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MEASUREMENT OF VAPOR SORPTION EQUILIBRIA OF POLYMER SOLUTIONS AND COMPARATIVE CORRELATION BY G^E-MODELS AND LATTICE EQUATIONS OF STATE

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Abstract – Solvent sorption equilibrium data of binary solvent-polymer systems were measured with a vacuum electro-microbalance equilibrium cell. Tested solvents were benzene, *n*-pentane, cyclohexane, *n*-hexane, water and methanol. Polymers tested were poly(dimethylsiloxane), poly(iso-butylene), poly(propylene oxide) and poly(vinyl alcohol). Data obtained in the present study, together with existing literature data, were correlated by two g^E-models, such as UNIQUAC and the Flory-Huggins model, and four equations of state which stem from the lattice fluid theory, such as models proposed by Flory, Sanchez and Lacombe, Panayiotou and Vera, and the NLF model proposed recently by the present authors. For each solvent-polymer system, the provided models give a quantitative correlation. The advantages and drawbacks of the g^E-model and equation of state approaches are also discussed.

Key words: Experimental Method, Vapor Sorption Equilibria, Polymer Solutions, g^E-Model, Lattice Equations of State

INTRODUCTION

Understanding the sorption equilibrium characteristics of vapor-phase species in polymers is of prime importance in designing and operating industrial processes such as membrane separation of organics from waste streams [Baker et al., 1987; Matsumoto et al., 1991], and pervaporation processes [Maeda et al., 1991], separation of organics from polymer products [Danner and High, 1993], processing paint and coating agents [Napper, 1983], and acoustic-wave vapor sensors [Ballatine and Wohltjen, 1989; Grate et al., 1992].

A variety of experimental sorption equilibrium data of polymer solutions are reported in the literature. However, existing data are frequently available only in limited concentration ranges of the sorbed vapor component. Thus, in the present study, emphasis was given to the measurement of sorption equilibria of binary polymer solutions over an extended range of solvent concentration by an equilibrium cell apparatus (vacuum electro-microbalance). The polymers tested were poly(dimethylsiloxane, PDMS), poly(isobutylene, PIB), poly(propylene oxide, PPO) and poly(vinyl alcohol, PVA). These polymers were chosen on the basis of frequency of use in membrane separation processes. Selected solvents were *n*-hexane, benzene, cyclohexane, *n*-pentane, methanol and water.

To model the measured activities of solvents in a polymer solution, an equation of state (EOS) with an adequate mixing rule is sufficient for determining properties of pure solvents, polymers and their solutions. However, in many cases it is not practical to do so because most existing EOSs frequently do not correctly represent the volumetric behavior of macromolecules over an entire range of density from ideal state to condensed phase. To date, excess Gibbs energy (g^E) models of solutions (i.e., activity coefficient models) have been widely used to correlate the phase equilibria of polymer solutions in terms of departure function from ideal solution. The Flory-Huggins (FH) model [Flory, 1941, 1942; Huggins, 1941, 1942] and UNIQUAC [Abrams and Prausnitz, 1975] are typical examples of g^E-models in this genre which are applicable to macromolecular systems. These models, however, cannot be applicable to the configurational properties of pure fluids, and the uses of these models are sometimes limited for mixtures. The g^E-models also cannot be used to correlate the effect of pressure in liquid mixtures. Thus, in the past few decades, much attention has also been given to the formulations of EOSs that are applicable to pure r-mer fluids and their solutions.

A pioneering EOS theory for r-mer fluids is the new Flory theory (NF) [Flory, 1970]. This model, which is based on the cell theory of a liquid, was limitedly successful only for the liquid phase. It cannot be applied simultaneously to vapor- and liquid-phase equilibrium calculations. Thus it may not be regarded as a truly general theory. Since then, two categories of volumetric EOS theories were proposed as a result of subsequent search for more general EOSs. The first category consisted of perturbed hard chain theories (PHCTs) [Beret and Prausnitz, 1975b], and the second, of lattice-hole theories. Both theories are being investigated. The SAFT EOS [Huang and Radosz, 1991] may be regarded as a recent addition to the

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PHCTs. On the other hand, after Guggenheim [1952], there was a surge of lattice statistical-mechanical theory of r-mer systems.

Sanchez and Lacombe (SL)'s random [Sanchez and Lacombe, 1976a, b; 1978] and Panayiotou and Vera (PV)'s nonrandom [Panayiotou and Vera, 1982] EOSs are among frequently cited lattice-hole models which stem from the theory after Guggenheim. Vera and his coworkers [Panayiotou and Vera, 1980, 1981] discussed formal solutions of the lattice-hole theories. In recent years, the present authors, also, presented an NLF-EOS based on a generalized approximation of nonrandom lattice-hole theory [You et al., 1994a, b; Yoo et al., 1995a, b; Lee and Yoo, 1997]. Besides these models, there are several other thermodynamic theories and models in literature. However, we omit here further introduction of them. Interested readers may refer to a recent review article presented elsewhere by the present authors [Lee and Yoo, 1997].

Any thermodynamic model, whether it is a g^E-model or an EOS, is not complete for quantitatively correlating the experimental phase equilibrium data of polymer systems. Frequently, it is the case that process design engineers need to figure out which model is reliably applicable to correlate phase equilibrium properties of polymer systems among various thermodynamic models. Thus, in the present work, we have arbitrarily chosen some six well-known models and performed comparatively the VLE calculations based on the experimental data measured in the present work. The selected models are two g^E-models (FH and UNIQUAC) and four EOSs (NF, SL, PV, and NLF). Also, a discussion of the advantages and drawbacks of the g^E-models and the EOSs has been presented for modeling vapor-liquid equilibria of polymer solutions.

EXPERIMENTAL

1. Materials

Sample polymers were purchased from Aldrich chemical company (St. Louis, MO, United States) and Dow Corning chemical company (Midland, MI, United State). The number-average molecular weight (M_n) of PDMS was 6650, 26000 and 31300; 88000 for PVA; 1200,000 for PIB and 2000 for PPO. All solvents (*n*-hexane, benzene, cyclohexane, water, methanol, and *n*-pentane) were HPLC-grade ones purchased from J. T. Baker incorporation (Phillipsburg, NJ, United States).

2. Vapor Sorption Apparatus

The sorption apparatus used in the present experiment, shown in Fig. 1, consists of three major parts (gravimetric equilibrium measurement unit, vacuuming unit and solvent generation). To reduce flow and thermal fluctuation in the equilibrium cell, the whole unit was immersed in an air-bath.

The amount of sorbed solvent to a polymer was measured with a Sartorius M25D-V vacuum electro-microbalance (Goettingen, Germany). A calibrated weight was loaded on the left side of the balance as a reference weight and the polymer sample was loaded on the right side of the balance. The granular type of quartz was used as a reference weight in order to prevent possible condensation of solvents. A dish-type quartz sorption cell was used to load the polymer sample. Platinum wire was used to link both arms to the balance

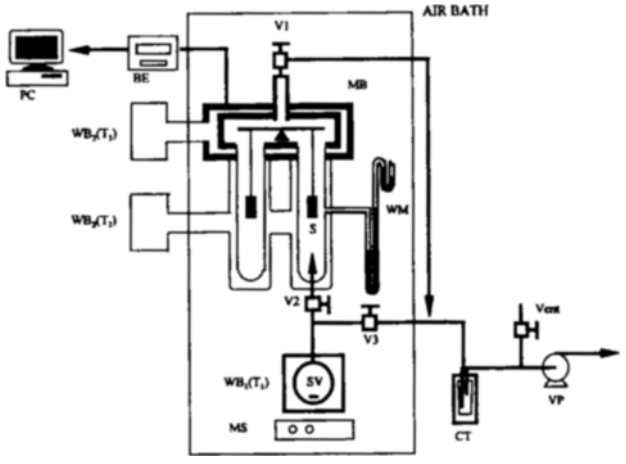

Fig. 1. Schematic diagram of vapor sorption apparatus

MB: Vacuum microbalance
WB: Water bath
WM: W-tube mercury manometer
SV: Solvent vessel
S: Polymer sample
V: High vacuum valves
CT: Cold trap
VP: Vacuum pump
PC: Personal computer
BE: Balance electronics
MS: Magnetic stirrer
$T_1<T_2<T_3$

to prevent possible oxidative corrosion of the arm by the solvent. Potential leakage of the system was checked by maintaining the pressure under 10^{-4} torr for a week with a precision vacuum pump (Chicago, IL, United States).

Water baths were installed in three regions for separately controlling temperatures to prevent temperature fluctuations that could result in condensation of solvent on the surface of the sorption cell. As one can see in Fig. 1, water bath 1 [WB_1] (Polyscience 9710, Niles, IL, United States) was used to control the solvent generation part. Since the vaporized solvent at the sorption area must be maintained in a saturated state, an accurate control of temperature was made. Water bath 2 [WB_2] was installed to control the sorption cell. Water bath 3 [WB_3] was installed to protect the essential part of the balance. The distribution of temperatures in each water bath was maintained differently such that the temperature of water bath 3 {T_3} > water bath 2 (T_2) > water bath 1 (T_1). Mercury head in the manometer was measured to within 0.01 mm using a cathetometer (Gaertner Scientific Co., Chicago, United States).

3. Experimental Procedure

After a polymer sample was loaded onto the sorption cell, valves 2 and 3 were closed (Fig. 1), and valve 1, which is connected to a vacuum pump, was opened to create a vacuum state within the cell. In this way, volatile low molecular weight substances and impurities including air were removed from the polymer sample. At high vacuum, if the weight of the polymer sample stayed within the fluctuation range within ± 1 μg for 3 hours, the measurement of the sorption equilibrium was started.

To absorb vapor-phase solvent by polymer sample, valves 1 and 2 were closed, and valve 2 was opened in order to transfer equilibrated vapor from the vapor generator. For PVA and PIB, a certain amount of sample was separately dissolved by

Table 1. Molecular weight of polymers, solutes and sorption experimental conditions and existing data sources

Polymers	Molecular weight, M_n^*	Solvent used	Measured temperature [K]
PDMS	26000, 6650, 31300	*n*-hexane	303.15
		n-pentane	303.15
PVA	88000	water	303.15
PIB	1200000	cyclohexane	298.15
PPO	2000	methanol	298.15
		benzene	298.15

*M_n: the number-average molecular weight

water and cyclohexane and poured into a horizontal petri dish and left until the solvents were evaporated. For PDMS and PPO, due to their high viscosity, each polymer was thinly coated onto the surface of a 200 mesh size stainless sieve.

The sorbed solvent was measured at 5 min intervals by a data processor. When the mass of absorbed solvent by a polymer stayed within the error range of ± 5 μg for 3 hours, we assumed that a sorptional equilibrium state was reached. Experimental conditions for each solvent-polymer system are summarized in Table 1.

DATA REDUCTION AND CORRELATION

1. Activities of Solvents from Experiment Data

Measured data were the vapor pressure of solvents (P_1) and the sorbed amount of solvent, w_1. From these data, the activities of a solvent in a polymer solution were calculated by:

$$a_1 = \frac{P_1}{P_1^{sat}} \exp\left(\frac{B_{11}(P_1 - P_1^{sat})}{RT}\right) \quad (1)$$

where P_1^{sat} is saturation pressure and B_{11} is the second virial coefficient. They were estimated by using existing correlations reported in the databooks [Reid et al., 1987; McGlashan and Wormald, 1964].

The equation of B_{11} is given by

$$\frac{B_{11}}{v_c} = 0.430 - 0.886\left(\frac{T}{T_c}\right)^{-2} - 0.0375(n-1)\left(\frac{T}{T_c}\right)^{-4.5} \quad (2)$$

where the subscript c stands for critical state. v is molar volume, n is the carbon number and T is temperature. Also, the saturation pressure at the system temperature for solvents except the case of water was estimated by

$$\ln\left(\frac{P^{vap}}{P_c}\right) = (1-x)^{-1}(Ax + Bx^{1.5} + Cx^3 + Dx^x), \; x = 1 - \frac{T}{T_c} \quad (3)$$

where P is pressure. The values of constants A, B, C and D were introduced from the literature [Reid et al., 1987]. The necessary physical properties of each solvent are summarized in Table 2.

2. Calculation of Activities of Solvents by EOS

Calculation of activities from the g^E-models (expressions of FH model and UNIQUAC are given in Appendix 1) is straightforward; thus, we omit further discussion regarding computational aspects of the g^E-models. However, further comment is warranted regarding the calculation of solvent activities from an EOS. For high molecular species such as polymers, vapor pressure is frequently not well known and is usually negligible. Thus, activities of solvents were determined from the equality criterion of chemical potential between equilibrated phases for component i, which is derived by the EOS, as follows:

$$\mu_{i,pure}^V(T, P) = \mu_i^L(T, P, \{x\}), \text{ and} \quad (4)$$

$$\mu_i^L = \mu_{i,pure}^L + RT \ln a_i; \quad (5)$$

where superscripts V and L denote vapor and liquid phase, respectively.

3. Selected Thermodynamic Models

Measured data were comparatively correlated by Flory-Huggins (FH) and UNIQUAC as the g^E-models, and by new Flory (NF), Sanchez-Lacombe (SL), Panayiotou-Vera (PV) and NLF as the EOS models. The theoretical basis of the selected models and the number of molecular parameters of each model are summarized in Table 2. Also, the pressure-explicit EOS and chemical potential expressions of each model are summarized in Appendix 1.

RESULTS AND DISCUSSION

1. Experimental Aspect

Isothermal-isobaric sorption equilibrium data were measured for *n*-hexane-PDMS, *n*-pentane-PDMS, cyclohexane-PIB, methanol-PPO, benzene-PPO and water-PPO systems as shown in Table 3. Also, the results of these systems compared with existing literature data and correlated with the six models are shown in Figs. 3-9, respectively. The measured data over a wide range of solvent concentration agree well with literature data.

Table 2. Thermodynamic models tested for the correlation of sorption data†

Type	Model	No. of parameters		Theoretical basis	Refs.¶
		Pure parameters	Binary parameter		
g^E	FH (Flory-Huggins)	1	2	Nonrandom two liquid rigid lattice	1
g^E	UNIQUAC	2	2	Random rigid lattice	2
EOS	NF (New Flory)	3	1	Free, Volume random rigid lattice	3
EOS	SL (Sanchez-Lacombe)	3	1	Random lattice-hole	4
EOS	PV (Panoyiotou-Vera)	2	1	Hole-free based nonrandom lattice-hole	5
EOS	NLF (Present authors)	2	1	Rigorous nonrandom lattice-hole	6

†The expression of each model is shown in Appendix 1.

¶1. Flory [1941, 1942], Huggins [1941, 1942]; 2. Abrams and Prausnitz [1975]; 3. Flory [1970]; 4. Sanchez and Lacombe [1976a, b; 1978]; 5. Panayiotou and Vera [1982]; 6. You et al. [1994a, b], Yoo et al. [1995a, b], Lee and Yoo [1997]

Table 3. Measured activity of solvent data in polymer-solvent systems

Polymers	Solvents	Measured temp. (K)	w_1 (Weight fract'n.)	a_1 (Activity)
PDMS (M_n: 26000)	*n*-hexane	303.15	.0203	.1071
			.0310	.1614
			.0421	.2175
			.0545	.2709
			.0677	.3248
			.0817	.3786
			.0971	.4327
			.1338	.5422
			.2424	.7537
			.4234	.9185
			.5688	.9719
			.7679	1.0071
PDMS (M_n: 6650)	*n*-hexane	303.15	.0225	.1119
			.0337	.1653
			.0454	.2213
			.0584	.2755
			.0719	.3294
			.0864	.3818
			.1027	.4379
			.1424	.5478
			.2552	.7614
			.4507	.9253
			.6010	.9772
			.8309	1.0087
PDMS	*n*-pentane	303.15	.0204	.1223
			.0714	.3424
			.1202	.5067
			.1937	.6693
			.3045	.8273
PIB	c-hexane	298.15	.0268	.1379
			.0461	.2083
			.0748	.3145
			.1059	.4080
			.1455	.5076
			.1924	.6116
			.2526	.7174
			.3381	.8194
			.4864	.9261
			.6688	.9828
			.7534	.9946
PVA	water	303.15	.0194	.1601
			.0503	.3202
			.0761	.4849
			.0947	.5970
			.1146	.6967
			.1681	.8254
			.1911	.8574
			.3341	.9571
PPO	methanol	298.15	.0068	.0859
			.0138	.1612
			.0220	.2372
			.0318	.3121
			.0445	.4004
			.0588	.4769
			.0761	.5519

(will be continued)

Table 3. continued

Polymers	Solvents	Measured temp. (K)	w_1 (Weight fract'n.)	a_1 (Activity)
PPO	methanol	298.15	.0993	.6299
			.1317	.7091
			.1828	.7898
			.2618	.8695
			.4226	.9439
PPO	benzene	298.15	.0308	.1110
			.1265	.3729
			.2305	.5599
			.3544	.7500
			.4735	.8556

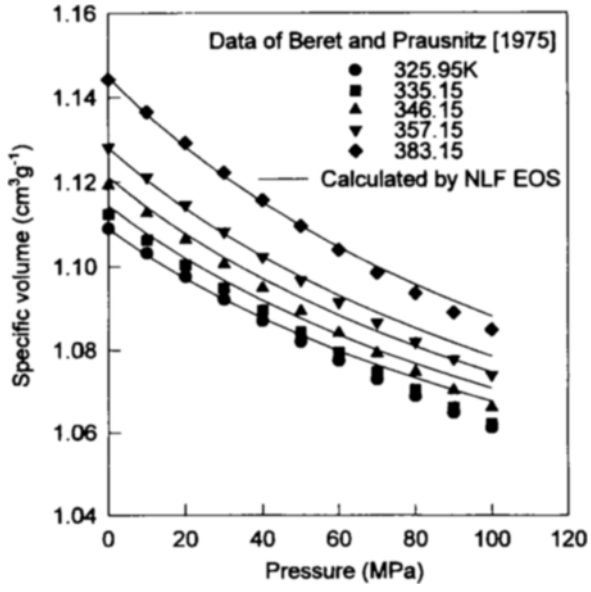

Fig. 2. Calculated specific volume of PIB by the NLF-EOS.

For *n*-hexane-PDMS [Sugamiya et al., 1974; Ashworth et al., 1984], and methanol-PPO system [Lakhanpol and Conway, 1960], sorption equilibrium data were reported only in a moderate concentration range of solvent. In the present work, measurement of activities of solvents was extended over a whole range of solvent concentrations. For an *n*-pentane-PDMS system, existing data were limitedly reported only for a diluted concentration of the solvent. Thus, in the present work, the entire range of the solvent concentrations was measured. For cyclohexane-PIB [Bawn and Patel, 1956; Eichinger and Flory, 1968], benzene-PPO [Booth and Devoy, 1971] and water-PVA [Sakurada et al., 1959] systems, experimental data were extended over a concentrated range of solvent concentrations.

In the case of rubbery PDMS with different molecular weights (i.e., M_n: 26,000 and 6,650), sorption equilibration behaviors of *n*-hexane and *n*-pentane were found to be similar. Also, for a given solvent (i.e., *n*-hexane), we found that there is no time difference of equilibration for different molecular weights (M_n: 26,000 and 6,650).

For a benzene-PPO (M_n: 2,000) sample, data were measured at 298.15 K in the present study. However, existing data for this system were only available for 320.35 K [Booth and Devoy, 1971]. Upon comparison of activities of benzene in PPO

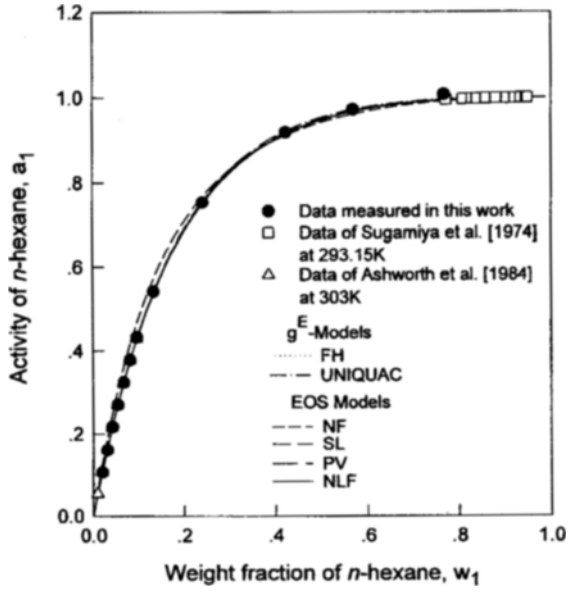

Fig. 3. Measured and calculated activities of *n*-hexane in PDMS (M_n:6,650) at 303.15 K.

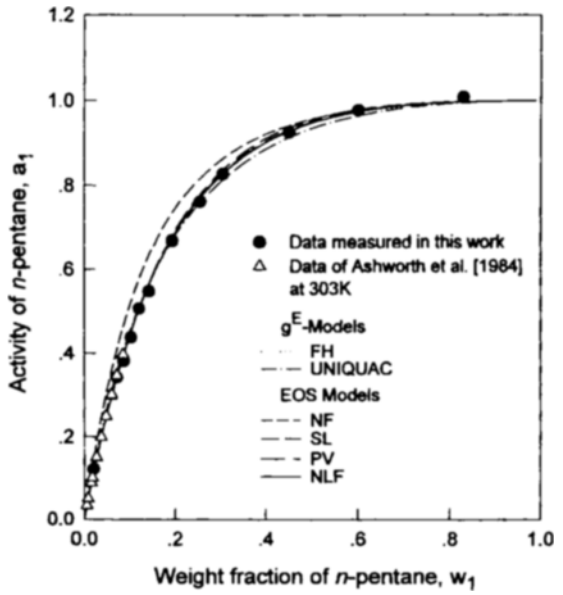

Fig. 5. Measured and calculated activities of *n*-pentane in PDMS (M_n:31,300) at 303.15 K.

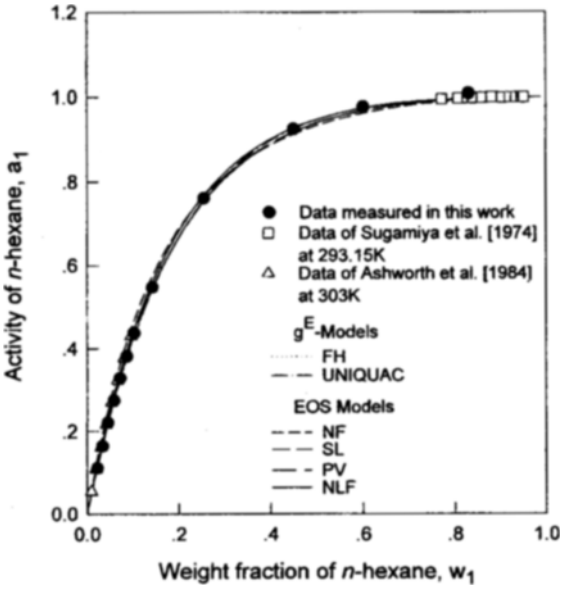

Fig. 4. Measured and calculated activities of *n*-hexane in PDMS (M_n:26,000) at 303.15 K.

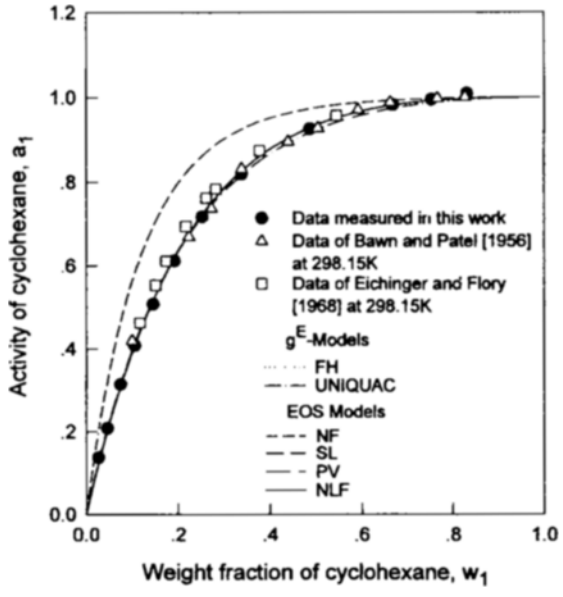

Fig. 6. Measured and calculated activities of cyclohexane in PIB (M_n:1,200,000) at 298.15 K.

at these different temperatures, we found that the effect of equilibrium temperature was negligible. Thus, we concluded that in solvent-sorption equilibrium of polymer systems, the sorption equilibrium behavior is highly dependent on the different types of solvents and relatively insensitive to the sorption temperature employed.

In Fig. 9, measured and existing sorption data of water in PVA [Sakurada et al., 1959] are shown. In contrast to other systems measured in this work, measured data do not agree well with existing data. In general, PVA is glassy rather than rubbery. At the same time, PVA and water have hydroxy groups and, thus, there is an effect of hydrogen bonding in the sorption of solvent into PVA. According to literature [Sakurada et al., 1959], water tends to desorb on the PVA surface rather than penetrate and sorb into PVA, and there exists serious hysteresis in the sorption and desorption for this system.

In recent years, several investigators have attempted to employ a vacuum electro-microbalance for the purpose of a sorption equilibrium cell since this device can easily interface to a computerized data acquisition system. However, they found that it is extremely difficult to eliminate experimental errors related to the buoyancy effect of vapor phase flow in the cell. Also, it is apt to increase the temperature distribution in different locations in the cell. However, in the present study, we put the whole system in a large-scale air bath, and as a result, the system can work very stably.

2. Model Correlational Aspect

To convert the measured sorption equilibrium data to the

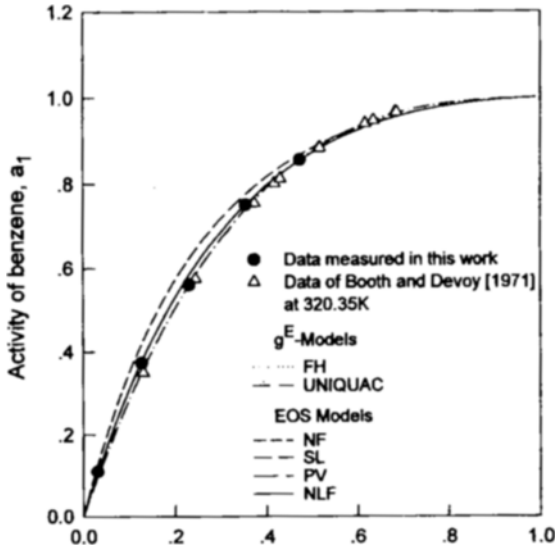

Fig. 7. Measured and calculated activities of benzene in PPO (M_n:2,000) at 298.15 K.

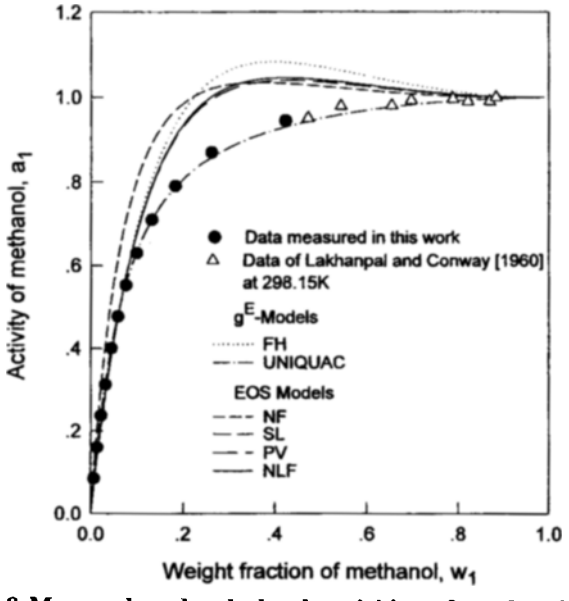

Fig. 8. Measured and calculated activities of methanol in PPO (M_n:2,000) at 298.15 K.

activities of the solvent, it is necessary to use Eqs. (2) and (3). The necessary physical constants of solvents employed in the present study are summarized in Table 4. These data were calculated by the methods described in the databooks [Reid et al., 1978; McGlashan and Wormald, 1964]. The specific volume (V_{sp}) for pure solvents and polymers necessary for the FH model is summarized in Table 5. Also, the estimated pure molecular surface area (Q_i) and the volume parameter (R_i) for the UNIQUAC model are summarized in Table 6.

The pure molecular characteristic parameters for each EOS were estimated from existing pure component data. These results are summarized in tables: parameters for NF EOS in Table 7, those for SL EOS in Table 8, those for PV EOS in Table 9, and those for NLF EOS in Table 10, respectively.

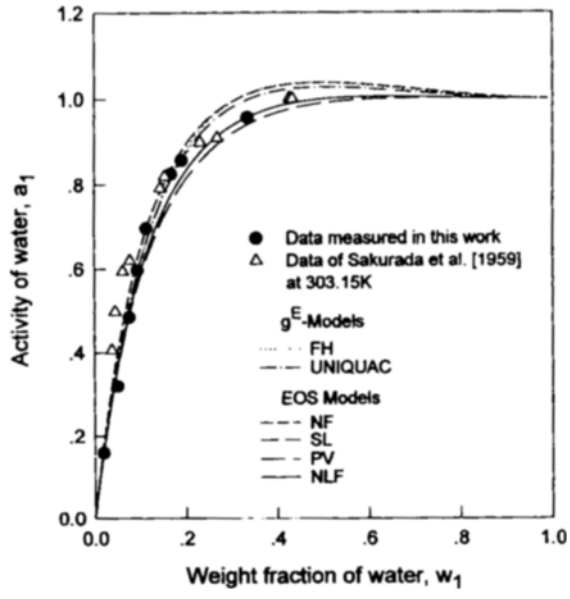

Fig. 9. Measured and calculated activities of water in PVA (M_n:88,000) at 303.15 K.

Table 4. Estimated physical constants for solvents

Solvents	T [K]	P_c [MPa]	V_c [$cm^3 \cdot mol^{-1}$]	T_c [K]	P^{sat} [MPa]	B_{11} [$cm^3 \cdot mol^{-1}$]
n-Hexane	303.15	3.01	370.0	507.5	0.02493	−1814.372
Water	303.15	22.12	57.1	647.3	0.00425	−264.142
c-Hexane	298.15	4.07	308.0	553.5	0.01304	−2045.434
n-Pentane	303.15	3.37	304.0	469.7	0.08183	−1120.190
Methanol	298.15	8.09	118.0	512.6	0.01697	−371.069
Methanol	288.15	-	-	-	0.00989	−394.400
Benzene	303.15	4.89	259.0	562.2	0.01267	−1803.485

Table 5. Estimated molecular parameters of Flory-Huggins model for pure fluids

Components	Temperature, [K]	V_{sp} [$cm^3 \cdot g^{-1}$]
PDMS	303.15	1.0359
PVA	303.15	0.7648
PIB	298.15	1.0906
PPO	298.15	1.0004
n-hexane	303.15	1.5337
n-pentane	303.15	1.6271
water	303.15	1.004
c-hexane	298.15	1.2992
methanol	298.15	1.2713
benzene	298.15	1.1446

Based on the sorption data measured in the present study together with the existing data in the literature [Ashworth et al., 1984; Sugiyama et al., 1974; Flory and Daoust, 1957; Bawn and Patel, 1956; Eichinger and Flory, 1968; Sakurada et al., 1959; Lakhanpal and Conway, 1960; Booth and Devoy, 1971; etc.], the binary adjustable interaction energy parameters for all the binary polymer solutions in the g^E-models (i.e., FH and UNIQUAC) and EOSs (i.e., NF, SL, PV and NLF) were regressed. These results are summarized in Table 11 for FH model, in Table 12 for UNIQUAC, in Table 13 for NF EOS,

in Table 14 for SL EOS, in Table 15 for PV EOS and in Table 16 for NLF EOS, respectively. In these tables, the percent of absolute average deviation (AAD%) of the activities of each solvent (i.e., *n*-hexane, *n*-pentane, water, methanol, benzene, etc.) and the related list of existing data sources are summarized.

Table 6. Estimated molecular parameters of UNIQUAC for pure fluids

Components*	R_i	Q_i
PDMS	2.9066	2.162
PVA	2.1213	1.968
PIB	2.6961	2.236
PPO	2.2663	1.856
n-Hexane	4.4998	3.856
n-Pentane	3.8254	3.316
Water	0.9200	1.40
c-Hexane	4.0464	3.240
Methanol	1.4311	1.432
Benzene	3.1878	2.400

*In the case of polymer, R_i and Q_i stand for the values of the repeating unit.

Table 7. Estimated molecular parameters of New Flory EOS for pure fluids

Components	Temp. [K]	V_{sp} [$cm^3 \cdot g^{-1}$]	Pure parameter T* [K]	P* [MPa]	v* [$cm^3 \cdot g^{-1}$]	Ref.¶
PDMS	303.15	1.0359	5563	339	0.8410	1
PVA	303.15	0.7648	4599	5217.3	0.5831	2
PIB	298.15	1.0906	7580	448	0.9493	1
PPO	298.15	1.0004	5973	505	0.8306	3
n-Hexane	303.15	1.5337	4445	422.3	1.1563	4
n-Pentane	303.15	1.6271	4170	404.4	1.1878	4
Water	303.15	1.004	6258	2671.4	0.8394	5
c-Hexane	298.15	1.2992	4721	530	1.0012	4
Methanol	298.15	1.2713	4361	1937.7	0.9548	4
Benzene	298.15	1.1446	4709	627.6	0.8860	4

¶1. Beret and Prausnitz [1975]; 2. Lucchelli et al. [1988]; 3. Kershaw and Malcolm [1968]; 4. Timmerma ns [1965]; 5. Smith and Van Ness [1987]

In contrast to g^E-models (i.e., UNIQUAC), an EOS can be applied to mixtures by using the pure properties. As an illustration, the experimental and calculated specific volume of PIB, as a function of pressure using the NLF-EOS, is shown in Fig. 2. This result was solely based on parameter values given in Table 10. Although we did not perform a detailed error analysis between the experimental and the calculated results by the NLF-EOS, the model values fit the specific volume of polymers well. Also, the EOS accurately predicted the configurational properties of pure solvents [Lee and Yoo, 1997].

The calculated and measured activities of *n*-hexane in PDMS in the present study with the existing data [Sugamiya et al., 1974; Ashworth et al., 1984] are shown in Fig. 3 for high molecular weight PDMS (M_n=26000) solution and in Fig. 4 for low molecular weight PDMS (M_n=6650). The effect of the molecular weight of PDMS on the sorption behavior of *n*-hexane is seen to be neglected. Indeed, when M_n of PDMS is greater than 6000, the number of chemical bonds per unit volume reaches a maximum, and the effect of temperature and density on the M_n becomes insignificant [Lichtenthaler et al., 1978]. To compare the correlation results by the FH and UNIQUAC g^E-models on a reasonable basis, the χ-parameter in the FH model is made temperature dependent. In these criteria, the AAD% for the case of UNIQUAC seemed

Table 8. Estimated molecular parameters of Sanchez-Lacombe EOS for pure fluids

Components	Pure parameters T* [K]	P* [MPa]	ρ^* [$g \cdot cm^{-3}$]	Ref.¶
PDMS	476	302	1.104	1
PVA	647	1372	1.311	2
PIB	643	354	0.974	1
PPO	571	1158	1.085	3
n-Hexane	476	298	0.775	4
n-Pentane	441	310	0.755	4
c-Hexane	497	383	0.902	4
Benzene	523	444	0.994	4
Methanol	468	1202	0.922	4
Water	623	2687	1.105	4

¶1. Sanchez and Lacombe [1978]; 2. Lucchelli et al. [1988]; 3. Booth and Devoy [1971]; 4. Sanchez and Lacombe [1976a]

Table 9. Estimated molecular parameters Panayiotou-Vera EOS for pure fluids

Components	Pure parameters E_a	E_b	E_c	V_a	V_b	V_c	Ref.¶
PDMS	66.993	0.073	0.	0.891	0.	0.	1
PVA	152.525	0.017	0.	0.821	0.	0.	2
PIB	95.858	0.062	0.	1.008	0.	0.	1
PPO	102.425	0.005	0.	0.916	0.	0.	3
n-Hexane	96.619	0.0372	0.0425	113.9811	-0.0125	-0.1045	4
n-Pentane	92.803	0.0799	0.2895	100.8218	-0.0944	-0.5542	4
c-Hexane	108.392	0.0102	-0.1034	97.7464	0.0166	0.0494	4
Benzene	119.737	-0.0087	-0.4477	82.3512	0.0198	0.0081	4
Methanol	188.794	-0.2681	0.0036	39.9034	0.0087	-0.1167	4
Water	406.843	-0.7105	-0.3273	18.0717	0.0036	-0.0364	5

¶1. Beret and Prausnitz [1975]; 2. Lucchelli et al. [1988]; 3. Kershaw and Malcolm [1968]; 4. Timmermans [1965]; 5. Smith and Van Ness [1987]

Table 10. Estimated coefficients in molecular parameters of NLF EOS for pure fluids

Components	Pure parameters						Ref.[¶]
	w_{ii}	H_{ii}	d_{ii}	a_i	b_i	v_i	
PDMS	69.543	0.0854	0	0.8998	0	0	1
PVA	156.344	0.0251	0	0.8247	0	0	2
PIB	90.376	0.1031	0	1.0183	0	0	1
PPO	109.011	0.0032	0	0.9204	0	0	3
n-Hexane	97.0823	0.0404	0.0312	112.227	−0.0802	0.3583	4
n-Pentane	93.3463	0.0854	0.2748	105.327	0.4536	−2.3503	4
c-Hexane	108.809	0.0144	−0.1102	96.5724	0.0017	0.0782	4
Benzene	120.161	−0.0055	0.0630	81.7062	0.0112	0.0548	4
Methanol	189.017	−0.2736	−0.0931	39.8148	0.0143	0.0495	4
Water	407.068	−0.7248	−0.4184	18.0677	0.0045	−0.0303	5

[¶]1. Beret and Prausnitz [1975]; 2. Lucchelli et al. [1988]; 3. Kershaw and Malcolm [1968]; 4. Timmermans [1965]; 5. Smith and Van Ness [1987]

Table 11. Best fitted temperature-dependent binary interaction parameters of Flory-Huggins model and the absolute average deviation

Systems	Binary parameters		Temp. range [K]	AAD%[†]	Ref.[¶]
	$\chi^{(0)}$	$\chi^{(1)}$			
PDMS(26000)/*n*-hexane	0.0094	0.0009	293.15-323.15	0.927	1,2
PDMS(6650)/*n*-hexane	0.1609	0.0006	293.15-323.15	1.459	1,2
PDMS(31300)/*n*-pentane	0.4007	−0.0002	303.00-303.15	1.625	1
PVA(88000)/water	0.7138	0.0007	281.15-338.15	4.086	3,4,5
PIB(1200000)/c-hexane	0.7046	0.0010	303.15	1.843	6
PPO(2000)/methanol	0.9936	0.0004	248.15-298.15	11.773	7
PPO(2000)/benzene	0.2654	−0.0002	298.15-347.15	1.718	8

[†]$AAD\% = |(a_i(exp) - a_i(cal)/a_i(exp)| \times 100$

[¶]1. Ashworth et al. [1984]; 2. Sugamiya et al. [1974]; 3. Flory and Daoust [1957]; 4. Bawn and Patel [1956]; 5. Eichinger and Flory [1968]; 6. Sakurada et al. [1959]; 7. Lakhanpal and Conway [1960]; 8. Booth and Devoy [1971]

Table 12. Best fitted binary interaction parameters of UNIQUAC model and the absolute average deviation

Systems	Binary parameters		Temp. range [K]	AAD%
	A_{12}	A_{21}		
PDMS(26000)/*n*-hexane	104.4	−49.9	293.15-323.15	0.788
PDMS(6650)/*n*-hexane	186.3	−123.1	293.15-323.15	1.264
PDMS(31300)/*n*-pentane	−188.6	292.0	303.00-303.15	1.175
PVA(88000)/water	147.7	50.0	281.15-338.15	4.311
PIB(1200000)/c-hexane	−122.7	249.6	303.15	1.370
PPO(2000)/methanol	−141.8	708.0	248.15-298.15	0.848
PPO(2000)/benzene	320.4	−216.3	−216.3	4.249

Table 13. Best fitted binary interaction parameter for New-Flory EOS and the absolute average deviation

Systems	Binary parameters χ_{12}	Temp. range [K]	AAD%	Ref.[¶]
PDMS(26000)/*n*-hexane	3.8248	293.15-323.15	2.152	1,2
PDMS(6650)/*n*-hexane	3.5343	293.15-323.15	2.556	1,2
PDMS(31300)/*n*-pentane	4.7099	303.00-303.15	1.299	1
PVA(88000)/water	40.7455	281.15-338.15	6.342	3,4,5
PIB(1200000)/c-hexane	5.4629	303.15	1.825	6
PPO(2000)/methanol	30.7289	248.15-298.15	8.513	7
PPO(2000)/benzene	3.5274	298.15-347.15	1.621	8

[¶]1. Ashworth et al. [1984]; 2. Sugamiya et al. [1974]; 3. Flory and Daoust [1957]; 4. Bawn and Patel [1956]; 5. Eichinger and Flory [1968]; 6. Sakurada et al. [1959]; 7. Lakhanpal and Conway [1960]; 8. Booth and Devoy [1971]

slightly better than the case of FH. Also, upon comparisons of AAD% among the four EOSs (i.e., NF, SL, PV and NLF), we found that the NLF was found to be better than the others, although the differences of the AAD% (Table 13-16) are not significant for each other. In general, the g^E-models show better results of correlations than those EOSs for sorption data of polymer solutions. However, at the same time, an EOS can be used to fit the configurational properties of pure polymers and pure solvents in addition to the solution equilibrium properties (Fig. 2).

As shown in Table 2, the NF EOS stemmed from a semi-empirical cell theory; and it requires three pure molecular parameters and one binary parameter for a binary polymer solution. The other EOSs (SL, PV, and NLF) were based on the same fundamental lattice-hole theory after Guggenheim [1952]. The SL EOS is based on a random-hole approximation that requires three pure molecular parameters and one binary parameter for a binary solution. The PV EOS is based on a non-random quasi-chemical approximation of the underlying theory. This model, however, has a quadratic expression of the nonrandomness factor, which can be solved analytically only up to binary systems. For multicomponent systems, the esti-

Table 14. Best fitted binary interaction parameter of Sanchez-Lacombe EOS and the absolute average deviation

Systems	Binary parameters δ_{ij}	Temp. range [K]	AAD%
PDMS(26000)/*n*-hexane	0.0173	293.15-323.15	0.939
PDMS(6650)/*n*-hexane	0.161	293.15-323.15	1.468
PDMS(31300)/*n*-pentane	0.0218	303.00-303.15	0.883
PVA(88000)/water	0.0615	281.15-338.15	18.49
PIB(1200000)/c-hexane	0.0476	303.15	4.793
PPO(2000)/methanol	0.0392	248.15-298.15	10.02
PPO(2000)/benzene	-0.0352	298.15-347.15	12.73

Table 15. Best fitted binary interaction parameter of Panayiotou and Vera EOS and the absolute average deviation

Systems	Binary parameters δ_{ij}	Temp. range [K]	AAD%
PDMS(26000)/*n*-hexane	0.009	293.15-323.15	0.8404
PDMS(6650)/*n*-hexane	0.008	293.15-323.15	1.3735
PDMS(31300)/*n*-pentane	0.014	293.15-323.15	1.7470
PVA(88000)/water	-0.078	303.00-303.15	5.8162
PIB(1200000)/c-hexane	0.016	281.15-338.15	1.7823
PPO(2000)/methanol	0.018	303.15	10.3171
PPO(2000)/benzene	0.005	248.15-298.15	1.7137

mation of the nonrandomness factor should be based on a numerical procedure. However, the NLF-EOS is one of the most recent models developed by the present authors [You et al., 1994a, b; Yoo et al., 1995a, b; Lee and Yoo, 1997] based on a rigorous approximation of nonrandom lattice-hole theory. This model is applicable to a general mixture without employing any numerical procedure. Although one cannot reach a sound conclusion as to which EOS is the best one in practice, it is the present authors' argument that the NLF shows better results than others tested in the present study.

In Fig. 6, the measured and calculated activities of cyclohexane in PIB at 298.15 K are shown. Except for the case of SL EOS, the other g^E-models and EOSs show comparable correlation capabilities. For further quantitative correlation results by FH, UNIQUAC, NF, PV, and NLF model, the results summarized in Tables 11-16 can be used a crude guide for selection. Similar correlations resulted for the activities of benzene in PPO at 298.15 K as shown in Fig. 7. We omit here further discussion of this system.

In Fig. 8, the activities of methanol in PPO at 298.15 K are shown. In this case, due to the effect of nonideal hydrogen bonding, only the fitting result by UNIQUAC seemed to be reliable, whereas the results by the others (FH, NF, SL, PV and NLF) are erroneous. The EOSs employed in the comparison cannot quantitatively take into account the effect of association such as hydrogen bonding, and it is necessary to further improve those models for systems with high association. We will not dwell on those problems in the present study. Similar deviations were found for the correlation of activities of water in PVA as shown in Fig. 9. The addition of the effect of association in the models tested in the present study remains to be resolved in the contemporary thermodynamic field. However, for practical purposes of calculating activities of solvents in polymer solutions, the UNIQUAC and the NLF-EOS show better results than other models. However, we would like to leave the matter of preferential choice of a g^E-model (i.e., FH and UNIQUAC) or of an EOS (NF, SL, PV and NLF) to the readers.

Table 16. Best fitted binary interaction parameter of NLF-EOS and the absolute average deviation

Systems	Binary parameters δ_{ij}	Temp. range [K]	AAD%
PDMS(26000)/*n*-hexane	-0.002	293.15-323.15	1.07
PDMS(6650)/*n*-hexane	-0.002	293.15-323.15	1.07
PDMS(31300)/*n*-pentane	0.0025	303.00-303.15	0.59
PIB(1200000)/c-hexane	0.0159	281.15-338.15	1.26
PVA(88000)/water	-0.0516	303.15	8.57
PPO(2000)/methanol	0.0144	248.15-298.15	5.78
PPO(2000)/benzene	0.0021	298.15-347.85	1.65

CONCLUSION

By using a vacuum electro-microbalance as an essential part of the equilibrium sorption apparatus, we measured the reliable sorption equilibria of several binary systems (*n*-hexane-PDMS, *n*-pentane-PDMS, water-PVA, cyclohexane-PIB, methanol-PPO, benzene-PPO and water-PVA). Special emphasis in performing the measurement was given to provide missing data in a certain range of solvent concentration for systems reported by other investigators.

To provide a crude guide, the data measured in the present study together with the data reported in the literature were used to provide model parameters for process design purposes. In the comparative correlation of such sorption data, two g^E-models (NF and UNIQUAC) and four EOSs (NF, SL, PV and NLF) were adopted.

In general, UNIQUAC and the NLF EOS show better correlation capabilities than other models.

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APPENDIX 1. EXPRESSIONS OF G^E-MODELS AND EOSs

Here the essential expressions of the two g^E-models (F-H and UNIQUAC) and four EOSs (N-F, S-L, P-V and NLF) employed in this work are presented. In case of EOSs, the expressions are for general multicomponent mixtures, and they can be reduced to the pure fluid forms in a straightforward manner. Detailed notations in each expression were omitted and, thus, interested readers may refer to the related references.

1. F-H Model [Flory, 1941, 1942; Huggins, 1941, 1942]

The chemical potential expression of the F-H model for component 1 in a polymer solution is written by

$$\mu_1 = RT\left[\ln(1-\phi_2) + \left(1-\frac{1}{r}\right)\phi_2 + \chi\phi_2^2\right] \quad \text{(A1)}$$

where we employed a linear temperature dependent χ parameter. It is given by

$$\chi = \chi^{(0)} + \chi^{(1)}T \quad \text{(A2)}$$

Here, ϕ_1 denotes volume fraction of solvent and r is the number of the segment. The best fitted binary parameters, $\chi^{(0)}$ and $\chi^{(1)}$, for the VLE correlation of the polymer solutions measured in the present study are summarized in Table 11.

2. UNIQUAC Model [Abrams and Prausnitz, 1975]

The chemical potential expression of UNIQUAC is given by

$$\frac{\mu_1}{RT} = \ln\frac{\Phi_1}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1\ln(\theta_1+\theta_2\tau_{21}) + \theta_2 q_{11}\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right) \quad \text{(A3)}$$

where, $l_1 = \frac{z}{2}(r_1-q_1)-(r_1-1)$, $\theta_i \equiv \frac{q_i N_i}{\sum_j q_j N_j}$ and $\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j}$.

In the case of polymer, $r_1 = N_{rep}\times R_1$, $q_1 = N_{rep}\times Q_1$ where, N_{rep} is the number of repeating units.

The binary adjustable parameter is given by

$$\tau_{ji} \equiv \exp\left\{-\left[\frac{u_{ji}-u_{ii}}{RT}\right]\right\} \equiv \exp\left\{-\left[\frac{A_{ji}}{RT}\right]\right\} \quad \text{(A4)}$$

where Φ_i denotes average segment fraction, θ_i the average area fraction and A_{ji} represents the UNIQUAC binary interaction parameter. The best fitted parameters for polymer systems tested in this work are summarized in Table 12.

3. N-F Model [Flory, 1970; Eichinger and Flory, 1968]

The reduced EOS is defined by

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{v}\tilde{T}} \quad \text{(A5)}$$

and the chemical potential for component 1 is given by

$$\mu_1 = p_1^* v_1^*\left\{3\tilde{T}_1\ln\left[\frac{\tilde{v}^{1/3}-1}{\tilde{v}^{1/3}-1}\right] + (\tilde{\rho}_1^{-1}-\tilde{\rho}_1^{-1})\right\} + \frac{v_1^*\chi_{12}}{\tilde{v}}\theta_2^2 \quad \text{(A6)}$$

where $\tilde{v} = v/v^* = 1/\tilde{\rho}$, $\tilde{T} = T/T^* = 2v^* cRT/s\eta$, $\tilde{p} = p/p^* = 2pv^{*2}/s\eta$, $p^* = cRT^*/v^*$, $\varepsilon^* = \sum\phi_i\varepsilon_{ii} - 2\sum_{j>1}\phi_i\phi_j w_{ij}$, $w_{ij} = \frac{1}{2}(\varepsilon_{ii}+\varepsilon_{jj}) - \varepsilon_{ij}$, $\varepsilon_{ij} = \varepsilon_{ji}$, $\chi_{12} = 4w_{12}$ and the surface area fraction, θ_i is defined by $\theta_i \equiv q_i N_i/\sum_j q_j N_j$, c denotes the amount of flexibility and rotation, and $s\eta$ is the interaction energy of the molecule per segment.

This EOS requires three molecular characteristic parameters, T^*, P^*, v^* for pure polymer. For mixtures these parameters are defined by $v^* = \sum_i \phi_i v_i^*$ $P^* = \varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1\theta_2\chi_{12}$, and $T^* = (\varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1\theta_2\chi_{12})(\varphi_1 P_1^*/T_1^* + \varphi_2 P_2^*/T_2^*)^{-1}$. Here the best-fitted binary adjustable parameters, χ_{12}, are summarized in Table 13.

4. S-L Model [Sanchez and Lacombe, 1976a, b, 1978]

The EOS for general mixtures and chemical potential for component 1 is given by

$$\frac{\tilde{p}}{\tilde{T}} = \ln\frac{\tilde{v}}{\tilde{v}-1} - \frac{(1-r_2^{-1})}{\tilde{v}} - \frac{1}{v^2\tilde{T}} \quad \text{(A7)}$$

$$\frac{\mu_1}{RT} = \ln\phi_1 + \left(1-\frac{r_1}{r_2}\right)\phi_2 + r_1^o\tilde{\rho}\left[\chi + \left(1-\frac{v_1^*}{v_2^*}\right)\lambda_{12}\right]\phi_2^2 + r_1^o\varepsilon_{11}^*\left\{-\tilde{p} = \tilde{P}_1\tilde{v} + \tilde{T}_1\left[(\tilde{v}-1)\ln(1-\tilde{\rho}) + \frac{1}{r_1^o}\ln\left(\frac{\tilde{\rho}}{w_1}\right)\right]\right\} \quad \text{(A8)}$$

where $\tilde{T}=T/T^*$, $T^*=\varepsilon^*/k$, $\tilde{P}=P/P^*$, $P^*=\varepsilon^*/v^*$, $\tilde{v}=V/V^*=1/\tilde{\rho}$, $V=N_r v^*$, $V^*=v^*\sum r_i N_i$, $\lambda_{12} = \frac{1}{\tilde{T}_1} - \frac{1}{\tilde{T}_2} + (\phi_1-\phi_2)\chi = -\lambda_{21}$

$\varepsilon^* = \sum\sum\phi_i\phi_j\varepsilon_{ij}^* = \sum\phi_i\varepsilon_{ii}^* - kT\sum\sum\phi_i\phi_j\chi_{ij}$,

$\chi_{ij} = (\varepsilon_{ii}^* + \varepsilon_{jj}^* - 2\varepsilon_{ij}^*)/kT$, $r_i = r_i^o(v_i^*/v^*)$,

$r = \sum x_i r_i$, $\phi_i^o = r_i^o N_i / \sum r_i^o N_i$, and.

Here V^* represents the closed-packed volume of a mer, r_i denotes the number of segments of a molecule of species i, θ_i is the surface area fraction, and is ϕ_i is the segment fraction of component i. This EOS contains three molecular parameters, T^*, P^*, v^* for a pure fluids. To apply the EOS to a binary mixture requires the mixed forms of v^* and ε^* and a binary adjustable parameter, δ_{12}. They are defined by $v^* = \sum_i \phi_i v_i^*$, and $\varepsilon_{12}^* = (\varepsilon_{11}^*\varepsilon_{22}^*)^{1/2}(1-\delta_{12})$. The best-fitted δ_{12} for the systems tested in the present study are summarized in Table 14.

5. P-V Model [Panayiotou and Vera, 1982]

The EOS for a mixture and chemical potential for component i are given by

$$\frac{\tilde{P}}{\tilde{T}} = \ln\frac{\tilde{v}}{\tilde{v}-1} + \frac{z}{2}\ln\frac{\tilde{v}+(q/r)-1}{\tilde{v}} - \frac{\theta^2}{\tilde{T}} \quad \text{(A9)}$$

$$\frac{\mu_1}{RT} = \ln\phi_1 + \ln\frac{\tilde{v}_1}{\tilde{v}} + q_1\ln\left(\frac{\tilde{v}}{\tilde{v}-1}\,\frac{\tilde{v}-1}{\tilde{v}}\right) + q_1\left(\frac{2\theta_{1,p}-\theta}{\tilde{T}_1} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_1}{2}\ln(\Gamma_{1i}) \quad \text{(A10)}$$

where $(\Gamma_{1i}) = \frac{2}{1+\sqrt{1-4\theta_1^2(1-G)}}$, $G = \exp\left(\frac{\varepsilon_{11}}{RT}\right)$,

$(\Gamma_{1H}) = \frac{2}{1+\sqrt{1-4\theta_1\theta_2(1-G)}}$, $G = \exp\left(\frac{\Delta\varepsilon}{RT}\right)$

where $\tilde{T}=T/T^*$, $T^*=\varepsilon^*/k$, $\tilde{P}=P/P^*$, $P^*=\varepsilon^*/v^*$, $\tilde{v}=V/V^*=1/\tilde{\rho}$, $V=N_r v^*$, $V^*=v^*\sum r_i N_i$, $\theta_i \equiv q_i N_i / \sum_j q_j N_j$ and $\phi_i = r_i N_i / \sum r_i N_i$. Here r_i denotes a number of segments of a molecule of species i, θ_i is surface area fraction ϕ_i and segment fraction of component i. This EOS contains two molecular parameters, T^*, P^*, v^* for a pure fluid. For a binary mixture, this model requires mixed forms of $v^* = \sum_i x_i v_i^*$, $\Delta\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}$ where $\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}(1-\delta_{12})$. The best-fitted binary adjustable parameters δ_{12} are summarized in Table 15.

6. NLF Model [You et al., 1994a, b; Yoo et al., 1995a, b; Lee and Yoo, 1997]

$$P=\frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-\ln(1-\rho)\right\}-\left(\frac{z}{2}\right)\theta^2\left(\frac{\varepsilon_M}{V_H}\right); \quad (A11)$$

$$\varepsilon_M=\frac{1}{\theta^2}\left\{\sum\sum\theta_i\theta_j\varepsilon_{ij}+\left(\frac{\beta}{2}\right)\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})\right\}; \quad (A12)$$

This model required a temperature-dependent molecular size parameter, r_i, and an interaction energy parameter, ε_{ii}, between component i-i given by

$$r_i=a_i+b_i(T-T_0)+c_i\left(T\ln\frac{T_o}{T}+T-T_0\right) \quad (A13)$$

$$\varepsilon_{ii}/k=w_{ii}+h_{ii}(T-T_0)+d_{ii}\left(T\ln\frac{T_0}{T}+T-T_0\right); \quad (A14)$$

where T_0=273.15 K. The best fitted values of the coefficients in Eqs. (A13) and (A14) are summarized in Table 10. To apply the model to a binary VLE, a cross interaction energy between species i and species j is necessary. It is given by $\varepsilon_{ij}=(\varepsilon_{ii}\varepsilon_{jj})^{0.5}(1-\lambda_{ij})$ where the estimated binary interaction parameters, λ_{ij} are summarized in Table 16.

NOMENCLATURE

A, B, C, D fitting constants given in Eq. (3)
a_1 : activity of component 1
B_{11} : second virial coefficient
k : Boltzmann constant
N : total number of molecules
P : pressure [MPa]
q_i : surface area parameter for molecule i
r_i : number of segment for molecule i
P : system pressure [MPa]
R : universal gas constant
T : temperature [K]
v : molar volume [cm^3mol^{-1}]
w : interchange energy
x_1 : liquid phase mole fraction for component 1
z : coordination number

Greek Letters

β : reciprocal temperature (1/kT)
δ_{ij} : binary adjustable interaction energy parameter
ε_{ii} : molecular interaction energy between component i and j
ρ : system density
ϕ_i : surface area fraction sites
θ_i : surface area fraction
μ_i : chemical potential for component i
λ_{ij} : adjustable binary interaction parameter
χ : Flory-Huggins interaction parameter
τ_{ij} : energy parameter
Γ_{11} : nonrandomness factor between for molecular species 1-1

Subscripts

~ : reduced properties
* : molecular characteristic properties
c : critical state
i : molecular index
M : mixture quantity

Superscripts

c : configurational quantity
H : unit lattice volume
M : mixed state
vap : vapor pressure
L : liquid property
V : vapor phase property

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