Vapour–Liquid Equilibria in the Polystyrene + Toluene System at Higher Concentrations of Solvent

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Vapour–liquid equilibria (VLE) were determined in the polystyrene + toluene system under isothermal conditions at 363.15, 373.15, and 383.15 K using an improved all-glass microebulliometer with circulation of the liquid phase for the dynamic measurement of total pressure over liquid mixtures. The experimental data were correlated using the UNIQUAC-free volume model and the applicability of three known predictive models was tested. It was found that prediction of VLE using the GC-Flory equation of state, the UNIFAC-vdw-FV and the Entropic-FV model are of the same quality.

Key words:
vapour–liquid equilibrium, polymer–solvent system, ebulliometer, experimental data, correlation

Introduction

This paper represents a continuation of the series concerning experimental determination of vapour–liquid equilibria (VLE) in diluted polymer + solvent systems. In the previous papers we dealt with the polymeric flow improvers + toluene, hexane, chloroform[1,2], poly(acrylic acid) + water[3], poly(methyl methacrylate) + acetone[3], and poly(methyl methacrylate) + 2-butanone[4] systems. The aim of this study is to provide new – and always welcome – experimental data on vapour–liquid equilibria (VLE) in the polystyrene (PS) + toluene system, determined under isothermal conditions at 363.15, 373.15, and 383.15 K using ebulliometric techniques infrequently exploited for the investigation of polymer solutions. Moreover, the three prediction models were tested against the new experimental data.

Experimental equipment and procedure

Experimental techniques are summarised and discussed in[5]. In our earlier study[1], we designed a micro-ebulliometer for the quick measurement of the total pressure of systems containing a solvent and a polymer or a non-volatile component, for which only a little amount of material is required. Detailed testing and a discussion about the error caused by a little hold-up of solvent in the vapour phase part of the equilibrium still was published in[1].

For this study, we exploited the improved original ebulliometer, which with simplified construction makes operation not only easier but more reliable. This ebulliometer was described in details recently[4]. The improved ebulliometer makes it possible to measure VLE with only a small amount of polymer available; 10 mL of liquid phase is required. As discussed in[2], the experimental uncertainty u in the composition and pressure are estimated as $u(w)$ = 0.0001, and $u(P)$ = 0.001 kPa, respectively.

Results and data processing

The quality and the source of the individual compounds are summarized in Table 1. Table 2 presents the experimental vapour pressure data expressed in terms of toluene activity, $a_1 = P_1/P_1^{o}$, in dependence on weight fraction of solvent w_1, where P_1 is partial pressure and P_1^{o} is vapour pressure of pure solvent. For illustration, the experimental data are plotted in Figure 1.

The obtained experimental data were correlated using the UNIQUAC-FV model[6], which includes the three contributions: combinatorial, residual, and free-volume. The first two contributions are identical to the original UNIQUAC model described in the DECHEMA Data Collection[5]. The free–volume contribution, which enables better description of polymer–solvent system, is calculated by means of the Flory expression[6]. The complete procedure is described in[4].

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Table 1 – *Description of compounds*

Compound	CAS No.	Denotation	Source	Specification
Polystyrene	9003-53-6	PS	Acros Organics	$M_w = 250000$ g mol^{-1} $M_w/M_n = 1.2$
Toluene, puriss. p. a.	108-88-3		Fluka AG	purity >99.5 %

Table 2 – *Total pressure P and toluene activity a_1 versus weight fraction w_1 in the toluene (1) + PS (2) system*

w_1	P (kPa)	a_1
T = 363.15 K; P_1^o = 54.379 kPa		
1.0000	54.379	1.0000
0.9910	54.374	0.9999
0.9742	54.358	0.9996
0.9620	54.344	0.9993
0.9465	54.324	0.9990
0.9371	54.311	0.9988
0.9252	54.295	0.9984
T = 373.15 K; P_1^o = 74.313 kPa		
1.0000	74.313	1.0000
0.9910	74.301	0.9998
0.9742	74.274	0.9995
0.9620	74.254	0.9992
0.9465	74.223	0.9988
0.9371	74.206	0.9986
0.9252	74.183	0.9982
T = 383.15 K; P_1^o = 99.748 kPa		
1.0000	99.748	1.0000
0.9910	99.726	0.9998
0.9742	99.681	0.9993
0.9620	99.652	0.9990
0.9465	99.609	0.9986
0.9371	99.584	0.9984
0.9252	99.552	0.9980

Standard uncertainties u are $u(w)$ = 0.0001, $u(P)$ = 0.001 kPa

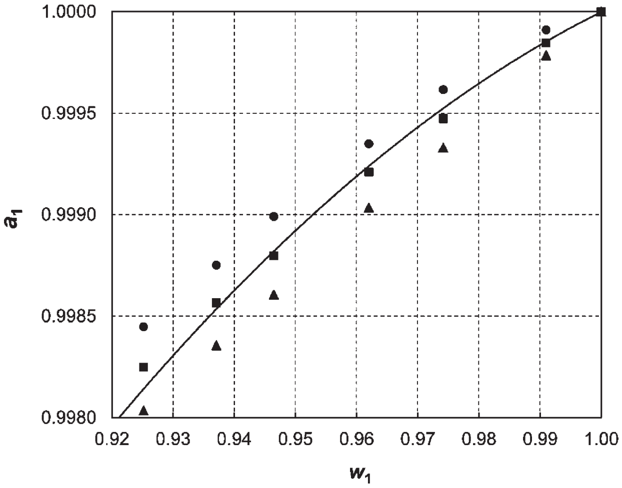

Fig. 1 – *Activity a_1 of toluene in PS as a function of toluene weight fraction w_1. Experimental data at (●) 363.15 K, (■) 373.15 K and (▲) 383.15 K. Solid line represents predicted activities at 373.15 K using the UNIQUAC-FV parameters estimated using all data within temperature range 363.15–383.15 K.*

The calculation method requires as input data the densities of the solvent and of the polymer at the temperature of polymer solution, molecular weight of the repeating unit of component *i*, van der Waals volume parameters and the surface area parameters of the repeating unit of component *i*. The densities are estimated using the DIPPR data bank[7] for the solvent and the Tait equation parameters obtained by Rodgers[8] for polymer. The van der Waals volumes and the surface area parameters of the repeating units are calculated using the group contributions values by Bondi[9], but normalized using the volume and external area of the CH_2 unit in the polyethylene[5].

Table 3 – *A_{12} and A_{21} interaction parameters in the UNIQUAC-FV model for the toluene (1) + PS (2) system*

Type of calculation	T (K)	No. of data points	A_{12} (K)	A_{21} (K)	Δa
Estimation	363.15 – 383.15	21	84.79	–64.34	0.0002
Prediction	363.15	7			0.0002
Prediction	373.15	7			0.0002
Prediction	383.15	7			0.0003

Δa = average absolute deviation in calculated activity

The UNIQUAC-FV energy parameters A_{12} and A_{21} have been estimated by minimizing differences between experimental and calculated activities. In Table 3 are presented the estimated values within the temperature range 363.15–383.15 K together with average absolute deviation in calculated activity. Additionally, these parameters were used to predict activities at the three particular isotherms and corresponding average absolute deviations in activities are summarised in Table 3, too. It can be seen that activities are well predicted; therefore, we can conclude that parameters are practically temperature independent. Figure 1 additionally illustrates successful prediction of data at 373.15 K with the UNIQUAC-FV model.

Note that the simple sorption method, often referred to as total pressure measurement, usually provides data only from the concentration range with a lower solvent content. Such type of data for the PS + toluene system are available in literature[4,10–12] but the dynamic total pressure method for boiling point measurement used in this work can provide data at high solvent concentrations. For further analyses of the obtained data, our data (M_w = 250000 g mol^{-1}) were compared with the experimental data[10] (M_w = 275000 g mol^{-1}) determined at 383.15 K as illustrated in Figure 2. It is obvious that data are well complementing each other.

We opted also for the prediction of phase behaviour using group-contribution predictive models developed earlier: the GC-Flory EoS model[13] the UNIFAC-vdw-FV model[14], and the Entropic-FV model[15]. These models were used to predict the activities of toluene in mixtures with PS, because input values for all necessary group parameters for the models have already been published. Models are described in detail in[13–15], where necessary equations, calculation procedure, and parameters are presented.

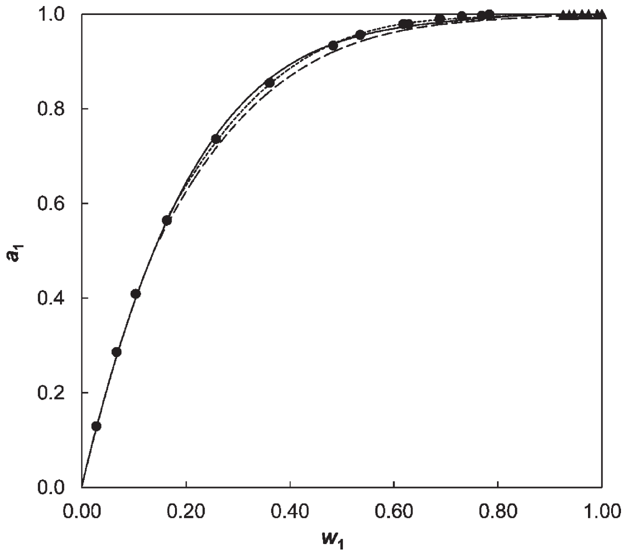

Fig. 2 – *Activity a_1 of toluene in PS as a function of toluene weight fraction w_1. Experimental data at 383.15 K: (▲) this work; (●)[10], M_w = 275000 g mol^{-1}. Prediction of activities: ——— GC-Flory EoS model; - - - - - - UNIFAC-vdw-FV model; – – – Entropic FV model.*

The reliability of all mentioned models is illustrated in Figure 2 for 383.15 K. It can be seen that the predictions of activity versus concentration using the GC-Flory EoS, the UNIFAC-vdw-FV, and the Entropic-FV models are almost of the same quality. It is obvious that the models are mutually comparable and in good agreement. It should be pointed out that prediction procedures were used not for validation of the experimental data but rather to give an idea of the trend of activity as a function of concentration.

Conclusions

Total pressures over the PS + toluene system were determined ebulliometrically at three isotherms in the region of diluted concentrations of polymer and expressed in terms of solvent activity. These data complete existing literature data and were successfully correlated using the UNIQUAC-FV model. Three known predictive models were tested against the obtained experimental data to see how applicable they may be for practical use. It was found that all three models can be used for prediction of VLE in the studied system.

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List of symbols

a_i – activity of component i
A_{ij} – UNIQUAC parameter for interaction $i - j$, K
i, j – component
M_n – number average molecular weight, g mol^{-1}
M_w – weight average molecular weight, g mol^{-1}
P – total pressure, kPa
P_i – pressure of component i, kPa
P^o – vapour pressure of pure solvent, kPa
T – temperature, K
u – uncertainty of measurements
w_i – weight fraction of component i

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Erratum

“Vapour–Liquid Equilibria in the Polystyrene + Toluene System at Higher Concentrations of Solvent” by J. Pavlíček, G. Bogdanić, and I. Wichterle, published in Chemical and Biochemical Engineering Quarterly, **29** (1), 1–4 (2015),

there are wrongly printed dimensions of interaction parameters A_{12} and A_{21}. Correct dimensions are (cal mol^{-1}) instead of (K) in both the Tables 3 and Lists of symbols.

The authors and publisher apologize for these errors.