Vapor Liquid Equilibrium Data of Binary Polymer Solutions by Vacuum Electromicrobalance

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Vapor liquid equilibrium data of nine binary solvent + polymer systems were measured by a vacuum electromicrobalance cell. Solvents used were hexane, pentane, water, methanol, and ethanol. Polymers tested were poly(dimethylsiloxane), M_n, 26 000; poly(propylene oxide), M_n, 2000; poly(vinyl alcohol), M_n, 88 000; poly(acrylic acid), M_n, 1 250 000; and polycarbonate, M_n, 24 000. Measured equilibrium data were tabulated and discussed.

Introduction

Despite the need for vapor−liquid equilibrium characteristics of polymer solutions in various polymer-processing design industries (Baker et al., 1987; Matsumoto et al., 1991; Maeda et al., 1991; Danner and High, 1993; Ballatine and Wohltjen, 1989; Grate et al., 1992), experimental information of such systems is scarce (Kim et al., 1998). Also, existing data are frequently available only over a limited concentration range of sorbed vapor components. Thus, in the present study, emphasis was given to vapor sorption equilibria measurements both of new systems and of existing systems over the extended range of solvent concentration. In the measurement, an equilibrium cell made by a vacuum electromicrobalance is used. The polymers tested are poly(dimethylsiloxane), PDMS, M_n, 26 000; poly(propylene oxide), PPO, M_n, 2000; poly(vinyl alcohol), PVA, M_n, 88 000; poly(acrylic acid), PAA, M_n, 1 250 000; and polycarbonate, PC, M_n, 24 000. Selected solvents are hexane, pentane, water, methanol, and ethanol.

Experiment Section

1. Materials and Apparatus. Polymer PDMS was purchased from Dow Corning Co. (Midland, MI) PPO, PVA, PAA were from Aldrich Co. (St. Louis, MO), and PC was from Dow Chemical Co. (Midland, MI). The number average molecular weight (M_n) of PDMS was 26 000, PPO was 2000, PVA was 88 000, PAA was 1 250 000, and PC was 24 000. All solvents (hexane, pentane, water, methanol, and ethanol) were HPLC-grade ones purchased from J. T. Baker (Phillipsburg, NJ).

The schematic diagram of the sorption apparatus used in the experiment is shown in Figure 1. It consists of three major parts (gravimetric equilibria measurement unit, vacuuming unit, and solvent generation unit). 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 electromicrobalance [MB], which has an accuracy of ±0.001 mg (Goettingen, Germany). A calibrated mass was loaded to the left side of the balance as a reference mass, and the polymer sample was loaded on 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 Scientific vacuum pump (Chicago, IL).

Water baths were installed in three regions for separately controlling temperatures to prevent temperature fluctuation, which could result in condensation of solvent on the surface of the sorption cell. Water bath 1 [WB_1], which has an accuracy of ±0.01 °C (Polyscience 9710, Niles, IL), 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], which has an accuracy of ±0.01 °C (Polyscience 9710, Niles, IL), was installed to control the sorption cell. Water bath 3 [WB_3], which has an accuracy of ±0.01 °C (Polyscience 9710, Niles, IL) 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 [WM] was measured to within ±0.01 mmHg using a cathetometer (Gaertner Scientific Co., Chicago, IL).

2. Experiment. After a polymer sample was loaded to the sorption cell, valve 2 [V_2] and valve 3 [V_3] were closed, and valve 1 [V_1], which is connected to vacuum pump, was opened to create a vacuum state within the cell. This way, volatile low molecular weight substances and impurities including air were removed from the polymer sample. At the high-vacuum state, if the mass of the polymer sample stayed within the fluctuation range within ±0.001 mg for 3 h, the measurement of the sorption equilibrium was started.

To absorb vapor-phase solvent by polymer sample, valve 1 [V_1] and 3 [V_3] were closed, and the valve 2 [V_2] was opened in order to transfer equilibrated vapor from the vapor generation unit.

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

Results and Discussion

New sorption equilibrium data were measured by the experimental apparatus shown in Figure 1. The measured

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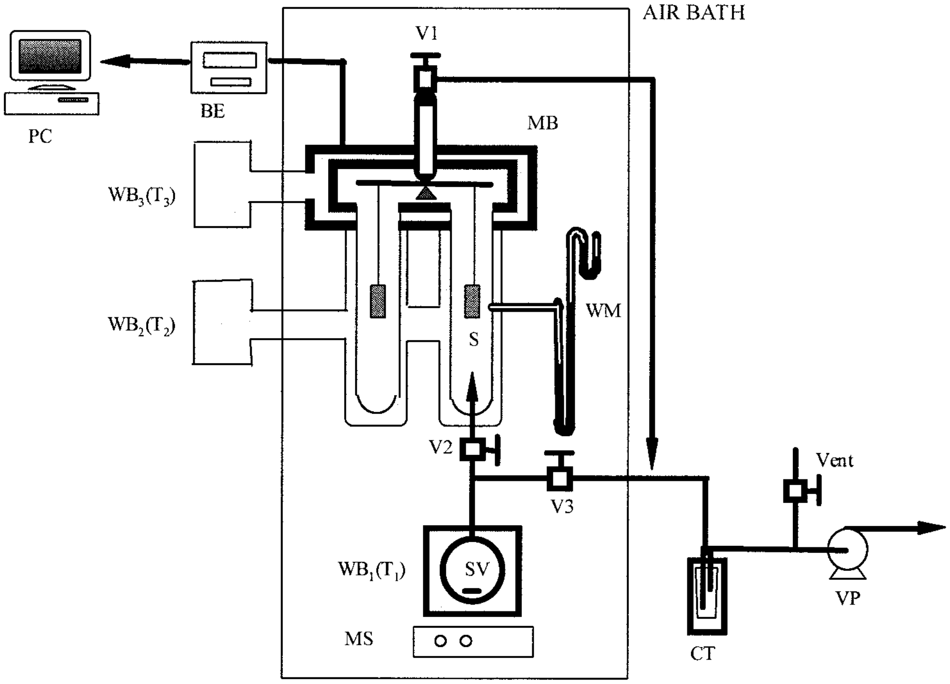

Figure 1. Schematic diagram of vapor sorption apparatus: PC, personal computer; MB; microbalance; BE, balance electronics; $WB_1(T_1)$, water bath 1; $WB_2(T_2)$, water bath 2; $WB_3(T_3)$, water bath 3; V1, valve 1; V2, valve 2; V3, valve 3; WM, W-tube mercury manometer; S, polymer sample; SV, solvent vessel; MS, magnetic stirrer; CT, cold trap; VP, vacuum pump.

Table 1. Measured Presssure of Solvent in Polymer + Solvent Systems

polymer	solvent	T^a/K	$w_1{}^b$	$P_1{}^c$/kPa	polymer	solvent	T^a/K	$w_1{}^b$	$P_1{}^c$/kPa
poly(acrylic acid)	water	303.15	0.0262	0.334	poly(vinyl alcohol)	water	303.15	0.0233	0.968
			0.0303	0.617				0.0341	1.164
			0.0426	0.990				0.0614	1.803
			0.0596	1.398				0.0783	2.371
			0.0843	1.959				0.1076	2.919
			0.1456	2.593				0.1852	3.643
			0.2006	3.101				0.3515	4.188
			0.2836	3.586					
			0.5479	4.019	polycarbonate	pentane	303.15	0.0149	7.347
								0.0191	11.444
poly(acrylic acid)	ethanol	303.15	0.0004	1.535				0.0246	18.281
			0.0015	2.011				0.0269	23.740
			0.0027	2.819				0.0306	32.600
			0.0058	4.576				0.0333	39.862
			0.0097	5.806				0.0355	46.546
								0.0389	53.419
poly(dimethylsiloxane)	hexane	313.15	0.0218	4.341				0.0418	60.685
			0.0442	8.205				0.0553	72.321
			0.0699	12.355				0.0629	80.761
			0.0920	16.787					
			0.1247	20.493	polycarbonate	ethanol	303.15	0.0084	0.663
			0.1665	24.468				0.0133	1.374
			0.2933	31.808				0.0170	2.210
			0.3907	35.227				0.0208	2.962
								0.0346	4.787
poly(dimethylsiloxane)	pentane	313.15	0.0212	14.610				0.0391	5.496
			0.0626	35.226				0.0486	6.925
			0.1121	56.840				0.0572	8.226
			0.1590	70.639				0.0699	9.554
			0.2048	81.187				0.0794	10.332
			0.2644	91.348				0.0887	10.404
			0.3211	98.301					
					polycarbonate	water	303.15	0.0017	0.293
poly(propylene oxide)	methanol	313.15	0.0094	3.042				0.0027	0.526
			0.0153	5.148				0.0038	0.913
			0.0212	6.896				0.0049	1.266
			0.0313	9.599				0.0070	1.934
			0.0429	12.598				0.0096	2.375
			0.0643	16.742				0.0110	2.811
			0.0891	20.732				0.0164	3.654
			0.1736	27.179				0.0324	4.311
			0.2413	29.893					

[a] T: temperature (±0.01 °C). [b] w_1: weight fraction of solvent. [c] P_1: measured pressure of solvent (±0.001 kPa).

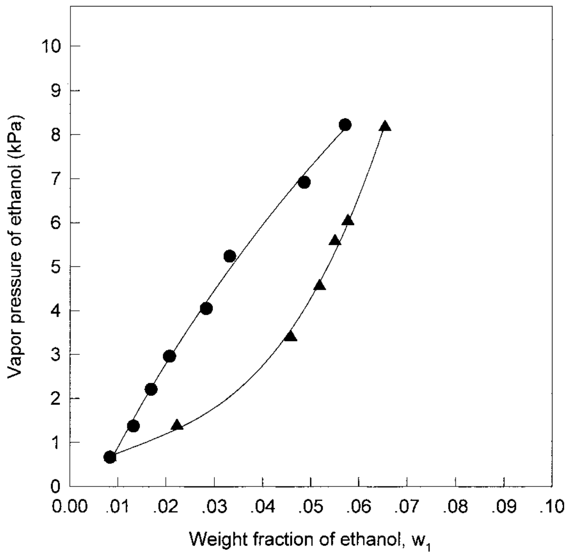

Figure 2. Hysteresis example of absorption−desorption behavior of ethanol + polycarbonate system: (●) sorption data measured in this work; (▲) desorption data measured in this work.

systems are hexane + PDMS, pentane + PDMS, methanol + PPO, water + PVA, water + PAA, ethanol + PAA, pentane + PC, water + PC, and ethanol + PC. These raw data are summarized in Table 1.

For the hexane + PDMS (M_n, 26 000) system, existing data (Kim et al., 1998; Ashworth et al., 1984; Sugamiya et al., 1974) are reported for only a limited weight fraction range of solvent. Ashworth et al. (1984) used a gravimetric sorption method, and data were measured over limited weight fraction of hexane (0.1). Also, Sugamiya et al. (1974) used an osmotic pressure method and reported data up to the weight fraction of hexane (0.5). Thus, in the present work, sorption data were measured over the entire range of the weight fraction of hexane. Flory and Shih (1972) and Chahal et al. (1973) provided a comprehensive analysis of the thermodynamic properties of the PDMS mixture.

For the methanol + PPO (M_n, 2 000) system, PPO is in the liquid state. Lakhpanol and Conway (1960) reported similar data over a wide weight fraction range of methanol by vapor pressure measurement. However, it is generally pointed out that this method is not accurate in a high concentration of solvent (i.e., above 0.5 weight fraction of solvent).

For the water + PAA and ethanol + PAA systems, we found that ethanol tends to be sparingly sorbed into PAA while water is easily sorbed into PAA. According to Allan (1995), when a polymer material that bonded by carboxyl group (−COOH) is to dissolve into water, the carboxyl group tends to dissociate into carboxylate ion (−COO−) and this carboxylate ion forms hydrogen bonding with water. This is one of reasons why water is sorbed much better in PAA than ethanol. In addition, though water and ethanol have the same hydroxy group (−OH), in the case of ethanol, it has relatively large ethyl group (C_2H_5-), which may cause steric effect, and this difference resulted in the different sorption characteristics.

Perhaps because polycarbonate is a substance with a strong kinetic barrier, no experimental sorption data with solvents are reported to date in the literature. Existing vapor liquid equilibria measurements of polycarbonate were limited to the solvent that has strong solvating power such as toluene and dichlorobenzene and, these data were obtained by IGC (inverse gas chromatography) (Ward et al., 1981). Thus in the present work, measurements of sorption equilibria of pentane, water, and ethanol with polycarbonate were carried out. We found that most of the solvents tend to be very sparingly sorbed into polycarbonate. To figure out whether these sorption characteristics are due to simple surface adsorption rather than absorption into the micropores of polycarbonate, an experimental hysteresis measurements with water, ethanol, and pentane was carried out. One hysteresis example of absorption−desorption behavior of ethanol + polycarbonate system is shown in Figure 2. The different absorption and desorption curves tell us that the absorption of solvent into polycarbonate is not a simple surface adsorption.

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