

## Vapor pressure and Flory-Huggins interaction parameters in binary polymeric solutions

Milad Asgarpour Khansary<sup>†</sup>

Young Researchers and Elite Club, South Tehran Branch, Islamic Azad University, Tehran, Iran

(Received 19 August 2015 • accepted 11 December 2015)

**Abstract**—This communication reports two unique relationships for (1) Flory-Huggins interaction parameter ( $\chi$ ) and (2) vapor pressure of solvent (P), which explicitly show their composition dependency. There is no empirical constant in the proposed relationships, and no trial and error and/or data-fitting optimization is required for determination and/or correlation of vapor pressure and Flory-Huggins interaction parameter. A straightforward computational technique for implementation of models is provided. For a number of systems, the calculated data have been compared and evaluated against experimental ones and the reliability and accuracy of proposed relationships was assured. IARD (%) values on the order of 0.05 demonstrate the accuracy of the proposed method.

**Keywords:** Binary Polymeric Solution, Vapor Pressure, Flory-Huggins Interaction Parameter, Thermodynamic Equilibrium, Free Energy of Mixing

### INTRODUCTION

Phase behavior of polymeric solutions and its related theoretical calculations and experimental investigations are of much interest in many applications, such separation of gaseous and liquid mixtures using polymeric membranes, swelling of polymers, gas solubility and diffusion [1-4]. For a substantial number of binary polymeric systems, equilibrium vapor pressures have been reported in the literature [5-7], and the composition dependency of vapor pressure of polymer solutions has been observed [5-7], for which an accurate and predictive model is still lacking [8].

Here, attempts were made to develop a model of vapor pressure of solvent in binary polymeric solutions, by combination of two regular solution models of free energy of mixing, where, in addition, a model for Flory-Huggins interaction parameter was obtained. The idea was the presentation of a solely predictive model that requires no experimental measurement and data. The details of theoretical development are presented below.

### MODEL DEVELOPMENT

The regular solution free energy of mixing per unit volume has been given as Eq. (1) by Flory and Huggins [9]:

$$\frac{\Delta g_{mix}}{kT} = \frac{\phi_A}{N_A v_A} \ln \phi_A + \frac{\phi_B}{N_B v_B} \ln \phi_B + \frac{\phi_A \phi_B}{\sqrt{v_A v_B}} \chi \quad (1)$$

Here,  $\phi_i$  indicates volume fraction,  $N_i$  number of segments of volume  $v_i$  for molecules  $i$ ,  $k$  the Boltzmann constant and  $\chi$  Flory-Huggins interaction parameter. The subscripts A and B indicate the components, respectively, solvent and polymer.

Ruzette and Mayes [9] developed following regular solution free energy of mixing per unit volume (Eq. (2)):

$$\frac{\Delta g_{mix}}{kT} = \frac{\tilde{P}_A \phi_A}{N_A v_A} \ln \phi_A + \frac{\tilde{P}_B \phi_B}{N_B v_B} \ln \phi_B + \phi_A \phi_B \tilde{P}_A \tilde{P}_B (\delta_{A,0} - \delta_{B,0})^2 + \phi_A \phi_B (\tilde{P}_A - \tilde{P}_B)(\delta_A^2 - \delta_B^2) \quad (2)$$

The Flory-Huggins interaction parameter ( $\chi$ ) can be obtained by equating these two expressions (Eq. (1)-(2)) of free energy of mixing per unit volume as given by Eq. (3):

$$\chi = (\tilde{P}_A - 1) \frac{\sqrt{v_A v_B} \phi_A}{N_A v_A \phi_B} \ln \phi_A + (\tilde{P}_B - 1) \frac{\sqrt{v_A v_B} \phi_B}{N_B v_B \phi_A} \ln \phi_B + \tilde{P}_A \tilde{P}_B \sqrt{v_A v_B} (\delta_{A,0} - \delta_{B,0})^2 \cdots + (\tilde{P}_A - \tilde{P}_B)(\delta_A^2 - \delta_B^2) \sqrt{v_A v_B} \quad (3)$$

At this step, note that the accuracy of the Flory-Huggins model depends on the robustness and reliability of the employed interaction parameter ( $\chi$ ) [10,11], which can be measured experimentally or calculated by some phase equilibria calculations as found elsewhere [10-15]. The relationship obtained in Eq. (3), itself, can be used in such calculations to enhance the reliability and accuracy of phase calculations.

The relationship between Flory-Huggins interaction parameter ( $\chi$ ) and vapor pressure of solvent (P) in a binary polymeric solution is given by Eq. (4) [8,16], where  $P_0$  is the vapor pressure of the pure solvent.

$$\chi = \frac{\ln\left(\frac{P}{P_0}\right) - \ln(\phi_A) - \left(1 - \frac{v_A}{v_B}\right)\phi_B}{\phi_B^2} \quad (4)$$

Combining Eqs. (3) and (4), one can obtain the following expression (Eq. (5)) for vapor pressure of a solvent (P) in a binary polymeric solution:

$$\ln\left(\frac{P}{P_0}\right) = \ln(\phi_A) + \left(1 - \frac{v_A}{v_B}\right)\phi_B + (\tilde{P}_A - 1) \frac{\sqrt{v_A v_B}}{N_A v_A} \phi_A \phi_B \ln \phi_A$$

<sup>†</sup>To whom correspondence should be addressed.

E-mail: miladasgarpour@ut.ac.ir

Copyright by The Korean Institute of Chemical Engineers.

$$\begin{aligned}
& + (\bar{P}_B - 1) \frac{\sqrt{V_A V_B} \phi_B^3}{N_B V_B \phi_A} \ln \phi \cdots + [\bar{P}_A \bar{P}_B (\delta_{A,0} - \delta_{B,0})^2 \\
& + (\bar{P}_A - \bar{P}_B) (\delta_A^2 - \delta_B^2)] \sqrt{V_A V_B} \phi_B^2
\end{aligned} \quad (5)$$

This expression (Eq. (5)) explicitly shows the composition dependency of vapor pressure of solvent (P) in a binary polymeric solution. As the compressible regular solution model parameters can be determined and calculated using some well-defined equation of state and group contribution method covered in next section, there's no empirical constant in this relationship (Eq. (5)) that requires the common trial and error methods and/or data-fitting optimization

for determination and/or correlation of vapor pressure. The method of implementation of these relationships, i.e., (1) Flory-Huggins interaction parameter ( $\chi$ ) and (2) vapor pressure of solvent (P), is illustrated in the following section.

### COMPUTATIONAL TECHNIQUE

The compressible regular solution models and Sanchez and Lacombe equation of state (SL-EoS) individually have been well-studied in the literature [1,17-23] and their parameters of pure components are available for a substantial number of materials

**Table 1. The collected experimental data together with the model-based calculate data for binary system of THF+PS**

$\phi_B$	P/P <sub>0</sub>		IARD (%)	log(P/P <sub>0</sub> )		IARD (%)
	Exp.	Cal.		Exp.	Cal.	
T=20 °C						
0.46689	0.82789	0.82709	0.097279	−0.08203	−0.08199	0.045795
0.50929	0.78486	0.78481	0.00615	−0.10521	−0.10515	0.054245
0.5614	0.73488	0.73443	0.061625	−0.13378	−0.13377	0.009624
0.59848	0.68495	0.68477	0.026132	−0.16434	−0.16423	0.07196
0.64527	0.62668	0.62633	0.054833	−0.20296	−0.20286	0.049733
0.70796	0.5476	0.54744	0.02832	−0.26154	−0.26141	0.050484
0.73795	0.48522	0.48487	0.071852	−0.31406	−0.31389	0.052235
0.77679	0.4339	0.43351	0.090413	−0.36261	−0.36248	0.036241
0.82004	0.36041	0.36036	0.012902	−0.4432	−0.4431	0.024068
0.85973	0.27724	0.277	0.088363	−0.55714	−0.55699	0.026057
			<b>Avg. IARD%=0.053787</b>	<b>Avg. IARD%=0.042044</b>		
T=40 °C						
0.46877	0.36877	0.36842	0.096606	−0.43324	−0.43295	0.066208
0.5147	0.4147	0.41456	0.034652	−0.38226	−0.38213	0.035858
0.56328	0.46328	0.46282	0.098382	−0.33416	−0.33397	0.055589
0.60124	0.50124	0.5011	0.026821	−0.29996	−0.29987	0.030269
0.64714	0.54714	0.54677	0.068383	−0.2619	−0.26171	0.071509
0.70894	0.60894	0.60877	0.027698	−0.21542	−0.21531	0.051276
0.73894	0.63894	0.63885	0.013706	−0.19454	−0.19439	0.078555
0.7769	0.6769	0.67666	0.03578	−0.16947	−0.1694	0.045013
0.82014	0.72014	0.71995	0.026591	−0.14258	−0.14257	0.008145
0.85984	0.75984	0.75914	0.092119	−0.11928	−0.11916	0.096585
			<b>Avg. IARD%=0.052074</b>	<b>Avg. IARD%=0.053901</b>		
T=60 °C						
0.47154	0.27154	0.27129	0.091612	−0.56616	−0.56565	0.090453
0.51835	0.31835	0.31831	0.01192	−0.4971	−0.49664	0.09125
0.56692	0.36692	0.36676	0.043485	−0.43543	−0.43522	0.049386
0.60487	0.40487	0.40473	0.034126	−0.39268	−0.39238	0.077237
0.65079	0.45079	0.45064	0.032042	−0.34603	−0.34589	0.041487
0.70992	0.50992	0.50943	0.096053	−0.2925	−0.29227	0.080359
0.7417	0.5417	0.54116	0.09916	−0.26624	−0.26624	0.003379
0.777	0.577	0.57668	0.056673	−0.23882	−0.23881	0.004113
0.81847	0.61847	0.61799	0.077468	−0.20868	−0.20853	0.072579
0.85906	0.65906	0.65852	0.082026	−0.18108	−0.18105	0.013981
			<b>Avg. IARD%=0.062456</b>	<b>Avg. IARD%=0.052422</b>		

**Table 2.** The collected experimental data together with the model-based calculate data for binary system of THF+PVME

$\phi_B$	P/P <sub>0</sub>		IARD (%)	log(P/P <sub>0</sub> )		IARD (%)
	Exp.	Cal.		Exp.	Cal.	
T=20 °C						
0.371	0.94252	0.94196	0.059854	−0.02571	−0.02569	0.083533
0.42669	0.90788	0.90697	0.099611	−0.04197	−0.04197	0.005137
0.47707	0.87739	0.87674	0.073539	−0.05681	−0.05679	0.033972
0.54777	0.82059	0.82043	0.019787	−0.08587	−0.08582	0.058774
0.56632	0.79568	0.79512	0.070128	−0.09926	−0.09923	0.028667
0.59106	0.76661	0.76611	0.064663	−0.11543	−0.11543	0.001092
0.62377	0.7472	0.74649	0.096076	−0.12656	−0.12649	0.053344
0.62995	0.74305	0.743	0.006965	−0.12898	−0.12893	0.043043
0.67853	0.65448	0.65391	0.088078	−0.1841	−0.184	0.057762
0.82253	0.43166	0.43125	0.095226	−0.36486	−0.36458	0.075052
0.84284	0.39568	0.39561	0.019638	−0.40265	−0.40258	0.019383
0.86844	0.32375	0.32345	0.090334	−0.4898	−0.48938	0.085102
0.93379	0.17985	0.17972	0.070308	−0.74509	−0.74493	0.022502
0.96469	0.09546	0.09537	0.09815	−1.02019	−1.01952	0.065368
Avg. IARD%=0.068025			Avg. IARD%=0.045195			
T=40 °C						
0.34719	0.24719	0.24707	0.049098	−0.60696	−0.60654	0.06915
0.37724	0.27724	0.27698	0.094363	−0.55715	−0.55667	0.085646
0.39847	0.29847	0.29837	0.031168	−0.52511	−0.52471	0.075836
0.43117	0.33117	0.33115	0.005804	−0.47996	−0.47978	0.037471
0.45151	0.35151	0.35143	0.021487	−0.45407	−0.4539	0.036862
0.48242	0.38242	0.38206	0.096424	−0.41746	−0.41731	0.035799
0.50807	0.40807	0.40804	0.006652	−0.38926	−0.38921	0.014733
0.54077	0.44077	0.44067	0.021366	−0.35579	−0.35554	0.070726
0.5664	0.4664	0.46597	0.092098	−0.33125	−0.33093	0.094635
0.56992	0.46992	0.46982	0.019971	−0.32798	−0.3279	0.02626
0.59378	0.49378	0.49344	0.068227	−0.30647	−0.30647	0.000215
0.60527	0.50527	0.50495	0.063253	−0.29648	−0.29644	0.013245
0.62823	0.52823	0.52818	0.010717	−0.27717	−0.27692	0.090231
0.63265	0.53265	0.53239	0.047696	−0.27356	−0.27332	0.087172
0.65386	0.55386	0.55358	0.051114	−0.2566	−0.25641	0.073679
0.68036	0.58036	0.57988	0.083157	−0.2363	−0.23618	0.049903
0.70245	0.60245	0.60191	0.089699	−0.22008	−0.21992	0.07069
0.73779	0.63779	0.63756	0.03577	−0.19533	−0.19529	0.017921
0.76693	0.66693	0.66644	0.07466	−0.17592	−0.17586	0.033986
0.7899	0.6899	0.68927	0.091376	−0.16121	−0.1612	0.005915
0.80226	0.70226	0.7017	0.080894	−0.1535	−0.15335	0.096581
0.82524	0.72524	0.7252	0.004886	−0.13952	−0.13943	0.067815
0.82876	0.72876	0.72874	0.003029	−0.13742	−0.1373	0.081506
0.84466	0.74466	0.74397	0.092488	−0.12804	−0.12798	0.050897
0.86145	0.76145	0.76089	0.072915	−0.11836	−0.11825	0.096899
0.87205	0.77205	0.77138	0.086873	−0.11236	−0.11226	0.085123
0.8959	0.7959	0.79525	0.080614	−0.09914	−0.09908	0.06125
0.93384	0.83384	0.83369	0.018822	−0.07892	−0.07885	0.078044
0.96035	0.86035	0.86008	0.031425	−0.06533	−0.06529	0.061007
0.96651	0.86651	0.86636	0.016974	−0.06223	−0.06222	0.017031
Avg. IARD%=0.051434			Avg. IARD%=0.056208			

[17,18,22]; however, here the method of computation of these parameters is briefly introduced.

The reduced density ( $\tilde{\rho}_i$ ) and the hard-core solubility parameter ( $\delta_i$ ) are given by Eq. (6) and Eq. (7), respectively [2,9,24], where  $\alpha_i$  and  $\rho_i^0$  are the hard-core volumetric coefficient of thermal expansion and density.  $\delta_i^2$  (298) can be calculated from a group contribution method such as the Hoftyzer and van Krevelen group contribution method [17].

$$\tilde{\rho}_i = \frac{\rho_i}{\rho_i^0} = \exp(-\alpha_i T) \quad (6)$$

$$\delta_i^2(T) = \delta_i^2(298) \frac{\rho_i(T)}{\rho_i^0(T)} \quad (7)$$

For calculation of  $N_i v_p$ , one might use  $N_i v_i = Mw/\rho^*$  equality [2,24], where  $Mw$  is the molecular weight of components (for polymer, the repeating unit).  $N_p$ , the number of segments in hard core, itself, can be obtained as  $N_i = MwP^*/RT^* \rho^*$ .  $\rho^*$  is the lattice-fluid (LF) scaling constant of Sanchez and Lacombe [18] and can be calculated using Boudouris et al. [24] modified group contribution method of Constantinou and Gani [22]. Noting that  $\alpha_i = -(1/\rho)(\partial\rho/\partial T)_p$ , the hard-core volumetric coefficient of thermal expansion ( $\alpha_i$ ) can

Table 2. Continued

$\phi_B$	P/P <sub>0</sub>		IARD (%)	log(P/P <sub>0</sub> )		IARD (%)
	Exp.	Cal.		Exp.	Cal.	
T=60 °C						
0.35519	0.15519	0.15508	0.072528	−0.80913	−0.80907	0.008096
0.37996	0.17996	0.17984	0.068745	−0.74483	−0.7445	0.044328
0.40558	0.20558	0.20549	0.040709	−0.68703	−0.68688	0.021655
0.43476	0.23476	0.2347	0.026335	−0.62937	−0.62909	0.045051
0.46038	0.26038	0.2603	0.031999	−0.58439	−0.58429	0.017504
0.48603	0.28603	0.28577	0.091427	−0.54359	−0.5433	0.053225
0.51871	0.31871	0.3184	0.098827	−0.4966	−0.4965	0.019969
0.54875	0.34875	0.34854	0.060052	−0.45748	−0.45725	0.050157
0.57263	0.37263	0.37235	0.07733	−0.42872	−0.42858	0.031704
0.57262	0.37262	0.37229	0.086322	−0.42874	−0.42864	0.022661
0.60003	0.40003	0.39985	0.045698	−0.39791	−0.39787	0.008784
0.61062	0.41062	0.41054	0.018457	−0.38657	−0.38644	0.032725
0.63095	0.43095	0.43071	0.054704	−0.36557	−0.36555	0.007516
0.66275	0.46275	0.4623	0.098003	−0.33465	−0.33448	0.050604
0.68043	0.48043	0.48015	0.05904	−0.31837	−0.31834	0.007991
0.70694	0.50694	0.50672	0.043767	−0.29504	−0.29482	0.077535
0.71045	0.51045	0.51033	0.023163	−0.29205	−0.29203	0.006042
0.73963	0.53963	0.53926	0.068832	−0.26791	−0.26788	0.008775
0.73783	0.53783	0.53739	0.081613	−0.26935	−0.2691	0.093006
0.77496	0.57496	0.57485	0.020712	−0.24036	−0.24021	0.061805
0.77405	0.57405	0.57388	0.030121	−0.24105	−0.24101	0.017419
0.79174	0.59174	0.59173	0.001987	−0.22787	−0.22765	0.097756
0.80499	0.60499	0.60448	0.085548	−0.21825	−0.21814	0.049413
0.80762	0.60762	0.60759	0.004476	−0.21637	−0.21616	0.098257
0.82619	0.62619	0.62575	0.069609	−0.2033	−0.20314	0.075809
0.83413	0.63413	0.63358	0.087974	−0.19782	−0.19772	0.048999
0.84031	0.64031	0.64022	0.013616	−0.19361	−0.19357	0.023323
0.86062	0.66062	0.66031	0.047583	−0.18005	−0.18003	0.012017
0.86769	0.66769	0.6676	0.013201	−0.17543	−0.17527	0.087282
0.87387	0.67387	0.67362	0.03788	−0.17142	−0.17142	0.003557
0.89948	0.69948	0.69945	0.00519	−0.15522	−0.15515	0.051102
0.90123	0.70123	0.7011	0.018758	−0.15414	−0.15413	0.007002
0.92685	0.72685	0.72647	0.051722	−0.13856	−0.13846	0.067201
0.93037	0.73037	0.72971	0.090471	−0.13646	−0.1364	0.040763
0.94626	0.74626	0.74581	0.061493	−0.12711	−0.12706	0.038028
0.96216	0.76216	0.76159	0.07392	−0.11796	−0.11786	0.079463
Avg. IARD%=0.051717			Avg. IARD%=0.040737			

be calculated using Eq. (8) [2], where  $\rho = \tilde{\rho} \rho^*$  and  $\tilde{\rho}$  is obtained from the Sanchez and Lacombe's lattice-fluid (LF) equation of state [24] presented by Eq. (9):

$$\alpha_i = -\frac{\rho^*(\tilde{P} + \tilde{P}_2)}{\rho T^* \tilde{T}} \cdot \left( \tilde{T} \left( \exp \left[ \tilde{\rho} + \frac{\tilde{P}}{\tilde{T}} + \frac{\tilde{P}^2}{\tilde{T}} \right] - 1 \right) - 2\tilde{\rho} \right)^{-1} \quad (8)$$

$$\tilde{\rho} = 1 - \exp \left[ -\tilde{\rho} - \frac{\tilde{P}}{\tilde{T}} - \frac{\tilde{P}^2}{\tilde{T}} \right] \quad (9)$$

By an initial guess of  $\tilde{\rho} = 1$ , Eq. (9) can be solved numerically using an iterative root seeking method for any temperature and pressure condition of interest. For details of the application of the covered methods, the interested reader may refer to Ref. [2].

## RESULTS AND DISCUSSION

There is a substantial amount of experimental data for binary polymeric solution vapor pressure reported in the literature such as Ref. [6], which makes the validation of proposed relationship of vapor pressure an interesting but exhaustive work. To avoid a large database treatment and recalculation of known LS-EoS parameters, here a number of systems (THF+poly(vinylmethylether) and THF+polystyrene from [8]) were used that their LS-EoS parameters are already known [9,25]. The comprehensive study of data of Ref. [6] and extension of present proposed models for multicomponent systems might be covered in a future work. Individual absolute relative deviation (IARD) between calculated and experimental data was used to present the accuracy of calculations.

The experimental data of the selected systems together with the correlations results of models is provided in Table 1 and Table 2. IARD (%) ( $\text{IARD}(\%) = 100 \times |(P/P_0)_{\text{exp}} - (P/P_0)^{\text{cal}}| / (P/P_0)^{\text{exp}}$ ) values on the order of 0.05 demonstrate the accuracy of the proposed method. Note that in proposed method no fitting of data was required. For both binary systems of THF+PS and THF+PVME, the averaged IARD % (*avg. IARD*) are in the range of 0.05% to 0.07% as seen from correlations results reported in Table 1 and Table 2, which indicates the reliability of models for calculation of considered properties.

In these proposed methods, using well-defined physicochemical property estimation/calculation methods, the composition dependence of vapor pressures and Flory-Huggins interaction parameter were mathematically represented. Having these two proposed methods available, comparison of different systems would be no more than doing some simple thermodynamic calculations. As a side, reasonable estimation can be made for expected behaviors of the studied systems. While the necessity of knowing densities of the components for calculation of volume fractions may be inconvenient, for practical purposes, however, one can simply relate volume fractions weight fractions [26].

## CONCLUSION

For Flory-Huggins interaction parameter ( $\chi$ ) and vapor pressure of solvent (P) in binary polymeric solutions, two reliable and consistent relationships were developed and examined. The composition dependency of these two properties is explicitly incorpo-

rated in the proposed relationships. The validation was made using a number of binary polymeric solutions data obtained from the literature. IARD (%) values on the order of 0.05 demonstrate the accuracy of the proposed method.

## LIST OF SYMBOLS

$g$	: gibbs free energy
IARD	: individual absolute relative deviation
$K$	: Boltzmann constant
$M_w$	: the molecular weight of components
$N_i v_i$	: product of number of hard cores in molar volume of each core
$N_p$	: number of data points
$P$	: pressure
$P_i^{\text{sat}}$	: saturation vapor pressure of pure component
$\tilde{P}$	: reduced pressure (hard-core pressure)
$R$	: the universal gas constant
$T$	: temperature
$\tilde{T}$	: reduced temperature (hard-core temperature)
$\alpha_i$	: coefficient of thermal expansion
$\chi_{ij}$	: interaction parameters in Flory-Huggins (FH) theory
$\rho$	: density
$\tilde{\rho}$	: reduced density (hard-core density)
$\rho^*$	: scaled density the modified Sanchez-Lacombe Lattice Fluid model (SL-LF) in Boudouris et al.
$\delta_i$	: solubility parameter
$\delta_d$	: dispersion solubility parameter
$\delta_p$	: polar solubility parameter
$\delta_h$	: hydrogen bonding solubility parameter
$\delta_{i,0}$	: solubility parameter in 298 K
cal	: calculated data
exp	: experimental data
$\Delta$	: difference in property

## REFERENCES

1. John M. Prausnitz and Rudiger N. Lichtenthaler, Edmundo Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria* 3ed., Prentice Hall (1998).
2. L. Keshavarz, M. A. Khansary and S. Shirazian, *Polymer*, **73**, 1 (2015).
3. M. Mulder, *Basic Principles of Membrane Technology*, 2 Ed., Springer Netherlands, Kluwer, Netherlands, Dordrecht (1996).
4. M. Mulder, *MEMBRANE PREPARATION | Phase Inversion Membranes*, Elsevier Science Ltd. (2000).
5. C. Wohlfarth, *CRC Handbook of Thermodynamic Data of Copolymer Solutions*, CRC Press (2001).
6. C. Wohlfarth, *CRC Handbook of Thermodynamics Data of Polymer Solutions at Elevated Pressures*, CRC Press (2005).
7. C. Wohlfarth, *CRC Handbook of Liquid-liquid Equilibrium Data of Polymer Solutions*, CRC Press (2007).
8. M. Bercea, J. Eckelt and B. A. Wolf, *Ind. Eng. Chem. Res.*, **48**, 4603 (2009).
9. A.-V. G. Ruzette and A. M. Mayes, *Macromolecules*, **34**, 1894 (2001).
10. M. Asgarpour Khansary and M. A. Aroon, *Fuel*, **140**, 810 (2015).

11. D. J. Geveke and R. P. Danner, *Polym. Eng. Sci.*, **31**, 1527 (1991).
12. C. Barth, *Polymer*, **41**, 8587 (2000).
13. B. Cao and M. A. Henson, *Annals of the New York Academy of Sciences*, **984**, 370 (2003).
14. M. A. Khansary and M. A. Aroon, *Fuel*, **142**, 306 (2015).
15. A. Mejía and H. Segura, *Fuel*, **140**, 812 (2015).
16. Polymer Thermodynamics: Liquid Polymer-Containing Mixtures, Springer Verlag Berlin Heidelberg (2011).
17. D. W. V. Krevelen and K. T. Nijenhuis, Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions, 4 Ed., Elsevier (2008).
18. I. Sanchez and M. Stone, *Statistical Thermodynamics of Polymer Solutions and Blends*, Wiley (2000).
19. *CRC Handbook of Chemistry and Physics*, 90 Ed., CRC Press (2010).
20. R. P. Danner and H. Martin S, *Handbook of Polymer Solution Thermodynamics*, American Institute of Chemical Engineers, 345 East 47 Street, New York (1993).
21. G. M. Kontogeorgis and G. K. Folas, *Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories*, 1 Ed., Wiley (2010).
22. B. E. Poling, J. M. Prausnitz and J. P. O'Connell, *Properties of Gases and Liquids*, 4 Ed., McGraw-Hill Professional (1987).
23. S. I. Sandler, *Models for Thermodynamic and Phase Equilibria Calculations*, CRC Press (1993).
24. D. Boudouris, L. Constantinou and C. Panayiotou, *Ind. Eng. Chem. Res.*, **36**, 3968 (1997).
25. P. A. Rodgers, *J. Appl. Polym. Sci.*, **48**, 1061 (1993).
26. R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, 2 Ed., Wiley (2006).