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Vapor–liquid equilibrium of polymer + solvent systems: Experimental data and thermodynamic modeling

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Abstract

In this work, experimental vapor–liquid equilibrium (VLE) data for binary systems polymer + solvent were obtained using a gravimetric sorption apparatus. The studied systems were benzene + polystyrene, hexane + polystyrene, benzene + poly(methyl methacrylate), benzene + poly(ethyl methacrylate), hexane + poly(vinyl chlorate) and water + poly(vinyl chlorate), in the range of 30–40 °C.

The experimental data were modeled with two group contribution models for the activity coefficient, Elbro-FV and UNIFAC-Zhong; the latter method considers the free-volume of molecules of high molecular weight, such as polymers. UNIFAC groups in the literature as well as new groups that were proposed for the monomers were used. The necessary energy interaction parameters between these groups were estimated. There were observed mean deviations between experimental and calculated mass fractions of about 8.5% with Elbro-FV, and about 17% with UNIFAC-Zhong when original groups were used, while there were observed mean deviations of about 7% with Elbro-FV and about 16% with UNIFAC-Zhong when new groups were used. The Elbro-FV model represents the experimental data with better precision in both cases; on the other hand, the data were better correlated with both models when new groups were used.

Keywords: Polymers; Gravimetric sorption; Group contribution

1. Introduction

The knowledge of the vapor–liquid equilibrium (VLE) of polymeric solutions is of extreme importance for the development of products and processes in several industrial sectors such as, for example, surface acoustic-wave vapor sensors [1,2], optimum formulation of paints and coatings [3], properties of the water transport in of contact lenses [4], development and use of new materials, polymer devolatilization and other polymeric membrane-separation processes [5], recovery of organic vapors from waste-air streams using a polymeric membrane [6], fuel cells [7], vapor-phase photo-grafting [8] and pervaporation [9].

Polymers have enormous commercial interest because of their unique physical properties, such as mechanical and thermal resistance, flexibility, molecular structure, monomer ratio and distribution in the chain, morphology, glass transition temperature, rheology, crystallinity, molecular weight, etc. The production of polymers in world has been continuously rising over the last 20 years [10]. In the last few years there have been an increase in publications on the VLE for systems + solvent; however, the quantity of polymers studied is still small and more research must be made. Some papers have presented significant contributions to the field: the original method was proposed by Panayiotou and Vera [11], while several authors [12–25] further developed the method, with application to diverse polymeric systems.

In this work experimental VLE data were obtained for binary systems homopolymer + solvent using a gravimetric sorption apparatus. The experimental data were correlated with the Elbro-FV and Zhong group contribution models for the activity

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coefficient. Two approaches were used, one that uses UNIFAC functional groups already available from literature, and another that considers new functional groups for monomers.

2. Experimental

2.1. Procedure and experimental apparatus

Several experimental methods are available for measuring the vapor pressure of a solvent in a polymeric solution [26]. These include inverse gas chromatography, piezoelectric sorption, gravimetric sorption, light scattering and turbidimetry analysis. In this work a gravimetric sorption technique was used; this technique allows the determination of VLE data when the polymeric solution is very rich in polymer and very diluted in solvent.

The gravimetric sorption technique gives direct measurement of the VLE of polymer + solvent systems. This method was originally proposed by Panayiotou and Vera [11], and later improved by Prausnitz and co-workers [15–18,20,21,27] and Kim and co-workers [28,29]. Fig. 1 gives a schematic view of the apparatus.

A sample of known mass (25–50 mg) of copolymer is loaded on a clock glass, weighed and placed in an evacuated glass chamber, which is kept at constant temperature by using a Tecnal TE-184 thermostatic bath with precision of 0.1 °C. The vacuum is used to remove any trace moisture, oligomers or monomers present. After a period that can vary, in the case of the polymers of this work, between 10 and 36 h, the solvent is introduced in the glass chamber by quickly opening and closing the solvent valve. The system is allowed to equilibrate for several hours, in this case, between 12 and 16 h, and the pressure is read by a U-mercury manometer connected to the glass chamber. The pressure was measured with a precision of 0.01 mmHg. The sample is quickly withdrawn and weighed in order to determine the mass of solvent absorbed by the sample. The mass was measured using an Ohaus Explorer Pro analytical balance with a precision of 0.01 mg. Subsequent measures of pressure and new experimental points are obtained by increasing the amount of solvent in the chamber. All experiments are at pressures below 90% of the saturation vapor pressure to avoid solvent condensation in the system. Solvent weight fraction w_1 uncertainty is less than 1% and reliability of the apparatus and experimental procedure were established by reproducing published experimental vapor–liquid equilibrium data [15].

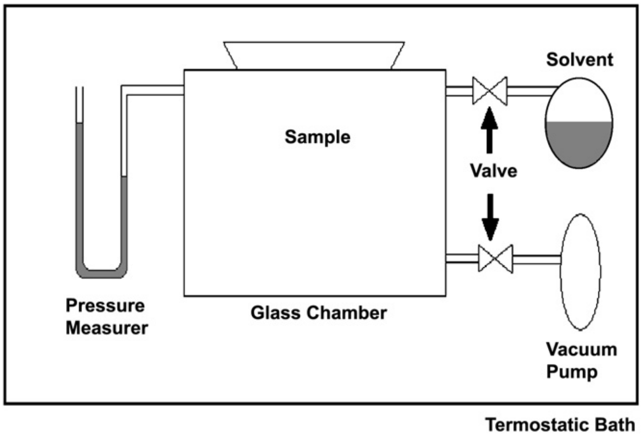

Fig. 1. Schematic view of the experimental apparatus.

2.2. Materials

The homopolymers and solvents used in this work are listed in Table 1. For the solvents used, the values of maximum saturation vapor pressure for the gravimetric sorption technique, calculated by the DIPPR vapor pressure equation, are shown in Table 2.

3. Experimental results

Table 3 and Figs. 3–5 show the experimental data of VLE for the binary systems homopolymers + solvents. These results are analyzed and commented in the Sections 5 and 6, together with the results of the thermodynamic modeling.

4. Thermodynamic models

4.1. Elbro-FV model

The Elbro-FV model [30], in contrast with the UNIFAC-FV model [31], does not include an additional term to account for the free-volume differences between solvents and polymers. In the Elbro-FV model, the combinatorial and free-volume effects are both included in a combinatorial-FV expression, similar to the Flory-Huggins one, where free-volume fractions are used instead of volume fractions:

$$\ln \gamma_i^{c-\mathrm{fv}} = 1 - \frac{\phi^{\mathrm{fv}}}{x_i} + \ln \frac{\phi^{\mathrm{fv}}}{x_i} \tag{1}$$

Table 1
Polymers and solvents

Reagents	PM (g/mol)	Supplier
Polystyrene (PS)	50,000	Polysciences
Polymethyl methacrylate (PMM)	125,000	
Polyethyl methacrylate (PME)	850,000	Aldrich
Polyvinyl chloride (PVC)	175,000	Scientific Polymer Products
Benzene	P.A.	Fluka
Hexane	P.A.	Sigma-Aldrich

Table 2
Maximum saturation vapor pressure for the reagents[a]

Reagents	Maximum vapor pressure (10^4) Pa			
	30 °C	40 °C	60 °C	70 °C
Water	0.38231	0.66477	–	–
Benzene	1.42677	2.18691	–	6.60204
Hexane	2.25684	3.37005	6.88716	9.48438

[a] DIPPR equation.

Table 3
VLE for homopolymer + solvent system (mass fraction)

P (kPa)	w_1	P (kPa)	w_1	P (kPa)	w_1
Benzene + polystyrene					
$T = 30$ °C					
1.1	0.020	5.7	0.051	9.6	0.085
1.7	0.027	6.3	0.055	10.8	0.093
2.1	0.031	7.1	0.060	11.5	0.096
3.7	0.040	8.2	0.073	12.9	0.104
4.0	0.042	8.6	0.079	14.2	0.111
5.3	0.050	9.1	0.081		
$T = 40$ °C					
11.6	0.050	15.3	0.100	21.3	0.183
12.9	0.063	18.7	0.137		
14.7	0.084	20.1	0.154		
Hexane + polystyrene					
$T = 30$ °C					
11.8	0.010	16.5	0.061	21.6	0.112
13.3	0.021	19.7	0.094	22.1	0.120
14.9	0.043	20.3	0.103		
$T = 40$ °C					
20.1	0.030	27.4	0.073	31.8	0.132
21.4	0.042	28.3	0.085		
23.2	0.057	30.1	0.101		
Benzene + poly(methyl metacrylate)					
$T = 30$ °C					
7.3	0.023	10.8	0.045	13.6	0.060
7.6	0.027	11.2	0.046	14.1	0.063
8.8	0.032	11.6	0.049		
10.1	0.041	12.9	0.057		
$T = 40$ °C					
12.9	0.020	17.3	0.037	20.5	0.061
15.4	0.031	18.1	0.043	21.3	0.070
Benzene + poly(ethyl metacrylate)					
$T = 30$ °C					
3.0	0.010	8.9	0.039	12.3	0.074
6.0	0.025	10.5	0.053	13.6	0.080
7.3	0.030	11.2	0.069		
$T = 40$ °C					
9.1	0.015	12.9	0.049	16.6	0.082
10.3	0.023	13.2	0.063	17.4	0.091
12.5	0.045	14.2	0.071	18.3	0.123
Hexane + poly(vinyl chloride)					
$T = 30$ °C					
18.0	0.008	20.3	0.029	22.1	0.057
18.5	0.012	20.8	0.033	22.5	0.060
19.1	0.019	21.2	0.045		
19.6	0.025	21.7	0.052		
Hexane + poly(vinyl chloride)					
$T = 40$ °C					
20.7	0.003	27.2	0.021	35.1	0.058
21.6	0.005	29.4	0.035	36.3	0.067
22.4	0.009	30.9	0.039		
25.1	0.013	32.3	0.042		
Water + poly(vinyl chloride)					
$T = 30$ °C					
1.7	0.001	2.6	0.012	3.7	0.032
2.1	0.003	2.8	0.016	3.8	0.040
2.2	0.007	3.1	0.023		
2.5	0.010	3.5	0.027		
$T = 40$ °C					
2.5	0.001	3.6	0.015	6.0	0.053
2.7	0.002	4.1	0.027	6.2	0.055
2.8	0.004	4.5	0.031		
3.0	0.008	5.3	0.045		

where ϕ^{fv} is the free-volume fraction:

$$\phi^{\mathrm{fv}} = \frac{x_i V_{\mathrm{f}i}}{\sum_j x_j V_{\mathrm{f}i}}. \tag{2}$$

The free-volume $V_{\mathrm{f}i}$, which is the volume inaccessible to other molecules, is expressed as:

$$V_{\mathrm{f}i} = V_i - V_{\mathrm{w}i} \tag{3}$$

where V_i is the volume of the component i and $V_{\mathrm{w}i}$ is the van der Waals volume as calculated by the method of Bondi [32]. The Elbro-FV model uses the classical UNIFAC residual term:

$$\ln \gamma_i^{\mathrm{res}} = \sum_k^{\mathrm{groups}} \nu_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \tag{4}$$

with the residual activity coefficient:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \tag{5}$$

where Q_k is the van der Waals group surface area [32] and Θ_m is the area fraction of group m, calculated as:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{6}$$

with X_m being the molar fraction of the group m in the compound:

$$X_m = \frac{\sum_i^M \nu_m^{(i)} x_i}{\sum_i^M \sum_j^N \nu_j^{(i)} x_i} \tag{7}$$

and Ψ_{mn} are the energy interaction parameters between the groups m and n:

$$\Psi_{mn} = \exp\left[-\frac{U_{mn} - U_{nn}}{RT} \right] = \exp\left(-\frac{a_{mn}}{RT} \right). \tag{8}$$

4.2. UNIFAC-Zhong model

The UNIFAC-Zhong model [33] introduced a modified van der Waals volume parameter value r for the polymer in the Flory-Huggins term of UNIFAC, which, according to the authors, is able to account for the free-volume effect, though no explicit free-volume term is involved.

For an n-mer chain molecule, the volume parameter was set equal to:

$$r(n) = 0.6583nr(1) \tag{9}$$

where $r(1)$ is the volume parameter for the monomer, given by

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{10}$$

where R_k is the van der Waals group volume [32]. Thus, the modified combinatorial term is given by:

$$\ln \gamma_i^c = \ln \frac{\phi_i'}{x_i} - \frac{\phi_i'}{x_i} + 1 - \frac{z q_i}{2}\left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i}\right] \tag{11}$$

where:

$$\phi_i' = \frac{x_1 r_1}{x_1 r_1 + x_2[0.6583nr(1)]} \tag{12a}$$

$$\phi_2' = \frac{x_2[0.6583nr(1)]}{x_1 r_1 + x_2[0.6583nr(1)]} \tag{12b}$$

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2[nr(1)]} \tag{13a}$$

$$\phi_2 = \frac{x_2[nr(1)]}{x_1 r_1 + x_2[nr(1)]}. \tag{13b}$$

The Zhong model also uses the classical UNIFAC residual term, Eqs. (4)–(8), with the temperature-independent interaction parameters proposed by Hansen et al. [34].

4.3. Parameters for the models

In both group contribution models, Elbro-FV and Zhong, there have been used both original UNIFAC functional groups [35] and new functional groups proposed in this work, which consider the monomer of a polymer as a single functional group. The new functional groups proposed in this work and their respective structural group volume and surface area parameters R and Q are shown in Table 4, while the original UNIFAC groups and their respective structural parameters R and Q are shown in Table 5. The structural parameters for the new groups were calculated according to Gmehling et al. [36] and Bondi [32]. The representation of the monomers that had been used as new UNIFAC groups for each polymer is shown in Fig. 2.

Table 4
New functional groups and their structural parameters

Polymer	Group	R	Q
PS	$C_6H_5HC_2H_3$	3.5228	3.6561
PMM	$C_3H_5COOCH_3$	3.1675	3.3975
PME	$C_4H_7COOCH_3$	3.8000	4.1056
PVC	CH_2CHCl	1.6244	1.7208

Table 5
Original functional groups and their structural parameters

Polymer	Group	R	Q
PS	ACCH	0.9100	0.3769
	CH_2	0.6325	0.7081
PMM	CH_2	0.6325	0.7081
	CH_3	0.6325	1.0608
	CH_3COO	1.2700	1.6286
	C	0.6325	0.0000
PME	CH_2	0.6325	0.7081
	CH_3	0.6325	1.0608
	CH_3COO	1.2700	1.6286
	C	0.6325	0.0000
	CH_2COO	1.2700	1.4228
PVC	CH_2	0.6325	0.7081
	CHCl	0.9919	1.0127

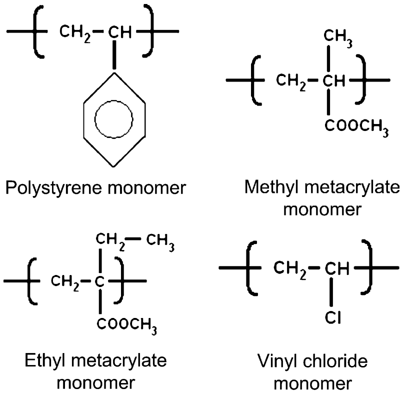

Fig. 2. Graphical representation of monomers of each polymer.

The procedure of parameters estimation is based on the Simplex method [37] and consists in minimization of the objective function below, following an algorithm developed by Stragevitch and d'Ávila [38]:

$$S = \sum_{k=1}^{d} \sum_{j=1}^{N_k} \left\{ \left(\frac{P_{jk} - P_{jk}^{\mathrm{m}}}{\sigma_{P_{jk}}}\right)^2 \left(\frac{T_{jk} - T_{jk}^{\mathrm{m}}}{\sigma_{T_{jk}}}\right)^2 + \sum_{i=1}^{C_k - 1}\left[\left(\frac{wl_{jk} - wl_{jk}^{\mathrm{m}}}{\sigma_{wl}}\right)^2 + \left(\frac{wv_{jk} - wl_{jk}^{\mathrm{m}}}{\sigma_{wv}}\right)^2\right]\right\} \tag{14}$$

where d is the number of data set, N_k and C_k are the number of data points and components in the data set k, σ_P, σ_T (fixed at 0.1 K) are the mean deviations in pressure and temperature, while σ_{wl} and σ_{wv} (fixed at 0.0005) are the mean deviations in the liquid and vapor equilibrium phase compositions (mass fraction), respectively, and the superscript 'm' stands for measured. The estimated energy interaction parameters for the new groups are presented in Table 6.

Table 6
Parameters of energy interaction for the new UNIFAC groups

	$C_6H_5C_2H_3$	$C_3H_5COOCH_3$	$C_4H_7COOCH_3$	C_2H_3Cl
CH_2	1621.8	–	–	938.30
	−274.00	–	–	−418.40
CH_3	293.70	–	–	1293.9
	−477.74	–	–	549.05
H_2O	–	–	–	−140.86
	–	–	–	678.65
ACH	−315.70	−292.94	−145.11	–
	2323.7	1447.7	562.63	–

The mean deviations in experimental compositions are given by:

$$\left(\sum \frac{w_{\text{calculated}} - w_{\text{experimental}}}{w_{\text{experimental}}}\right) \times 100. \qquad (15)$$

5. Results and discussion

The experimental results are presented in Figs. 3–5, which show the systems with each homopolymer. In this way, the effect of solvent and temperature can be observed on the behavior of the system. The predictions of the models Elbro-FV and Zhong are presented in Figs. 6–11. In this case, the data calculated by both models with original functional groups and with new groups are presented for each polymer separately. The deviations between calculated and experimental compositions are shown in Table 7.

In Fig. 3, it is observed that the best solvent for PS is benzene, whose absorption increases when the temperature increases from 30 °C to 40 °C. Hexane does not present an increase of absorption in PS when the temperature is raised. It can be observed that, in all the cases, the vapor pressure for

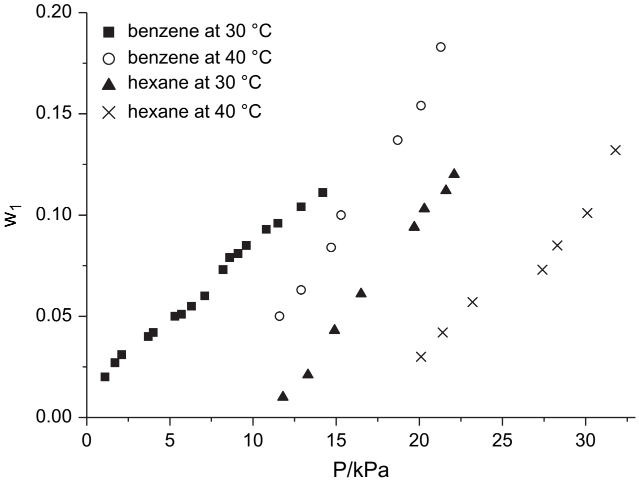

Fig. 3. Experimental data for the systems benzene + PS and hexane + PS.

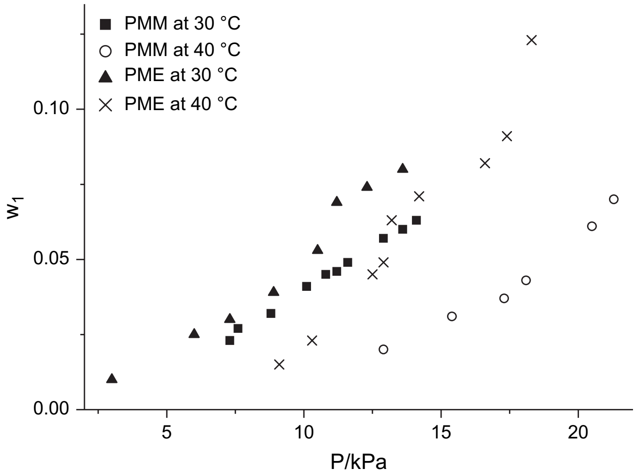

Fig. 4. Experimental data for the systems benzene + PMM and benzene + PME.

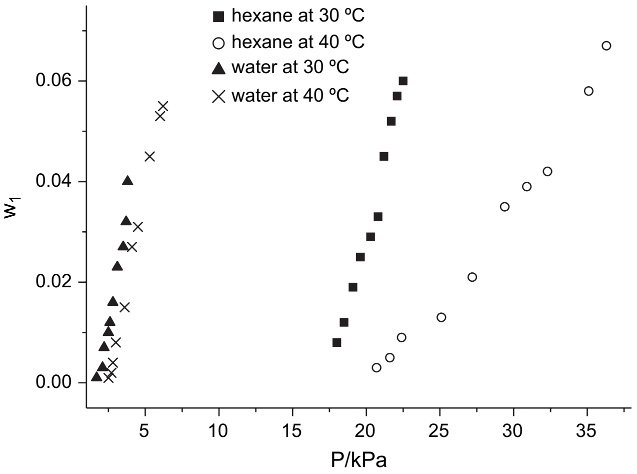

Fig. 5. Experimental data for the systems hexane + PVC and water + PVC.

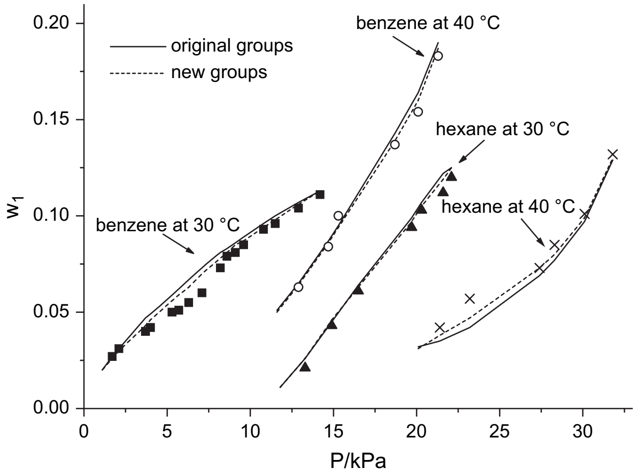

Fig. 6. Systems benzene + PS and hexane + PS described by the Elbro-FV model.

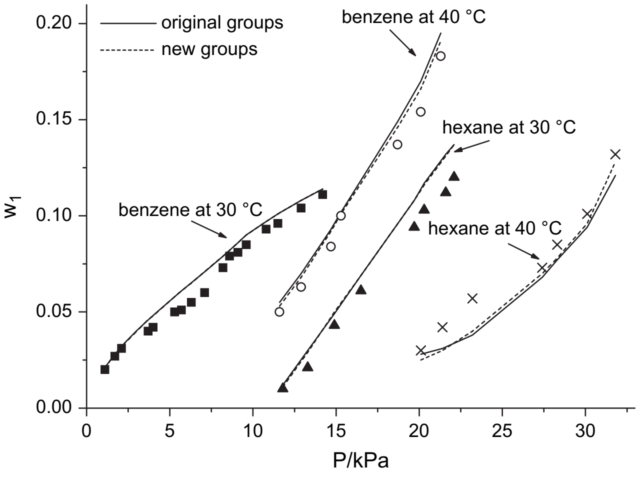

Fig. 7. Systems benzene + PS and hexane + PS described by the Zhong model.

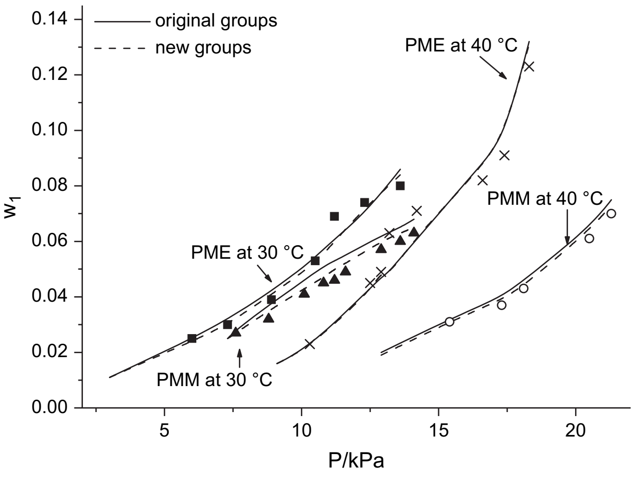

Fig. 8. Systems benzene + PMM and benzene + PME described by the Elbro-FV model.

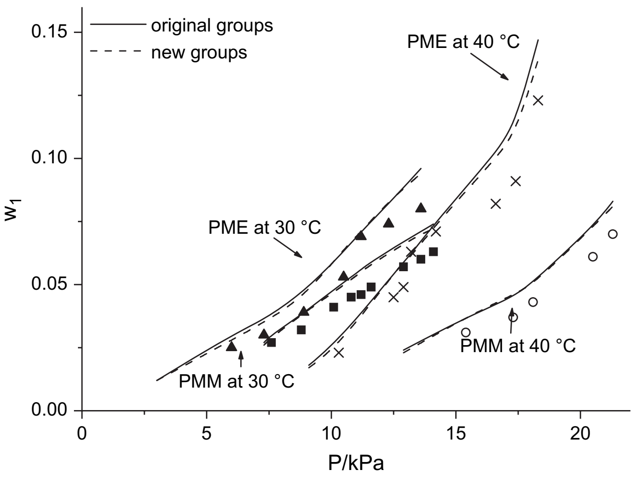

Fig. 9. Systems benzene + PMM and benzene + PME described by the Zhong model.

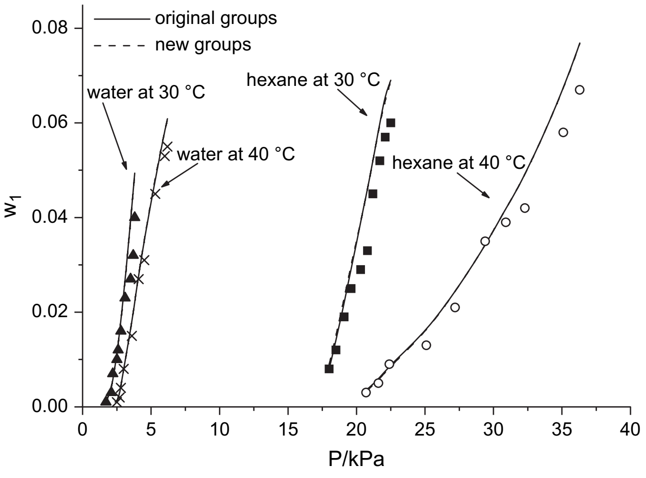

Fig. 10. Systems hexane + PVC and water + PVC described by the Elbro-FV model.

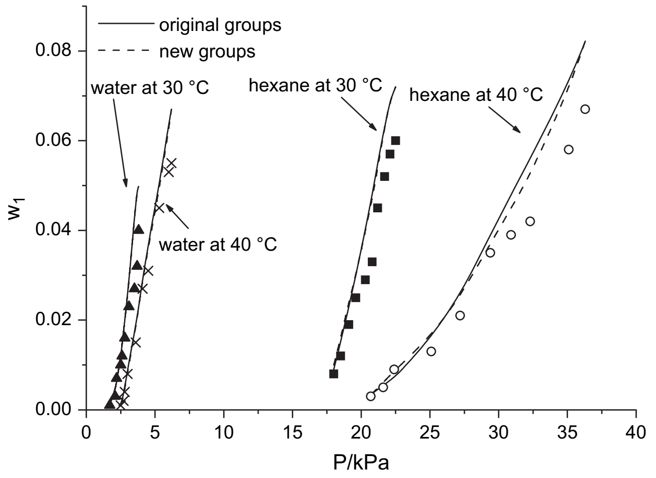

Fig. 11. Systems hexane + PVC and water + PVC described by the Zhong model.

Table 7
Mean deviations in the mass fraction for systems with homopolymer

Systems	Mean deviation (%)			
	Original UNIFAC groups		New UNIFAC groups	
	Elbro-FV	Zhong	Elbro-FV	Zhong
Benzene + PS 30 °C	2.85	4.50	2.27	4.23
Benzene + PS 40 °C	4.06	8.36	2.24	6.21
Hexane + PS 30 °C	5.37	15.03	5.10	12.92
Hexane + PS 40 °C	5.34	15.28	3.36	14.16
Benzene + PMM 30 °C	8.14	18.08	5.01	14.23
Benzene + PMM 40 °C	7.61	18.35	4.26	17.10
Benzene + PME 30 °C	7.50	19.82	4.53	17.52
Benzene + PME 40 °C	6.79	21.03	5.39	17.35
Hexane + PVC 30 °C	15.16	21.74	15.11	20.26
Hexane + PVC 40 °C	15.77	23.37	15.06	22.26
Water + PVC 30 °C	12.48	22.73	11.23	22.22
Water + PVC 40 °C	11.54	20.83	11.54	19.95
Global variation (%)	8.55	17.43	7.09	15.70

the hexane mixtures are greater than that for the benzene mixtures. This means that, for the same absorption, a greater amount of hexane in the system is needed. However, since hexane is less toxic, its use is recommended.

In Fig. 4 it is observed that PME presents greater benzene absorption than PMM, especially at 40 °C. For both polymers, the absorption is improved as the temperature increases.

Fig. 5 indicates that PVC absorbs a little more hexane than water, and this absorption increases with the temperature. Water, although a worse solvent than hexane, has the advantage of being a cheap, nontoxic solvent. Thus, the water is more recommended. It can also be verified that PVC only absorbs at pressures next to the limit of 90% of the saturation pressure.

In Figs. 6 and 7 it can be observed that there is little difference in the data fit when the original and the new groups are used with both models for the systems with polystyrene. For both solvents, benzene and hexane, the fit is closer at 30 °C, while, at 40 °C, the deviations are greater as the vapor pressure of the solvent increases. The Elbro-FV model shows a slightly better fit than the Zhong model.

Figs. 8 and 9 show the results for the systems with PMM and PME; in these cases, independent of the temperature of the system, the Elbro-FV model yield a better fit when original groups were used, with global deviations of 8.14% at 30 °C and 7.61% at 40 °C. When new groups are used, again the Elbro-FV model yield a better fit, with deviations of 5.01% and 4.26%, at 30 and 40 °C, respectively.

In all cases, the fit obtained with the new groups was better than the one obtained with the original groups. As already observed with polystyrene, the new groups demonstrate a significant improvement for both Elbro-FV and Zhong models, although the Elbro-FV model was always better.

Figs. 10 and 11 show the results for the system containing PVC. In these cases, the fit with original and new groups was basically the same for the Elbro-FV model, while the variation is more significant for the Zhong model. However, the data fit with the Elbro-FV model was better than the one obtained with the Zhong model for both temperatures.

From Figs. 6–11 and deviations in Table 7, it can be concluded that, for the studied systems at 30 °C and 40 °C, the Elbro-FV model was capable to represent the experimental data with greater precision. This model showed a global deviation of 8.55%, while the Zhong model showed a global deviation of 17.43%, when the original groups are used. In a similar way, when the new groups are used, the Elbro-FV model also showed a global deviation much lesser than the Zhong model, about 7% and 16%, respectively.

The new groups showed a good performance compared with the original groups. In all the cases, the new groups showed a better fit than the original groups, for both the Elbro-FV and Zhong models.

6. Conclusion

Experimental VLE data have been determined for binary mixtures including polystyrene (PS), poly(vinyl chloride) (PVC), poly(methyl metacrylate) (PMM) and poly(ethyl metacrylate) (PME), with common solvents such as water, benzene and hexane. For the studied systems, it is clear that the increase of the temperature improves the absorption of the solvent. Among the studied solvents, the best is benzene, but due its toxic character, other alternatives must be studied.

The data were modeled by two group contribution models for the activity coefficient, the Elbro-FV and Zhong models, both with original functional groups and new functional groups proposed in this work. In all cases, the Elbro-FV model was capable to describe the experimental data with greater precision than the Zhong model, with global mean deviations of 8.5% against 17.4%, respectively, when using original groups, and 7% against 15.7%, respectively, when new groups were used.

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