Measurements and Correlation of Hydrogen-Bonding Vapor Sorption Equilibrium Data of Binary Polymer Solutions

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Abstract−Vapor sorption equilibrium data of ten binary polymer/solvent systems were measured using sorption equilibrium cell equipped with a vacuum electromicrobalance. Tested solvents were water, methanol, ethanol and n-propanol and polymer solutes were poly(ethylene glycol), poly(propylene glycol), poly(tetramethylene glycol) and poly(ethylene oxide). The measured sorption obtained in the present work, were compared with existing literature data and the degree of reliability of the measured data was discussed. Vapor sorption equilibrium data obtained in the present study were correlated by UNIQUAC model and the multi-fluid non-random lattice fluid hydrogen bonding equation of state (MF-NLF-HB EOS) recently proposed by the present authors.

Key words: Vapor Sorption Equilibrium, Polymer-Solvent Systems, UNIQUAC Model, MF-NLF-HB EOS

INTRODUCTION

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

Despite the various sorption equilibria data of polymer solutions were reported in the literature, existing data are scarce and frequently available only in a limited range of the concentration of solvent species. Especially, the systems with no existing data source were selected in this work to provide sorption data for the first time.

In the present study, emphasis was given to the measurement of sorption equilibrium data of binary polymer solution containing interaction of hydrogen bonding by an apparatus based on the principle of the vacuum electromicrobalance. Besides, some complimentary measurement of data was made to enhance the utility of the existing systems over an extended range of solvent concentrations. The polymers tested were poly(ethylene glycol), poly(propylene glycol), poly(tetramethylene glycol) and poly(ethylene oxide) and solvents were used water, methanol, ethanol and n-propanol.

To model the measured activity of solvents in polymer solutions, one of well-known g^E model, UNIQUAC [Abrams and Prausnitz, 1975] was used. Also, the same data were tried to correlate by the MF-NLF-HB EOS which was recently formulated by the present authors based the multi-fluid approximation of the non-random lattice fluid theory [Yeom et al., 1999] with the combination of the theory of hydrogen bonding after Veytsman [Veytsman, 1990].

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EXPERIMENTAL SECTION

1. Materials and Apparatus

For polymers, PEG and PPG were purchased from Fluka Chemie AG (Buchs, Switzerland). PEO and PTMG were purchased from Aldrich Co. (St. Louis, MO, United States). The number of average molecular weight (Mn) of PEG was 600, of PPG was 400, of PTMG was 1400, of PEO was 600000. These sample polymers were used directly without further purification. Water, methanol, ethanol and n-propanol were purchased from Aldrich Co. All sol-
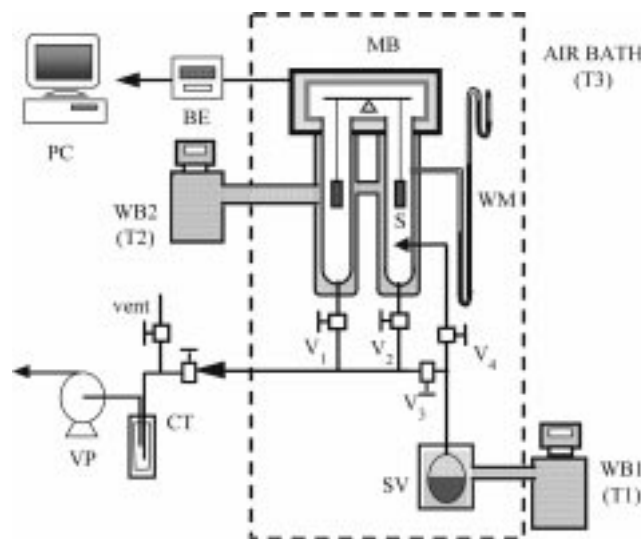

Fig. 1. Schematic diagram of vapor sorption apparatus: PC, personal computer; MB, microbalance; BE, balance electronics; WB1 (T1), water bath1; WB2 (T2), water bath2; WM, W-tube mercury manometer; S, polymer sample; SV, solvent vessel; CT, cold trap; VP, vacuum pump; V, valve.

vents were HPLC-grade and these were used directly without further purification.

The schematic diagram of the sorption apparatus used in the experiment is shown in Fig. 1. To reduce flow and thermal fluctuations 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 Satorius M25D-V vacuum electro-microbalance (Goettingen, Germany), which has the accuracy of ±0.001 mg. A calibrated mass was loaded to the left side of the balance as a reference mass and the polymer sample was put to the right side of the balance. A dish-type quartz sorption cell was used to load the polymer sample. Platinum wire was used to link both arms to the balance for preventing possible oxidative corrosion of the arm by the solvent. Potential leakage of the system was checked by maintaining the pressure under 1.3×10^{-2} Pa for a week using a Precision Science vacuum pump (Chicago, IL. USA).

Water baths were installed in two regions for separately controlling temperature to prevent temperature fluctuation which could result in condensation of solvent on the surface of the sorption cell. Water bath 1 [WB1] which has the accuracy of ±0.01 °C (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 bath2 [WB2] which has the accuracy of ±0.01 °C (Polyscience 9710) was installed to control the sorption cell. The distribution of temperatures in each water bath was maintained differently such that the temperature of air bath (T3)>water bath 2 (T2)>water bath 1 (T1). Mercury head in the manometer [WM] was measured to within±0.01 mmHg using a cathetometer (Gaertner Scientific, Chicago, United States).

2. Experimental Procedure

A polymer sample was loaded to the sorption cell. For PEG, PPG and PTMG, each polymer was thinly coated onto the surface of a 200 mesh stainless sieve. For PEO, a certain amount of sample was separately dissolved by acetone and coated onto the surface of 200 mesh stainless sieve and left until the solvent was evaporated.

The system temperature was controlled by WB2 and temperature in the air bath (T3) was maintained 4 °C higher than T2 throughout experiment. The sorption cell was evacuated the vacuum pump by close valves 3 and 4 and open valves 1 and 2, respectively. In this step, the low volatile gaseous impurities in the polymer samples were removed before measuring the equilibrium data. Also, when the system is under high vacuum state for approximately 5 hours and checked where there is any leak or not, then when the weight fluctuation stays within±0.001 mg, the valves 1 and 2 were closed. Temperature in WB1 is lowered up to the freezing point of the solvent and opened valve 3 to remove rest of impurities in solvent vessel (SV) by vacuum pump. Then, after close the valve 3 and set the temperature of WB1 to measure the vapor pressure of the tested solvent.

To absorb vapor-phase solvent by polymer sample, the valve 1 [V$_1$], 2 [V$_2$] and 3 [V$_3$] were closed and the valve 4 [V$_4$] was opened in order to transfer equilibrated vapor from the vapor generation unit.

The sorbed solvent was measured with 5 min interval by a data processor [PC]. When the mass of absorbed solvent by polymer stayed within the error range of ±0.005 mg for 3 hours, we assumed that a sorption equilibrium state was reached.

DATA REDUCTION AND CORRELATION

1. Activities of Solvents from Experiment

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

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

where P_1^{sat} is saturation pressure and B_{11} is the second virial coefficient. These values were estimated using existing correlation methods reported in the data book [Reid et al., 1988; McGlashan and Wormald, 1964].

2. MF-NLF-HB EOS

Measured sorption data were comparatively correlated using UNIQUAC as a g^E model and using MF-NLF-HB EOS. The EOS was proposed recently by the present authors. From the previous work of the present authors [Shin et al., 1999; Yeom et al., 1999; Yoo et al., 1997], the MF-NLF-HB EOS for general multi-component hydrogen bonding mixtures is derived by

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \ln(1-\rho) - \nu_{HB}\rho + \frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}} - 1\right)\right\} \tag{2}$$

where, $q_u = \sum x_i q_i$, $r_u = \sum x_i r_i$, $\rho = \sum \rho_i$, $\rho_i = V_i^*/V$, $V_i^* = N_a r_i V_H$ and x_i is the mole fraction of species i in a mixture. The fraction of hydrogen bonds in the system, ν_{HB}, is given by the summed fraction of pairs of hydrogen bonds as follows

$$\nu_{HB} = \sum_{k=1}^{K}\sum_{l=1}^{L}N_{kl}^{HB}\bigg/\sum_{i=1}^{c}N_i r_i \tag{3}$$

There are apparently four molecular parameters in the EOS for pure fluids; z, V_H, r_1, ε_{11}. As in the previous study [Shin et al., 1999, 2000; Yeom et al., 1999; Yoo et al., 1997], we set z=10 and V_H= 9.75 cm^{3}mol^{-1}. Thus, for a pure fluid we need to determine only two independent molecular parameters, r_1 and ε_{11}. The parameters, r_1 and ε_{11} are regressed at each isotherm and represented as functions of temperature.

$$\varepsilon_{11}/k = E_a + E_b(T-T_0) + E_c[T \ln(T_0/T) + T - T_0] \tag{4}$$

$$r_1 = R_a + R_b(T-T_0) + R_c[T \ln(T_0/T) + T - T_0] \tag{5}$$

where T_0=273.15 K is a reference temperature.

We have one binary energy parameter λ_{12} for a binary, which is defined by

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{12})^{1/2}(1-\lambda_{12}) \tag{6}$$

where λ_{12} is determined by data fitting and may be temperature dependent.

RESULTS AND DISCUSSION

The sorption equilibrium data were measured by the vacuum electromicrobalace as shown in Fig. 1. Measured systems were PEG+ n-propanol, PPG+water, PPG+methanol, PPG+ethanol, PEO+water, PEO+methanol, PEO+ethanol, PTMG+water, PTMG+methanol,

Table 1. Measured pressure and activities of solvent in solvent(1)+polymer(2) system

Polymer	Solvent	T^a/K	w_1^b	P_1^c/kPa	a_1	Polymer	Solvent	T^a/K	w_1^b	P_1^c/kPa	a_1
PEO	Water	303.15	0.0114	1.3866	0.2057	PTMG	Water	303.15	0.0023	1.1492	0.1523
			0.0219	1.8465	0.3140				0.0041	1.4772	0.2296
			0.0313	2.3598	0.4349				0.0072	1.7425	0.2921
			0.0453	3.0491	0.5971				0.0109	2.2105	0.4023
			0.0569	3.4664	0.6953				0.0148	2.5091	0.4726
			0.0777	3.9130	0.8004				0.0177	2.7998	0.5410
			0.1114	4.5956	0.9609				0.0254	3.3077	0.6605
PEO	Methanol	303.15	0.0850	5.1089	0.2348	PTMG	Methanol	303.15	0.0319	4.9863	0.2042
			0.1114	6.3128	0.2899				0.0491	6.0208	0.2517
			0.1430	8.0540	0.3697				0.0584	7.0101	0.2971
			0.1883	10.3098	0.4729				0.0744	8.2660	0.3546
			0.3095	12.6256	0.5786				0.0861	9.1659	0.3958
PEO	Ethanol	303.15	0.0288	2.4905	0.2387				0.1017	10.2525	0.4460
			0.0359	3.5557	0.3406				0.1171	11.3151	0.4940
			0.0515	4.7356	0.4534				0.1489	13.1296	0.5769
			0.0689	5.8289	0.5577				0.1846	15.2854	0.6752
			0.0886	7.1487	0.6835				0.2164	16.9453	0.7507
			0.1531	8.6780	0.8291				0.2650	18.8291	0.8366
PPG	Water	303.15	0.0094	1.2172	0.1674	PTMG	Ethanol	303.15	0.0141	2.3598	0.1766
			0.0137	1.4892	0.2315				0.0205	2.8198	0.2207
			0.0213	1.9865	0.3486				0.0295	3.4557	0.2816
			0.0304	2.2825	0.4183				0.0424	4.2157	0.3542
			0.0404	2.7064	0.5181				0.0618	4.8996	0.4196
			0.0549	3.1131	0.6138				0.0841	5.7489	0.5007
			0.0762	3.6264	0.7345				0.1113	6.7408	0.5953
									0.1371	7.3367	0.6522
PPG	Methanol	303.15	0.0354	5.1089	0.2123	PEG	n-Propanol	303.15	0.0246	1.8225	0.2593
			0.0555	6.8101	0.2903				0.0525	2.1945	0.3829
			0.0771	8.4126	0.3637				0.0829	2.5931	0.5344
			0.1043	10.3831	0.4538				0.1264	3.0864	0.6402
			0.1353	12.1243	0.5334				0.1805	3.5597	0.7615
			0.1693	14.1415	0.6254				0.2354	4.1397	0.8662
									0.2354	4.1397	0.8662
PPG	Ethanol	303.15	0.0282	3.0851	0.2428						
			0.0460	4.0597	0.3360						
			0.0732	5.1329	0.4386						
			0.1049	6.3261	0.5525						
			0.1320	7.2861	0.6440						

[a]T: temperature (± 0.01 °C).

[b]w_1: weight fraction of solvent.

[c]P_1: measured pressure of solvent (± 0.001 kPa).

PTMG+ethanol. Measured data and their experimental conditions were summarized in Table 1.
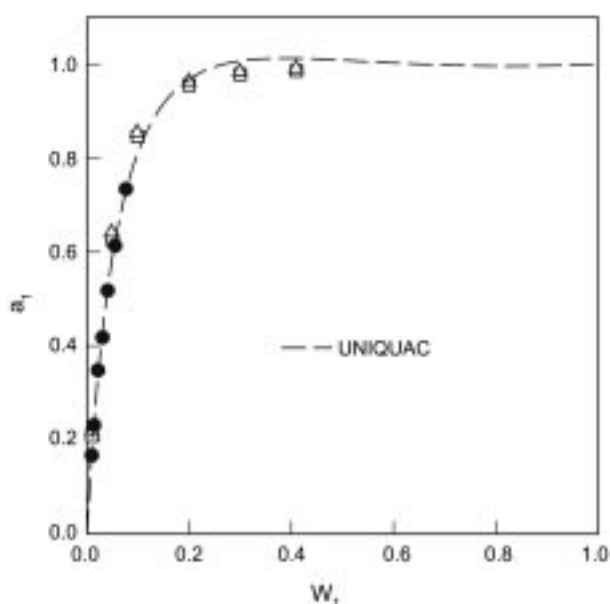
From the sorption data obtained in the present study and other existing data, the activities of solvents in various polymers were calculated using both UNIQUAC model and MF-NLF-HB EOS. The best-fitted UNIQUAC binary parameters, A_{12}, A_{21} and MF-NLF-HB EOS binary interaction parameters, λ_{12} were summarized

in Table 2. Since the PVT data of PPG was not available in literature, the λ_{12} for system with PPG was assumes as zero.

The reliability of the apparatus was repeatedly verified by the present authors and reported them elsewhere. Thus, in this work, by simply choosing PPG+water system, comparison of the data obtained in this work and the data by other investigator [Malcolm and Rowlinson, 1957] were compared together in Fig. 2. Also, the
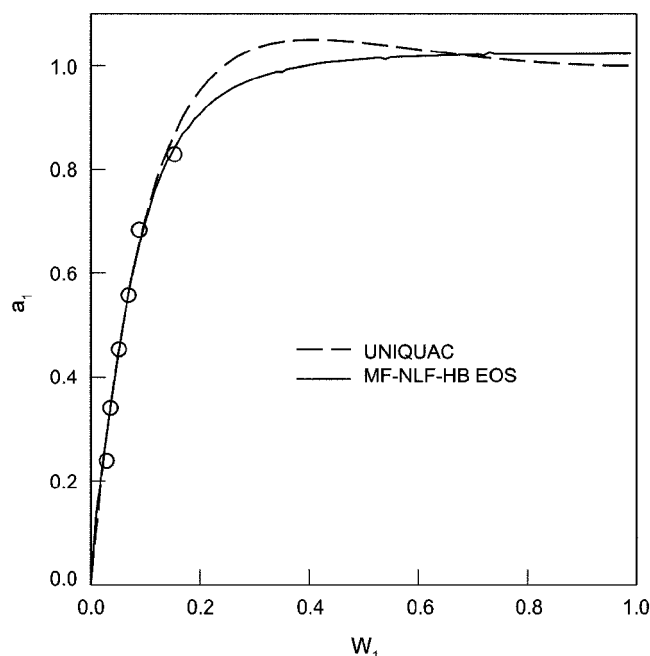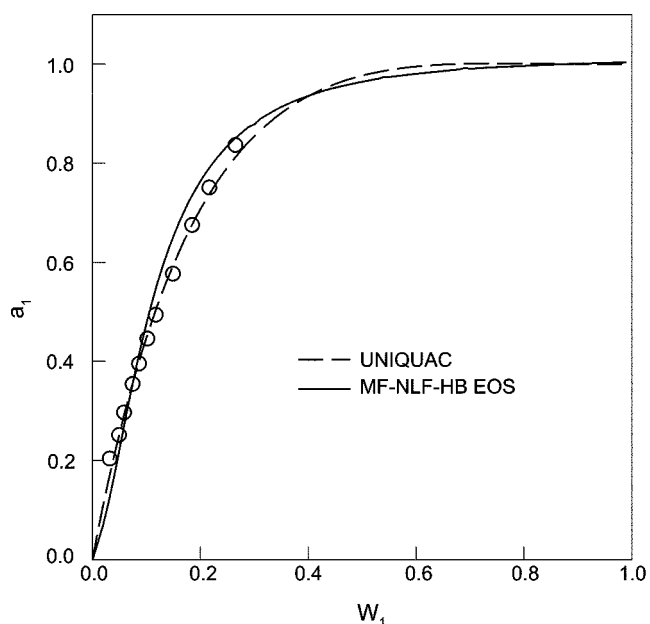
Table 2. Estimated binary interaction parameters of UNIQUAC and MF-NLF-HB EOS

System	UNIQUAC		MF-NLF-HB	T/K
	A_{12}	A_{21}	λ_{12}	
PEG+n-propanol	−69.611	579.901	−0.0019	303.15
PEO+water	350.726	−77.654	-	303.15
PEO+methanol	351.136	−351.164	−0.1874	303.15
PEO+ethanol	118.217	237.305	−0.0520	303.15
PPG+water	−267.092	615.912	-	303.15
PPG+methanol	−221.279	344.110	-	303.15
PPG+ethanol	−186.145	572.231	-	303.15
PTMG+water	−327.823	1044.250	-	303.15
PTMG+methanol	498.551	−198.787	−0.0395	303.15
PTMG+ethanol	−289.722	735.196	−0.0189	303.15

Fig. 3. Measured and calculated activities, a_1 of ethanol (1) in poly (ethylene oxide, Mn : 600000) at 303.15 K: (◯) sorption data measured in this work.

Fig. 2. Measured and calculated activities, a_1 of water (1) in poly (propylene glycol, Mn: 400) at 303.15 K: (●) sorption data measured in this work; (□) Malcolm et al. at 303.15 K; (△) Malcolm et al. at 323.15 K.

Fig. 4. Measured and calculated activities, a_1 of methanol (1) in poly(tetramethylene glycol, Mn: 1400) at 303.15 K: (◯) sorption data measured in this work.

data were correlated by UNIQUAC model. In Fig. 3, the measured sorption data of PEO+ethanol system was shown with the correlated results by the UNIQUAC and MF-NLF-HB model. Both models found to be qualitatively useful for the calculation of activities of sorbed species in polymers. However, the MF-NLF-HB model is an EOS which can be used to calculate thermodynamic properties of pure systems and mixtures while the UNIQUAC cannot be used to calculate pure properties. In this regard, EOS approach should be more useful than g^E model approach.

In Figs. 4 and 5, the measured sorption data for PTMG+methanol and PTMG+ethanol system was shown, respectively. As one can see from these figures, the UNIQUAC and the MF-NLF-HB model fit the data equivalently well. Although we omit further graphical demonstration, the two models fit quantitatively well the data of PEG+n-propanol, PEO+methanol systems. Also, in a region of low mass fraction, the activities of alcohols tend to increase with

increasing the carbon number. This trend was identically applicable to systems containing PEO, PPG or PTMG.

CONCLUDING REMARKS

The sorption data for several solvent-polymer systems with the hydrogen bonding was measured by a vacuum electromicrobalance. Most of the systems chosen in this work, existing data are not
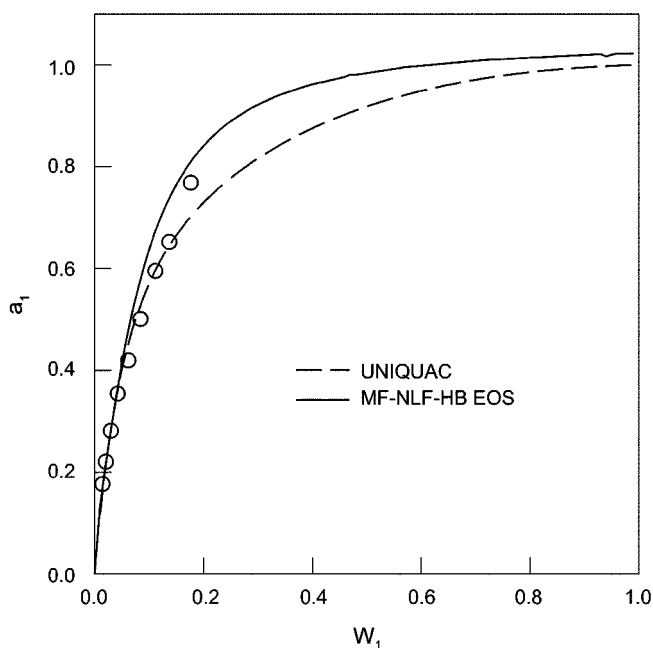
Fig. 5. Measured and calculated activities, a_1 of ethanol (1) in poly (ethylene glycol, Mn: 1400) at 303.15 K: ($\bigcirc$) sorption data measured in this work.

available in literatures. Thus, it will be a new release of such data in thermodynamic society. Upon comparative correlation of these sorption data of hydrogen bonding with the UNIQUAC model as a g^E approach and the MF-NLF-HB model as a EOS approach, it was found that both model equivalently fit well the data. However, the EOS approach found to be more versatile than the g^E model since an EOS approach can be used to calculate other thermodynamic properties of pure compounds.

NOMENCLATURE

a_1 : activity of a solvent
B_{11} : second virial coefficient
N_a : Avogadro's number
N_i : number of molecular species i
P : pressure [MPa]
P_1 : vapor pressure of a solvent [kPa]
P_1^{sat} : saturation pressure of a solvent [kPa]
q_i : surface area parameter
q_M : mole fraction average of q_i
R : gas constant
r_i : segment number
r_M : mole fraction average of r_i
T : temperature [K]
V : molar volume [cm^{3}mol^{-1}]
V^* : characteristic volume of component i [cm^{3}mol^{-1}]
V_H : volume of a unit cell [cm^3]
z : lattice coordination number

Greek Letters

ε_{ij} : interaction energy for i-j segment contacts [J]

λ_{ij} : binary interaction parameter for i-j contacts
ρ : total segment fraction
ρ_i : segment fraction of component i
θ_i : surface area fraction of component i
τ_{ij} : nonrandomness factor

Superscript
HB : chemical contribution by Hydrogen Bongding

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