MEASUREMENT AND PREDICTION OF SOLUBILITIES OF ETHYLBENZENE VAPOR IN STYRENE-BUTADIENE RUBBERS

YOSHIO IWAI, SHINJI MIYAMOTO, KATSUYUKI NAKANO AND YASUHIKO ARAI

Department of Chemical Engineering, Kyushu University, Fukuoka 812

Key Words: Phase Equilibrium, Solubility, Ethylbenzene, Styrene-Butadiene Rubber, UNIFAC FV Model, Absorption

Introduction

In the polymer industry, separation equipment is required to separate unreacted monomers and solvents from the polymers produced. To design such equipment, the solubilities of hydrocarbon vapors in molten polymers are needed as fundamental data. As reported in a previous paper[2], the authors measured the solubilities of hydrocarbon vapors in polystyrene and polybutadiene by sorption apparatus with a quartz spring. A UNIFAC-FV model was applied to predict the activities of solutes in polymer solutions. In the present work, the solubilities of ethylbenzene in styrene-butadiene rubbers (SBR) have been measured by the same apparatus at 100 and 130 °C. No previous measurements for these systems at finite concentration are known. Three kinds of SBR were used. The concentrations of styrene in SBR were 30, 45 and 77 mass% for each polymer. To show the applicability of the UNIFAC-FV model proposed previously[2], the model was used to predict the solubilities of ethylbenzene vapor in SBR.

1. Experimental

1.1 Materials

SBR of 30 and 45 mass% styrene, represented as SBR (30) and SBR (45), was obtained from Scientific Polymer Products, Inc. and SBR (77) was obtained from Denki Kagaku Industry, Inc. The weight-average molecular weights of SBR (30), SBR (45) and SBR (77) measured by GPC are 1.4×10^5 ($M_w/M_n=1.3$), 6.0×10^5 ($M_w/M_n=4.6$) and 2.0×10^5 ($M_w/M_n=1.7$), respectively.

Ethylbenzene used was reagent grade obtained from Nakarai Chemical, Ltd. and was used for the present experiments without further purification. The purity is believed to be more than 98%.

1.2 Apparatus

The solubilities of ethylbenzene vapor in SBR were measured by a sorption apparatus with a quartz spring at 100 and 130°C. Details of the experimental procedure have been reported in previous papers[2,3]. In brief, a film of SBR coated on a thin aluminum plate was suspended by a sensitive quartz spring in an evacuated glass column. Ethylbenzene vapor was supplied into the column from a flask. During the sorption experiment, ethylbenzene liquid in the flask was maintained at a constant temperature lower than that of the column (equilibrium temperature) to generate constant-pressure vapor. The increase in mass of the film due to sorption of vapor was measured as a function of time by observing the extension of the spring through a cathetometer. When the film reached equilibrium with the surrounding vapor, i.e., no extension of the spring was observed, the solubility of ethylbenzene in SBR could be determined by the mass difference between initial and equilibrium conditions. The vapor pressure of ethylbenzene supplied from the flask was given from the Antoine equation shown in the literature[4] by measuring the temperature inside the flask.

1.3 Results

Tables 1 to **3** show the solubilities thus obtained for ethylbenzene in SBR. From their reproducibility, the accuracy of the present solubility data is believed to be within 3%.

2. Prediction

2.1 UNIFAC-FV model

It is very useful to be able to estimate the solubility of hydrocarbon vapor in polymer by a predictive method, without any information about the mixture. In the previous paper[2], the authors applied a UNIFAC-FV model to predict the activities of solutes in polymer solutions. In this work, the same model is used. Details of the model and calculation procedure were shown previously.[2] In brief, the UNIFAC-FV model is given as

$$\ln a_1=\ln a_1^{C}+\ln a_1^{R}+\ln a_1^{FV} \qquad (1)$$

* Received November 29, 1989. Correspondence concening this artivcle should be addressed to Y. Iwai.

Table 1. Solubilities of ethylbenzene vapor in SBR (30)

100°C		130°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0296	3.87	0.0248	7.93
0.0472	5.83	0.0308	9.73
0.0760	8.79	0.0357	11.1
0.0902	10.0	0.0418	12.3
0.0978	10.7	0.0467	13.8
0.124	13.0	0.0491	14.7
0.145	14.8	0.0591	17.1
0.164	16.1	0.0632	18.2
0.187	17.8	0.0730	20.4
		0.0804	22.2
		0.0855	23.5
		0.0945	25.6
		0.0958	25.7
		0.105	27.9
		0.114	29.6
		0.130	33.0
		0.140	34.8
		0.149	37.1
		0.166	39.7

Table 2. Solubilities of ethylbenzene vapor in SBR (45)

100°C		130°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0283	4.00	0.0209	7.14
0.0411	5.42	0.0262	8.79
0.0548	6.92	0.0277	9.45
0.0552	6.89	0.0361	11.4
0.0752	9.10	0.0413	12.6
0.0888	10.0	0.0441	13.8
0.0978	11.1	0.0461	14.3
0.117	12.6	0.0506	15.7
0.161	16.1	0.0593	18.1
0.162	16.1	0.0667	19.7
		0.0668	20.5
		0.0692	20.4
		0.0759	22.0
		0.0771	22.2
		0.0890	25.6
		0.0919	26.5
		0.0964	27.1
		0.108	29.6
		0.115	31.3
		0.121	32.0
		0.155	38.7

where a_1^C, a_1^R and a_1^{FV} are respectively the combinatorial, residual and free-volume terms of the activity of solute. The temperature-dependent coordination number and the interaction parameters given by Skjold-Jørgensen *et al.*[5] are adopted and other parameters are adopted from the original UNIFAC[1] in the combinatorial and residual terms. The free-volume term is given as

$$\ln a_1^{FV} = C_1\left[\ln\frac{\tilde{v}_{f,1}}{\tilde{v}_{f,M}} + \frac{\tilde{v}_1^{5.66}}{(\tilde{v}_1-1)^4\exp(0.3\tilde{v}_1)} \times \frac{1}{(1.66-0.3\tilde{v}_1)}\left\{\frac{\exp(0.3\tilde{v}_1)}{\tilde{v}_1^{1.66}} - \frac{\exp(0.3\tilde{v}_M)}{\tilde{v}_M^{1.66}}\right\}\right] \quad (2)$$

where

$$\tilde{v}_f = (\tilde{v}-1)\exp\left\{-\frac{18(\tilde{v}-1)^2+9(\tilde{v}-1)+2}{6(\tilde{v}-1)^3}\right\} \quad (3)$$

$$\tilde{v}_1 = v_1/v_1^* \quad (4)$$

$$\tilde{v}_M = \frac{v_1w_1+v_2w_2}{v_1^*w_1+v_2^*w_2} \quad (5)$$

where C_1 is the one-third external degree of freedom for solute, v is the specific volume, v^* is the specific hard-core volume, and subscript M denotes the property of mixture. The values of the parameters in the free-volume term were given previously[2].

Table 3. Solubilities of ethylbenzene vapor in SBR (77)

100°C		130°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0220	3.85	0.0256	10.0
0.0307	4.85	0.0315	11.8
0.0386	5.81	0.0428	14.7
0.0480	7.17	0.0539	18.2
0.0681	9.10	0.0598	20.0
0.0734	9.69	0.0642	21.0
0.0860	11.1	0.0646	21.6
0.102	12.6	0.0768	24.3
0.119	14.7	0.0787	25.0
0.131	15.2	0.0974	29.6
0.154	17.1	0.0996	30.4
0.160	17.6	0.106	32.1
		0.122	35.0
		0.144	40.8

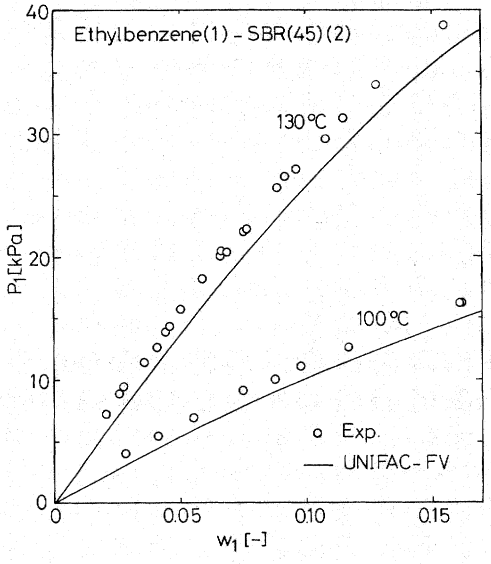

Fig. 1. Solubilities of ethylbenzene vapor in SBR (45)

2.2 Results

Figure 1 shows the solubilities of ethylbenzene

vapor in SBR (45). The calculated results by the UNIFAC-FV model are in good agreement with the experimental data. Almost the same results are obtained for the ethylbenzene-SBR (30) and ethylbenzene-SBR (77) systems.

Conclusion

The solubilities for ethylbenzene vapor in SBR were measured by a sorption apparatus with a quartz spring at 100 and 130°C.

It is shown that the UNIFAC-FV model is useful for predicting the solubilities of ethylbenzene in SBR.

Acknowledgement

We gratefully acknowledge the financial support provided by the Asahi Glass Foundation of Industrial Technology (1984, 1985).

Nomenclature

a	=	activity	[—]
C	=	one-third external degrees of freedom	[—]
M_n	=	number-average molecular weight	[—]
M_w	=	weight-average molecular weight	[—]
P	=	pressure	[Pa]
v	=	volume	$[m^3 \cdot kg^{-1}]$
v_f	=	free volume	$[m^3 \cdot kg^{-1}]$
v^*	=	hard-core volume per kg	$[m^3 \cdot kg^{-1}]$
w	=	mass fraction	[—]

〈Subscripts〉

M	=	mixture property
1	=	solute (ethylbenzene)
2	=	polymer (SBR)

〈Superscripts〉

C	=	combinatorial term
FV	=	free volume term
R	=	residual term
~	=	reduced property

Literature Cited

1) Fredenslund, Aa., J. Gmehling, M. L. Michelsen, P. Rasmussen and J. M. Prausnitz: *Ind. Eng. Chem., Process Des. Dev.*, **16**, 450 (1977).
2) Iwai, Y. and Y. Arai: *J. Chem. Eng. Japan*, **22**, 155 (1989).
3) Iwai, Y., M. Kohno, T. Akiyama and Y. Arai: *Rep. Asahi Glass Found. Ind. Technol.*, **48**, 71 (1986).
4) "Kagaku Binran II", Maruzen, Tokyo (1965).
5) Skjold-Jørgensen, S., P. Rasmussen and Aa. Fredenslund: *Chem. Eng. Sci.*, **35**, 2389 (1980).