangled network. When placed in contact with an appropriate solvent, the network expands to a certain degree. As a consequence of the cross-linked structure, the polymer shows quasi-perfect insolubility toward the solvent phase. Because it is impossible for the polymer to transfer to the fluid phase, the polymer term can be eliminated in the Gibbs–Duhem equation applied to the solvent phase.
2. Another important characteristic is that at equilibrium (when no tendency toward change occurs with time), the pressure in the polymer is different from the pressure in the fluid phase (Table 1, case II).

It follows that the set of equilibrium conditions for a cross-linked polymer coexisting with a surrounding fluid phase can be summarized by (Guggenheim, 1965)

$$dT = 0 \qquad dP^{\text{polymer}} = 0 \qquad dP^{\text{liquid}} = 0 \qquad dG = 0. \quad (2)$$

Recently, Maurer and Prausnitz (1996) reexamined the implications of this condition. The polymer phase has to be seen as a bulk phase surrounded by an elastic membrane with interfacial tensions. By analogy with osmotic pressure, the elastic properties of this membrane create a difference in pressure between the inner and outer polymer phases resulting from what Guggenheim (1965) called a membrane equilibrium.

As expansion continues, the elastic retractive force caused by the network structure is opposed to the sorption of the liquid placed in contact; in other words, to the diluting force. A state of equilibrium is reached when these two forces are in balance. According to Flory (1953), the elastic reaction can be interpreted as pressure acting in the polymer phase and increasing with the amount of solvent incorporated in the polymer.

Characteristics 1 and 2 discussed earlier lead to an equilibrium situation that differs from the classic vapor–liquid equilibrium. Therefore, the derivation of a thermodynamic consistency test needs to be reexamined. The starting point remains the Gibbs–Duhem equation.

Gibbs–Duhem Equation

The Gibbs–Duhem equation (Null, 1970) reads as follows:

$$-SdT + VdP - \sum_i n_i d\mu_i = 0. \quad (3)$$

Binary Case: Solvent S1 + Polymer P. In the polymer phase at constant temperature, Eq. 3 becomes (Table 1; case II)

$$V'dP - n'_1 d\mu_1 - n'_p d\mu_p = 0. \quad (4)$$

From the equality of chemical potential at equilibrium (see Appendix A), the expression of chemical potential differential of component i in the polymer as a function of solvent activity in the vapor phase (under the sole assumption of constant temperature) can be deduced as follows:

$$d\mu_{i,\text{pol}} = RTd \ln (a_i^{\text{vap}}) = RT \frac{da_i^{\text{vap}}}{a_i^{\text{vap}}}. \quad (5)$$

Substituting $d\mu_1$ from Eq. 5 into 4 gives

$$dP = \frac{n'_1 RT}{V'} \frac{da_1}{a_1} + \frac{n'_p}{V'} d\mu_p. \quad (6)$$

In terms of volume fraction,

$$n'_i = \frac{\phi_i V'}{v^*_{i,\text{liq}}} \quad (7)$$

where $v_i = v^*_{i,\text{liq}}(T)$ is the molar volume of component i at temperature T.

Combining Eqs. 6 and 7, we obtain

$$dP = \frac{\phi_1 RT}{v_1 a_1} da_1 + \frac{n'_p}{V'} d\mu_p. \quad (8)$$

This equation can be integrated at constant temperature, P_d being the polymer internal pressure in the dry state:

$$P_1 - P_d = \int_{P_d}^{P_1} dP = RT \int_0^{a_1} \frac{\phi_1}{v_1 a_1} da_1 + \int_d^{s1} \frac{n'_p}{V'} d\mu_p. \quad (9)$$

The lefthand term corresponds to the pressure increase in the polymer phase during the expansion. The first term of the righthand term of Eq. 9 can be simply assessed from experimental equilibrium data [$\phi = f(a)$]. On the other hand, pressure variation as well as polymer chemical potential variation are not accessible from experiments.

Binary Case: Solvent S2 + Polymer P. The previous procedure can be applied to solvent 2 in the same way as to solvent 1, which leads to the final integrated equation:

$$P_2 - P_d = \int_{P_d}^{P_2} dP = RT \int_0^{a_2} \frac{\phi_2}{v_2 a_2} da_2 + \int_d^{s2} \frac{n'_p}{V'} d\mu_p. \quad (9')$$

Table 1. Three Cases of Equilibria between Two Phases under Isothermal Conditions

Case I	Case II	Case III
Vapor Phase P, V, y_1, y_2	*Vapor Phase* $P, V, n_1, n_p = 0$	*Liquid Phase* $P, V, x_1, x_2, x_p = 0$
Liquid Phase P, V', x_1, x_2	*Polymer Phase* P', V', ϕ_1	*Polymer Phase* P', V', ϕ_1, ϕ_2

Ternary Case: Two Solvents S1/S2 + Polymer P. In the polymer phase at constant temperature, Eq. 3 becomes (Table 1, case III):

$$V'dP - n'_1 d\mu_1 - n'_2 d\mu_2 - n'_p d\mu_p = 0. \tag{10}$$

In the liquid phase, at constant temperature and constant pressure and always assuming the insolubility of the polymer in the liquid phase, the Gibbs-Duhem equation (Eq. 3) can be expressed as

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{11}$$

$$d\mu_2 = -\frac{x_1}{x_2} d\mu_1. \tag{12}$$

Substituting $d\mu_2$ from Eq. 12 into Eq. 10 and replacing n'_i using Eq. 7 gives

$$V'dP = \left(\frac{\phi_1 V'}{v_1} - \frac{x_1}{x_2} \frac{\phi_2 V'}{v_2} \right) d\mu_1 + n'_p d\mu_p. \tag{13}$$

Based on the equality of chemical potential at equilibrium (see Appendix B), the expression of chemical potential differential of component i in the polymer as a function of solvent activity in the liquid phase (under the sole assumption of constant temperature) can be deduced as follows:

$$d\mu_{i,\text{pol}} = RTd \ln a_i^{\text{liq}} = RT \frac{da_i^{\text{liq}}}{a_i^{\text{liq}}}. \tag{14}$$

Substituting $d\mu_1$ from Eq. 14 into Eq. 13 leads to

$$dP = \frac{RT}{x_2 a_1} \left(\frac{\phi_1 x_2}{v_1} - \frac{\phi_2 x_1}{v_2} \right) da_1 + \frac{n'_p}{V'} d\mu_p.$$

Integration gives

$$P_1 - P_2 = \int_{P_2}^{P_1} dP = RT \int_0^{a_1} \left(\frac{\phi_1 x_2}{v_1} - \frac{\phi_2 x_1}{v_2} \right) \frac{da_1}{x_2 a_1} + \int_{s2}^{s1} \frac{n'_p}{V'} d\mu_p. \tag{15}$$

The difference in pressure given by Eq. 15 corresponds to the variation of pressure of a polymer swelled by a pure solvent S2 to a pure solvent S1 (covering the entire range of composition).

The Thermodynamic Consistency Test

The sorption isotherms must obey the integral thermodynamic consistency dictated by Eqs. 9, 9′, and 15. Furthermore, the following relationship has to be satisfied:

$$(P_1 - P_2) + (P_2 - P_d) + (P_d - P_1) = 0. \tag{16}$$

The following equation, which corresponds to the polymer term, is verified:

$$\int_d^{s2} \frac{n'_p}{V'} d\mu_p + \int_{s2}^{s1} \frac{n'_p}{V'} d\mu_p + \int_{s1}^{d} \frac{n'_p}{V'} d\mu_p = 0. \tag{17}$$

Coupling Eqs. 16 and 17 leads to the final expression of the consistency test:

$$\int_0^{a_1} \left(\frac{\phi_1 x_2}{v_1} - \frac{\phi_2 x_1}{v_2} \right) \frac{da_1}{x_2 a_1} + \int_0^{a_2} \frac{\phi_2}{v_2 a_2} da_2 - \int_0^{a_1} \frac{\phi_1}{v_1 a_1} da_1 = 0. \tag{18}$$

Two points concerning Eq. 18 are worth noting:

1. The equation can be easily checked, since its only requirement is knowledge of the raw equilibrium data (a, ϕ).
2. It is based on a combination of three equilibrium data sets, including two binaries and one ternary. This somewhat complicated condition is caused by the impossibility of deriving a simple expression for a binary system involving a cross-linked polymer, an impossibility similar to the one in adsorption equilibria on solids (Rao and Sircar, 1996).

Nevertheless the new proposed consistency test offers the unique opportunity of validating different sets of data, provided the latter were obtained with the same polymer. Later in the article, the applicability of Eq. 18 is investigated with the few data fulfilling these conditions.

Experimental Determination of Sorption Equilibria

The thermodynamic equilibrium between a solvent and a cross-linked polymer can best be measured using the gravimetric method. The experimentally obtained isotherm is usually represented, in terms of volume fractions, as a function of solvent activities in the fluid phase.

In the binary case (a polymer swelled by a single component), the entire activity range is covered by putting pure solvent vapor with various activities in contact with the polymer sample. Measurement of the variation in weight of the polymer phase allows us to determine the expansion factor, plus the volume fraction of solvent in the polymer (Enneking et al., 1993). An example of the isotherm (benzene/polyurethane system) extracted from the experimental data assessed below is shown on Figure 1.

In a ternary mixture (a polymer P swelled by the binary mixture of solvents S1 and S2), the isotherm is obtained by putting different liquid mixtures with a variety of compositions into contact with a polymer sample. The activity of each solvent, which depends on its concentration in the liquid phase, can be computed by classic vapor-liquid equilibria equations (NRTL, Uniquac, Wilson, and so on) (Gmehling and Onken, 1977). After attaining equilibrium, the weight of

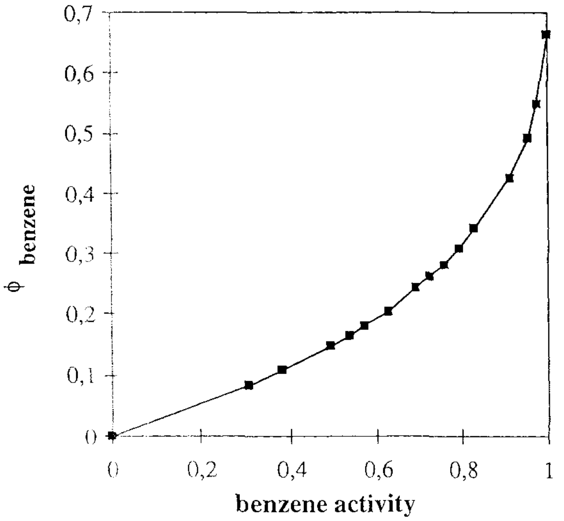

Figure 1. Sorption isotherm of benzene in polyurethane at 60°C: volume fraction of benzene in polymer as a function of benzene activity.

From Enneking et al. (1993).

the swelled polymer sample is measured in order to calculate the swelling factor. After desorption of the sorbed molecules, the amount of each species sorbed in the polymer is determined by chromatographic analysis, which yields the volume fraction of each component (Enneking et al., 1993).

Application to Experimental Data

Four sets of data previously reported in the literature have been studied. The calculation of each integral as well as the test results are summarized in Table 2.

An example of a numerical application of Eq. 18 to data is shown on Figure 2, where the different functions below the different integrals are plotted vs. solvent activities. The proposed thermodynamic consistency criterion implies that the sum of areas above the X-axis is equal to the area below.

The different data sets have been integrated graphically and errors calculated similar to the expression proposed in thermodynamic data banks (Gmehling and Onken, 1977):

$$\text{Error} = 100\,\frac{|(P_1-P_2)+(P_2-P_d)+(P_d-P_1)|}{|P_1-P_2|+|P_2-P_d|+|P_d-P_1|}\ (\%).$$

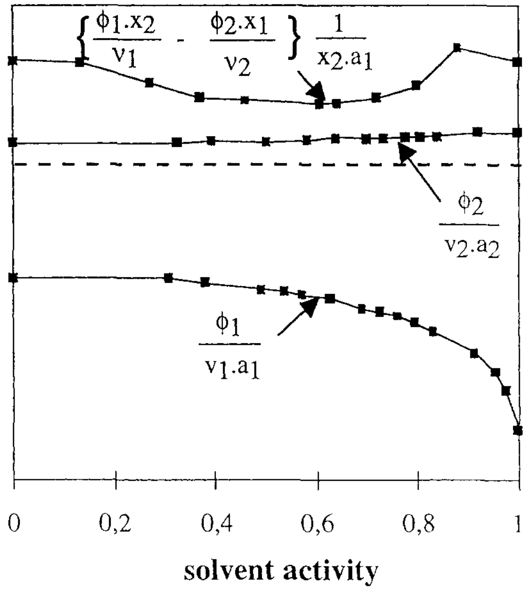

Figure 2. Numerical application of Eq. 18 to benzene(1)-cyclohexane(2)-polyurethane system (60°C).

Dashed line: X-axis. From Enneking et al. (1993).

The final error values vary considerably from one system to the other. It is worth recalling that a deviation of a few percent is considered to be acceptable for such consistency tests when applied to classic vapor–liquid equilibria (Gmehling and Onken, 1977).

Based on this criterion, the only conclusion we can draw concerns the thermodynamic consistency of systems shown in columns 2 and 3 of Table 2. These systems provide excellent results within the limits of experimental error, especially if one considers that three sets of experimental data are involved in the global uncertainty assessment.

The same statement does not hold for the other two systems (columns 4 and 5), which correspond to polymers used for dense membrane separations: cellulose acetate (an amorphous polymer often proposed for reverse osmosis applications) and polyvinylalchohol (a cross-linked semicrystalline polymer used for pervaporation applications) (Bitter, 1991).

The system shown in column 4 involves sorption data (water–ethanol–cellulose acetate) reported by different authors. In this case, it is noticeable that a large discrepancy is

Table 2. Calculation of Different Integrals and Test Results for Four Experimental Systems*

Exp. System	Benzene (1) Cyclohexane (2) PU	Ethanol (1) Toluene (2) PDMS	Ethanol (1) Water (2) CA	Ethanol (1) Water (2) PVA
Solvent(1) + Solvent(2) + Polymer S1–S2	2,748	−1,600	−15,812	−5,121
Solvent(2) + Polymer S2–D	1,036	2,352	7,062	10,968
Solvent(1) + Polymer D–S1	−3,789	−693	−3,586	−2,262
Sum	−26	66	−12,336	3,584
Error (%)	0.06	1.26	46.6	19.5

*Benzene–cyclohexane–polyurethane (PU) at 60°C (Enneking et al., 1993); ethanol–toluene–polydimethylsiloxane (PDMS) at 40°C (Favre, 1994; Favre et al., 1994); ethanol–water–cellulose acetate (CA) (Burghoff and Pusch, 1976; Bitter, 1991; Perrin, 1994); ethanol–water–polyvinylalcohol (PVA) at 60°C (Heintz and Stephan, 1994).

obtained, suggesting the unreliability of these different data sources. This might be explained by differences in either operating conditions or in polymer samples.

The results reported in column 5 are not satisfactory (water–ethanol–PVA). The high error value can be explained by the peculiarity of the polymer studied. Indeed, PVA is a semicrystalline polymer that constitutes a two-phase system at a microscopic level. The failure observed suggests that the amorphous and the crystalline phases should be considered separately (the Gibbs–Duhem equation can only be applied to one homogeneous phase). Furthermore, the incorporation of water in a PVA matrix modifies the structure of the crystalline phase, since sorbed water molecules induce crystal dissolution. Consequently, the procedure proposed here cannot be directly applied to such a complex system.

Conclusion

A procedure to evaluate the reliability of experimental measurements is an essential requirement of the study of polymer-solvent equilibria. To date, no procedure has been proposed to achieve this goal, despite the many applications faced with multicomponent equilibria involving a cross-linked polymer. The aim of this work was to investigate the possibility of deriving a consistency test suitable for cross-linked polymers. While this possibility is already known to fail for binary systems, it has been shown that an easy-to-check expression can be derived, providing that several sets of equilibrium data are combined. The newly proposed test, which only demands the knowledge of raw data, has been successfully applied to amorphous polymeric networks. Discrepancies have been seen either for semicrystalline networks or in data obtained with different polymer samples.

It is clear that the criticisms commonly directed at consistency tests remain: first, whereas the test provides an efficient tool for finding inconsistencies, it cannot explain why the agreement is not satisfactory. Second, the test cannot be used to choose which set of data must be eliminated to check the consistency. Moreover, it must be remembered that the consistency test proposed here is an integral test that implicitly shows major limitations, in contrast to differential or point-by-point tests. The test can lead to the cancellation of errors, just like any integration, and requires experimental data that covers the entire composition range. These drawbacks can be overcome, provided that an equivalent to the Van-Ness-Byer–Gibbs test or a differential test can be derived.

Finally, it should also be remembered that the applicability of a test is a necessary but not sufficient condition for thermodynamic consistency (Jackson and Wilsak, 1995). Nevertheless, it is hoped that this preliminary work will stimulate efforts in the field of multicomponent polymer solvent equilibria, which still suffers from a lack of either fundamental or applied studies. It is clear that the procedure developed in this article can be easily extended to sorption equilibria involving gases in polymers, or to the combination of three ternary data sets. This work is currently being carried out.

Notation

a_i = activity of component i
γ = activity coefficient
G = Gibbs free energy
n_i = number of mole of component i
P^* = vapor pressure
S = entropy
μ = chemical potential
v_i = molar volume of component i
V = volume
x_i = mole fraction of component
ϕ = volume fraction
φ = fugacity coefficient

Abbreviations

$$S1-S2=\int_0^{a_1}\left(\frac{\phi_1 x_2}{v_1}-\frac{\phi_2 x_1}{v_2}\right)\frac{da_1}{x_2 a_1}$$

$$S2-D=\int_0^{a_2}\frac{\phi_2}{v_2 a_2}\,da_2$$

$$S1-D=\int_0^{a_1}\frac{\phi_1}{v_1 a_1}\,da_1$$

Subscripts

1 = solvent 1
2 = solvent 2
d = polymer in dry state
p = polymer
$s1$ = polymer swelled by solvent 1
$s2$ = polymer swelled by solvent 2

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Appendix A: Determination of Chemical Potential Differential (The Vapor/Polymer Equilibrium Case)

Consider a vapor–polymer system at temperature T. Because of the nature of such a system (difference of pressure between the two phases), equilibrium is reached when the system's temperature, pressure in the polymer phase P' and in the vapor phase P, and the chemical potential of the solvent are constant. The chemical potential of the polymer is not defined in the vapor phase because it is assumed that the polymer does not disperse.

Thus, at equilibrium we can write

$$\mu_{i,\mathrm{vap}}(T,P,y)=\mu_{i,\mathrm{polym}}(T,P',x'). \tag{A1}$$

Chemical potential can then be expressed taking as reference state:

- For a component in the vapor phase, the perfect gas at the same temperature T and the same pressure P: $\mu_i^{\cdot}(T,P)$;
- For a component in the polymer phase, the pure liquid at the same temperature T and same pressure P': $\mu^*_{i,\mathrm{liq}}(T,P')$;

leading to

$$\mu_{i,\mathrm{vap}}(T,P,y)=\mu_{i,\mathrm{vap}}(T,P)=\mu_i^{\cdot}(T,P)+RT\ln\varphi_i^*(T,P). \tag{A2}$$

where, $\varphi_i^*(T,P)$ corresponds to the fugacity coefficient of pure component i. Here we have considered a pure-component vapor, which corresponds to our experimental conditions.

$$\mu_{i,\mathrm{pol}}(T,P',x')=\mu^*_{i,\mathrm{liq}}(T,P')+RT\ln x_i'\gamma_i^{\mathrm{pol}}(T,P',x'), \tag{A3}$$

where $\gamma_i^{\mathrm{pol}}(T,P',x')$ is the activity coefficient of component i in the polymer phase, and $a_i^{\mathrm{pol}}(T,P',x')=x_i'\gamma_i^{\mathrm{pol}}(T,P',x')$ corresponds to the activity of component i in the polymer phase.

For a pure component, we can write

$$\mu^*_{i,\mathrm{liq}}(T,P')=\mu^*_{i,\mathrm{liq}}(T,P)+\int_P^{P'}v^*_{i,\mathrm{liq}}(T)\,dP, \tag{A4}$$

where $v^*_{i,\mathrm{liq}}(T)$ is the molar volume of component i at temperature T.

When Eqs. A2, A3, and A4 are incorporated into the equality of potential (Eq. A1), we obtain

$$\mu^*_{i,\mathrm{liq}}(T,P)-\mu_i^{\cdot}(T,P)=RT\ln\varphi_i^*(T,P)-RT\ln x_i'\gamma_i^{\mathrm{pol}}(T,P,x)-\int_P^{P'}v^*_{i,\mathrm{liq}}(T)\,dP. \tag{A5}$$

To determine the righthand term corresponding to the difference in reference chemical potential, we consider the pure component i in a vapor–liquid equilibrium at the same temperature T and same pressure P. In that case, the total pressure is equal to the saturated vapor pressure of pure component i, $P_i^s(T)$, and the criterion for phase equilibrium is

$$\mu^*_{i,\mathrm{liq}}[T,P_i^s(T)]=\mu^*_{i,\mathrm{vap}}[T,P_i^s(T)]. \tag{A6}$$

The chemical potentials can be expressed, respectively, by

$$\mu^*_{i,\mathrm{liq}}[T,P_i^s(T)]=\mu^*_{i,\mathrm{liq}}(T,P)+\int_P^{P_i^s(T)}v^*_{i,\mathrm{liq}}(T)\,dP \tag{A7}$$

and

$$\mu^*_{i,\mathrm{vap}}[T,P_i^s(T)]=\mu_i^{\cdot}(T,P)+RT\ln\frac{P_i^s(T)\varphi_i^*[T,P_i^s(T)]}{P}. \tag{A8}$$

Coupling Eqs. A6, A7, and A8 leads to

$$\mu^*_{i,\mathrm{liq}}(T,P)-\mu_i^{\cdot}(T,P)=RT\ln\left[\frac{P_i^s(T)\varphi_i^*[T,P_i^s(T)]}{P}\exp\left(\frac{1}{RT}\int_{P_i^s(T)}^{P}v^*_{i,\mathrm{liq}}(T)\,dP\right)\right]. \tag{A9}$$

The difference in the reference chemical potential given by Eq. A9 can then be incorporated into Eq. A5, giving the general relationship for the vapor–polymer equilibrium:

$$\underbrace{P\cdot\frac{\varphi_i^*[T,P]}{\varphi_i^*[T,P_i^s(T)]}\exp\left(\frac{1}{RT}\int_P^{P_i^s(T)}v^*_{i,\mathrm{liq}}(T)\,dP\right)}_{C_i}=P_i^s(T)x_i'\gamma_i^{\mathrm{pol}}(T,P',x')\exp\left(\frac{1}{RT}\int_P^{P'}v^*_{i,\mathrm{liq}}(T)\,dP\right).$$

Because of the low-pressure difference between $P_i^s(T)$ and P, deviation of C_i from unity can be neglected. On the other hand, the last exponential term involving the pressure difference (P and P') between the two coexisting phases has to be considered.

Then, the previous equation reduces to the final relationship between the activity of component i in the vapor and polymer phase:

$$a_i^{\mathrm{vap}}=\frac{P}{P_i^s(T)}=x_i'\gamma_i^{\mathrm{pol}}(T,P',x')\exp\left(\frac{1}{RT}\int_P^{P'}v^*_{i,\mathrm{liq}}(T)\,dP\right). \tag{A10}$$

It can be seen that, contrary to classic vapor–liquid equilibrium, the activity of component i is not the same in both phases. The exponential term corresponds to the increase in pressure from the surrounding phase. Neglecting this term can lead to significant errors, as has already been stated by Maurer and Prausnitz (1996).

Because the objective is to determine the chemical potential term $d\mu_i$ in the Gibbs–Duhem equation, differentiation of Eq. A3 leads to

$$d\mu_{i,\mathrm{pol}}(T,P',x') = d\mu^*_{i,\mathrm{liq}}(T,P') + RdT \ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x') + RTd\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x') \quad \text{(A11)}$$

with

$$d\mu^*_{i,\mathrm{liq}}(T,P') = -s^*_i dT + v^*_i dP. \quad \text{(A12)}$$

At constant temperature and incorporating Eq. A12 into Eq. A11, we obtain

$$d\mu_{i,\mathrm{pol}}(T,P',x') = v^*_{i,\mathrm{liq}} dP + RTd\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x'). \quad \text{(A13)}$$

It is easier to work with the activity of the component in the vapor phase because it can be evaluated simply and experimentally by $a_i^{\mathrm{vap}} = P/(P_i^s(T))$. Using the relation (Eq. A10) between the activity of component i in the vapor and the polymer phases, we can write

$$d\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x') = d\ln a_i^{\mathrm{vap}}(T,P,x) - \frac{1}{RT} v^*_{i,\mathrm{liq}}(T)\,dP. \quad \text{(A14)}$$

Coupling Eqs. A13 and A14, we finally obtain

$$d\mu_{i,\mathrm{pol}}(T,P',x')v^*_{i,\mathrm{liq}} = dP + RTd\ln a_i^{\mathrm{vap}}(T,P,x) - v^*_{i,\mathrm{liq}}\,dP$$

$$d\mu_{i,\mathrm{pol}}(T,P',x') = RTd\ln a_i^{\mathrm{vap}}(T,P,x) = RT\frac{da_i^{\mathrm{vap}}}{a_i^{\mathrm{vap}}}. \quad \text{(A15)}$$

Appendix B: Determination of Chemical Potential Differential (Liquid/Polymer Equilibrium Case)

We consider an isothermal system (temperature T) with a solvent mixture in equilibrium with a cross-linked polymer.

The criterion for phase equilibrium is

$$\mu_{i,\mathrm{liq}}(T,P,x) = \mu_{i,\mathrm{polym}}(T,P',x'). \quad \text{(B1)}$$

The chemical potential is then expressed taking as reference state:

- For a component in the liquid phase, the pure liquid at the same temperature T and the same pressure P;
- For a component in the polymer phase, the pure liquid at the same temperature T and the same pressure P'.

Assuming these conditions, it follows that

$$\mu_{i,\mathrm{pol}}(T,P',x') = \mu^*_{i,\mathrm{liq}}(T,P') + RT\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x') \quad \text{(B2)}$$

$$\mu_{i,\mathrm{liq}}(T,P,x) = \mu^*_{i,\mathrm{liq}}(T,P) + RT\ln x_i\gamma_i^{\mathrm{liq}}(T,P,x), \quad \text{(B3)}$$

where $x'_i\gamma_i^{\mathrm{pol}}(T,P',x')$ and $x_i\gamma_i^{\mathrm{liq}}(T,P,x)$ are the activity of component i in, respectively, the polymer phase and the liquid phase.

Coupling Eqs. B1, B2, and B3, we obtain

$$\mu^*_{i,\mathrm{liq}}(T,P) + RT\ln x_i\gamma_i^{\mathrm{liq}}(T,P,x) = \mu^*_{i,\mathrm{pol}}(T,P') + RT\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x'). \quad \text{(B4)}$$

For a pure component, we can write

$$\mu^*_{i,\mathrm{liq}}(T,P') = \mu^*_{i,\mathrm{liq}}(T,P) + \int_P^{P'} v^*_{i,\mathrm{liq}}(T)\,dP. \quad \text{(B5)}$$

Then, eliminating the reference chemical potential by putting Eq. B5 into Eq. B4 leads to the final relationship between the activity of component i in the liquid and polymer phases:

$$x_i\gamma_i^{\mathrm{liq}}(T,P,x) = x'_i\gamma_i^{\mathrm{pol}}(T,P',x')\exp\left[\frac{1}{RT}\int_P^{P'} v^*_{i,\mathrm{liq}}(T)\,dP\right]. \quad \text{(B6)}$$

Differentiating Eq. B2 leads to

$$d\mu_{i,\mathrm{pol}}(T,P',x') = d\mu^*_{i,\mathrm{liq}}(T,P') + RdT\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x') + RTd\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x'), \quad \text{(B7)}$$

with

$$d\mu^*_{i,\mathrm{liq}}(T,P') = -s^*_i dT + v^*_i\,dP \quad \text{(A8)}$$

and at constant temperature,

$$d\mu_{i,\mathrm{pol}}(T,P',x') = v^*_{i,\mathrm{liq}}\,dP + RTd\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x'). \quad \text{(B9)}$$

It is more convenient to work with component activity in the liquid phase because it can be evaluated experimentally from molar fraction by the classic activity coefficient equations (NRTL, Uniquac, etc). By using the relationship (Eq. 6) between activity in the polymer phase and the liquid phase, we obtain

$$d\ln x'_i\gamma_i^{\mathrm{pol}}(T,P',x') = d\ln x_i\gamma_i^{\mathrm{liq}}(T,P,x) - \frac{1}{RT}v^*_{i,\mathrm{liq}}(T)\,dP. \quad \text{(B10)}$$

Thus, we finally obtain

$$d\mu_{i,\mathrm{pol}}(T,P',x') = v^*_{i,\mathrm{liq}}\,dP + RTd\ln x_i\gamma_i^{\mathrm{liq}}(T,P,x) - v^*_{i,\mathrm{liq}}\,dP$$

$$d\mu_{i,\mathrm{pol}}(T,P',x') = RTd\ln a_i^{\mathrm{liq}}(T,P,x) = \frac{RTda_i^{\mathrm{liq}}}{a_i^{\mathrm{liq}}}.$$

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