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Modeling of the phase equilibria of polystyrene in methylcyclohexane with semi-empirical quantum mechanical methods I

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Abstract A method for calculating interaction parameters traditionally used in phase-equilibrium computations in low-molecular systems has been extended for the prediction of solvent activities of aromatic polymer solutions (polystyrene+methylcyclohexane). Using ethylbenzene as a model compound for the repeating unit of the polymer, the intermolecular interaction energies between the solvent molecule and the polymer were simulated. The semiempirical quantum mechanical method AM1, and a method for sampling relevant internal orientations for a pair of molecules developed previously were used. Interaction energies are determined for three molecular pairs, the solvent and the model molecule, two solvent molecules and two model molecules, and used to calculate UNIQUAC interaction parameters, a_{ij} and a_{ji} . Using these parameters, the solvent activities of the polystyrene 90,000 amu+methylcyclohexane system, and the total vapor pressures of the methylcyclohexane+ethylbenzene system were calculated. The latter system was compared to experimental data, giving qualitative agreement.

Keywords Molecular interactions · Solvent activities · Polystyrene solutions

Introduction

There are plenty of experimental data for the liquid–liquid equilibria (LLE) of polymer/solvent and polymer blend/solvent in the literature. In general polymers have limited solubility in organic solvents. The solubility of a given

polymer depends on many factors, like the temperature, pressure, and molecular weight of the polymer, its polydispersity and in particular the solvent. [1, 2, 3, 4].

The thermodynamic theory of phase transitions in polymer solutions, as well as polymer blends, is in principle the same as that used to describe phase separation in mixtures of small molecules. If the free energy of mixing can be calculated for all possible compositions of the mixture of interest, it is possible to determine under which conditions (pressure, temperature and composition) the mixture separates into two phases. In reality, it is much more difficult to carry out such calculations for polymer solutions than for organic solvents, and due to the size difference, the same thermodynamic models cannot be used.

There are many models describing LLE of polymer solutions in the literature. Among them are three main approaches. In the first group of methods, LLE is described semi-quantitatively in terms of the polymer solubility. The second group of methods includes various equations of state. Finally, a very popular group of methods uses the connection between to excess Gibbs free energy (G^E) and coexistence curves; this includes various group-contribution methods. The Flory–Huggins theory, [1] one of the mean field theories widely used in the calculation of phase behavior of polymer solution, falls in the last category.

Kontogeorgis et al. [5] calculated LLE of a range of polymer solutions with different lattice-based excess Gibbs free energy models, using interaction parameters obtained from vapor–liquid equilibrium (VLE) data. Sanches and Panayiotou [6] give an overview of some lattice-based equations of state for calculating LLE and VLE of polymer solutions. Recently, Kontogeorgis [7] has written a review about a variety of methods used for calculations of phase behavior of polymer solutions, including group-contribution methods, and cubic and non-cubic equations of state.

Jónsdóttir et al. [8, 9] have developed a method for predicting UNIQUAC interaction parameters used in phase-equilibrium calculations, based on Molecular Me-

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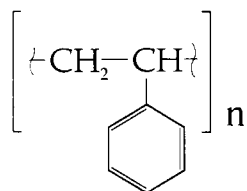


Fig. 1 Drawing of the repeat unit (segment) in a polystyrene chain

chanics computations of the system of interest. The method has been used to predict the phase behavior of a variety of systems, giving results in good agreement with experimental data. This includes organic solvent-solvent systems [8, 9, 10], polyalcohols and saccharides in aqueous solution [11, 12], and polymer solutions [13, 14]. In this method, interaction energies between pairs of molecules (molecular clusters made of two molecules) were calculated with a molecular mechanics method called the Consistent Force Field (CFF) [15, 16]. For a binary mixture, three pairs of molecules need to be considered, two pairs of like molecules and one pair of unlike molecules. For accurate determination of the interaction energy it is important to sample the conformational space of each pair of molecules adequately. Two different methods have been developed for this purpose. The direct search method [8, 9] is very good for small molecules exhibiting limited conformational flexibility, but for larger and more flexible molecules Monte Carlo search methods [10, 13, 17] are used. See the cited references for more detailed information.

For polymer solutions, interaction energies are calculated between the solvent molecule and a model compound of similar size to the solvent molecule. The model compound typically contains one or two repeating units, segments, from the polymer molecule. The assumption behind this approach is that each solvent molecule can only interact with a small part of the polymer at a given time. Because the interaction parameters are defined as interactions per surface area, this simple model is sufficient for describing the interactions in the system.

The VLE (solvent activities) for polypropylene in diethylketone were calculated using this method [13], where isohexane (2-methylpentane) was used as a model molecule for the polymer. Isohexane contains two repeating units of the polymer molecule and is of comparable size to the solvent molecule, diethylketone. The results obtained were in excellent agreement with experimental data, and showed that it is indeed possible to predict VLE of polymer solutions from these relatively simple calculations.

Polystyrene chains are essentially different from polymers like polyethylene and polypropylene due to the presence of aromatic rings. A sketch of the repeat unit of polystyrene is shown in Fig. 1. Due to the delocalized electrons in the aromatic rings, the intermolecular interactions occurring in polystyrene solution are more complicated to describe than in the case of aliphatic polymer solutions. The contribution of the delocalized

electrons to the intermolecular interactions in such systems is thus the main problem that needs to be solved. Molecular Mechanics methods treat the electrons as charges absorbed into the nuclei and are thus not particularly suitable for calculating accurate interaction energies for aromatic compounds.

This work is the first step towards modeling L-L phase equilibria in polystyrene-solvent solutions. The ethylbenzene+methylcyclohexane system is used as a model system, and a semi-empirical quantum mechanical method, Austin Model 1 (AM1) [18, 19], is used to calculate the intermolecular interaction energies. The system studied is polystyrene 90,000 amu dissolved in methylcyclohexane, which is one of the systems for which experimental LLE data have been measured [20]. The solvent activities are calculated with the Elbro free volume method [21, 22]. The UNIQUAC interaction parameters, a_{ij} and a_{ji} acquired for ethylbenzene+methylcyclohexane system were also used to calculate the total vapor pressure as a function of composition for binary mixture formed by ethylbenzene and methylcyclohexane. The results obtained are compared with experimental data.

Methods

Theoretical background.

For a given polymer solution, the solvent activity (a_i) is calculated as a product of the mole fraction (x_i) of the solvent and its activity coefficient (γ_i) according to the simple relation:

$$a_i = x_i \gamma_i \quad (1)$$

The activity coefficient, which is one for an ideal solution, can be calculated with the Elbro free volume method (also called entropic free volume method) [15]. In this method, the natural logarithm of the activity coefficient is defined as a sum of a residual term and a so-called free volume and combinatorial term:

$$\ln \gamma_i = \ln \gamma_i^R + \ln \gamma_i^{fv} \quad (2)$$

The residual term ($\ln \gamma_i^R$) represents the energetic interactions between the molecules in the solution and is identical to the residual term used in the UNIQUAC method, originally introduced by Abrams and Prausnitz in 1975 [23]. The residual contribution is calculated with the relation:

$$\ln \gamma_i^R = q_i \left\{ 1 - \left(\ln \sum_j \theta_j \tau_{ji} \right) - \sum_j \left[\theta_j \tau_{ij} / \left(\sum_k \theta_k \tau_{kj} \right) \right] \right\} \quad (3)$$

where: q_i is the van der Waals surface area parameter of component i in the mixture, defined as $q_i = (A_i^{vdw} / 2.5 \times 10^9 \text{ cm}^2 \text{ mol}^{-1})$, A_i^{vdw} is the van der Waals surface area determined by Bondi's method [24], θ_i is the surface area fraction of component i and is given by the relation $\theta_i = q_i x_i (\sum_j q_j x_j)^{-1}$. The parameter τ_{ij} is defined as

$$\tau_{ij} = \exp[-(\Delta U_{ij} - \Delta U_{ii}) / q_i RT] = \exp(-a_{ij} / T) \quad (4)$$

where ΔU_{ij} represents the interaction energy between two different molecules in the system, and a_{ij} is the UNIQUAC interaction parameter. Note that $a_{ij} \neq a_{ji}$ and then consistently $\tau_{ij} \neq \tau_{ji}$.

The so-called free volume and combinatorial term ($\ln \gamma_i^{fv}$) describe the free volume difference between the polymer melt and the solvent, as well as the difference in the size of the polymer and solvent molecules. In Elbro's method the relation is as follows:

$$\ln \gamma_i^{fv} = \ln(\phi_i^{fv} / x_i) + 1 - (\phi_i^{fv} / x_i) \quad (5)$$

Table 1 The molar volumes (V), as well as the UNIQUAC volume (r_i) and surface area (q_i) parameters for ethylbenzene, methylcyclohexane and polystyrene

Main group	V (cm ³ mol ⁻¹)	r_i	q_i
Methylcyclohexane	131.2	4.7200	3.776
Ethylbenzene		4.5972	3.508
Polystyrene, Mw=90,000 amu	85500.	3777.	2765.

where $\phi_i^{fv} = x_i(V_i - V_i^{vdW}) / [\sum_j x_j(V_j - V_j^{vdW})]$, x_i is the mole fraction, V_i the molar volume and V_i^{vdW} the van der Waals volume (the so-called hard-core volume) of component i , respectively. V_i^{vdW} values are calculated with Bondi's method [24]. The relationship between the UNIQUAC volume parameter (r_i) and the van der Waals volume of component i is defined as $r_i = (V_i^{vdW} / 15.17 \text{ cm}^3 \text{ mol}^{-1})$ [23]. Optionally q_i and r_i values can be evaluated by summing the UNIFAC group values Q_k and R_k [25], as described later. In cases where the polymer and the solvent are made of the same functional groups, like polyethylene dissolved in a small alkane, both τ_{ij} parameters become almost zero, and relation (2) reduces to the free volume term.

Kontogeorgis et al. [22] have added an empirical Staverman-Guggenheim (SG) correction term to the free volume activity coefficient expression of component i in the Elbro method. This is done to incorporate the differences in shape between the solvent and segment of the polymer. The resulting equation they obtained for the free volume term is:

$$\ln \gamma_i^{fv} = \ln(\phi_i^{fv} / x_i) + 1 - \left(\phi_i^{fv} / x_i \right) - 5q_i [\ln(\phi_i / \theta_i) + 1 - (\phi_i / \theta_i)] \quad (6)$$

where $\phi_i = x_i r_i / (\sum_j x_j r_j)$ and $r_i = \sum_k v_{ki} R_k$, R_k is the volume parameter for group k and v_{ki} is the number of groups of type k in molecule i .

When a polymer solution separates into two coexisting liquid phases at a given temperature, the activity of the solvent and the polymer are equal in both phases. By calculating solvent and polymer activity as a function of composition, it is possible to find the liquid-liquid demixing conditions.

For modeling phase equilibria for a real polymer solution, it is important to choose an appropriate way for determining the strength of intermolecular interaction parameters for the system under consideration. The method of theoretically determined interaction parameters is particularly useful for systems with significant residual contribution to the activity coefficient.

Procedure for determining the intermolecular interaction parameters and other relevant parameters

The system under study is the polystyrene+methylcyclohexane system. The ethylbenzene molecule was selected as a model compound, as it represents the repeat unit (segment) of the polystyrene chain. Monodispersity of the polymer was assumed, meaning that the all polymer molecules are considered to be of the same size, and identical to the average length of the polymers in the sample.

Various geometrical parameters were calculated for the isolated molecules. Surface area and volume parameters based on Bondi's method [24] for van der Waals surface areas and volumes were determined using the UNIFAC tables [25]. Methylcyclohexane is made up of (5CH₂+1CH+1CH₃) groups, and ethylbenzene of (1CH₃+5ACH+1ACCH₂) groups, where A stands for the benzene ring. Values of the r_i and q_i parameters for these molecules are given in Table 1.

Likewise, the r and q parameters for polystyrene 90,000 are listed in Table 1, as well as the molar volume (V) of the polymer and the solvent. The molar volume of the polymer was determined with a correlated equation given by Rodgers [26], and the liquid density of the solvent was obtained from the DIPPR data bank [27]. The van der Waals volume (V_i^{vdW}), used in the Elbro free volume method, can be calculated from the r_i parameters ($V_i^{vdW} = r_i \times 15.17 \text{ cm}^3 \text{ mol}^{-1}$).

The AM1 method [18, 19] was used to calculate the equilibrium structures and corresponding potential energies of the methylcyclohexane molecule and the ethylbenzene molecule. The energy was minimized (i.e. the geometry was optimized) for every conformer (equilibrium conformation) of the individual molecules. A quantum-mechanically based method was chosen because we found it more suitable for treating systems containing delocalized electrons than a Molecular Mechanics method. The AM1 method was chosen because it is one of the most widely used semiempirical quantum chemical methods. Semiempirical methods are much faster than full scale ab initio calculations, but at the same time, they are electronic calculations. Although less accurate than ab initio methods, it is useful to examine how well these methods perform for the problem at hand.

Molecular complexes were built from one conformer of each molecule, and several energy minimizations were performed in order to find the global minimum of the potential-energy surface of each pair of conformers. To ensure that the global energy minimum for each pair of conformers was found, a large number of energy minimizations were performed with different starting geometries, employing the direct search method developed by Jónsdóttir et al. [8]. In this method, by fixing one of the molecules in space, and rotating the other molecule against the fixed molecule through a predefined pattern, the starting geometries are created. The starting geometries are then energy minimized, relaxing all degrees of freedom.

All calculations for single molecules and pairs of conformers were carried out using the Spartan program [SPARTAN IBM, Version 5.1.3X11, Wavefunction Inc., Irvine, Calif., USA], using the AM1 method. The three molecular pairs studied here are: ethylbenzene+methylcyclohexane, ethylbenzene+ethylbenzene, and methylcyclohexane+methylcyclohexane.

The interaction energy was calculated as the difference between the potential energy of a pair of molecules isolated in a space and the potential energies of the individual molecules. For a unlike pair the equation is as follows:

$$\Delta U = U(\text{pair}) - U(\text{molecule 1}) - U(\text{molecule 2}) \quad (7)$$

with $U(\text{pair}) = U_{12} = U_{21}$.

The total interaction energy for a particular pair of molecules was computed as a weighted thermodynamic average of the interaction energies for all possible pairs of conformers. Usually, this is done by calculating the Gibbs free energy at 298.15 K for each pair of conformers, and to calculate their relative probabilities with Boltzmann statistics. The procedure is described in detail by Jónsdóttir et al. [8, 17]. In our calculation we used the calculated potential energies, which neglects the entropy factor.

Having determined the interaction energies between all three different types of molecules in a binary mixture (ΔU_{11} , ΔU_{22} , and ΔU_{12}) the interactions parameters a_{12} and a_{21} were found for the model mixture (ethylbenzene+methylcyclohexane) according to the following relations:

$$a_{12} = (\Delta U_{12} - \Delta U_{22}) / Rq_2 \quad (8)$$

and

$$a_{21} = (\Delta U_{12} + \Delta U_{11}) / Rq_1 \quad (9)$$

where R is the gas constant and q_i are the surface area parameters.

Based on these results, solvent activities of the polymer solution, as well as the VLE data of the organic mixture, the model system, were calculated. For the binary solvent-solvent mixture, methylcyclohexane+ethylbenzene, the VLE data were calculated with the UNIQUAC method. The solvent activities of the polymer solution,

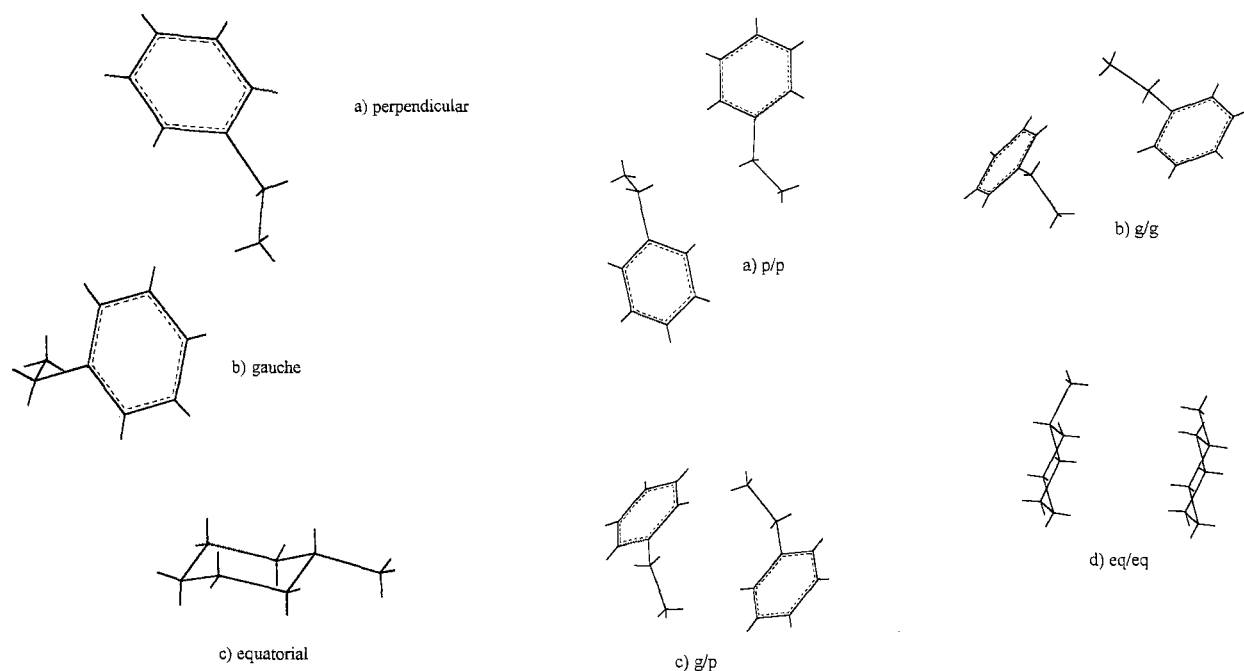


Fig. 2 Minimized structures of the equatorial isomer of methylcyclohexane (c), and the two possible conformers of ethylbenzene: **b** *gauche* (g); **a** *perpendicular* (p)

polystyrene 90,000 amu+methylcyclohexane, were calculated with the Elbro free volume method.

Results and discussion

Possible conformations of the individual molecules were studied. Conformers for single isolated methylcyclohexane and ethylbenzene molecules are presented in Fig. 2 and their potential energies are listed in Table 2. The six-member ring in the methylcyclohexane molecule occurs exclusively as a chair conformer, where the aliphatic methyl group can take up both *axial* and *equatorial* positions, and thus form two isomers. The equatorial form is the preferable isomer from an energetic point of view, and thus this isomer was used in the calculations. For ethylbenzene, two possible conformers were found: *gauche* with a torsional angle of 72° , and *perpendicular* with a torsional angle of 90° , referring to the orientation of the ethyl group compared to the aromatic ring. Both these conformers were taken into account in the calculations.

The potential energies for all relevant pairs of molecules were then determined according to the procedure described in the previous section. During the minimization for the molecular pairs, the torsional angle

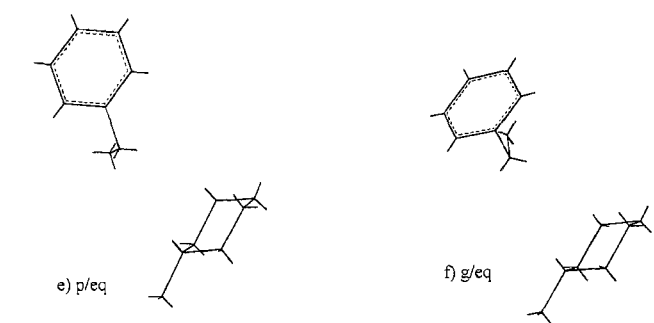


Fig. 3 Internal orientations of molecular conformers giving the global minimum: **a, b, c** ethylbenzene+ethylbenzene; **d** methylcyclohexane+methylcyclohexane; **e, f** methylcyclohexane+ethylbenzene

defining the two conformers of ethylbenzene was kept fixed at the value obtained for isolated conformers, and all other degrees of freedom were relaxed. The energy barrier between the two conformers was shown to be relatively low, and the bottoms of the potential energy wells are relatively broad. Therefore, it was necessary to fix the torsion angle. The numerical values obtained are given in Table 3. The most energetically favorable intermolecular orientations (global minima) for all significant pairs of conformers are shown in Fig. 3. Table 3 lists the

Table 2 Potential energies calculated for the individual molecules

Component	Isomer/conformer	U (kJ mol ⁻¹)
Methylcyclohexane	Equatorial	-182.955
Ethylbenzene	<i>Gauche</i> (g) (with torsional angle of 72°)	36.149
	<i>Perpendicular</i> (p) (with torsional angle of 90°)	36.262

Table 3 Potential energies and interaction energies for a molecular pairs formed from ethylbenzene (ethbenz) and methylcyclohexane (mch)

System	Pair of molecules	U_{pair} (kJ mol ⁻¹)	$\Delta U_{\text{int.}}$ (kJ mol ⁻¹)
mch–mch	eq/eq	-370.909	-4.999
ethbenz–ethylbenz	g/g	68.429	-3.869
	g/p	68.358	-4.053
	p/p	68.898	-3.626
ethbenz–mch	g/eq	-149.808	-3.002
	p/eq	-150.273	-3.580
			-3.264^a

^a Total interaction energy of the pair of molecules (ethbenz–ethylbenz and ethbenz–mch) are computed as a weighted thermodynamic average of the interaction energies for all possible pairs of conformers with their relative probabilities calculated with Boltzmann statistics

Table 4 UNIQUAC interaction parameters for methylcyclohexane(1)+ethylbenzene(2) system

Source	a_{12} (K)	a_{21} (K)	$a_{12}+a_{21}$ (K)
AM1	20.6	55.2	75.8
Literature ^a	-130.21	201.86	60.55

^aInteraction parameters adjusted to experimental VLE data [28]

calculated values of the total interaction energies for three molecular pairs.

The UNIQUAC interaction parameters a_{ij} determined with the AM1 method, as well as values adjusted to the experimental VLE data [28] are listed in Table 4. The sums of the parameters are also listed in Table 4. Pairs of interaction parameters, adjusted to experimental data, are inter-correlated. The values of the theoretically obtained interaction parameters can, therefore, not be compared directly to the adjusted parameters. On the other hand, the sum of the interaction parameters is a measure of the total strength of the interaction in the system. It is noteworthy that the sum of the theoretically obtained interaction parameters is very similar to the sum of adjusted parameters, which indicates that the interaction parameters are determined with reasonable accuracy.

Having determined a_{ij} parameters for the methylcyclohexane+ethylbenzene mixture, solvent activities at 316 K were calculated for polystyrene 90,000 amu in methylcyclohexane. The calculated solvent activities are shown in Fig. 4. The curve obtained with the theoretically determined interaction parameters is compared to another curve where interaction parameters, adjusted to experimental VLE data [28] for the ethylbenzene+methylcyclohexane system, are used.

Vapor pressures as a function of the composition for the binary mixture consisting of ethylbenzene and methylcyclohexane at 313 K were also calculated. Calculations were carried out with the theoretically obtained interaction parameters, a_{ij} , and compared to a curve calculated using the adjusted parameters. The adjusted interaction parameters are fitted to experimental VLE data for this system, and, therefore, the curve shown represents the experimental data. The results obtained with the interaction parameters determined with the AM1

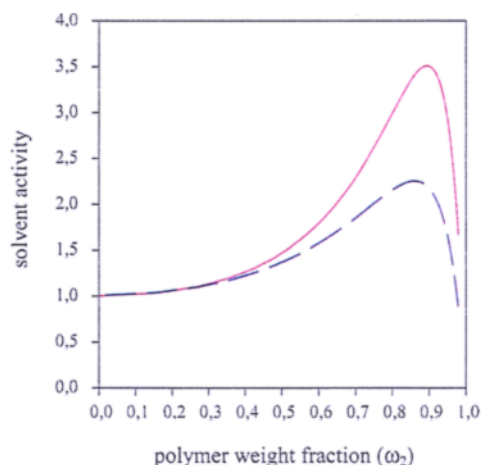


Fig. 4 Solvent activities for the methylcyclohexane(1)+polystyrene(2) system at 316 K. Parameters a_{ij} (pink line) obtained with the AM1 method; parameters a_{ij} (blue line) from VLE data for the ethylbenzene+methylcyclohexane system [28]. The abscissa is the polymer weight fraction defined as $\omega_2(x_1)=(1-x_1)M_2/[x_1M_1+(1-x_1)M_2]$, where x_1 is the solvent mole fraction and M_i are the molecular weights of the components

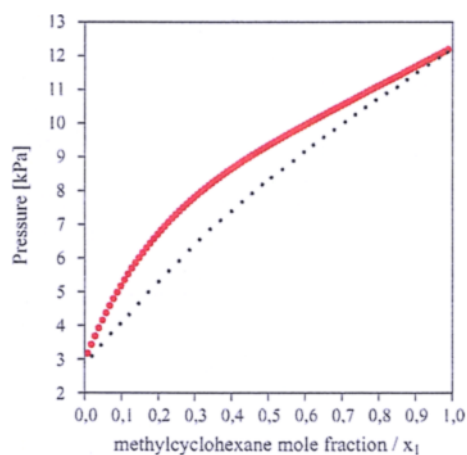


Fig. 5 Vapor pressure at 313 K for the methylcyclohexane(1)+ethylbenzene(2) binary mixture as a function of composition. Red-line parameters: $a_{12}=20.6$ K, $a_{21}=55.2$ K determined with AM1 method. Black-line parameters: $a_{12}=201.86$, $a_{21}=-30.21$ K fitted to the VLE data [28]

method are in qualitative agreement with the experimental data, see Fig. 5.

Conclusions

Interaction energies and interaction parameters for the methylcyclohexane+ethylbenzene system were calculated with the AM1 semiempirical quantum chemical method. The parameters obtained were used to describe intermolecular interactions of a solution of polystyrene 90,000 amu dissolved in methylcyclohexane. Solvent activities predicted with the Elbro free volume method for this solution are in qualitative agreement with results obtained with interaction parameters fitted to experimental VLE data for a binary mixture of methylcyclohexane and ethylbenzene.

The calculations for the solvent-solvent system are carried out with the UNIQUAC method. Vapor pressure as a function of composition is predicted for the binary mixture ethylbenzene+methylcyclohexane, giving a qualitative agreement to the experimental data.

The main conclusion is that the AM1 method can be useful to calculate vapor-liquid equilibria for polymer solutions containing aromatic groups in a polymer chain, but quantitative agreement with experimental data was not achieved. The method can also be useful to determine if a liquid-liquid phase split occurs or if it does not. For obtaining a more quantitative description, calculations would have to be carried out with the more accurate and very time consuming quantum mechanical ab initio calculations.

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