# Concentration-Dependent Thermodynamic Interaction Parameters for Polymer Solutions: Quick and Reliable Determination via Normal Gas Chromatography

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ABSTRACT: Equilibrium vapor pressures were determined by combining a head-space sampler with a gas chromatograph for the system cyclohexane/polystyrene in the temperature range from 35 to 65 °C. From these measurements the Flory–Huggins interaction parameter $\chi$, its variation with $\varphi_2$, the volume fraction of the polymer, and its enthalpy part were calculated; $\chi(\varphi_2)$ was represented by an analytical expression given by Koningsveld and Kleintjens and compared with different experimental findings reported in the literature. All measurements agree reasonably well at 35 °C (in the vicinity of the $\Theta$ temperature of the system). Differences develop as $T$ is raised; at 65 °C $\chi$ and its concentration dependence are found to be less pronounced than reported. Under these conditions there also exists a discrepancy between the values calculated from $\chi(\varphi_2)$ for vanishing polymer concentration and those directly measured. The reasons for that observation are discussed. The present work demonstrates that the new method yields quick and reliable information on $\chi(\varphi_2;T)$.

## Introduction

For many theoretical considerations as well as for numerous practical applications the knowledge of the Gibbs energy of mixing as a function of composition is of utmost importance. Despite this need there is only a little experimental information due to the fact that considerable labor is required to obtain these data. Normally it is necessary to combine different kinds of measurements, among them that of vapor pressure as a function of polymer concentration, and these—when performed in the usual way—are rather time consuming.

For the above reasons it was checked whether a normal gas chromatograph in combination with a head-space sampler could be used to obtain the equilibrium vapor pressures of polymer solutions. This procedure would—in contrast to the traditional measurements—not require the removal of air; furthermore, it could be easily automatized. The system cyclohexane/polystyrene (CH/PS) was chosen to test out the new method, since it is probably the one studied in greatest detail.

## Experimental Section

**Apparatus.** The different instruments and their setup can be seen in Figure 1.

A pneumatically driven thermostated head-space sampler (Dani HSS 3950, Milano, Italy) takes 20 $\mu$L of the gas phases in equilibrium with the polymer solutions and injects it into a gas chromatograph (Shimadzu GC 14A, Kyoto, Japan). A glass column packed with 10% Apiezon M on Chromosorb W was used. A flame ionization detector ($H_2$ of 99.9% purity and dried pressurized air) served to measure the amount of solvent contained in the injected gas volume. The signals were integrated and registered by means of an integrator (Shimadzu Chromatopac C-R6A).

**Procedures.** Polymer solutions (3 mL), contained in crimp-top vials (capacity 5 mL) sealed with air-tight septa, were rotated at the equilibrium temperature for typically 5 days on a wobble mixer (IDL, TRM-V, Nidderau-Heldenbergen, Germany) to guarantee the establishment of the correct vapor pressure. Then the vials were transferred into the head-space sampler and conditioned for 1.5 h. Typically one injection was performed per minute.

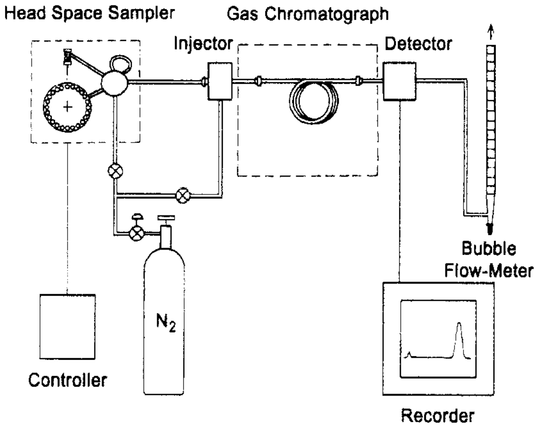

**Figure 1.** Scheme of the experimental setup for the determination of vapor pressures by means of gas chromatography.

The transfer line was kept at a temperature ca. 10 °C higher than the sampler in order to avoid condensation. The injector and the detector temperatures were 140 °C, and that of the column was 120 °C. The flow rates of $N_2$ (carrier gas, 0.8 bar), of $H_2$, and of the pressurized air were 500, 60, and 500 mL/min, respectively. After each series of measurements the vials were weighted to check their tightness.

Although it is possible to obtain absolute values for the vapor pressures $p_1$ of the solvent via calibration, these figures were not calculated since it is only the ratio $p_1/p_1^o$ (the index o standing for the pure solvent) that is required for the calculation of the thermodynamic data and $p_1/p_1^o$ is directly accessible from the ratio of the corresponding integrated detector signals.

**Materials.** Cyclohexane (p.a., Merck, Darmstadt, Germany) was kept over a molecular sieve of 3 Å. The weight-average molecular mass of the polystyrene sample PS 233 (PSS; Mainz, Germany) is 233 kg/mol; its molecular nonuniformity ($M_w/M_n$) − 1 is <0.01 according to the suppliers and as checked by GPC.

**Tests of Feasibility.** The reproducibility of the vapor pressure data was checked by means of several pure solvents and different solutions of PS 233 in CH for different temperatures. The standard deviation was in all cases less than 1%. In the case of pure solvents these data were evaluated with respect to the heat of vaporization according to eq 1

$$\ln \frac{p_1(T_2)}{p_1(T_1)} = \frac{\Delta \bar{H}_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

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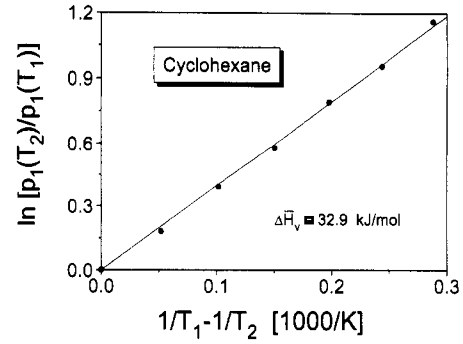

**Figure 2.** Test of the reliability of the gas chromatographic vapor pressure measurements by means of eq 1 for pure cyclohexane.

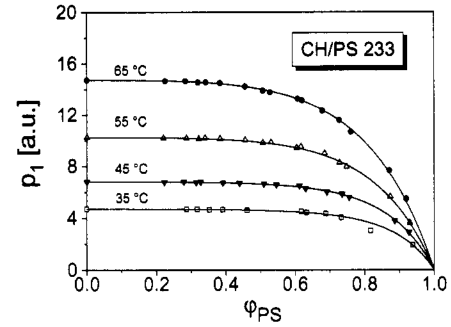

**Figure 3.** Dependence of the vapor pressures $p_1$ (given in arbitrary units) on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane, for the indicated temperatures. The full lines connecting the data points are calculated from eqs 8 and 9 by means of the parameters collected in Table 1 for the evaluation not considering $\chi_0$.

as shown in Figure 2 for cyclohexane. The value for the heat of vaporization given in this graph agrees well with the figure given in the literature[2] (32.8 kJ/mol).

Furthermore, the influence of an external pressure on the equilibrium vapor pressure was checked. The vapor pressure $p_1{}^*$ in the presence of air, i.e., under the external pressure $p_{tot}$, as compared with the equilibrium value $p_1$, can be obtained from eq 2

$$\ln\frac{p_1{}^*}{p_1} = \frac{\bar{V}_1}{RT}(p_{tot} - p_1) \qquad (2)$$

According to calculations for representative systems and conditions, the increase of the vapor pressure of the solvent by the presence of air remains below 0.2% in all cases, in agreement with a corresponding discussion in the literature.[3]

Tests were performed to ascertain that equilibria are attained in the course of the normal procedures; to that end some polymer solutions were kept at constant temperature for several weeks and $p_1$ was measured as a function of time. No changes outside the normal scattering of data could be observed.

## Results and Discussion

The vapor pressures of CH in the system CH/PS 233 are shown in Figure 3 as a function of $\varphi_2$, the volume fraction of the polymer, for different constant temperatures. For the reasons explained in the introduction $p_1$ is given in arbitrary units. The curves connecting the data points are calculated by means of eqs 8 and 9, where the parameters of eq 9 were determined from vapor pressures only.

The determination of the Flory–Huggins interaction parameter $\chi$ starts from eq 3, which expresses the molar Gibbs energy of mixing in terms of the mol fractions $x_i$ and the volume fractions $\varphi_i$ of the components, plus an integral interaction parameter $g$, normally varying with composition.

$$\Delta\bar{G}_M/RT = x_1 \ln \varphi_1 + x_2 \ln \varphi_2 + g x_1 \varphi_2 \qquad (3)$$

Upon differentation of eq 3 with respect to the number of moles of solvent, one obtains $\Delta\bar{G}_1$, the chemical potential of the solvent

$$\Delta\bar{G}_1/RT = \ln \varphi_1 + (1 - 1/N_2)\varphi_2 + \chi\varphi_2{}^2 \qquad (4)$$

where $N_2$ is the ratio of the molar volumes of solute and solvent (proportional to the degree of polymerization) and $\chi$ the differential interaction parameter for the solvent (usually the only one experimentally accessible); $\chi$ is defined in terms of the partial molar residual Gibbs energy of mixing of this component as

$$\chi = \Delta\bar{G}_1{}^{R}/RT = g - (1 - \varphi_2)\ \partial g/\partial\varphi_2 \qquad (5)$$

Since Gibbs energy and vapor pressures are interrelated by

$$\Delta\bar{G}_1/RT = \ln(p_1/p_1{}^{\circ}) \qquad (6)$$

if one neglects the small corrections for the nonideality of the vapor, the Flory–Huggins interaction parameter $\chi$ is experimentally accessible from the ratio of $p_1$ and $p_1{}^{\circ}$, the vapor pressures above the solution and above the pure solvent, respectively, according to

$$\frac{\ln(p_1/p_1{}^{\circ}) - \ln \varphi_1 - (1 - 1/N_2)\varphi_2}{\varphi_2{}^2} = \chi \qquad (7)$$

The parameters of equations describing $\chi(\varphi_2)$ are then obtained from the condition that

$$\sum_i (\chi_i{}^{\mathrm{exp}} - \chi_i{}^{\mathrm{theor}})^2 \rightarrow \text{minimum} \qquad (7a)$$

For the evaluation of data eq 7 is often rearranged as shown in eq 8

$$\ln(p_1/p_1{}^{\circ}) - \ln \varphi_1 - (1 - 1/N_2)\varphi_2 = \chi\varphi_2{}^2 \qquad (8)$$

so that the condition for the best fit now reads

$$\sum_i (\chi_i{}^{\mathrm{exp}}(\varphi_2{}^2)_i - \chi_i{}^{\mathrm{theor}}(\varphi_2{}^2)_i)^2 \rightarrow \text{minimum} \qquad (8a)$$

Normally $\chi$ is found to vary with composition; its dependence on $\varphi_2$ is often quantitatively described by the relation of Koningsveld and Kleintjens[4]

$$\chi = \alpha + \frac{\beta(1 - \gamma)}{(1 - \gamma\varphi_2)^2} \qquad (9)$$

where $\alpha$, $\beta$, and $\gamma$ are constants for a given system and temperature. The entropical parameter $\alpha$ should be independent of $T$, and $\beta$ should vary according to

$$\beta = \beta_0 + \beta_1/T \qquad (10)$$

The parameter $\gamma$ takes account of the fact that $\sigma$, the molecular surface areas per segment, are normally different for solvent and solute in the following way:

$$\gamma = 1 - \sigma_2/\sigma_1 \qquad (11)$$

Since the concentration dependence of $\chi$, as determined by means of vapor pressures, is only accessible for moderate to high concentrations, it is often mandatory to supplement this information with data referring to dilute solutions;

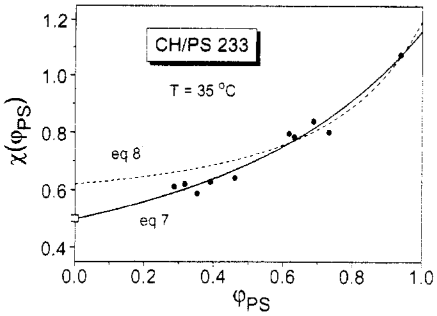

**Figure 4.** Graph demonstrating the differences in the Flory–Huggins interaction parameters $\chi$ resulting from the evaluation of the vapor pressures on the basis of eqs 7 and 8. The open square gives $\chi_0$ as determined from light scattering.[5,6]

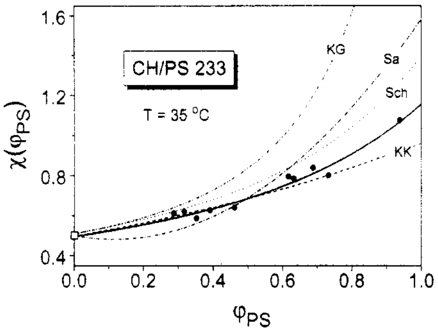

**Figure 5.** Dependence of the Flory–Huggins interaction parameter $\chi$ on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane for 35 °C. The full line connecting the data points is calculated from eq 9 by means of the parameters collected in Table 1 for the evaluation *not* considering $\chi_0$. The abbreviations inserted into the broken lines denote the authors who have published this information. KK: Koningsveld and Kleintjens.[4] Sch: Scholte.[7] Sa: Sanchez.[8] KG: Krigbaum and Geymer.[9] The open square indicates the $\chi_0$ value calculated from light scattering measurements.[5,6]

$\chi_0$, the limiting value of $\chi$ for infinite dilution, can be easily obtained from the second osmotic virial coefficients, $A_2$, knowing the molar volume $\bar{V}_1$ of the solvent and the density $\rho_2$ of the polymer, by means of eq 12.

$$\chi_0 = 0.5 - A_2\bar{V}_1\rho_2^{\,2} \qquad (12)$$

In Figure 4 this information concerning the dilute state is also given (open square); it demonstrates that the evaluation should only be performed according to eq 7 and not according to eq 8. The reason is that the latter procedure underrates the information for low $\varphi_2$ values considerably, as can be seen from the comparison of eqs 7a and 8a.

**Concentration Dependence.** The variation of $\chi$ with $\varphi_2$, the volume fraction of the polymer, is shown in the Figures 5–8 for different temperatures, together with experimental results reported in the literature. The solid curves drawn through the data points of the present measurements were calculated by means of eq 9 and the parameters resulting from the corresponding fits (see Table 1). In these diagrams the $\chi_0$ values[5,6] are also indicated for the sake of comparison; they were, however, not taken into account in the evaluation.

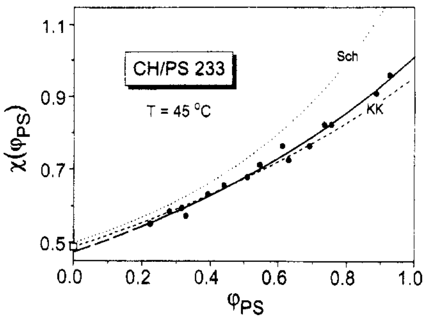

**Figure 6.** Dependence of the Flory–Huggins interaction parameter $\chi$ on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane for 45 °C. The full line connecting the data points is calculated from eq 9 by means of the parameters collected in Table 1 for the evaluation *not* considering $\chi_0$. The abbreviations inserted into the broken lines denote the authors who have published this information. KK: Koningsveld and Kleintjens.[4] Sch: Scholte.[7] The open square indicates the $\chi_0$ value calculated from light scattering measurements.[5,6]

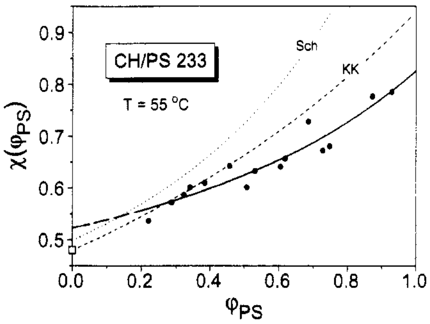

**Figure 7.** Dependence of the Flory–Huggins interaction parameter $\chi$ on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane for 55 °C. The full line connecting the data points is calculated from eq 9 by means of the parameters collected in Table 1 for the evaluation *not* considering $\chi_0$. The abbreviations inserted into the broken lines denote the authors who have published this information. KK: Koningsveld and Kleintjens.[4] Sch: Scholte.[7] The open square indicates the $\chi_0$ value calculated from light scattering measurements.[5,6]

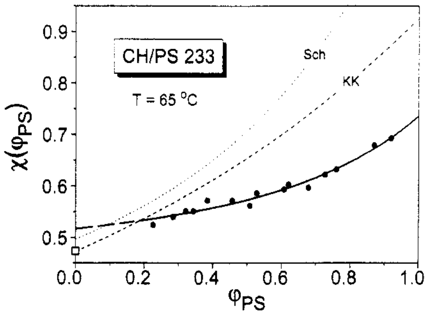

**Figure 8.** Dependence of the Flory–Huggins interaction parameter $\chi$ on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane for 65 °C. The full line connecting the data points is calculated from eq 9 by means of the parameters collected in Table 1 for the evaluation *not* considering $\chi_0$. The abbreviations inserted into the broken lines denote the authors who have published this information. KK: Koningsveld and Kleintjens.[4] Sch: Scholte.[7] The open square indicates the $\chi_0$ value calculated from light scattering measurements.[5,6]

At the lowest temperature, which lies within the range reported for the Θ temperature of the system (34–35 °C), two of the four reported dependencies agree well with the present findings within the region of moderate polymer concentration. The relation reported by Koningsveld and Kleintjens[4] (KK), who evaluated critical data, deviates close to the pure polymer only. The agreement of the data of Scholte[7] (Sch), which stem from equilibrium measurements on an ultracentrifuge, is somewhat worse. Only the results reported by Sanchez[8] (Sa) and by Krigbaum and Geymer[9] (KG) deviate considerably. All curves intersect the ordinate close to the independently determined $\chi_0$ value. However, as $T$ is raised this coincidence gets lost and the information obtained at higher concentration and extrapolated to lower concentrations leads to totally unrealistic values at high dilution.

The reason for the increasing discrepancies between the $\chi_0$ values calculated from eq 9 and those actually measured

**Table 1. Evaluation of Vapor Pressure Data on the Basis of Equations 9 and 10**

| | fits according to eq 9 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | excluding $\chi_0$ | | | fixed to experimental $\chi_0$[a] | | | | simultaneous fit according to eqs 9 and 10 | | | | |
| $T$ (°C) | $\alpha$ | $\beta$ | $\gamma$ | $\chi_0$ | $\alpha$[a] | $\beta$ | $\gamma$ | $\alpha$ | $\beta_0$ | $\beta_1$ (K) | $\beta$[b] | $\gamma$ |
| 35 | 0.21 | 0.52 | 0.45 | 0.500 | 0.20 | 0.53 | 0.44 | 0.47 | −1.47 | 533 | 0.26 | 0.63 |
| 45 | −0.10 | 0.80 | 0.28 | 0.495 | 0.05 | 0.65 | 0.33 | 0.47 | −1.47 | 533 | 0.21 | 0.63 |
| 55 | 0.26 | 0.33 | 0.36 | 0.488 | −0.17 | 0.80 | 0.19 | 0.47 | −1.47 | 533 | 0.15 | 0.63 |
| 65 | 0.46 | 0.14 | 0.50 | 0.480 | −0.01 | 0.59 | 0.17 | 0.47 | −1.47 | 533 | 0.11 | 0.63 |

[a] $\alpha = \chi_0 - \beta(1 - \gamma)$. [b] $\beta$ calculated according to eq 10.

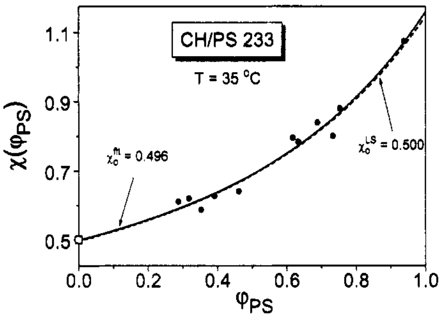

**Figure 9.** Dependence of the Flory–Huggins interaction parameter $\chi$ on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane, for 35 °C. The broken line connecting the data points is calculated from eq 9 by means of the parameters collected in Table 1 for the evaluation *considering* $\chi_0$ (stemming from light scattering data, open squares); the full line of the corresponding Figure 5 is also given.

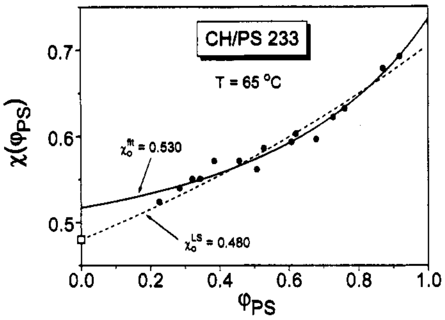

**Figure 10.** Dependence of the Flory–Huggins interaction parameter $\chi$ on $\varphi_{PS}$, the volume fraction of polystyrene in mixtures with cyclohexane, for 65 °C. The broken line connecting the data points is calculated from eq 9 by means of the parameters collected in Table 1 for the evaluation *considering* $\chi_0$ (stemming from light scattering data, open squares); the full line of the corresponding Figure 8 is also given.

(squares stemming from light scattering data) is obvious: Close to the Θ conditions the size of the polymer coils is practically independent of composition, whereas it increases markedly under good thermodynamic conditions as solvent is added and the chain overlap goes down; this situation leads to additional contributions to $\chi$ due to these changes[10] which cannot be felt at high concentrations and which are outside the scope of eq 9 which assumes that the polymer segments of a given solution are equally distributed over the entire volume.

The comparison of $\chi(\varphi_2)$ for the higher temperatures demonstrates that the dependencies of KK and of Sch are both shifted relative to the present results to higher $\chi$ values and intersect the results from the vapor pressure measurements at moderate polymer concentrations. The discrepancies in the case of KK are probably due to the fact that this information is extrapolated from a temperature region within which the solvent is very poor to one where it is considerably improved in quality. At present no explanation can be offered for the still larger deviations in the case of Sch.

In view of the problems with the poor representation of the variation of $\chi$ in the region of high dilution by eq 9 for which the parameters are exclusively determined from vapor pressures, it was interesting to check whether the situation improves if the information concerning $\chi_0$ is included in the evaluation. Expectedly there is practically no change for 35 °C (Figure 9). For 65 °C, on the other hand, $\chi(\varphi_2)$ can be forced through $\chi_0$ (Figure 10) but only at the cost of a considerably worse agreement with the other data points.

The comparison of the data collected in the first two sections of Table 1 demonstrates that the parameters $\alpha$ and $\gamma$ of eq 9 which should—according to theory—be independent of $T$ vary considerably and unsystematically. It was therefore checked how the entire set of experimental information can be represented if one fits the concentration and the temperature dependence in one step, i.e., forces $\alpha$ and $\gamma$ to become constant. The results of this evaluation are collected in the third section of Table 1. Expectedly the standard deviation of the simultaneous fit turns out to be 1 order of magnitude worse than that of the individual ones.

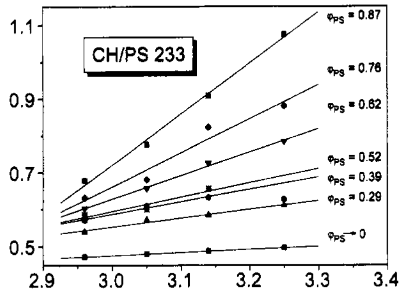

**Figure 11.** Evaluation of $\chi(T^{-1})$ according to eq 13 for the indicated volume fractions of the polymer.

**Temperature Dependence.** From the present experimental material it is also possible to calculate $\chi_H$, the enthalpy part of $\chi$, as a function of composition, which is related to $\Delta\bar{H}_1$, the heat of dilution, by

$$\chi_H = \frac{\Delta\bar{H}_1}{RT\varphi_2^2} = \frac{1}{T}\left(\frac{\partial\chi}{\partial(1/T)}\right) \tag{13}$$

$\chi_S$, the entropy part of $\chi$, constitutes the difference between $\chi$ and $\chi_H$ and measures $\Delta\bar{S}_1^R$, the residual Gibbs entropy of dilution

$$\chi_S = \chi - \chi_H = -\Delta\bar{S}_1^R/R\varphi_2^2 \tag{14}$$

Figure 11 shows the evaluation of $\chi$ according to eq 13 for the different indicated polymer concentrations. In agreement with the general experience the slope of the lines in this graph, i.e., $\chi_H$, increases markedly as $\varphi_2$ becomes larger. How the Flory–Huggins interaction parameter $\chi$ is made up from its constituents, $\chi_H$ and $\chi_S$, at different concentrations is demonstrated in Figure 12.

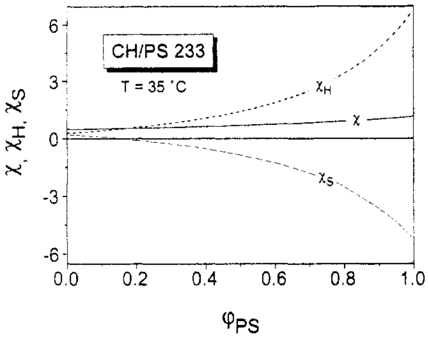

**Figure 12.** Dependence of $\chi$ and of its enthalpic and entropic constituents $\chi_H$ and $\chi_S$ (eqs 13 and 14) on the volume fraction of the polymer.

The data on the dilute side are already well established.[11,12] The information that is available to check the present findings for higher polymer contents is practically restricted to the results of inverse gas chromatography. This method yields the limit of $\chi$ for vanishing solvent concentration and is therefore physically unrealistic if applied below the glass transition temperature of the polymer which is ca. 100 °C for PS. Therefore, the results from higher temperatures must be extrapolated into the temperature range of present interest. The same argument holds true for the extrapolation of our isothermal data to $\varphi_2 \rightarrow 1$. In view of these difficulties the value of $\chi_H = 6.5$ that results from Figure 12 agrees reasonably with those reported in the literature if extrapolated to 35 °C ($\chi_H$ = 5.8[13] and 2.3[14]).

The $\chi_H$ values calculated from eqs 9, 10, and 13 by means of the parameters (collected in the third section of Table 1) resulting from the simultaneous fit of all data are about three times larger in the limit of $\varphi_2 \rightarrow 0$ and only ca. $^2/_3$ as large for $\varphi_2 \rightarrow 1$ as compared with that of the direct evaluation.

## Outlook

The results reported above demonstrate that the Flory–Huggins interaction parameters can be determined in a reliable and quick manner via the measurement of the vapor pressures of the solvent by means of gas chromatography. Since this new method can be easily automatized, it makes the required thermodynamic data more readily available.

In our group the new procedure is presently applied to several binary systems to study the variation of $\chi$ with composition in the range within which the coils change upon dilution from their unperturbed to their equilibrium dimension at infinite dilution. In addition, it is also applied to ternary systems, consisting of two incompatible polymers and a common solvent, to obtain information on the interaction between the polymers.

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