J. PAVLÍČEK et al., Vapour–Liquid Equilibria in the Poly(methyl methacrylate) +…, *Chem. Biochem. Eng. Q.*, **28** (4) 447–450 (2014)

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Vapour–Liquid Equilibria in the Poly(methyl methacrylate) + + 2-Butanone System Containing Lower Concentrations of Solute at Normal or Reduced Pressures

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Dedicated to Professor Egon Bauman on his 90th birthday

Vapour–liquid equilibria (VLE) were determined in the poly(methyl methacrylate) + 2-butanone system under isothermal conditions at 333.15, 343.15, and 353.15 K using an improved all-glass micro-ebulliometer with circulation of the liquid phase for the dynamic measurement of total pressure over liquid mixtures. The experimental data were correlated using the UNIQUAC-FV model and the applicability of three known predictive models was tested. It was found that only the UNIFAC-vdw-FV model gives excellent prediction of VLE for the studied system.

Key words:

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

Introduction

Many industrial processes face a variety of issues related to the thermodynamics of polymer solutions. To evaluate the thermodynamic properties of industrial systems we need experimental data, which are often missing. Alternatively, we can resort to models based on the structure–property relationship to estimate and/or predict the thermodynamic properties, or phase equilibria in particular.

The aim of this study was to provide new – and always welcome – experimental data on vapour-liquid equilibria (VLE) in the poly(methyl methacrylate) [PMMA] + 2-butanone (methyl ethyl ketone) system, determined under isothermal conditions at 333.15, 343.15, and 353.15 K using techniques infrequently exploited for the investigation of polymer solutions. Additionally, three group contribution prediction models developed earlier were tested against the obtained experimental data to see how applicable they may be for practical use.

Experimental equipment and procedure

Experimental techniques are summarised and discussed in[1]. In our earlier study[2], 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 the same paper. It was also concluded that the accuracy given in 4 digits in composition was reliable.

For this study however, we improved the original ebulliometer inasmuch as we not only simplified the construction to make operation easier, but also to make it more reliable. The improved ebulliometer is shown in Figure 1. The boiler is now
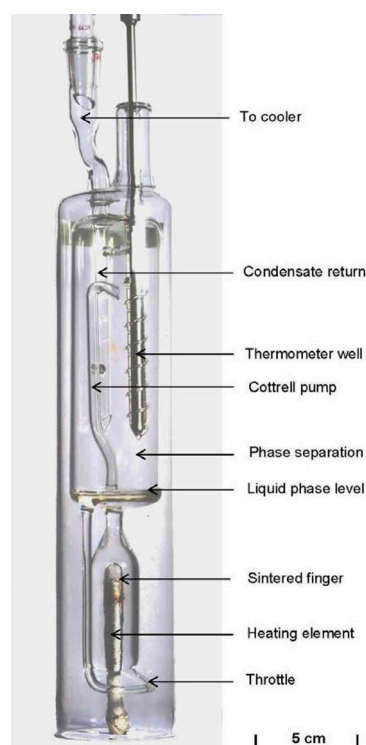

F i g. 1 – *Modified ebulliometer*

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Ta b l e 1 – *Description of compounds*

Compound	CAS No.	Denotation	Source	Specification
Poly(methyl methacrylate)	9011-14-7	PMMA	Acros Organics	M_w = 15 000 g mol^{-1}; M_w/M_n = 1.18
2-Butanone, ACS reagent	78-93-3		Sigma-Aldrich	purity >99.0 %

broader in order to minimise the possibility of caking of the polymer on the boiler finger. The separator of the vapour and liquid phases has been removed, because separation occurs in the whole volume around the thermometer well.

With the improved device, equilibrium data can be collected with only a small amount of polymer available. The experimental uncertainty u in the composition and pressure are estimated as $u(w) = 0.0001$, and $u(P) = 0.001$ kPa, respectively, as discussed in[3].

Results and data processing

Table 1 shows the quality and the source of the compounds. The PMMA + 2-butanone system was studied at three isotherms: 333.15, 343.15, and 353.15 K. Table 2 summarises the vapour pressure data expressed in terms of 2-butanone activity, $a_1 = P_1/P_1^\circ$, where P_1 is partial pressure and P_1° is vapour pressure of pure solvent.

The obtained experimental data were correlated using the UNIQUAC-FV model[4], which includes a contribution for free–volume differences between polymer and solvent molecules, what enables better description of polymer–solvent system. The expression for the activity of a solvent, i, in a polymer is used:

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

where a_i is the activity of solvent i at solution temperature T, a_i^C is the combinatorial contribution to the activity providing the contributions due to differences in molecular size, and a_i^R is the residual contribution, providing contributions due to molecular interactions to the activity. Both contributions are identical to the original UNIQUAC model described in the DECHEMA Data Collection[1]. The free–volume contribution to the activity, a_i^{FV}, is calculated by means of the Flory expression:

$$\ln a_i^{FV} = 3c_i \ln\left[\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}_M^{1/3}-1}\right] - c_i\left[\left(\frac{\tilde{v}_i}{\tilde{v}_M}-1\right)\left(1-\frac{1}{\tilde{v}_i^{1/3}}\right)^{-1}\right] \quad (2)$$

where c_i denotes an external degree of freedom parameter, $\tilde{v}_i$ is the reduced volume of component i, and $\tilde{v}_M$ is the reduced volume of mixture. Despite the fact that the values of c_i could be discussed[5] or

Ta b l e 2 – *Total pressure P and 2-butanone activity a_1 versus mass fraction w_1 in the 2-butanone (1) + PMMA (2) system*

w_1	P (kPa)	a_1
T = 333.15 K; P_1° = 52.07 kPa		
1.0000	52.070	1.0000
0.9524	52.050	0.9996
0.8998	51.997	0.9986
0.8471	51.920	0.9971
0.7995	51.840	0.9956
0.7497	51.706	0.9930
0.6993	51.500	0.9891
T = 343.15 K; P_1° = 74.087 kPa		
1.0000	74.087	1
0.9524	74.042	0.9994
0.8998	73.953	0.9982
0.8471	73.842	0.9967
0.7995	73.716	0.9950
0.7497	73.509	0.9922
0.6993	73.190	0.9879
T = 353.15 K; P_1° = 102.96 kPa		
1.0000	102.967	1
0.9524	102.895	0.9993
0.8998	102.750	0.9979
0.8471	102.586	0.9963
0.7995	102.380	0.9943
0.7497	102.081	0.9914
0.6993	101.618	0.9869

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

taken as adjustable parameters, in this paper $c_i = 1.1$ is considered.

The calculation procedure requires 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[6] for the

T a b l e   3 – A_{12} and A_{21} interaction parameters in the UNI-QUAC-FV model for the 2-butanone (1) + PMMA (2) system

Calculation procedure	T [K]	No. of data points	A_{12} [K]	A_{21} [K]	Δa
Estimation	333.15–353.15	21	–206.65	513.48	0.0005
Prediction	333.15	7			0.0005
Prediction	343.15	7			0.0003
Prediction	353.15	7			0.0007

Δa = average absolute deviation in calculated activity

solvent and the Tait equation parameters obtained by Rodgers[7] 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[8], but normalized using the volume and external area of the CH_2 unit in the polyethylene[1].

The UNIQUAC-FV interaction parameters A_{12} and A_{21} have been estimated from the experimental solvent activity data by minimizing the following objective function:

$$O.F. = \frac{1}{n} \sum_{k=1}^{n} \frac{\left| a_{1k}^{calc} - a_{1k}^{exp} \right|}{a_{1k}^{exp}},$$

where n is the number of data points, a_1^{exp} and a_1^{calc} are the experimental and calculated solvent activities, respectively. Table 3 shows the estimated set of A_{12} and A_{21} interaction parameters in the UNIQUAC-FV model for the temperature range 333.15–353.15 K together with average absolute deviations in calcu-
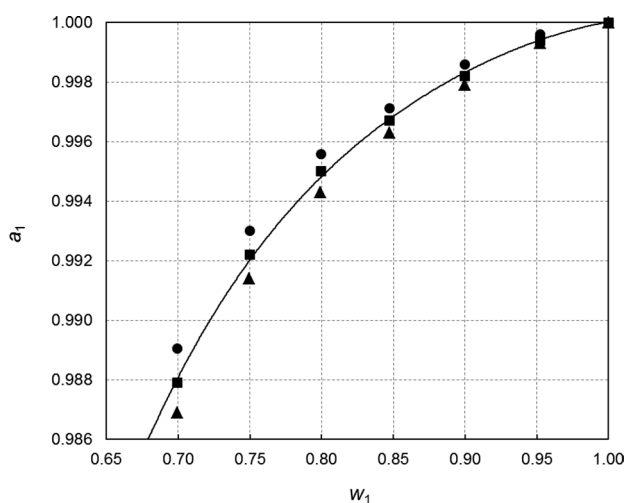
lated activities. These parameters were used to predict activities at the three particular isotherms. The average absolute deviations in predicted activities are also summarised in Table 3. It can be seen that activities are well predicted using the estimated set of interaction parameters A_{12} and A_{21}, and therefore it can be concluded that parameters are practically temperature independent. Figure 2 additionally illustrates successful prediction of data at 343.15 K using 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 PMMA + 2-butanone system are available in literature[9–11] 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, we opted for the prediction of phase behaviour using group-contribution predictive models developed earlier: the Entropic-FV model[12], the GC-Flory EOS model[13], and the UNIFAC-vdw-FV model[14]. These were used to predict the activities of 2-butanone in mixtures with PMMA, because values for all necessary group parameters for all models have already been published. Models are described in detail in[12–14], where necessary equations, calculation procedure, and parameters are presented.

It was found that the Entropic-FV model overestimates while the GC-Flory EOS model underestimates experimental data; only the UNIFAC-vdw-FV gives excellent prediction of the concentration vs. activity dependence. The reliability of the UNIFAC-vdw-FV model is illustrated in Figure 3 for 343.15 K.
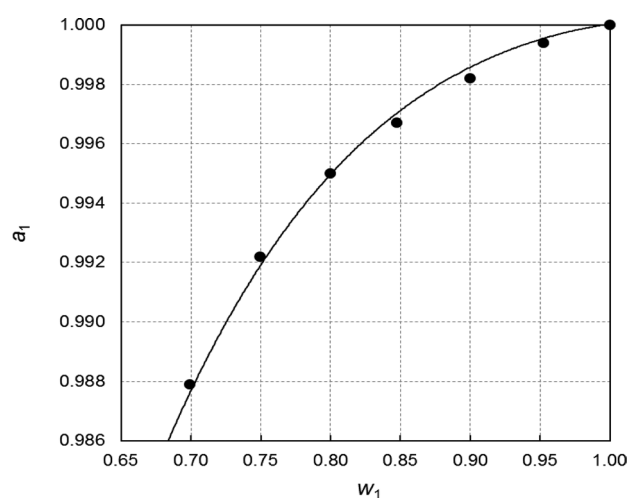

F i g . 2 – *Activity a_1 of 2-butanone in PMMA as a function of 2-butanone mass fraction w_1. Experimental data at (●) 333.15 K, (■) 343.15 K and (▲) 353.15 K. Solid line represents predicted activities at 343.15 K using the UNIQUAC-FV parameters estimated using all data within temperature range 333.15–353.15 K.*

F i g . 3 – *Activity a1 of 2-butanone in PMMA as a function of 2-butanone mass fraction w_1. Experimental data at (●) 343.15 K. Solid line represents predicted activities at 343.15 K using the UNIFAC-vdw-FV model.*

Conclusions

Total pressures over the PMMA + 2-butanone system were determined ebulliometrically in a modified still at three isotherms in the region of diluted concentrations of polymer and expressed in terms of activity. The data obtained 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 only the UNIFAC-vdw-FV model gives excellent prediction of VLE for the studied system.

List of symbols

a_i – activity of component i

a_i^C – combinatorial contribution to the activity providing the contributions due to differences in molecular size

a_i^R – residual contribution, providing contributions due to molecular interactions

a_i^{FV} – free–volume contribution to the activity

c_i – external degree of freedom parameter

A_{ij} – UNIQUAC parameter for interaction $i-j$, K

$calc$ – calculated

exp – experimental

i, j – component

M_n – number average molar mass, g mol^{-1}

M_w – weight average molar mass, g mol^{-1}

n – number of experimental points

n_i^{rep} – number of repeating units of component i

$O.F.$ – objective function

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

Δa – average absolute deviation in activity

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Erratum

"Vapour–Liquid Equilibria in the Poly(methyl methacrylate) + 2-Butanone System Containing Lower Concentrations of Solute at Normal or Reduced Pressures" by J. Pavlíček, G. Bogdanić, and I. Wichterle, published in Chemical and Biochemical Engineering Quarterly, **28** (4), 447–450 (2014),

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.