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Vapor Pressures of Polymer Solutions and the Modeling of Their Composition Dependence

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Equilibrium vapor pressures, p , are reported for the systems tetrahydrofuran + poly(vinyl methyl ether) and tetrahydrofuran + polystyrene at 20, 40, and 60 °C. These data plus information from the literature serve to demonstrate that the composition dependence of p can be modeled quantitatively for polymer solutions in thermodynamically very different solvents by means of three, physically meaningful parameters.

Introduction

By means of this contribution we would like to demonstrate the benefit of a recently established relation, modeling the composition dependence of the Flory–Huggins interaction parameter χ , for a quantitative description of the composition dependence of the vapor pressures above polymer solutions.

First we present the results of vapor pressure and light scattering measurements for the systems THF + poly(vinyl methyl ether) [PVME] and THF + polystyrene [PS]. After that we model these results in terms of Flory–Huggins interaction parameters and composition dependent vapor pressures. The present data are complemented by published material to demonstrate the capability of the concept.

Experimental Section

The PVME sample (Lutonal), which is a liquid at room temperature, was supplied by BASF (Germany). Polystyrene (a white powder) was a commercial product purchased from PSS (Polymer Standard Service, Mainz, Germany). The molar masses and the polydispersity indices of these components are given in Table 1. They have been obtained by means of GPC measurements in THF at room temperature (columns, PSS SDV Gel, 10², 10⁴, 10⁵ nm, supplied by Polymer Standards Service (PSS), Mainz, Germany; detectors, RI-detector (Shodex RI-71) and UV-detector (Spectra-Physics 200)). Polystyrene standards (PS) served for calibration. In the case of PVME we employed the universal calibration using the following Kuhn–Mark–Houwink parameters for THF: $K_{PS} = 0.0136$ mL/g, $a_{PS} = 0.714$ (at 25 °C),¹ $K_{PVME} = 0.0135$ mL/g, and $a_{PVME} = 0.739$ (at 30 °C).² All samples were filtered through 0.45 μ m Millipore membrane filters Membrex 13 PET (membraPure, Bodenheim, Germany) before injection. The errors remain below 10% as usual.

The densities of the polymers, required for the calculation of the number of polymer segments, were taken from the literature: for PVME from ref 3 and for PS from ref 4. The densities of the THF were calculated according to the relation: ρ_{THF} (g/cm³) = 0.8892 – (9.37 \times 10^{–7}) t (°C).

Vapor pressure measurements were carried out as described in the literature^{5,6} by means of an apparatus consisting of the

headspace-sampler Dani HSS 3950, Milano (Italy) and a normal gas chromatograph Szimadzu GC 14B Kyoto (Japan). This procedure gives access to the amount of the volatiles in a constant volume of the vapor phase, which is in thermodynamic equilibrium with the polymer solution. From these data it is possible to determine p , the partial vapor pressures of a certain volatile above the solution, divided by p_o , the vapor pressure of the pure solvent. This ratio can be easily converted into composition dependent vapor pressures by means of published p_o data.

Light scattering measurements were performed with a modified (SLS, G. Bauer, Freiburg, Germany) static light scattering apparatus Fica 50 (Sofica, Paris) using a laser (632.8 nm) and measuring angles from 20° to 145°. PVME + THF solutions with concentrations in the range of 1 to 2.5 g/dL were prepared one day in advance and kept at 50 °C in an oven. Prior to measurements, they were filtered through a 0.45 μ m membrane filter (Millipore) directly into the thoroughly cleaned optical cells (Helma, Müllheim, Germany) and thermostatted in the light scattering apparatus for 15 min. The refractive index of the solvent (n_o) was determined by means of an Abbé refractometer, Carl Zeiss, Germany). The refractive index increments (dn/dc), were measured at 20, 30, and 40 °C by means of an instrument described in the literature.⁷ The values of n_o , dn/dc , and second virial coefficient (A_2) are listed in Table 2.

For the vapor pressure measurements, samples with weight fractions of the polymer ranging from 0.35 to 0.965 and total volumes of 2 mL were prepared in crimp top vials of 10 mL, by loading the polymer with solvent via the gas phase, after which the vials were sealed with airtight septa. To guarantee the attainment of thermodynamic equilibria, the polymer +

Table 1. Characteristic Data of the Polymer Samples

	M_w (g/mol)	M_w/M_n
PVME 50	50 500	2.6
PS 30	29 800	1.1

Table 2. Refractive Indices, Refractive Index Increments and Second Osmotic Virial Coefficients for Solutions of PVME in THF at Different Temperatures

	20 °C	30 °C	40 °C	60 °C ^a
n_o	1.4076	1.4022	1.3971	–
dn/dc (mL g ^{–1})	0.0677 ₄	0.0691 ₅	0.0668 ₁	–
$A_2 \times 10^4$ (mol mL g ^{–2})	2.87	3.19	4.44	5.85 ₅

^a Extrapolated because of the high volatility of the solvent at that temperature.

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solvent mixtures were kept in an oven at 50 °C for 10 days and were constantly agitated by means of a rolling-mixer.

The reproducibility of the data was checked in multiple headspace extractions by means of five independent measurements for each sample. The amount of solvent vapor decreases slightly from extraction to extraction in a linear manner. The equilibrium vapor pressure was determined by plotting the measured peak area as a function of the number of extractions and extrapolating to the first extraction. The experimental error in p/p_o was typically on the order of 1–2%.

Vapor Pressure and Flory–Huggins Interaction Parameters. The fugacity of the solvent (which is in many cases practically identical with its vapor pressure (p)) constitutes the most important source of experimental information on the Flory–Huggins interaction parameter χ , which is calculated according to the following relation:⁸

$$\chi = \frac{\ln\left(\frac{p}{p_o}\right) - \ln(1 - \varphi) - \left(1 - \frac{1}{N}\right)\varphi}{\varphi^2} \quad (1)$$

φ stands for the volume fraction of the polymer in the mixture and N represents the number of polymer segments defined by the ratio of the molar volumes of the polymer and of the solvent. For experimental reasons the practical use of the above relation is restricted to sufficiently high polymer concentrations (large enough difference between p and p_o , the vapor pressure of the pure solvent) and to suitably low viscosities (to reach equilibria). This implies that additional information is required, at least on the dilute side, to obtain reliable data on the composition dependence of χ .

The limiting value of the interaction parameter for very dilute solutions (i.e., in the range of pair interaction between the solute), χ_o , can be calculated according to the following relation:⁹

$$\chi_o = \frac{1}{2} - A_2 \rho_2^2 \bar{V}_1 \quad (2)$$

from measured second osmotic virial coefficients A_2 obtained from osmosis or light scattering experiments; ρ_2 is the density of the polymer, and \bar{V}_1 is the molar volume of the solvent. Because A_2 produces only a small addendum to 0.5, the errors in χ_o can usually be neglected as compared with the errors in the χ values resulting from vapor pressures.

The following theoretically founded relation¹⁰ has proven to model the composition dependence of the Flory–Huggins interaction parameter for all binary systems studied so far:

$$\chi = \frac{\chi_o + \xi\lambda}{(1 - \nu\varphi)^2} - \xi\lambda(1 + 2\varphi) + \varpi\varphi(3\varphi - 2) \quad (3)$$

The system specific parameter $\xi\lambda$ accounts for the fact that the conformation of the polymer chain before the separation and after the separation of intermolecular contacts between its segments differs in the general case. Equation 3 constitutes a simplified version of the original approach accounting for the fact that λ is always very close to 0.5 for polymer solutions; under these circumstances the parameters ξ and λ can be merged to $\xi\lambda$. The normally dissimilar surface to volume ratios of polymer segments and of solvent molecules (which are important for the interaction between these entities) are quantified by the parameter ν . Finally, the parameter ϖ , modeling particularly strong interactions between the solute, was hitherto only required for aqueous

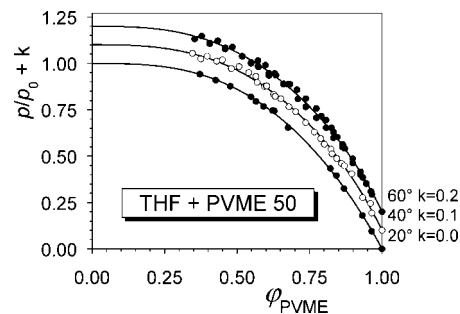


Figure 1. Dependence of the vapor pressure of THF on the volume fraction of PVME 50 in the solution for the indicated temperatures. For better discernability of the individual data points, the curves are shifted by the additive term k .

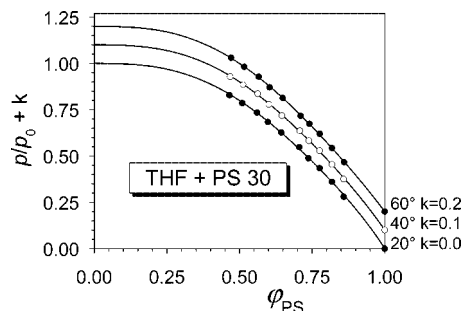


Figure 2. As Figure 1 but for the system THF + PS.

Table 3. Parameters of Equations 3 and 4 for the Present Polymer Solutions and for the Systems Toluene + Polystyrene (TL + PS, ref 12, 13) and Water + Pullulan (W + PUL, ref 10); the χ_o Values Were Calculated from the A_2 Values, Obtained from Light Scattering Measurements, by Means of Equation 2

T (°C)	χ_o	$\xi\lambda$	ν	ϖ
THF + PVME 50				
20	0.474	0.66 ± 0.05	0.257 ± 0.016	0
40	0.462	0.71 ± 0.07	0.287 ± 0.016	0
60	0.451	0.71 ± 0.05	0.293 ± 0.012	0
THF + PS 30				
20	0.419	1.26 ± 0.05	0.324 ± 0.016	0
40	0.417	1.18 ± 0.07	0.310 ± 0.016	0
60	0.416	1.11 ± 0.05	0.295 ± 0.012	0
TL + PS 180				
20	0.452	0.48 ± 0.05	0.305 ± 0.013	0
W + PUL 280				
37.5	0.488	-0.858 ± 0.05	0.753 ± 0.014	2.183 ± 0.286

solutions of some polysaccharides; in all other cases it could be set equal to zero.

Combining the phenomenological eq 1, defining the Flory–Huggins interaction parameter, with eq 3, its modeled composition dependence, yields eq 4, which represents the vapor pressure of the solvent as a function of polymer concentration.

$$\ln\left(\frac{p}{p_o}\right) = \left(\frac{\chi_o + \xi\lambda}{(1 - \nu\varphi)^2} - \xi\lambda(1 + 2\varphi) + \varpi\varphi(3\varphi - 2)\right)\varphi^2 + \ln(1 - \varphi) + \left(1 - \frac{1}{N}\right)\varphi \quad (4)$$

Knowing the physical data of the polymer (molar mass and density) and of the solvent (vapor pressure p_o and molar volume)

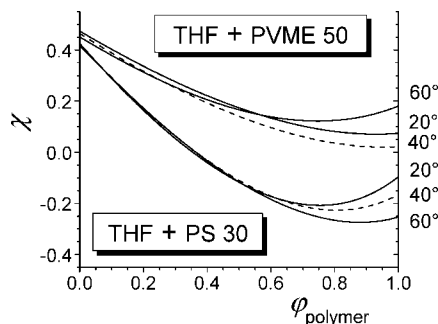


Figure 3. Composition dependence of the Flory–Huggins interaction parameter for the indicated systems and temperatures.

it is possible to calculate $p(\varphi)$ from experimentally determined χ_o , ν , and $\zeta \lambda$ values (plus ϖ , if required).

Results and Discussion

For the system THF + PVME we have performed two independent sets of experiments (Figure 1) to demonstrate the reproducibility and reliability of the HS-GC method. This procedure yields reduced vapor pressures p/p_o , where p_o can for THF be obtained from published data.¹¹ In the case of THF + PS (Figure 2) the data stem from one set of measurements. The curves shown in these graphs are calculated according to eq 4 by means of the parameters of Table 3 (fitted to the measured composition dependence of the vapor pressures).

The system specific parameters collected in Table 3 supply the information required to assess the thermodynamic quality of a certain solvent for a given polymer. According to the original Flory–Huggins theory the knowledge of χ_o should suffice for this purpose, where the solvent with the least χ_o value is considered to be the best. Because of the well-established composition dependence of χ the situation is much more complicated, as demonstrated for the present solutions in Figure 3.

According to Figure 3 the interaction between THF and PVME as well as between THF and PS becomes particularly favorable at a characteristic composition in the range of high polymer concentrations. Such minima in $\chi(\varphi)$ are not uncommon but represent only one possibility out of a large number of different behaviors ranging from linear dependencies, with positive or negative slope, to even more complicated functionalities exhibiting points of inflection. In this context it is interesting to note that the “individuality” of a certain system is in most cases developed at high polymer concentrations only; in the dilute range the favorable entropies of mixing are obscuring these details to a great extent. That statement also holds true for the temperature influences, which are often much more pronounced at large φ values, like in Figure 3. For THF + PS the dilution process takes place practically athermally in the range of low polymer concentrations, whereas it becomes endothermal as φ is raised. The system THF + PVME is slightly endothermal at high dilution, as seen from the χ_o values, but the temperature influences become more complicated at high φ values, where it must presently remain unclear because of experimental uncertainties whether $\chi(T)$ really passes a minimum in that range. In view of well-documented complicated temperature effects, including inversions in the sign of the heat of mixing, such extrema may well exist.

The thermodynamic quality of a given solvent for a certain polymer at a given composition can be directly seen from

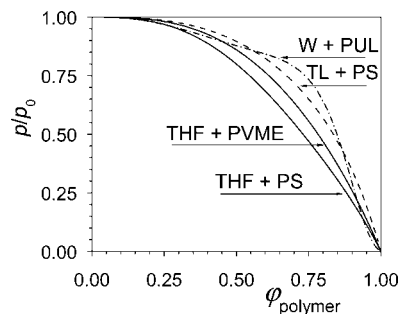


Figure 4. Vapor pressure curves calculated for the indicated systems by means of equation 4 and the parameters collected in Table 3.

the vapor pressure curves of present interest by the extent to which p is diminished with respect p_o . This situation is exemplified in Figure 4 for some typical systems.

Figure 4 testifies that the vapor pressures may differ tremendously in the range of high polymer concentrations even for solvents, which are according to common belief comparably good solvents, like TL or THF for polystyrene. With aqueous solutions of biopolymers the situation can become even more drastic as demonstrated for pullulan. In this case the system behaves in the usual way only at sufficiently high dilution; upon an increase in polymer concentration the reduction of the vapor pressure is much less pronounced than normal up to a characteristic point after which it falls rapidly.

Outlook

Over a mere mathematical representation of experimental data concerning the composition dependence of vapor pressures, the present approach has the advantage of using physically meaningful parameters, which ease the comparison of different systems and a reasonable estimation of expected behaviors. The volume fractions used here as composition variables for theoretical reasons, may be inconvenient for practical purposes, because they require the knowledge of the densities of the components and need corrections as the temperature varies. However, these relations can be easily reformulated in terms of weight fractions instead of volume fractions leading to different numerical values of the system specific parameters but enabling an easier application of the present concept in the field of engineering.

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