

Modeling Vapor Pressure Data of Ternary α -Methylstyrene-Toluene-Poly(α -methylstyrene) System

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ABSTRACT: The overall interaction parameter for the ternary polymer solution formed by: α -methylstyrene(1)-toluene(2)-poly(α -methylstyrene)(3) was determined from static vapor pressure using a binary liquid mixture computation method. The obtained parameter was used along with available data for three binary interaction parameters in order to deduce the specific ternary interaction parameters of the type χ_{123} . The yielded negative values for the latter were mainly attributed to some entropic contribution into the whole ternary mixing process.

KEY WORDS Interaction Parameter / Modeling / Ternary / Vapor Pressure / Computation Method /

In recent works,¹⁻⁴ the thermodynamic behavior of some equilibrium ionic polymerizations in solution have been adequately described by only three binary interaction parameters of monomer-solvent, solvent-polymer and monomer-polymer mixtures, respectively. These parameters have usually been evaluated at corresponding composition of each binary mixture in order to take the concentration dependences into account. The relative success of this method proved that the Flory-Huggins ternary model⁵ could be accurate enough, within the experimental accuracy limit, for handling a ternary mixture where the two polymer-liquid interactions are not much different from each other; and the nonideal behavior of the binary liquid mixture is not excessively strong, such as in hydrogen bonding systems. Efforts have been made² using vapor pressure data of ternary mixture to discover whether or not a specific ternary interaction of the type χ_{123} , introduced by Scatchard,⁶ should be required for the above

ternary systems. However, the magnitudes of the obtained parameters were not large enough over various sources of experimental errors to convince us about the necessity of that parameter.

A treatment for the equilibrium data of a ternary mixture was first proposed by Scott⁷ using a single-liquid approximation. According to that proposal, ternary systems of polymer-mixed solvent can be treated in an analogous way to binary systems with a single interaction parameter. The binary solvent mixture was assumed to be a single solvent with properties corresponding to the average of the two solvents. However, Scott's simplified treatment could not quantitatively handle the ternary experimental data, especially in systems with synergistic effects like cosolvency. Later, in dealing with light scattering data for the preferential adsorption measured on the systems polystyrene-benzene-cyclohexane,⁸ Read needed to arbitrarily select some value for χ_{123} to fit the data, Pouchly *et al.*,⁹ in analyzing

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experimental data of dialysis equilibrium and intrinsic viscosity on the system poly(methyl methacrylate)–benzene–methanol, have introduced a composition-dependent ternary parameter to obtain agreement between the theories and the experimental data. Munk *et al.*¹⁰ made detailed thermodynamic analyses of the solvent mixtures to obtain the binary interaction functions and evaluated the ternary functions from the data of the preferential adsorption coefficient and the second virial coefficient. Recently, Nakata *et al.*¹¹ has successfully applied these thermodynamic relations to the study of PMMA in the binary mixture 1 chlorobutane–2–methoxyethanol. Meanwhile, Horta¹² and others,^{13,14} used the Flory–Prigogine–Patterson equation-of-state theory for interpreting the ternary experimental data.

Either with the lattice model theory or with the EOS theory, the straight deduction of the ternary interaction parameter from ternary mixture data appeared to be more substantial than the method of arbitrarily selecting the ternary parameter to fit the experimental data. In the present work, the vapor pressure data of the ternary mixture formed by α -methylstyrene(1)–toluene(2)–poly(α -methylstyrene) (3) will be handled to yield first the overall interaction parameter, χ_{12T} , for the system.

This result will be then combined with the available data of the three binary parameters, χ_{12} , χ_{13} , and χ_{23} , to deduce the specific ternary parameter, χ_{123} , as defined by Scatchard.⁶

COMPUTATION METHOD

Overall Interaction Parameter χ_{12T}

In the proposed method, the ternary mixture formed by liquids 1 and 2 with polymer 3 should be considered as a “quasi-binary liquid mixture.” The interactions between the polymer and both liquids, represented by χ_{13} and χ_{23} , ought to have the effect of transforming the binary liquid mixture interaction, χ_{12} , into the overall ternary parameter χ_{12T} , which accounts for all interactions existing in the

whole system. Using this model, the χ_{12T} parameter may be calculated from experimental vapour pressure data, P , by applying the same method as for a binary liquid mixture. This quasi-binary concept is similar to the one used by Fujita’s group^{15–18} for dealing with polymer–polymer–solvent systems.

According to the Flory–Huggins theory, χ_{12T} parameter can be related to the excess of free energy of mixing, ΔG^E , through⁵:

$$\chi_{12T} = \frac{\Delta G^E}{RTx'_1\phi'_2} \quad (1)$$

where R is the gas constant, T is the absolute working temperature, x'_1 and ϕ'_2 are respectively the mole fraction of liquid 1 and volume fraction of liquid 2 forming the binary liquid part of the ternary mixture. These fractions should be calculated using only the mole numbers, n_1 and n_2 , of both liquids forming the ternary system:

$$x'_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad \phi'_2 = \frac{x'_2 V_2}{x'_1 V_1 + x'_2 V_2} \quad (2)$$

where $x'_2 = (1 - x'_1)$ and V_1 , V_2 are the molar volumes of the pure liquid components.

The question is how to deduce ΔG^E from P data? This can be done by means of the activity coefficients,¹⁹ γ_1 and γ_2 , for both liquid components in the quasi-binary liquid mixture, which are related to ΔG^E and P through:

$$\frac{\Delta G^E}{RT} = x'_1 \ln \gamma_1 + x'_2 \ln \gamma_2 \quad (3)$$

$$\text{and} \quad P = P_1^0 x'_1 \gamma_1 \Phi_1 + P_2^0 x'_2 \gamma_2 \Phi_2 \quad (4)$$

where P_1^0 , P_2^0 are, respectively, the vapor pressure of pure liquid components at the studied temperature. Φ_1 and Φ_2 are correction factors for the non-ideality of the vapor phase. In case where P is well below 1 atm., as in the present work, Φ_1 and Φ_2 would be very close to unity. It follows that eq 4 becomes:

$$P = P_1^0 x'_1 \gamma_1 + P_2^0 x'_2 \gamma_2 \quad (4')$$

The activity coefficients γ_1 , γ_2 (and hence

ΔG^E) can be computed from the set of experimental data of P , expressed as function of x'_1 , by means of eq 4', with the help of some empirical expression relating γ_1 , γ_2 to x'_1 through some empirical constants. Among many available expressions, the one proposed by Wilson²⁰ appeared to be suitable for most binary liquid mixtures:

$$\ln \gamma_1 = -\ln(x'_1 + A_{12}x'_2) + x'_2 \left(\frac{A_{12}}{x'_1 + A_{12}x'_2} - \frac{A_{21}}{x'_2 + A_{21}x'_1} \right) \quad (5a)$$

$$\ln \gamma_2 = -\ln(x'_2 + A_{21}x'_1) + x'_1 \left(\frac{A_{12}}{x'_1 + A_{12}x'_2} - \frac{A_{21}}{x'_2 + A_{21}x'_1} \right) \quad (5b)$$

where A_{12} and A_{21} are adjustable semi-empirical parameters.

The computation process is a nonlinear regression method, which is used to solve for those values of A_{12} and A_{21} that accurately fit the experimental data.

Introducing arbitrary values for A_{12} and A_{21} at the beginning of the computation program has the effect of creating an error, ΔP , on each experimental value of P such that:

$$\Delta P = \left(\frac{\partial P}{\partial A_{12}} \right) \Delta A_{12} + \left(\frac{\partial P}{\partial A_{21}} \right) \Delta A_{21} \quad (6)$$

$$\text{where } \Delta A_{12} = A_{12} - A_{12}^{\text{sup}}$$

$$\Delta A_{21} = A_{21} - A_{21}^{\text{sup}}$$

$$\text{and } \Delta P = P - P_{\text{cal}} = P - (x'_1 P_1^0 \gamma_1 + x'_2 P_2^0 \gamma_2) \quad (7)$$

Partial differentiation upon eq 4', 5a, 5b give rise to:

$$\frac{\partial P}{\partial A_{12}} = -\frac{x'_1 \gamma_1 P_1^0 A_{12} x_2'^2 + x'_2 \gamma_2 P_2^0 x_1'^2}{(x'_1 + A_{12} x_2')^2} \quad (8a)$$

$$\frac{\partial P}{\partial A_{21}} = -\frac{x'_1 \gamma_1 P_1^0 x_2'^2 + x'_2 \gamma_2 P_2^0 A_{21} x_1'^2}{(x'_2 + A_{21} x_1')^2} \quad (8b)$$

For a set of N experimental values of P , the use of eq 8a and 8b leads to N equations of

the form eq 6 which relate A_{12} and A_{21} . The summation of those N equations results in two equations that can be readily solved to yield ΔA_{12} and ΔA_{21} values:

$$\sum^N \Delta P_i (\partial P_i / \partial A_{12}) = \Delta A_{12} \sum^N (\partial P_i / \partial A_{12})^2 + \Delta A_{21} \sum^N (\partial P_i / \partial A_{12}) (\partial P_i / \partial A_{21}) \quad (9)$$

$$\begin{aligned} & \sum^N \Delta P_i (\partial P_i / \partial A_{21}) \\ & = \Delta A_{12} \sum^N (\partial P_i / \partial A_{12}) (\partial P_i / \partial A_{21}) \\ & + \Delta A_{21} \sum^N (\partial P_i / \partial A_{21})^2 \end{aligned} \quad (10)$$

The iterative computation is now repeated using the new values for A_{12} and A_{21} :

$$A_{12} = A_{12}^{\text{sup}} + \Delta A_{12} \quad (11a)$$

$$A_{21} = A_{21}^{\text{sup}} + \Delta A_{21} \quad (11b)$$

until ΔA_{12} and ΔA_{21} become smaller than 0.01% of the preceded values of A_{12} and A_{21} . The final values of these constants are used to deduce ΔG^E . χ_{12T} can then be calculated for the ternary mixture at any composition using eq 2 and 1. The performance of the computation method can be checked by estimating the average error percentage defined as:

$$\sigma = \frac{\sum^N |P_i - P_{i\text{cal}}| / P_i}{N} \times 100 \quad (12)$$

Specific Ternary Interaction Parameter χ_{123}

The excess of free energy of mixing for a ternary mixture can be expressed by means of three binary interaction parameters, χ_{12} , χ_{13} , and χ_{23} , plus a specific ternary interaction parameter of the type χ_{123} such as proposed by Scatchard⁶:

$$\begin{aligned} \frac{\Delta G^E}{RT} & = x_1 \phi_2 \chi_{12} + x_1 \phi_3 \chi_{13} + x_2 \phi_3 \chi_{23} \\ & + x_1 x_2 \phi_3 \chi_{123} \end{aligned} \quad (13)$$

where x and ϕ are the mole and volume fractions of the components in the ternary mixture, calculated by:

$$x_1 = \frac{n_1}{n_1 + n_2 + n_3}; x_2 = \frac{n_2}{n_1 + n_2 + n_3};$$

$$x_1 + x_2 + x_3 = 1.0 \quad (14)$$

and

$$\phi_2 = \frac{n_2 V_2}{n_1 V_1 + n_2 V_2 + n_3 V_3};$$

$$\phi_3 = \frac{n_3 V_3}{n_1 V_1 + n_2 V_2 + n_3 V_3} \quad (15)$$

where n_1 , n_2 are the mole numbers of the two liquids and n_3 is the base-mole number of the polymer forming the ternary mixture. V_1 , V_2 have previously been defined and V_3 is the base-molar volume of the polymer.

The values obtained for ΔG^E from the preceding solution may now be substituted into eq 13 along with the available data for the three binary parameters χ_{12} , χ_{13} , and χ_{23} in order to provide the specific ternary interaction parameter χ_{123} . Since all binary parameters, to some extent, are concentration dependent, therefore, their values should be directly extrapolated from their respective graphs by referring to the corresponding binary volume fraction defined as:

– for the binary 1–2: $\phi'_{21} = \frac{n_2 V_2}{n_1 V_1 + n_2 V_2}$ (16a)

– for the binary 1–3: $\phi'_{31} = \frac{n_3 V_3}{n_1 V_1 + n_3 V_3}$ (16b)

– for the binary 2–3: $\phi'_{32} = \frac{n_3 V_3}{n_2 V_2 + n_3 V_3}$ (16c)

This manner of calculating the binary compositions within the ternary system is very similar to the method used by Fujita's group^{15–18} to deduce the interaction parameters from the excess Rayleigh ratios obtained from light scattering measurements of binary and ternary polymer mixtures.

EXPERIMENTAL

Materials

The toluene and α -methylstyrene used were the best available reagents. They were kept over CaH₂ and degassed on the vacuum manifold for several days. They were then distilled under vacuum, the head and the tail fractions being discarded, the middle fraction was kept under vacuum for use in preparing the mixtures. Two grades of poly(α -methylstyrene) were used in separate application. One, from Polyscience, has $\bar{M}_n = 53000$ with a polydispersity index smaller than 1.10; the second, prepared in our laboratory by anionic polymerization of α -methylstyrene (α MS) in toluene, has been characterized by size exclusion chromatography yielding a polydispersity index smaller than 1.30 and $\bar{M}_n = 60000$.

Apparatus

The apparatus used for measurements of static vapor pressure of polymer solutions has been described elsewhere.²¹ It consisted of an MKS Baratron pressure gauge, a mixture cell, a reference cells, and a vacuum manifold. The mixture cell contained the polymer solution and the reference cell contained pure toluene (TOL) so that the vapor pressure of the polymer solution was differentially measured against that of pure TOL. Both cells were immersed in a controlled temperature chamber where maximum fluctuation of the temperature was $\pm 0.01^\circ\text{C}$. Under these conditions, differential pressures with a maximum fluctuation of $\pm 3 \times 10^{-3}$ mmHg were measured.

Measurement Procedure

The key idea for the applicability of the proposed computation method is to be able to obtain the vapor pressure data for a set of more than six ternary mixtures with a fixed polymer volume fraction (in this work it was $\phi_3 = 0.20 \pm 0.01$), and variable binary liquid compositions. In order to prepare such mixtures, about 1.0 g of previously desiccated P α MS was

Table I. Vapor pressure, molar volume for α -methylstyrene, toluene, and poly(α -methylstyrene) at various temperatures

T/K	P°/mmHg		$V/\text{l mol}^{-1}$		
	αMS	TOL	αMS	TOL ^b	P αMS (base-mole) ^a
298	2.75	29.10	0.12966	0.10595	0.1071
303	3.57	37.48	0.13031	0.10660	0.1073
308	4.75	47.36	0.13102	0.10723	0.1075
313	5.94	61.75	0.13171	0.10789	0.1078

^a Extrapolated from ref 18. ^b TOL, toluene.

inserted into the mixture cell. Then the predetermined amounts of purified TOL and αMS , which satisfied the criterion: $(\phi_1 + \phi_2) = 0.80 \pm 0.01$, were successively inserted into the cell with precision syringes. The exact amounts were accurately checked by weighing the cell after each insertion of liquid. The cell was then placed on the vacuum manifold and the whole mixture was then thoroughly frozen degassed. After degassing the cell was set communicated to the pressure gauge and was allowed to reach the working temperature. The static equilibrium between the liquid and vapor phases was effectively assumed by a stirring magnetic bar driven by an external rotor. The differential vapor pressure between the two cells usually stabilized within an hour.

Molar Volume Determination

In order to obtain the volume fractions used in computation processes, the molar volumes of the liquid components as well the base-molar volume of P αMS are needed. The formers were determined using a SODEV, model 02, digital densimeter with an estimated accuracy of ± 2 ppm. The operation of the densimeter is based on measuring the period of oscillation of a vibrating U-shaped tube filled with liquid substance. The densimeter had previously been calibrated using purified air and redistilled water as reference samples. Meanwhile, the base-molar volume of P αMS is extrapolated from ref 22 for temperatures higher than 25°C. All these volumes are presented in Table I.

RESULTS AND DISCUSSION

Overall Parameter χ_{12T}

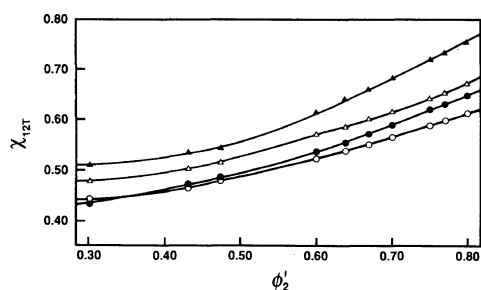
According to the quasi-binary liquid model, only the mole fractions x'_1 and $x'_2 = (1 - x'_1)$, of the binary liquid mixture in the ternary system are accounted for in the computation of ΔG^E and χ_{12T} . The values of x'_1 were deduced from the amounts of both liquids, W_1 and W_2 , forming the ternary system. Vapor pressures, and molar volumes, of the pure liquids needed for computations are presented in Table I for various temperature. Experimental and calculated vapor pressures for the αMS -TOL-P αMS mixtures are listed, as function of x'_1 , in Table II at four temperatures from 298 to 313 K. The nonlinear regression program was written in TURBO-BASIC language and performed on a PC-10 computer. Owing to the weak extent of nonideal behavior of the binary αMS -TOL mixture, the iterative process converged rapidly to accepted limit of 0.01% for A_{12} and A_{21} values. The final values of these constants as well those of $\Delta G^E/RT$ and χ_{12T} are tabulated in Table III as function of ϕ'_2 (for the studied temperatures). Due to the dependence of molar volumes of liquids on temperature, the volume fraction ϕ'_2 is usually varied with temperature for each mole fraction. However, that variation was so small that only the average values of ϕ'_2 are presented in Table III and Figure 1. Usually, the overall error of the χ_{12T} parameter was estimated as ± 0.005 arising mainly from errors on liquid compositions and on vapor

Table II. Vapor pressure (in mmHg) in function of binary mole fraction for the α -methylstyrene-toluene-poly(α -methylstyrene) mixture, at $\phi_3=0.20$ and various temperatures

x'_1	298 K		303 K		308 K		313 K	
	P_{ex}	P_{cal}	P_{ex}	P_{cal}	P_{ex}	P_{cal}	P_{ex}	P_{cal}
0.1733	25.18	25.15	32.95	32.73	41.66	41.59	55.08	54.92
0.1975	24.71	24.70	32.20	32.16	40.92	40.87	54.14	54.03
0.2133	24.42	24.40	31.81	31.78	40.45	40.39	53.53	53.44
0.2613	23.48	23.47	30.59	30.60	38.91	38.91	51.55	51.56
0.2863	22.98	22.98	29.90	29.96	38.18	38.12	50.47	50.54
0.3167	22.31	22.36	29.04	29.15	37.03	37.12	49.11	49.24
0.3551	21.52	21.55	28.02	28.10	35.71	35.82	47.38	47.51
0.4779	18.85	18.76	24.54	24.41	31.41	31.26	41.57	41.37
0.5236	17.58	17.62	22.91	22.91	29.38	29.41	38.83	38.84
0.6560	13.77	13.74	17.97	17.92	23.04	22.95	33.32	33.25
$\sigma/\%$	0.16		0.25		0.20		0.21	

Table III. Excess free energy and overall interaction parameter in function of binary volume fraction for the α -methylstyrene-toluene-poly(α -methylstyrene) mixture, at $\phi_3=0.20$ and various temperatures

ϕ'_2	298 K		303 K		308 K		313 K	
	$\Delta G^E/RT$	χ_{12T}	$\Delta G^E/RT$	χ_{12T}	$\Delta G^E/RT$	χ_{12T}	$\Delta G^E/RT$	χ_{12T}
0.7965	0.0849	0.614	0.0896	0.648	0.0927	0.671	0.1058	0.766
0.7693	0.0913	0.600	0.0959	0.630	0.0997	0.656	0.1127	0.742
0.7517	0.0949	0.592	0.0993	0.619	0.1037	0.646	0.1166	0.727
0.6988	0.1036	0.567	0.1074	0.588	0.1132	0.619	0.1253	0.686
0.6217	0.1069	0.556	0.1103	0.573	0.1167	0.606	0.1282	0.666
0.6391	0.1098	0.542	0.1127	0.556	0.1198	0.591	0.1305	0.645
0.5985	0.1119	0.526	0.1141	0.537	0.1221	0.574	0.1317	0.620
0.4727	0.1091	0.483	0.1093	0.483	0.1190	0.526	0.1249	0.536
0.4275	0.1049	0.469	0.1045	0.467	0.1145	0.511	0.1190	0.532
0.3002	0.0866	0.440	0.0855	0.432	0.0960	0.485	0.0994	0.505
A_{12}	1.51537		1.60948		1.49377		1.62939	
A_{21}	0.28351		0.23739		0.26947		0.19151	

**Figure 1.** Overall parameter χ_{12T} for α MS-TOL-P α MS mixture at (●) 298 K, (○) 303 K, (△) 308 K, (▲) 313 K.

pressure readings caused by temperature fluctuation.

The small values of σ (average error between experimental and calculated P , Table II), well below overall error, showed that the proposed computation method was suitable for the actual ternary mixture. This is due to the moderate nonideal behavior of the α MS-TOL mixture where the mixing process was assumed only by entropic interaction rather than specific enthalpic interaction. Furthermore, interaction

contributions from P α MS against α MS and TOL, according to ref 23, were judged as being normal and moderate without any special interactive phenomena. For the same temperature, the values of χ_{12T} are slightly different from those of the corresponding binary parameter χ_{12} (ref 21). The values of χ_{12T} should incorporate some contributions from the binary χ_{13} and χ_{23} parameters, and probably from some specific ternary interaction χ_{123} .

Specific Ternary Parameter χ_{123}

The values of ΔG^E (or χ_{12T}) obtained from the preceding computation may now be substituted into eq 13 in order to evaluate the χ_{123} parameter. In doing so, it is necessary to extrapolate or interpolate the values of χ_{12} , χ_{13} and χ_{23} from available data sources 21, 23. Before extrapolation or interpolation, the volume fraction for each corresponding binary mixture 1–2, 1–3, or 2–3 should be evaluated. They were evaluated from the mole numbers n_1 , n_2 , n_3 of the three components forming the ternary mixture, along with their molar volume, by using eq 16a, 16b, and 16c. The overall error on χ_{123} is comprised of the errors on the ternary and binary parameters, including those arising from the extra or interpolation processes plus errors on compositions. That overall error was evaluated as ± 0.06 for the $(\phi_3\chi_{123})$ term or ± 0.30 for χ_{123} parameter.

The calculations gave rise to negative values for the χ_{123} parameter presented in Table IV as a function of the volume fraction ϕ'_2 . Although the magnitude of χ_{123} seemed to be exaggeratedly large compared to those of the binary and χ_{12T} parameters, but according to the Scatchard expression, the true contribution of specific ternary interaction is the $(\phi_3\chi_{123})$ term (Table IV and Figure 2), rather than χ_{123} itself. The negative values of the former (or latter) mean that the presence of P α MS has the effect of making the binary liquid mixture α MS–TOL more compatible than the original

Table IV. Average values of χ_{123} parameter and $(\phi_3\chi_{123})$ term in function of binary volume fraction ϕ'_2

ϕ'_2	χ_{123}	$(\phi_3\chi_{123})$
0.7965	-0.60	-0.12
0.7517	-0.65	-0.13
0.6988	-0.65	-0.13
0.6391	-0.65	-0.13
0.5985	-0.70	-0.14
0.4727	-0.85	-0.17
0.4275	-0.95	-0.19
0.3002	-1.40	-0.28

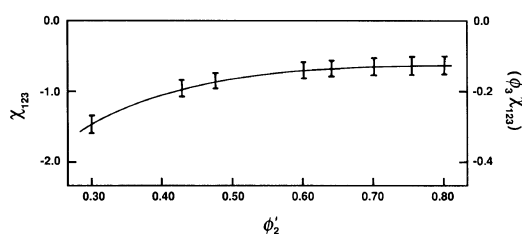


Figure 2. Average specific parameter χ_{123} and $(\phi_3\chi_{123})$ for α MS–TOL–P α MS mixture.

mixture. According to the chemical structure of three components, there may not be strong attractive forces between any pair of components so that the mixing process in all three binary mixtures is guessed to be mainly assumed by the entropy contribution, ΔS_M . This is reflected by relatively large positive values of all three binary parameters^{21,23}: about 0.35 for χ_{12} , 0.40 for χ_{13} and 0.45 for χ_{23} . Thus, the observed improvement on the compatibility of the ternary system might not be attributed to the enthalpic level but rather the noncombinatorial entropy part of the whole interactive pattern. This favorable entropic contribution may result in free volume effects on mixing caused by the encumbering configuration of α MS molecules as well as structural units of the P α MS chains. It was found out that the χ_{123} parameter varied slightly with concentration. This variation appeared similar to that of the binary parameter χ_{12} , arising from some shortcomings of the lattice model on which the

Flory–Huggins theory is based.

CONCLUDING REMARKS

The vapor pressures of the ternary mixtures formed by α MS–TOL–P α MS with a fixed volume fraction of P α MS were successfully treated using the so-called “quasi-binary liquid mixture” model. The iterative computation method based on the semiempirical equation of Wilson was suitable for the investigated mixture. This is reflected by the small values of average errors between experimental and calculated vapor pressures. The overall interaction parameter χ_{12T} is somewhat different from its counterpart, χ_{12} , for the binary mixture α MS–TOL since the former should contain the contributions from the other parameters χ_{13} , χ_{23} and probably χ_{123} . Along with the available data of three binary parameters, some negative values for χ_{123} have been deduced, which was attributed to the specific entropic contribution to the whole ternary mixing process.

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