

Determination of solvent/polymer interaction parameters of moderately concentrated polymer solutions by vapor pressure osmometry

M. Karimi^{a,*}, W. Albrecht^b, M. Heuchel^b, Th. Weigel^b, A. Lendlein^b

^a Amirkabir University of Technology, Department of Textile Engineering, Hafez Avenue, 15914 Tehran, Iran

^b GKSS Research Center Geesthacht GmbH, Institute of Polymer Research, Kantstr. 55, D-14513 Teltow, Germany

ARTICLE INFO

Article history:

Received 27 November 2007
Received in revised form 21 February 2008
Accepted 26 March 2008
Available online 28 March 2008

Keywords:

Immersion precipitation
Thermodynamics
Solvent/polymer interaction

ABSTRACT

The paper describes the application of vapor pressure osmometry (VPO) to determine solvent/polymer interaction parameters for various polymer solutions containing high-molecular weight polymers in the semi-diluted concentration range. The theoretical basis for the data evaluation is the Flory–Huggins (FH) model and a virial expansion up to the third virial term. For validation already well characterized polymer/solvent systems poly(vinylpyrrolidone)/water, polysulfone/*N,N*-dimethylformamide (DMF), and poly(ether sulfone)/DMF were investigated. In the second part interaction parameters of poly(ether imide) (PEI) in solvents with technical relevance for membrane formation (DMF, *N*-methylpyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc)) were examined at different concentrations and temperatures. The results document that VPO is a fast and promising method for characterization of semi-diluted polymer solutions containing polymers with higher molecular weight. Results confirm the decrease of solvent power for PEI in the series: NMP > DMAc > DMF.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The immersion precipitation process, in which a homogeneous polymer solution is separated by the addition of a nonsolvent through solvent/nonsolvent exchange into two phases (a polymer-rich and a polymer-lean phases), is the most commonly used one to fabricate polymeric membranes with various morphologies for different applications. The diffusive exchange between both liquid phases through the interface leads to changes in the composition resulting in a phase demixing. Besides the kinetics of the phase separation process, the thermodynamic state of the ternary non-solvent (1)/solvent (2)/polymer (3) system plays a crucial role in the creation of a specific morphology.

The classical Flory–Huggins (FH) model [1] is commonly used for the thermodynamic analysis of the phase behavior during membrane formation. The model results in an expression for the Gibbs free energy of mixing of the system per mole of segments. For a ternary system, the Gibbs free energy of mixing ΔG_M can be presented in form of Tompa's extension [2] as

$$\frac{\Delta G_M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12}(u_2)n_1\phi_2 + \chi_{23}(\phi_3)n_2\phi_3 + \chi_{13}n_1\phi_3 \quad (1)$$

where R is the gas constant, T is the absolute temperature, n_i and ϕ_i are the number of moles and the volume fraction of components i , respectively, and χ_{ij} are the i/j interaction functions. u_2 is the volume fraction of solvent in a pseudo-binary nonsolvent/solvent mixture defined as: $u_2 = \phi_2/(\phi_1 + \phi_2)$. The application of Eq. (1) requires three precisely and independently determined (binary) interaction parameters or interaction parameter functions. Knowing the interaction parameters between the three components, it is possible to calculate binodal, spinodal, tie lines, and critical points for the ternary system. More information about the mathematical/numerical treatment may be found, e.g., in Ref. [3].

The solvent/polymer interaction parameter χ_{23} is one of these three essential parameters. It is often assumed as concentration dependent. The physical basis of its experimental determination is the measurement of the reduced solvent vapor pressure above a binary polymer mixture with respect to the state of pure solvent. Experimental data can be found either for the diluted concentration range ($c_3 \leq 2.0$ wt.%) of the polymer, measured with osmometry, light scattering, or viscosimetry [4], or for a very high concentration range (≥ 50 wt.%), derived, e.g., from sorption experiments [5,6]. However, for the typical concentration range of membrane formation (polymer concentration between about 10 and 30 wt.%) only very few suitable χ_{23} data (not to mention their concentration dependencies) can be found. Recently, Barth and Wolf [7] introduced headspace gas chromatography as a method to measure partial pressures of volatile components (solvents) in different homogeneous binary systems. However, precise measurements

* Corresponding author. Tel.: +98 21 6454 2658; fax: +98 21 6640 0245.
E-mail address: mkarimi@aut.ac.ir (M. Karimi).

Nomenclature and abbreviations

Abbreviation

DMAc	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
FH	Flory–Huggins
NMP	<i>N</i> -methylpyrrolidone
PEI	poly(ether imide)
PES	poly(ether sulfone)
PSU	polysulfone
PVP	poly(<i>N</i> -vinylpyrrolidone)
VPO	vapor pressure osmometer

Nomenclature

ϕ	volume fraction
G	Gibbs free energy (J mol^{-1})
μ	volume fraction in binary system
T	absolute temperature (K)
R	gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
n	number of moles
χ	interaction parameter
P	vapor pressure (Pa)
x	mole fraction
ΔH	enthalpy difference (J)
$\Delta_{\text{v}}H$	heat of vaporization
$\Delta\phi_{\text{el}}$	voltage difference (V)
v	molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
\bar{v}	partial molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
ρ	density (g cm^{-3})
π	osmotic pressure (Pa)
M	molecular weight
c	concentration (g/ml)
A	virial coefficient ($\text{cm}^3 \text{ mol g}^{-2}$)
V	volume (cm^3)
$\Delta\mu$	chemical potential differences
a	activity
K	calibration constant (V g mol^{-1})

Index

1	nonsolvent
2	solvent
3	polymer as well as order of virial coefficient
M	mixture

require concentrations higher than 25 wt.%. These concentrations lie already on the upper limit, applied for membrane formation.

The experimental determination of solvent/polymer interaction parameter for the typical concentration range of the polymer membrane formation was carried out by high-pressure membrane osmometry [8,9] or light scattering [10,11]. Practically, these (limited) data are the basis of all reported thermodynamic studies of membrane formation in ternary systems. Most recently, Wei et al. [12] estimated interaction parameters on the basis of solubility parameters, but the relevance of the obtained χ_{23} values is questionable because of the data precision.

The vapor pressure osmometry (VPO) is a method that operates typically (i.e., with high precision) in the infinite diluted concentration range for polymer solutions containing polymers with molecular weights significantly smaller than 10 000 Da. Despite that Burge [13] showed that the thermoelectric differential vapor pressure method is valid for a wide variety of electrolytes up to moderate concentrations, VPO methods have obtained only a little attention [14] as a source for thermodynamic data in the range of

semi-dilute polymer solution and polymers with molecular weight $M_w \geq 10\,000$ Da typical for VPO. The quickness and convenience of this measurement make the method very promising in studies, where isopiestic methods are too time consuming, in general. In contrast to other techniques, very small pressure differences can be detected and transformed into relatively large temperature differences making VPO beneficial in comparison to direct measurements of the pressure difference. The open question is: Is the application of VPO also successfully possible in the range of *moderately concentrated* polymer solutions containing polymers with *high* molecular weight, which are commonly investigated by membrane osmometry? Obviously their application in the range of infinite diluted polymer solutions is not possible because of the low pressure difference between polymer solution and solvent. As a consequence, the precision of the osmotic data is too low. However, the pressure difference rises rapidly as a function of polymer volume fraction [15,16] and one may expect a successful application of VPO in the range of moderately concentrated polymer solutions. Therefore, the VPO technique may allow a new pathway to data for solvent/polymer interaction parameters in the moderate concentration range applied, e.g., for membrane formation.

In the present work, vapor osmotic pressure data are reported for moderately concentrated binary polymer solutions containing polymers with high molecular weight. Based on the data, the second and third virial coefficients for these binary polymer solutions are extracted and the FH interaction parameters are calculated. The aim of this investigation is the development of experimental data sources for the thermodynamic analysis of phase demixing processes during membrane formation. Also, these data are interesting for a completion of the concentration dependence of solvent/polymer interaction parameters in the (limited) concentration range between diluted and high where the standard experimental techniques do not work precisely. In realization of this aim the first part discusses the concentration dependency of the interaction parameter in well-investigated semi-diluted polymer solutions. With it, both the experimental technique and the principal data evaluation shall be validated. The second part presents solvent/polymer interaction parameters for poly(ether imide) (PEI) in different solvents including their concentration dependencies. According to the obtained results, VPO is applicable and represents a promising high precision technique for an inexpensive and quick determination of the solvent/polymer interaction parameter χ_{23} .

2. Background of vapor pressure osmosis (VPO) and data evaluation

2.1. Vapor pressure osmometry (VPO)

The equilibrium vapor pressure p_2 of a solvent over a solution is lower than the vapor pressure p_2^0 over the pure solvent at the same temperature and pressure. If x_3 is the mole fraction of the polymer component in a binary solution, the pressure difference can be expressed via Raoult's law as $p_2^0 - p_2 = \Delta p_2 = x_3 p_2^0$. This pressure difference can be detected easily by a VPO device. In a VPO device, two thermistors are placed in the measuring chamber. These thermistors, forming two arms of a Wheatstone bridge, are suspended in a saturated solvent atmosphere of a closed chamber, whose temperature is carefully controlled. This chamber contains a reservoir of solvent and two wicks to provide a saturated solvent atmosphere around the thermistors. Under these conditions, if pure solvent is placed on both thermistor surfaces with the same temperature, the bridge can be adjusted to 0 to establish the reference condition. Then the solvent on one thermistor is replaced by a drop of solution. Condensation from the saturated atmosphere warms the thermistor resulting in a change of its resistance and an unbalance of the bridge. The condensation will continue until the thermistor

temperature is raised enough to bring the solvent vapor pressure of the solution up to that of the pure solvent at the surrounding chamber temperature. The experimentally observed quantity is the amount of resistance change required to rebalance the bridge, which can be related to the temperature change of the thermistors. Thus a temperature difference will be attained between the two thermistors which is according to the Clausius–Clapeyron equation directly related to the vapor pressure of the solution by

$$\frac{dp_2}{dT} = \frac{p\Delta_v H}{RT^2} \quad (2)$$

where p_2 is the vapor pressure of the solvent and $\Delta_v H$ is the heat of vaporization of the pure solvent at this temperature and the ambient (atmospheric) pressure p . For the very small temperature changes that are associated with VPO, it is assumed that T , $\Delta_v H$, and p are constant and Eq. (2) can be integrated to yield the temperature difference

$$\Delta T = \left(RT^2/p\Delta_v H \right) \Delta p_2 \approx \left(RT^2/\Delta_v H \right) \chi_3 \quad (3)$$

which is proportional to the pressure difference.

In the operating range of the osmometer, $|\Delta T|$ is always small enough so that the temperature dependence of $\Delta_v H$ is negligible with respect to other sources of uncertainties. Thus, the constancy of $\Delta_v H$ is justified. The temperature difference ΔT is transferred into a voltage difference $\Delta\Phi_{el}$ (application of the Wheatstone bridge principle). On the basis of thermodynamic equilibrium considerations, Burge [13] as well as Brown [17] showed that the measured voltage is proportional to the chemical potential difference between states of pure solvent and of solution, $\Delta\Phi_{el} \propto \Delta\mu_2$. This chemical potential difference of the solvent can be expressed by the osmotic pressure π as $\Delta\mu_2 = -\pi v_2$, where v_2 is molar volume of the solvent. Therefore, the measured voltage difference has the following relation to the osmotic pressure π

$$\frac{\pi}{RT} = \frac{\Delta\Phi_{el}\rho_2}{1000K} \quad (4)$$

where ρ_2 is the density of solvent and K is a calibration constant.

2.2. Data evaluation

VPO is a standard method if infinite diluted polymer solutions containing low-molecular weight polymers are investigated. Insofar the data evaluation of VPO can be realized similar to the established data evaluation technique applied for low-molecular weight polymer solutions [18]. However, the influence of additional interactions has to be considered [19]. Herein two data evaluation techniques are used: virial expansion and Flory–Huggins model. It will be turned out that the obtained values of the solvent/polymer interaction parameters depend on the applied model. Therefore, we think that it is necessary to evaluate the data due to both models and to show briefly the underlying model assumptions.

2.2.1. Virial expansion

The chemical potential (μ_2) and the solvent activity (a_2) in the solution are related to the osmotic pressure π by

$$\Delta\mu_2 = \mu_2 - \mu_2^0 = RT \ln a_2 = -v_2\pi \quad (5)$$

The osmotic pressure of polymer solutions can be described by virial coefficients, which may be evaluated from cluster expansion methods [20] as

$$\frac{\pi}{RT} = \frac{1}{M_3}c_3 + A_2c_3^2 + A_3c_3^3 + \dots \quad (6)$$

where c_3 is the concentration of the polymer (expressed in g/ml), M_3 is the molecular mass of the polymer, and A_2 and A_3 are the

second and the third osmotic virial coefficients of the polymer in the solvent, respectively. c_3 can be related to ϕ_3 , the volume fraction of the polymer, by $\phi_3 = \bar{v}_3c_3/M_3$, in which \bar{v}_3 is partial molar volume of the polymer in the solution. The partial molar volume can be obtained through $\bar{v}_3 \equiv (\partial V/\partial n_3)_{T,P,n_2}$, where V is the total volume and n_i is the number of moles of component i . Commonly, the higher order of virial coefficients (A_3, \dots) are neglected and their contributions become part of an effective second virial coefficient. This model is the basis of data evaluation in diluted regimes.

2.2.2. Flory–Huggins model

A statistical thermodynamic approach, such as this model [21,22], provides a good description of the steeply increasing osmotic pressure with polymer concentration. The basic relation may be obtained by deriving $\Delta\mu_2$, the excess chemical potential of component 2 in the binary solvent (2)/polymer (3) system, from Eq. (1) assuming $\phi_1=0$ and calculating the first derivative of the Gibbs free energy of mixing with respect to n_2 , i.e., $\Delta\mu_2 = [\partial(\Delta G)/\partial n_2]_{T,P,n_3}$. It results

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 + (1 - v_2/v_3)\phi_3 + \chi_{23}\phi_3^2 \quad (7)$$

where $v_2/v_3 \approx 0$ is the ratio of molar volumes of solvent and polymer. Using Eq. (7) the measured solvent activity from VPO data can be used to calculate the solvent/polymer interaction parameter according to

$$\frac{\ln(a_2/\phi_2) - \phi_3}{\phi_3} = \chi_{23}\phi_3 \quad (8)$$

The interaction parameter χ_{23} is obtained as slope of a fitted straight line if $(\ln(a_2/\phi_2) - \phi_3)/\phi_3$ data are plotted versus ϕ_3 . This model is the basis of data evaluation in concentrated polymer solutions.

Polymer solutions, located in between the both regimes, behave differently. Usually, the FH model is also applied to describe semi-diluted polymer solutions, investigated herein. However, it has been recognized [23] that the FH model neglects certain correlations between adjacent (and even more distant) monomer units resulting in density fluctuations. How two monomer units on the same chain are spatially correlated is described with monomer density correlations [24]. Therefore, the FH model gives an inaccurate description of the virial coefficients for moderately concentrated polymer solution.

For the description of especially semi-diluted solutions, a virial expansion series with higher order interactions was proposed [19,25]. Due to this model, the basic equation for the thermodynamic properties is a power series for the osmotic pressure.

$$\ln a = -v_2 \left(\rho_3 \frac{1}{M_3} \phi_3 + \rho_3^2 A_2 \phi_3^2 + \rho_3^3 A_3 \phi_3^3 \right) \quad (9)$$

where ρ_3 is the density of the polymer which is assumed to be equal to the partial density of polymer, $\bar{\rho}_3$. The third term in Eq. (9) represents three-body interactions not considered in the FH model.

To find the “true” interaction parameter in semi-diluted region, it is assumed that the concentration dependency of the interaction parameter includes both; two and three-body interactions. Several theories exist for the description of this dependence. The following is used here [8]

$$\chi_{23}(\phi_3) = a + b\phi_3 \quad (10)$$

where a and b are adjustable parameters. According to Eq. (1) the chemical potential of solvent 2 in binary mixture of a solvent (2)/polymer (3) system can be represented by

$$\frac{\Delta\mu_2}{RT} = \ln a = \ln(1 - \phi_3) + (1 - v_2/v_3)\phi_3 + \left[\chi_{23}(\phi_3) - (1 - \phi_3) \left(\frac{\partial \chi_{23}(\phi_3)}{\partial \phi_3} \right) \right] \phi_3^2 \quad (11)$$

With Eq. (10) follows then

$$\ln a = \ln(1 - \phi_3) + (1 - v_2/v_3)\phi_3 + (a - b)\phi_3^2 + 2b\phi_3^3 \quad (12)$$

To express Eq. (12) as virial expansion series, a linear approximation $\ln(1 - \phi) \approx -\phi - (1/2)\phi^2 - (1/3)\phi^3$ should be used. This approximation is valid in the semi-dilute regime. Accordingly, the virial expansion (Eq. (6)) completely has been identified with FH model (Eq. (12)). However, it has been recognized that the FH model cannot explain osmotic pressure of polymer solution in semi-dilute regime precisely. In principle, the osmotic pressure (π) in the semi-diluted regime measures the number of contacts. Thus, according to virial expansion, the second and higher order virial coefficients are involved in the energetic interaction of contacts. On the other hand, the first two terms in the right hand side of Eq. (12) show entropy contribution of chemical potential in which they are disappeared if a linear approximation $\ln(1 - \phi) \approx -\phi$ is used. This approximation is valid if $\phi \rightarrow 0$. The second virial coefficient which shows the interaction of contacts is equal to $\chi/\rho_3^2 v_2$. In consequence, the interaction parameter is 0 if the solution behaves ideally. Traditionally, a linear approximation $\ln(1 - \phi) \approx -\phi - (1/2)\phi^2$ is used to present the FH model as virial expansion. Based on this point, the second virial coefficient is expressed by $(\chi - 0.5)/\rho_3^2 v_2$. It means that the interaction parameter is equal to 0.5 if the solution behaves ideally. We would accept this agreement and employ two terms of Taylor series in order to transfer the FH model to virial expansion. Therefore, by considering the third virial term in Eq. (5) as a contribution of three-body interactions, the concentration dependency of the interaction parameter will be included. The adjustable parameters of the interaction function (10) result from a comparison of Eqs. (9) and (12)

$$\begin{aligned} a &\equiv (1/2) + b - \rho_3^2 v_2 A_2 \\ b &\equiv -(1/2)\rho_3^2 v_2 A_3 \end{aligned} \quad (13)$$

3. Experimental

3.1. Material

The following polymers were investigated: poly(ether imide) (PEI), type Ultem[®] 1000 (General Electric, USA); polysulfone (PSU), type Ultrason[®] S3010; poly(ether sulfone) (PES), type Ultrason[®] E6020 (both BASF, Germany) as well as poly(*N*-vinylpyrrolidone) (PVP) (Sigma–Aldrich, Germany). Polymers were dried before use for 4 h at 100 °C in an oven. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP) were obtained from Sigma–Aldrich as water-free solvents and applied as received. Ultrapure water was purchased by Merck, Germany. Benzil (Merck, Germany) was applied as calibration substance for organic solvents and recrystallized twice from ethanol before application, whereas urea (p.a.) (Merck, Germany) was used (applied as purchased) for aqueous solvents. Characteristic data of the polymers and solvents are listed in Table 1.

3.2. Methods

3.2.1. Preparation of polymer solutions

The polymers were dissolved in solvents using closed bottles. Depending on the kind of polymer, solvent, or concentration, the solutions were prepared either at room temperature (22 °C) or in an oven at 80 °C under gentle stirring until a clear polymer solution

Table 1
Characteristic data of the solvents and the polymers investigated

Materials	Molar volume (cm ³ /mol)	Molecular weight (g/mol)	Density (g/cm ³)
Benzil	–	210.23	–
Urea	–	60.06	–
NMP	96.52	99.13	1.027
DMAc	92.98	87.12	0.937
DMF	77.34	73.09	0.945
Water	18.05	18	0.997
PEI	25 486	32 800 ^a [26]	1.287 [28]
	13 986	18 000 ^b [27]	
PSU	31 452	39 000 ^b [7]	1.24 [7]
PES	35 766	49 000 ^b [7]	1.37 [7]
PVP	310 345	360 000 ^c	1.16 [29]

^a Weight average.

^b Number average.

^c Data of the supplier.

was obtained (usually over night for 12 h). After that the polymer solutions were cooled down and degassed by standing for a longer time at room temperature.

3.2.2. Vapor pressure osmometry

A Vapor Pressure Osmometer, Model 833 (U.I.C. Inc., USA), was assembled to measure temperature differences between pure solvent and polymer solutions of various concentrations. For each experiment with a certain solvent and at each temperature, the measuring chamber was filled with the solvent (about 20 ml) and then equilibrated. The vapor/solvent equilibrium was reached in the measuring chamber after about 8 h. The reproducibility of the instrument was frequently checked with pure solvent. Differently concentrated solutions of urea in water (0.21–0.78 wt.%) and of benzil in DMF (0.12–0.82 wt.%), DMAc (0.1–0.82 wt.%) and in NMP (4.9–9.8 wt.%) were prepared to calibrate the instrument. The obtained $\Delta\Phi_{el}$ values for the various solution concentrations and the pure solvents were divided by the concentration ($\Delta\Phi_{el}/c$) and plotted versus the concentration c . Then the best straight line fit was used for extrapolation to zero concentration. This extrapolated value of $\Delta\Phi_{el}/c$ was used to calculate the calibration constant K (Eq. (4)) by multiplying it with the molecular weight of the used calibration substance. To obtain correct $\Delta\Phi_{el}$ values, measurements at five concentration steps were repeated 8–10 times then averaged (standard deviation: $\pm 2\%$). A straight line was fitted by linear regression through the five concentration values and finally extrapolated to zero concentration to get the calibration constant. Additionally, calibrations were repeated after one or two weeks if experimental investigations of a polymer/solvent system exceeded this period of time. The values for the calibration constants used in this work are listed in Table 2.

Measurements for the different binary polymer/solvent systems were performed in the concentration range from 5 to 30 wt.% polymer in the solution. After every fourth or fifth measurement, a reference measurement with pure solvent was carried out to check the baseline for the potential measurement. Under these conditions, the measured voltages (and thus the osmotic pressures of the solutions) differed within $\pm 1\%$ from their mean value.

Table 2
Calibration constants K (Vg mol⁻¹) (see Eq. (4)) for the used vapor pressure osmometer

Solvent	Temperature (°C)				
	25	50	70	90	110
NMP	–	–	685	1246	1744
DMAc	–	–	3919	2978	–
DMF	–	1373	2394	4977	–
Water	509	832	–	–	–

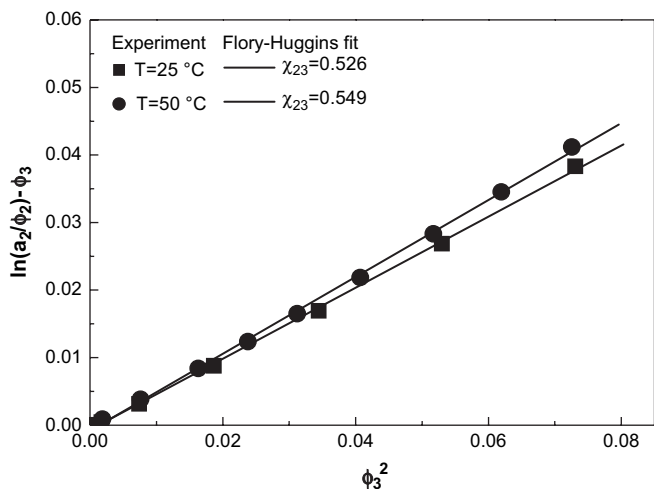


Fig. 1. Dependency of the activity on the polymer fraction of aqueous PVP solutions at 25 and 50 °C, according to the FH model (Eq. (8)).

4. Results and discussion

4.1. Reliability of the method

At first the VPO technique was applied to determine the interaction parameter χ_{23} for water/PVP (a system which is well reported in the literature for different concentration ranges, including the semi-diluted range [9]). Various concentrated aqueous PVP solutions (concentration range: 5–25 wt.%) were investigated at 25 and 50 °C. Results and typical data evaluation diagrams are presented in Fig. 1 on basis of the FH and Fig. 2 on basis of the virial expansion truncated at different virial terms.

The analysis leads in the semi-diluted regime to the following χ_{23} values: 0.54 ± 0.01 (FH model) and 0.415 ± 0.01 (virial expansion) (see Tables 3 and 4). According to the literature [30] the second virial coefficient of aqueous PVP solution (with the same characteristic data) was reported: $6.53 \times 10^{-4} \text{ cm}^3 \text{ mol g}^{-2}$ (measured at 25 °C), which is in agreement with our measurements: $5.024 \times 10^{-4} \text{ cm}^3 \text{ mol g}^{-2}$ at 25 °C and $6.78 \times 10^{-4} \text{ cm}^3 \text{ mol g}^{-2}$ at 50 °C.

Within the accuracy of the VPO method, for both models a constant interaction parameter was found for all investigated concentrations. In general, χ_{23} values derived from the virial expansion with higher order interaction are considered as more reliable in comparison to the FH model (see discussion later).

For the water/PVP system some parameter values are reported for different concentration ranges. For infinite diluted solutions, Cerny et al. [31] obtained a value of 0.48 (virial expansion truncated at second virial term) using membrane osmometry. Boom et al. [9] found in the concentration range of 2.5–30 wt.% a linear dependency of the interaction parameter on the concentration with parameter values between 0.475 (infinite diluted) and 0.63 (30 wt.%) at solution (FH model) using high-pressure membrane osmometry. A recalculation of the parameter with the procedures proposed herein using the data of Boom et al. [9] leads to $\chi_{23} = 0.59$ (FH model), and to $\chi_{23} = 0.47$ (virial expansion truncated at third virial term) with concentration dependency of $-0.014\phi_3$. Desbrieres et al. [32] reported from light scattering a water/PVP interaction parameter for infinite diluted solution of 0.49 (virial expansion truncated at second virial term). Sen et al. [33] as well as Kaplan and Güner [34] determined the interaction parameter for this system to 0.49 (no description of concentration range and used experimental technique). Rodriguez et al. [6] reported water/PVP interaction parameters in a range of 0.2–0.3 for 60–80 wt.% polymer “solutions” based on sorption measurements and data

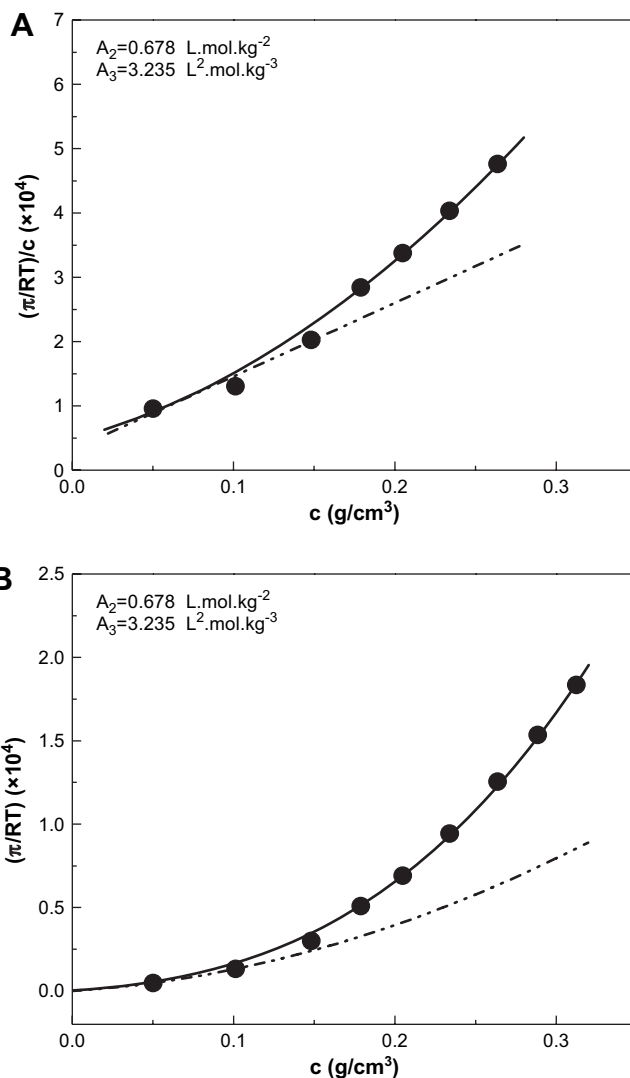


Fig. 2. Comparison of experimental osmotic pressure data (●) with calculations using the osmotic virial expansion truncated at the second virial coefficient term (---) and truncated at the third virial coefficient term (—) for PVP aqueous solution at 50 °C. (A) Plotting $(\pi/RT)/c$ against concentration, c ; (B) plotting π/RT against concentration, c . The virial coefficients are calculated from Eq. (6).

evaluation with the FH model. Finally Baulin and Halperin [35] discussed a constant water/PVP interaction parameter of 0.48 (two state models) in a concentration range up to 40 wt.%. At still higher concentration the parameter got a bit smaller. There is a good consistency between all these data, except Rodriguez’s result, but their concentration range is outside of the semi-diluted regime investigated here. The sorption method has the principal drawback that for high partial water pressures, corresponding to the semi-diluted concentration regime, the equilibrium water uptake cannot

Table 3

List of solvent/polymer interaction parameters χ_{23} evaluated from VPO measurements on the basis of FH model (see Eq. (8))

System	Temperature (°C)				
	25	50	70	90	110
PEI/NMP	–	–	0.56	0.57	0.58
PEI/DMAc	–	–	0.55	0.57	–
PEI/DMF	–	0.59	0.59	0.58	–
PSU/DMF	–	0.55	0.54	0.57	–
PES/DMF	–	0.47	0.47	0.48	–
PVP/water	0.53	0.56	–	–	–

Table 4

List of solvent/polymer interaction parameters χ_{23} evaluated from VPO measurements on basis of the virial expansion (see Eqs. (12) and (13))

Systems	Temperatures	$g(\phi) = a + b\phi$	
		a	b
PVP/water	25	0.417	-0.071
	50	0.437	-0.046
PSU/DMF	50	0.443	-0.017
	70	0.446	-0.003
	90	0.477	-0.008
PES/DMF	50	0.366	-0.061
	70	0.365	-0.05
	90	0.363	-0.057
PEI/DMF	50	0.498	0.008
	70	0.496	0.007
	90	0.494	-0.003
PEI/NMP	50	0.387	-0.11
	70	0.409	-0.089
	90	0.428	-0.071
PEI/DMAc	70	0.449	-0.024
	90	0.446	-0.026

be reached using water-soluble polymers. It can be expected that the water/PVP interaction parameter obtained by vapor sorption technique is increased with higher water uptake, as Chang et al [36] have shown for other polymer systems. By comparing the result, it is clear that all data are very similar.

According to statistical mechanics the second virial coefficient is a measure for the two-body interactions, while the higher order virial coefficient accounts for three-body interactions. The fundamental concept of this consideration suggests that the behavior of a solution can be described with only binary interactions if the second virial coefficient has a higher (or comparable) value compared to the next higher virial coefficients. In contrast, when in the solution the interacting pairs are affected by a third particle, then the third virial coefficient becomes higher. Plotting $(\pi/RT)/c$ against c , a linear behavior should result if three-body and higher order interactions do not exist. It can be seen in Fig. 2 that there is a deviation from the linearity which is related to three-body interactions. By considering the third virial coefficient in virial expansion, a good agreement is found between experimental osmotic pressure and calculations.

As second step, PSU and PES were investigated in the solvent DMF at different temperatures. The studied solvent/polymer systems are identical to systems investigated by Barth and Wolf [7] at concentration higher than 25 wt.% by headspace gas chromatography and at infinite diluted concentrations using light scattering. Therefore, the additional data can be included in the reported data to assess the concentration dependency of solvent/polymer interaction parameter in the semi-diluted regime. Data of investigation are summarized in Tables 3 (FH model) and 4 (virial expansion).

The results document the following:

- For PSU the interaction parameter, χ_{23} , calculated from VPO measurements is between 0.44–0.47 (virial expansion) and 0.54–0.57 (FH) and for PES between 0.36–0.34 (virial expansion) and 0.47–0.48 (FH). Data are practically identical with the data of Barth and Wolf [7] for infinite diluted solution (PSU: 0.46; PES: 0.37) and the lowest concentrated solution (25–30 wt.%) (PSU: 0.46) if data evaluation is based on virial expansion truncated at second virial term.
- The interaction parameter, χ_{23} , for PSU is constant in the investigated concentration range, but not for PES. The temperature dependency can be neglected, which is also in accordance with Barth and Wolf [7].
- Data evaluation using the FH model results in higher parameter values for χ_{23} compared to the virial expansion.

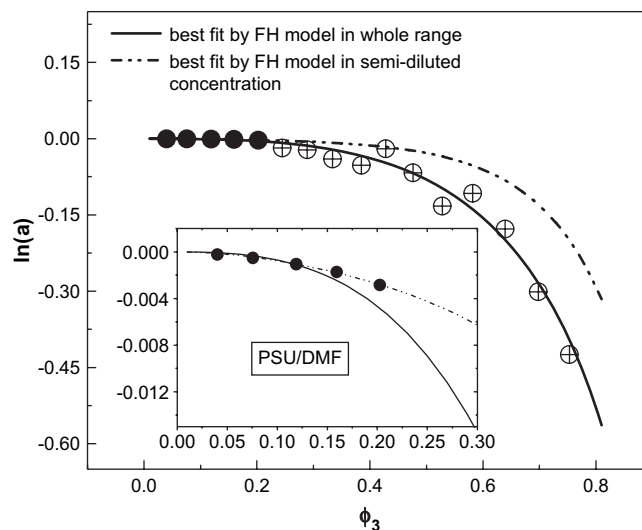


Fig. 3. Comparison of experimental reduced equilibrium vapor pressure with calculation using the FH model PSU/DMF system in which the interaction parameter has been obtained by means of FH model (---) and osmotic virial expansion truncated at third virial term (—) in semi-diluted regime. (⊕) Experimental data obtained from Ref. [7]; (●) experimental data obtained in this work. (The insert enlarges the semi-diluted concentration range.)

In summary, all obtained values based on VPO measurements are in good agreement with literature data if the evaluation was carried out with the virial expansion truncated at the third virial term. Up to about 25 wt.%, the concentration dependency is marginal when the solution behaves nearly ideal, and also the temperature dependence of the interaction parameter is very small. Differences are observed if different theoretical models are applied for the data evaluation. In general, the virial expansion gives a lower value for the solvent/polymer interaction parameter than the FH model.

4.2. Concentration dependency of the interaction parameter in the whole range

Fig. 3 displays, as an example, the experimental equilibrium vapor pressure of DMF as a function of the volume fraction of PSU, in both the semi-diluted and the concentrated regimes. Data in the semi-diluted regime were obtained in this work while for the concentrated regime experiments of Barth and Wolf [7] were used.

With the interaction parameter obtained from the virial expansion in the semi-diluted regime, the experimental data in the whole range of concentration can be well described. As expected the thermodynamic properties in the concentrated regime are better described by the FH model than by the virial expansion. An “accurate” interaction function for DMF/PSU is obtained by superposition of both approaches, virial expansion in semi-diluted regime and FH model in concentrated regime: $\chi_{23}(\phi_3) = 0.45 - 0.02\phi_3$. If the FH model is extended to the semi-dilute regime, the obtained interaction function is quite different: $\chi_{23}(\phi_3) = 0.66 - 0.25\phi_3$. By employing this interaction function, the calculated curve does not match the experimental data in the concentrated regime, as can be also seen in Fig. 3.

4.3. Determination of solvent/PEI interaction parameters in different solvents by VPO

PEI, an often used polymer for membrane formation by immersion precipitation, is almost not characterized with respect to their thermodynamic solution properties. The only experimentally determined values for solvent/polymer interaction parameters are

reported for NMP/PEI and methylene chloride/PEI by Young et al. [37] measured with membrane osmosis at infinite diluted concentration regime. (The correctness of these values is questionable, because, due to the common experience, NMP is a good solvent for PEI and that suggests solvent/polymer interaction parameters in the range of about 0.3.)

Therefore, in this part of our study, the interaction parameter χ_{23} was determined for PEI in three solvents (NMP, DMAc, and DMF), which have high relevance in practical membrane formation by VPO, at different temperatures. The measured data of the osmotic pressure are plotted in Fig. 4 in dependence on the solvent fraction in accordance to the virial expansion (truncated at third virial term) at different temperatures in the solvents NMP (A), DMAc (B) and DMF (C).

As can be seen, in all three cases a good fitting result with virial expansion was obtained in which it truncated at third virial term. In the case of NMP/PEI, the considerable value of third virial coefficient documents a dependence of the interaction parameters on the concentration in the range of moderately concentrated polymer solutions. In contrast, for DMF/PEI, the contribution of three-body interaction is not considerable so that the interaction parameter shows a concentration independency. For DMAc/PEI, the osmotic pressure scatters in the concentration range of 0.04–0.15 wt.% (see Fig. 4B). The reason is unknown; experimental errors can be excluded. Therefore, these data were not included in the data evaluation. For all three systems, the resulting values for the interaction parameters are listed in Tables 3 (FH model) and 4 (virial expansion truncated at third virial term).

According to these data, it can be clearly seen that NMP is (in difference to Ref. [37] but in accordance with experimental experience) a good solvent for PEI ($\chi_{23} = 0.57 \pm 0.01$ (FH); $\chi_{23} = [0.35, 0.42]$ (virial expansion)) while DMF is like a theta solvent ($\chi_{23} = 0.56 \pm 0.01$ (FH); $\chi_{23} = 0.5 \pm 0.005$ (virial expansion)). The solvent DMAc possess a better solvent quality than DMF but it is not as strong as solvency of NMP. The value of χ_{23} for DMAc/PEI is 0.56 ± 0.01 (FH) and 0.45 ± 0.01 (virial expansion). Based on these χ_{23} values the solvents can be sorted according to

NMP > DMAc > DMF.

This is a ranking for the solvent power in interaction with PEI in the solution state, valid for the moderately concentrated regime. (With FH model there differences between DMF and DMAc could not verified; only the virial expansion allows this conclusion.) An identical classification was reported in Ref. [38] based on solubility parameters. The strong interaction between PEI segments and NMP molecules causes the polymer chain to expand and to find a larger volume than ideal volume. In contrast, the interaction between PEI and DMF shows that the volume of a polymer chain is identical with the one of an ideal chain (theta condition). Therefore, it can be deduced that the system PEI/DMF has the potential to break down into two phases by decreasing the solvent quality only slightly, which is in strong accordance with the experimental experience. For instance, by cloud point measurements, it is clearly documented that the water tolerance (water is a strong nonsolvent for PEI) in DMF solutions is considerably lower than in NMP solutions [39].

5. Conclusions

The solvent/polymer interaction parameter χ_{23} characterizes the thermodynamic state of a polymer solution and is one of the three key parameters necessary to describe the thermodynamic behavior of phase demixing in a ternary nonsolvent (1)/solvent (2)/polymer (3) system. In this paper, vapor pressure osmometry (VPO) was introduced as an experimental technique for the χ_{23} determination in, e.g., membrane forming polymer systems containing high-molecular weight polymers in the (semi-diluted)

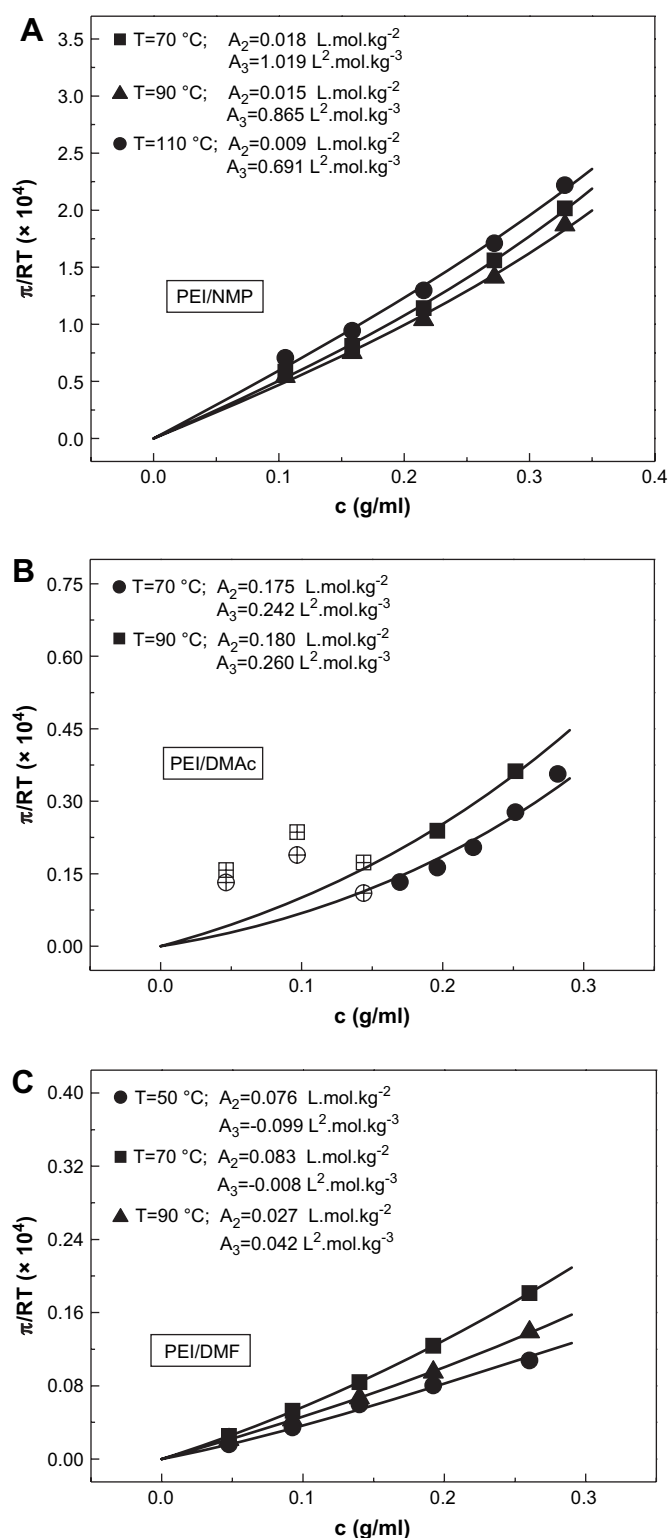


Fig. 4. Dependency of the osmotic pressure on the polymer fraction of PEI solutions at different temperatures in the solvents NMP (A), DMAc (B) and DMF (C). The virial coefficients are calculated from Eq. (6).

concentration range, typical for membrane preparations by non-solvent-induced phase separation. The results lead to the following conclusions:

- Investigations on the determination of solvent/polymer interaction parameters by VPO for systems, reported in the literature (such as water/PVP, DMF/PSU and DMF/PES), verify that

VPO is a fast and promising technique for the characterization of semi-diluted polymer solutions. Due to the principle of VPO the precision of measurement depends on the heat of condensation of the investigated solvent and the temperature of measurement. The selection of an optimal temperature in the experiment can be used for an increase in accuracy, because χ_{23} shows nearly no temperature dependence.

- Based on the documented accuracy of VPO, we found for infinite diluted and semi-diluted polymer solutions (up to 30 wt.%) for the solvent/polymer interaction only a marginal concentration dependency. Therefore, the application of a constant solvent/polymer interaction parameter, determined at infinite diluted concentration, is an good approximation if phase demixing of ternary systems is modeled as part of thermodynamic studies of membrane formation.
- The value of χ_{23} depends on the theoretical model applied for data evaluation. In this work two models have been considered, the FH and the virial expansion with contribution of third virial term. It can be expected that the “real” parameter value be obtained from the virial expansion model. Generally, the values obtained from the virial model are smaller than from the FH model. As a consequence of model assumptions and simplifications slightly different numeric values are obtained.
- The χ_{23} results for the polymer PEI in different solvents result in a series of decreasing solvent powers according to **NMP > DMAc > DMF**. This series is in accordance with our experimental experience at membrane formation [39] and an independent assessment on the basis of solubility parameters [38].

Acknowledgments

One of the authors (M. K.) thanks the GKSS for the financial support of this research project.

References

- [1] Flory PJ. Principle of polymer chemistry. Ithaca, New York: Cornell University Press; 1953.
- [2] Tompa H. Polymer solution. London: Butterworth; 1956.
- [3] Karimi M, Albrecht W, Heuchel M, Kish MH, Frahn J, Weigel Th, et al. J Membr Sci 2005;265(1–2):1–12.
- [4] Schuld N, Wolf BA. Polymer–solvent interaction parameter. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. New York: Wiley; 1999. p. 247–89.
- [5] Lai JY, Lin SF, Lin FC, Wang DM. J Polym Sci Polym Phys Ed 1998;36(4):607–15.
- [6] Rodriguez O, Fornasiro F, Arce A, Radke CJ, Prausnitz JM. Polymer 2003;44(20):6323–33.
- [7] Barth C, Wolf BA. Macromol Chem Phys 2000;201(3):365–74.
- [8] Altena FW. Phase separation phenomena in ternary cellulose acetate solutions: relation to membrane formation. Thesis. The Netherlands: University of Twente; 1984.
- [9] Boom RM, Reinders HW, Rolevink HHW, van den Boomgard Th, Smolders CA. Macromolecules 1994;27(8):2041–4.
- [10] Zeman L, Tkacik G. J Membr Sci 1988;36(1):119–40.
- [11] Lee JS, Lee HK, Kim SC. Polymer 2004;45(13):4491–8.
- [12] Wei YM, Xu ZL, Yang XT, Liu HL. Desalination 2006;192(1–3):91–104.
- [13] Burge DE. J Phys Chem 1963;67(12):2590–3.
- [14] Eliassi A, Modares H. J Chem Eng Data 1999;44(1):52–5.
- [15] de Gennes PG. Scaling concepts in polymer physics. Ithaca, New York: Cornell University; 1979.
- [16] Gao J, Weiner JH. J Chem Phys 1989;91(5):3168–73.
- [17] Brown W. J Appl Polym Sci 1967;11(11):2381–96.
- [18] Kurata M. Thermodynamics of polymer solutions. Harwood Academic Publishers; 1982.
- [19] Prausnitz JM. Molecular thermodynamics of fluid-phase equilibria. 3rd ed. Upper Saddle, New Jersey: Prentice Hall PTR; 1999.
- [20] Yamakawa H. Modern theory of polymer solutions. New York: Harper; 2001.
- [21] Dickman R, Hall CK. J Chem Phys 1986;85(7):4108–15.
- [22] Honnel KG, Hall CK. J Chem Phys 1989;90(3):1841–55.
- [23] Muthukumar M. J Chem Phys 1986;85(8):4722–8.
- [24] Edwards SF. Proc Phys Soc London 1965;85(4):613–24.
- [25] Haynes CA, Beynon RA, King RS, Blanch HW, Prausnitz JM. J Phys Chem 1989;93(14):5612–7.
- [26] Roesink HDW. Microfiltration: membrane development and module design. Thesis. The Netherlands: University of Twente; 1989.
- [27] Maggioni JF, Nunes SP, Nunes-Pires AT, Eich A, Horst R, Wolf BA. Polymer 1998;39(21):5133–8.
- [28] Rezac ME, Schöberl B. J Membr Sci 1999;156(2):211–22.
- [29] Güner A, Kara M. Polymer 1998;39(8–9):1569–72.
- [30] Comper WD, Checkley GJ, Preston BN. J Phys Chem 1984;88(6):1068–76.
- [31] Cerny LC, Helminiak TE, Meier JF. J Polym Sci 1960;44(144):539–45.
- [32] Desbrieres J, Borsali R, Rinaudo M, Milas M. Macromolecules 1993;26(10):2592–6.
- [33] Sen M, Pekel N, Güven O. Angew Makromol Chem 1998;257(1):1–6.
- [34] Kaplan H, Güner A. J Appl Polym Sci 2000;78(5):994–1000.
- [35] Baulin VA, Halperin A. Macromolecules 2002;35(16):6432–8.
- [36] Chang MJ, Myerson AS, Kwei TK. J Appl Polym Sci 1997;66(2):279–91.
- [37] Young TH, Tao CT, Lai PS. Polymer 2003;44(5):1689–95.
- [38] Wang D, Li K, Teo WK. J Appl Polym Sci 1999;71(11):1789–96.
- [39] Albrecht W, Weigel Th, Schossig-Tiedemann M, Kneifel K, Peinemann K-V, Paul D. J Membr Sci 2001;192(1–2):217–30.