Vapor Pressure and Flory-Huggins Interaction Parameters in Binary Polymeric Solutions

**Abstract**

This communication reports two unique relationships for (1) Flory-Huggins interaction parameter () and (2) vapor pressure of solvent () which explicitly show their composition dependency. There’s no empirical constant in 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 evaluation and comparison of calculated data against experimental ones have been made and the reliability and accuracy of proposed relationships was assured. IARD (%) values in the order of 0.05 demonstrate the accuracy of the proposed method.

**Keyword:** 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 and etc. [1-4]. For a substantial number of binary polymeric systems, equilibrium vapor pressures have been reported in literatures [5-7] and the composition dependency of vapor pressure of polymer solutions have been observed [5-7], for which accurate and predictive model is still lacked [8].

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

# Model development

The regular solution free energy of mixing per unit volume has been given as Eq. 1 by Flory and Higgins [9];

|  |  |
| --- | --- |
|  |  |

Here, indicates volume fraction,  number of segments of volume  for molecules,  the Boltzmann constant and  Flory-Huggins interaction parameter. The subscripts and indicates the components, respectively solvent and polymer.

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

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| --- | --- |
|  |  |

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

|  |  |
| --- | --- |
|  |  |

At this step, it might be worthwhile to mention that the accuracy of Flory-Huggins model depends on the robustness and reliability of employed interaction parameter () [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 () and vapor pressure of solvent () in a binary polymeric solution is given by Eq. 4 [8, 16], where  is the vapor pressure of the pure solvent.

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| --- | --- |
|  |  |

Combining Eq. 3-4, one would obtain following expression (Eq. 5) for vapor pressure of solvent () in a binary polymeric solution;

|  |  |
| --- | --- |
|  |  |

This expression (Eq. 5) explicitly shows the composition dependency of vapor pressure of solvent () 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 () and (2) vapor pressure of solvent (), is illustrated in following section.

# Computational technique

Although that the Compressible Regular Solution models and Sanchez and Lacombe equation of state (LS-EoS) individually have been well-studied in literatures [1, 17-23] and their parameters of pure components are available for a substantial number of materials [17, 18, 22], however, here the method of computation of these parameters is briefly introduced.

The reduced density () and the hard-core solubility parameter () are given by Eq. 6 and Eq. 7 respectively [2, 9, 24], where  and  are the hard-core volumetric coefficient of thermal expansion and density.  can be calculated from a group contribution method such as the Hoftyzer and van Krevelen group contribution method [17].

|  |  |
| --- | --- |
|  |  |
|  |  |

For calculation of, one might useequality [2, 24], where  is the molecular weight of components (for polymer, the repeating unit). , the number of segments in hard core, itself, can be obtained as.  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, the hard-core volumetric coefficient of thermal expansion () can be calculated using Eq. 8 [2], where and is obtained from the Sanchez and Lacombe’s lattice-fluid (LF) equation of state [24] presented by Eq. 9;

|  |  |
| --- | --- |
|  |  |
|  |  |

By an initial guess of, Eq. 9 can be solved numerically using an iterative root seeking method for any temperature and pressure condition of interest. For detailed instruction of the application of 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 literatures 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 are provided in Table 1-2. IARD (%) () values in the order of 0.05 demonstrate the accuracy of the proposed method. It must be noted 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 1-2, which indicates the reliability of models for calculation of considered properties.

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

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

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 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 () and vapor pressure of solvent () in binary polymeric solutions, two reliable and consistence relationships were developed and examined. The composition dependency of these two properties is explicitly incorporated in proposed relationships. The validation was made using a number of binary polymeric solutions data obtained from literatures. IARD (%) values in the order of 0.05 demonstrate the accuracy of the proposed method.

**List of Symbols**

|  |  |  |
| --- | --- | --- |
|  |  | Gibbs free energy |
|  |  | Individual Absolute Relative Deviation |
|  |  | Boltzmann constant |
|  |  | the molecular weight of components |
|  |  | Product of number of hard cores in molar volume of each core |
|  |  | number of data points |
|  |  | Pressure |
|  |  | saturation vapor pressure of pure component |
|  |  | reduced pressure (hard-core pressure) |
|  |  | the universal gas constant |
|  |  | Temperature |
|  |  | reduced temperature (hard-core temperature) |
|  |  | coefficient of thermal expansion |
|  |  | interaction parameters in Flory-Huggins (FH) theory |
|  |  | density |
|  |  | reduced density (hard-core density) |
|  |  | Scaled density the modified Sanchez-Lacombe Lattice Fluid model (SL-LF) in Boudouris et al. |
|  |  | Solubility parameter |
|  |  | Dispersion solubility parameter |
|  |  | Polar solubility parameter |
|  |  | Hydrogen bonding solubility parameter |
|  |  | solubility parameter in 298 K |
|  |  | calculated data |
|  |  | experimental data |
|  |  | Difference in property |

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  | | **IARD (%)** |  | | **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 |
|  |  | ***Avg. IARD%=0.053787*** | |  | ***Avg. IARD%=0.042044*** | |
| **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 |
|  |  | ***Avg. IARD%=0.052074*** | |  | ***Avg. IARD%=0.053901*** | |
| **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 |
|  |  | ***Avg. IARD%=0.062456*** | |  | ***Avg. IARD%=0.052422*** | |

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  | | **IARD (%)** |  | | **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*** | |
| **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*** | |