

On the equation of state of polymer solutions^{*)}

R. Simha and R. K. Jain¹⁾

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, U.S.A.

Abstract: The theory formulated for single and multicomponent systems is applied to polymer solutions. This follows earlier investigations on mixtures of low molecular weight compounds and a binary compatible polymer mixture. The requisite analysis of the polymer constituents, namely polyisobutylene and poly(dimethylsiloxane) shows good agreement between experiment and theory. Similar conclusions apply to the solvents, namely cyclohexane, benzene and hexa(methyl disiloxane). For the solutions, the theory makes predictions at elevated pressures, based on the equation of state of the constituents and low pressure experimentation for the mixtures. Satisfactory results obtain in this manner with deviations increasing with temperature and pressure (maximally 1 kbar). At low pressures, the agreement between experiment and theory is good for all temperatures and compositions.

Key words: Equation of state, polymer solution.

Introduction

As a sequel to formulation of an equation of state for chain molecular fluids [1] we have subsequently derived an extension to single phase, multicomponent systems [2]. Theory and experiment have been compared for some low molecular weight mixtures [2] and a compatible polymer pair [3], viz. Poly(2,6-dimethyl-1,4-phenylene ether)-polystyrene (PPO-PS), for which pressure-volume-temperature measurements had been undertaken [4].

The purpose of this paper is to explore the application of the theory to polymer solutions. A general prerequisite for the study of mixtures is PVT data for the components. Such are available in the cases of interest here for polymers as well as solvents.

Recapitulation of theory

The *scaled* equations of state of a mixture and of a homogeneous fluid are formally identical, and have the following form [2]:

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - \eta)^{-1} + 2Qy(AQ - B)/\tilde{T} \quad (1)$$

with $\eta = 1 - 2^{-1/6} \cdot y \cdot (y\tilde{V})^{-1/3}$, $Q = (y\tilde{V})^{-2}$, $A = 1.011$ and $B = 1.2045$. Here $1 - y$ is the fraction of vacant sites in the quasi-lattice which satisfies the minimum condition on the free energy, viz.:

$$\begin{aligned} & (s/3c) [(s - 1)/s + y^{-1} \ln(1 - y)] \\ & = (\eta - 1/3) (1 - \eta)^{-1} + Qy(2B - 3AQ)/6\tilde{T} \quad (2) \end{aligned}$$

where $3c$ denotes the number of effectively external degrees of freedom per molecule which has been subdivided into s segments. In what follows quantities referring to the constituents will be designated by subscripts. We consider only binary systems. The scaling parameters are then defined by the following relations:

$$T_i^* = q_i z \epsilon_i^* / c_i k, \quad P_i^* = q_i z \epsilon_i^* / s_i v_i^* \quad (3)$$

^{*)} Dedicated to Prof. Dr. Robert Kosfeld with best wishes on the occasion of his sixtieth birthday.

¹⁾ On leave from Rajdhani College, University of Delhi.

with

$$q_i z = s_i(z - 2) + 2; \quad i = 1, 2$$

ε_i^* represents the maximum intersegmental attractive energy, and the volume is scaled by the repulsive volume v_i^* per segment. Equation (3) is immediately generalized to the mixture. That is, c_i , s_i , T_i^* , P_i^* and v_i^* are replaced by averages over the mole fractions x_i , defined by the sets of equations below:

$$\begin{aligned} \langle c \rangle &= c_1 x_1 + c_2 x_2 & \langle s \rangle &= s_1 x_1 + s_2 x_2 \\ \langle T^* \rangle &= \langle qz \rangle \langle \varepsilon^* \rangle / \langle c \rangle k, & \langle P^* \rangle &= \langle qz \rangle \langle \varepsilon^* \rangle / \langle s \rangle \langle v^* \rangle \end{aligned} \quad (4)$$

and averages over self and cross-interactions

$$\begin{aligned} \langle \varepsilon^* \rangle \langle v^* \rangle^2 &= X_1^2 \varepsilon_{11}^* v_{11}^{*2} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*2} + X_2^2 \varepsilon_{22}^* v_{22}^{*2} \\ \langle \varepsilon^* \rangle \langle v^* \rangle^4 &= X_1^2 \varepsilon_{11}^* v_{11}^{*4} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*4} + X_2^2 \varepsilon_{22}^* v_{22}^{*4} \\ X_i &= x_i q_i / \Sigma x_i q_i. \end{aligned} \quad (5)$$

Equations (3) yield a relation between the scaling parameters:

$$P_i^* V_i^* s_i M_{oi} = c_i R T_i^* \quad (6)$$

where M_{oi} is the segmental molar mass and V_i^* is the scaling volume per unit mass. We continue with the universal assumption $3c_i/(s_i + 3) = 1$ for chain molecular systems [1-5]. Equation (6) defines for specified values of s_i and c_i the segment and its relations to the repeat unit in the polymer, or to the molecular unit in the solvent, once the scaling parameters have been obtained by superposition of the reduced theoretical $\tilde{P}_i \tilde{V}_i \tilde{T}_i$ on the experimental PVT surface.

An important relation follows from equations (4) and the generalization of equation (6), namely:

$$\langle P^* \rangle \langle V^* \rangle / \langle T^* \rangle = \langle c \rangle R / (\langle M_o \rangle \langle s \rangle) \quad (7)$$

with

$$\langle M_o \rangle = \Sigma M_{oi} s_i x_i / \langle x \rangle, \quad i = 1, 2. \quad (7a)$$

The averages $\langle V^* \rangle$ and $\langle T^* \rangle$ can be obtained from the thermal expansion of the mixture for $\tilde{P} \rightarrow 0$, i.e., atmospheric pressure. The average $\langle P^* \rangle$ and hence the volume at elevated pressures can then be predicted without further recourse to experiment.

Determination of scaling parameters

1. The constituents

We start with the atmospheric pressure results. As previously [2, 3], an excellent linear approximation of the coupled equations (1) and (2) at $\tilde{P} \rightarrow 0$ is employed, viz.

$$\ln \tilde{V} = A(s, c) + B(s, c) \times \tilde{T}^{3/2}. \quad (8)$$

For an infinite s -mer, $A = -0.1034$ and $B = 23.835$ ($0.95 \leq \tilde{V} \leq 1.40$) with $3c = s$ [6]. Equation (8) implies an analogous relation for experimental data, that is:

$$\ln V = C + D \times T^{3/2}. \quad (9)$$

Application of equations (8) and (9) then yields the scaling temperature and volume through the relations:

$$V^* = \exp(C - A) \quad \text{and} \quad T^* = (B/D)^{2/3}. \quad (10)$$

To obtain the scaling pressure, a series of theoretical isotherms are computed by means of equations (1) and (2). A sequence of P_j^* 's is derived from the corresponding experimental series P_j , T_j , and V_j , since

$$P_j^* = (P_j V_j / T_j) (\tilde{P} \tilde{V} / \tilde{T})^{-1}. \quad (11)$$

An average of the P_j^* over all isotherm is accepted as the final P^* .

A slight change of this procedure is required to analyze the equation of state of polymer solutions. We need a specific numerical assignment to the number of segments per chain molecule s_i . For this purpose M_{oi} is computed from equation (6) with V_i^* , T_i^* and P_i^* derived with $s_i \rightarrow \infty$. This value of M_{oi} is employed to calculate s_i from the number average molecular weight of the polymer. The numerical values of A and B are then derived through a least square fit to the coupled equations (1) and (2) at $P = 1$ bar and $3c_i = s_i + 3$, over the experimental temperature range. V_i^* , T_i^* are then recomputed by means of equation (10), and P_i^* follows from equation (6). Results for the characteristic parameters of poly(dimethyl siloxane) (PDMS) and polyisobutylene (PIB) derived from PVT data [7-9] in this manner are shown in table 1.

Two solvents considered in this study, namely, C_6H_6 and $c\text{-}C_6H_{12}$ were previously [2, 10] treated as monomers, $s = 1$. We now recompute the scaling parameters by considering them as dimers ($s = 2$) in order to maintain the requisite similarity in respect to size the segments of the two species in the solution. In

Table 1. Characteristic parameters for constituents

Polymer/Solvent	T, K	C	$D \times 10^5$	s	$3c$	$-A$	B	$V^*, \text{cm}^3 \text{g}^{-1}$	T^*, K	P^*, bar	$M_o, \text{g mole}^{-1}$
PDMS	298–343	−0.14489	3.4120	1070	1073	0.10109	23.597	0.9572	7820	5144	44.14
PIB	293–383	−0.01860	2.0490	450	453	0.10441	24.070	1.0908	11199	7134	40.15
C_6H_6	298–348	−0.10984	4.7554	2	3.9	0.11552	22.614	1.0057	6093	8383	39.06
HMDS	298–343	−0.01108	5.5579	3.5	6.5	0.11270	21.731	1.1070	5347	5359	46.39
$c\text{-C}_6\text{H}_{12}$	288–338	0.01287	4.7313	2	4.5	0.10986	21.265	1.1299	5859	7684	42.08

equation (6) s_i and M_{oi} are consequently known. The parameter c_i is then obtained by trial and error. That is, a first value is assigned to c_i , A and B in equation (8) are computed, and P_i^* then follows from equation (6). The procedure is repeated, until a best set of parameters in accord with the experimental isotherms [8,11,12] emerges. The results are displayed in table 1.

Table 1 also contains the parameters for hexa(dimethylsiloxane) (HMDS), the third solvent to be considered. Here the best assignment to represent the experiment [13] is $s = 3.5$ and $3c = s + 3 = 6.5$.

2. Solutions

Having extracted the numerical values of the characteristic parameters for the constituents, the corre-

sponding quantities for the mixtures follow immediately. Equations (4) and (7 a) provide $\langle s \rangle$, $\langle c \rangle$ and $\langle M_o \rangle$ for a specified composition. The coefficients A and B then follow from the appropriate solutions of the coupled equations (1) and (2), as described earlier. With the experimental isobars at $P = 1$ bar and thus C and D known, $\langle V^* \rangle$ and $\langle T^* \rangle$ are derived by means of equation (10), and $\langle P^* \rangle$ is predicted from equation (7).

Comparison of theory and experiment

1. Polymers

Theoretical and experimental isobars of PIB are compared in figure 1. The line for $P = 1$ bar results from equation (8) with parameters in table 1. The triangles represent the solutions of the coupled equations (1) and (2), and the circles are experimental points [9]. Several other lines which appear in this figure represent the linear approximations to the solutions of equations (1) and (2) at elevated pressures. Clearly, these approximations to the theoretical equation of state are valid at elevated pressures and are in good agreement with the data computed from a Tait equation [7]. Thus isobaric thermal expansivities can be computed from equations (8) and (9), provided the coefficients have been determined as functions of pressure. Polynomials for $A(\bar{P})$ and $B(\bar{P})$ for $s \rightarrow \infty$ have been given previously [3]. Deviations between theory and measurements increase with increase in P and T , reaching a maximum value of 0.1 % in V for the highest pressure. At $P = 1$ bar, the maximum discrepancy is 0.05 %. It should be noted at this point that the scaling parameters are treated as true constants of the system. In figure 2 we present two isotherms for PIB at extreme temperatures [7]. The deviations change sign as we go from the lowest to the highest T employed. This figure also contains two similar isotherms of PDMS ($M_n = 47,200$). The lines are computed from the theory, equations (1) and (2), and the circles represent the data

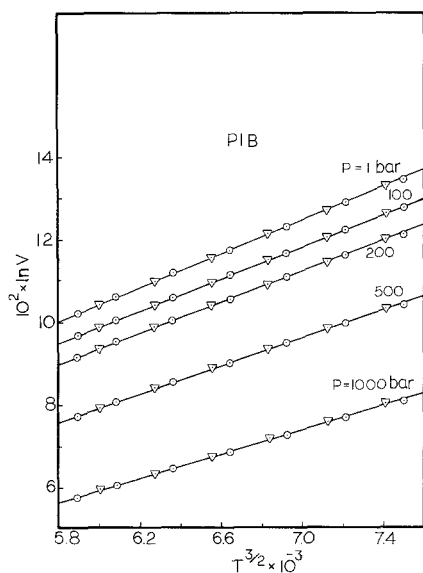


Fig. 1. Isobars of PIB between 52 and 110°C: Triangles, theory, equations (1) and (2); lines, least square fits to these; circles, experiment

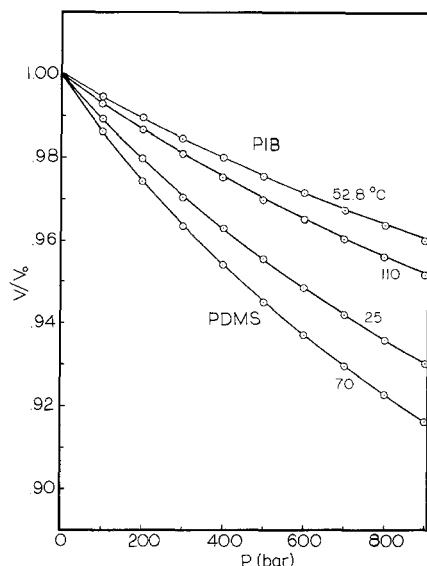


Fig. 2. Isotherms of PIB and PDMS: Lines, theory; circles, experiment

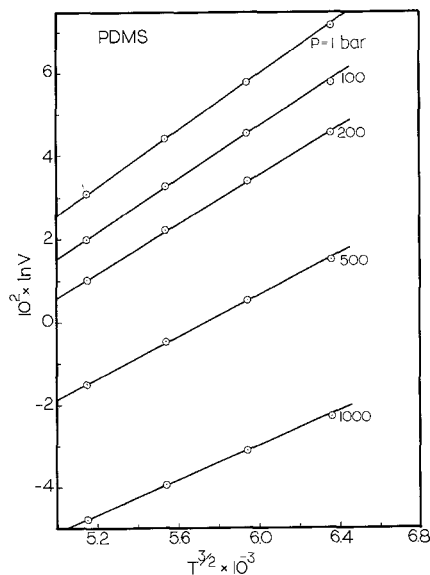


Fig. 3. Isotherms of PDMS: Lines, least square fits to theory; circles, experiment

derived from a Tait equation [7]. Excellent agreement between theory and measurement is seen, the maximum deviation being only 0.03 % in V/V_0 . Several isobars for PDMS are shown in figure 3, as $\ln V$ vs. $T^{3/2}$ plots obtained by means of equations (8) and (9), and with parameters from table 1. Once again a satisfactory representation of theory as well as experiment by

linear relations is observed at low and elevated pressures. The maximum deviation between theory and the data computed from a Tait equation [7] occurs again at the highest P , T and amounts to 0.07 % in V . However, these deviations do not exceed 0.03 % at atmospheric pressure.

2. Solvents

Cyclohexane and benzene have been previously analyzed by us [2, 5], by treating them as monomers, that is, $s = 1$. As explained in an earlier section, our new assignment, $s = 2$, is in accord with an assumption of the theory [14] involving the random mixing of different species in a mixture, and requiring similarity of sizes of the segments in the components. For $c\text{-C}_6\text{H}_{12}$, $3c = 4.5$ results in a satisfactory representation of the data [8, 12], as shown in figure 4. This figure also contains the results for C_6H_6 with $3c = 3.9$, and once more shows a good agreement between theory and experiment [8, 11] over the entire range of pressures and temperatures. The maximum deviations for these two solvents amount to 0.04 % in V . Again the linear representation of experimental and theoretical isobars turns out to be quite accurate at all pressures.

We now consider the third solvent, namely, HMDS for which comparison between theory and *raw* experi-

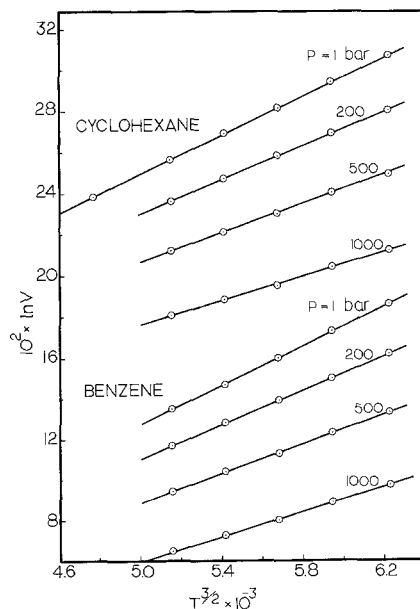


Fig. 4. Isotherms of $c\text{-C}_6\text{H}_{12}$ and C_6H_6 : Circles, experiment; lines, least square fits to theory

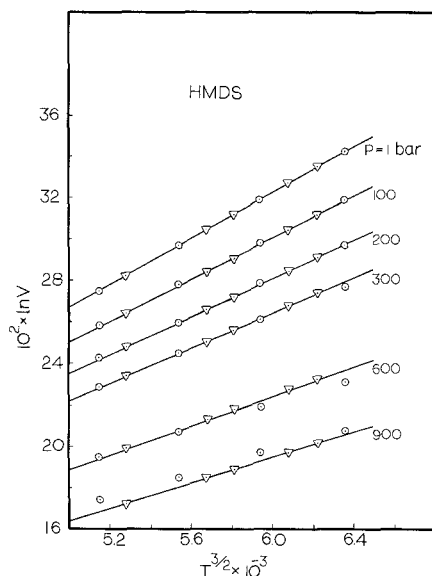


Fig. 5. Isobars of HMDS: Triangles, coupled equations (1) and (2); lines, least square fits to these; circles, experiment

mental data [13] is presented in figure 5. An excellent agreement is seen at atmospheric pressure, the maximum deviation being 0.02 % in V compared to the experimental uncertainty of 0.03 %. These discrepancies start increasing above 200 bar and are considerably enhanced at the highest pressure. A change in sign of these deviations seen between 600 and 900 bars indicates a possible increase in experimental error. The

authors [13] mention an overall uncertainty of 0.08 % for their relative-volume measurements. We find a maximum departure of 0.6 % in V for these two isobars.

3. Solutions

With the characteristic parameters for polymers and solvents at hand, we proceed to the solutions. Since experimental compositions [8] are reported as volume fractions, we compute the corresponding mole fractions by means of the relation

$$1/x_2 = 1 + (s_2 M_{o2}) V_2 \phi_1 / (s_1 M_{o1} V_1 \phi_2)$$

where $\phi_2 (= 1 - \phi_1)$ is the volume fraction of the polymer. The corresponding mole fraction x_2 is computed from the observed specific volumes at 25 °C (see below). Once x_2 for each polymer solution has been calculated, the averages $\langle s \rangle$, $\langle c \rangle$, $\langle M_o \rangle$ and the scaling parameters $\langle V^* \rangle$, $\langle T^* \rangle$, $\langle P^* \rangle$ are derived in the manner described in a previous section. The results are shown in table 2.

The computations for PIB in $c\text{-C}_6\text{H}_{12}$ and C_6H_6 at atmospheric pressure are presented in figure 6. Excellent agreement between theory and observations is seen for all compositions, the maximum deviation being 0.01 % in V . Isotherms for C_6H_6 + PIB solutions at the extremes of the temperature range are seen in figure 7. For solutions with the smallest and the largest polymer content, the measured compressions at 25 °C are in good agreement with the theoretical lines com-

Table 2. Characteristic parameters for polymer solutions

ϕ_2 Vol. fraction	$x_2 \times 10^3$ Mol. fraction	$\langle s \rangle$	$\langle 3c \rangle$	$\langle M_o \rangle$ g mol^{-1}	$-C$	$D \times 10^5$	$-A$	B	$\langle V^* \rangle$ $\text{cm}^3 \text{g}^{-1}$	$\langle T^* \rangle$ K	$\langle P^* \rangle$ bar
C_6H_6 ($s_1 = 2$) + PIB ($s_2 = 450$)											
0.1989	1.1215	2.5024	4.4037	39.28	0.08643	4.0487	0.10827	22.220	1.0221	6703	8143
0.4355	3.4765	3.5575	5.4614	39.54	0.05605	3.2979	0.10489	22.328	1.0501	7699	7889
0.5923	6.5266	4.9239	6.8313	39.71	0.04847	3.0334	0.10426	22.561	1.0574	8209	7516
$c\text{-C}_6\text{H}_{12}$ ($s_1 = 2$) + PIB ($s_2 = 450$)											
0.1971	1.3229	2.5927	5.0933	41.63	0.01128	4.1875	0.10590	21.289	1.0992	6370	7578
0.3731	3.2013	3.4342	5.9358	41.27	0.00269	3.5611	0.10342	21.445	1.1060	7131	7483
0.5445	6.4092	4.8713	7.3745	40.94	0.00229	3.0953	0.10300	21.872	1.1059	7933	7351
HMDS ($s_1 = 3.5$) + PDMS ($s_2 = 1070$)											
0.4370	3.4009	7.1270	10.1270	45.23	0.08598	4.5597	0.10350	22.021	1.0177	6156	5267
0.6497	8.0880	12.1259	15.1259	44.77	0.16668	4.9652	0.10419	22.670	0.9394	5929	4874
$c\text{-C}_6\text{H}_6$ ($s_1 = 2$) + PDMS ($s_2 = 1070$)											
0.5017	2.2036	4.3535	6.8546	43.18	0.07927	4.0098	0.10390	21.805	1.0249	6662	6568

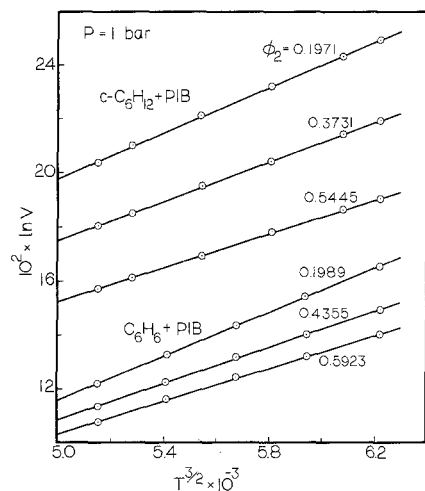


Fig. 6. Isobars for solutions of PIB in $c\text{-C}_6\text{H}_{12}$ and C_6H_6 at atmospheric pressure: Lines, least square fits to theory; circles, experiment; ϕ_2 , volume fraction of polymer

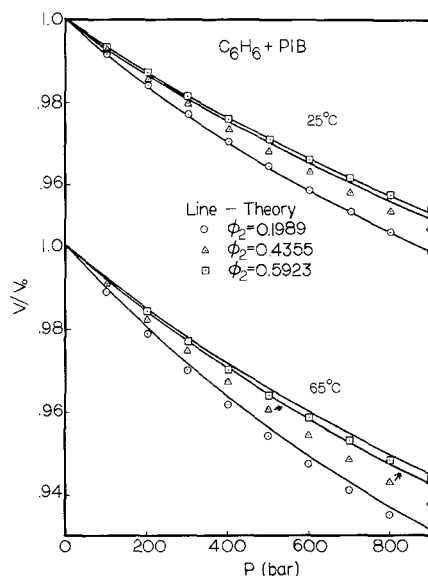


Fig. 7. Isotherms for solutions of PIB in C_6H_6 : Lines, theory; points, experiment; ϕ_2 , volume fraction of polymer

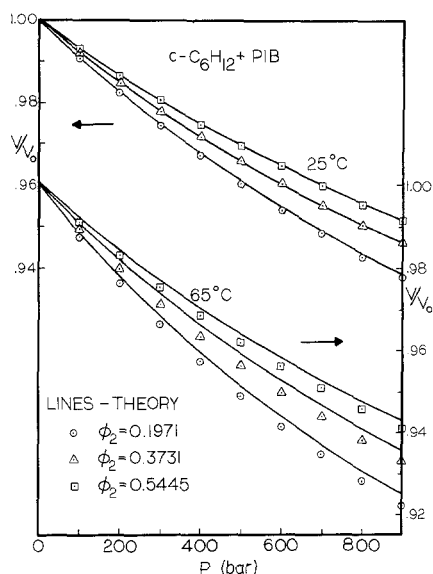


Fig. 8. Isotherms for solutions of PIB in $c\text{-C}_6\text{H}_{12}$: Lines, theory; points, experiment; ϕ_2 , volume fraction of polymer

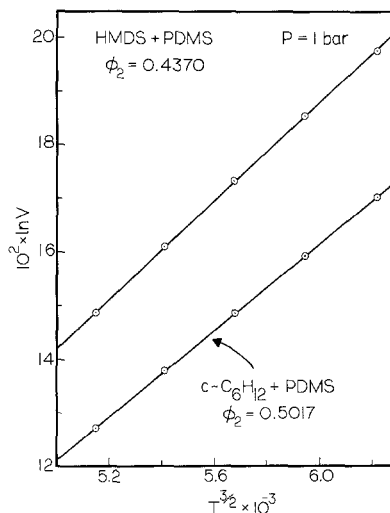


Fig. 9. Isobars for solutions of PDMS in HMDS and $c\text{-C}_6\text{H}_{12}$ at atmospheric pressure. Lines, least square fits to theory; circles, experiment

puted from the *predicted* $\langle P^* \rangle$ in table 2. For the intermediate composition theory predicts higher compressions over the entire range of pressures, the maximum deviation being 0.25 %. The same trend is seen for isotherms at 65 °C, but the deviations are now larger. The discrepancies for the extreme compositions do not exceed 0.2 %. For the intermediate polymer concentration they increase to 0.4 % at the highest pressure. In figure 8, the corresponding results for solutions of PIB

in $c\text{-C}_6\text{H}_{12}$ are exhibited. At 25 °C the predicted compressions are slightly higher than is observed, the maximum discrepancy being 0.08 %. These deviations increase to 0.25 % at 65 °C, the highest temperature for which data are reported [8].

Next consider the solutions of PDMS in $c\text{-C}_6\text{H}_{12}$ and HMDS. The isobars at atmospheric pressure are again linear and in satisfactory accord with experiment for both solutions as is seen in figure 9. The isotherms

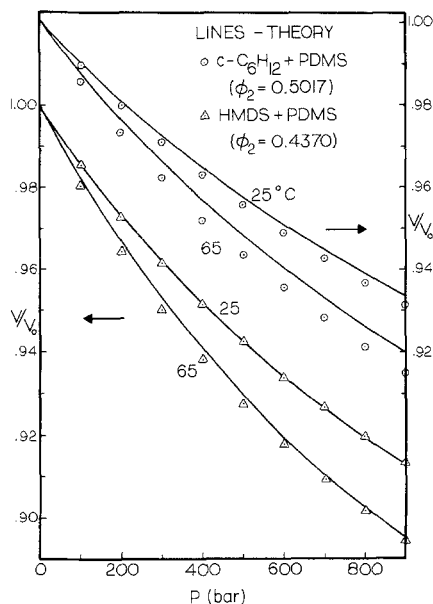


Fig. 10. Isotherms for solutions of PDMS in $c\text{-C}_6\text{H}_{12}$ and HMDS. Lines, theory; points, experiment; ϕ_2 , volume fraction of polymer

at the lowest and the highest available temperatures are displayed in figure 10. For PDMS in HMDS, the predicted isotherm at 25 °C is in good agreement with observations at all pressures, whereas at the highest T the theory predicts larger compressions throughout. However, the discrepancy does not exceed 0.2 %. For the second solution, i. e., PDMS in $c\text{-C}_6\text{H}_{12}$, the computed compressions are smaller at both temperatures, the deviations increasing with increase in T and P . They are maximally 0.2 and 0.5 % at 25 and 65 °C respectively. Larger deviations for this solution may in part be ascribed to the less satisfactory results for the solvent at elevated pressures, see figure 5. We omit consideration of the second composition ($\phi_2 = 0.3530$), since the data [8] lead to a higher thermal expansivity for this solution than for the solvent, $c\text{-C}_6\text{H}_{12}$. Specifically the values for $\alpha \times 10^3$ at 300 K are 2.67 and 1.23 respectively.

Table 2 contains the characteristic parameters for a second solution ($\phi_2 = 0.6497$) of PDMS and HMDS. We do not offer the results for this system, since unreasonably large discrepancies between predictions and observations prevent any meaningful comparisons at elevated pressures. The deviations in V vary between 2 to 2.5 % at the highest pressure as t increases from 25 to 65 °C. However, at $P = 1$ bar, the maximum discrepancy between theory and observations amounts to only 0.2 % in V .

Discussion

The theory successfully describes the PVT behavior of the two polymers and one of the solvents, thus increasing the number of systems examined so far. The two other solvents had been considered earlier [2, 10]. Appropriate linearization of the volume-temperature function at atmospheric as well as elevated pressure ensues, as has been seen previously for mixtures of low and high molecular weights [2, 3]. The largest deviations between theory and measurement occur in HMDS at the highest pressures reported [13]. Such discrepancies have not been encountered in other solvents or polymers. The reasons for such deviations are not clear.

For the solutions at atmospheric pressure, the excellent agreement between computation and measurement confirms the adequacy of the theory previously applied to polymer blends [3], mixtures of n -paraffins, and of solvents [2, 10]. In addition, we have shown the validity of the $\ln V$ versus $T^{3/2}$ representation of the theoretical isobars, both at low and elevated pressures. A trend for larger deviations at the higher temperature is discernible in all isotherms, although the increase differs in magnitude in each case. There is no systematic dependence of the deviations on composition. Numerically these discrepancies are smaller than those encountered for $n\text{-C}_6 + n\text{-C}_{16}$ solutions [2], where however the pressures extend to ~ 5 k bar. It should be noted that in all these comparisons, the data used were derived from empirical equations [8] except for HMDS [13].

For the number average molecular weights of PDMS a value of $\bar{M}_n = 47,200$ was used, as given in a previous paper [7] by the same authors. For PIB, on the other hand, only the viscosity average $\bar{M}_v = 3.6 \times 10^4$ was reported. We have used a value for $\bar{M}_n = 18,000$. An uncertainty in the molecular weight can affect the values of the computed mole fractions and hence of $\langle s \rangle$, $\langle c \rangle$ and the scaling parameters. Moreover, and as was mentioned previously, experimental volumes at 25 °C were employed to convert volume into mole fractions. A change of volume with temperature does not have an appreciable effect on the results for x_2 and consequently the scaling parameters. For example, $\langle V^* \rangle$, $\langle T^* \rangle$ and $\langle P^* \rangle$ change from 1.0501, 7699 and 7889 to 1.0500, 7706 and 7801 respectively, if the volumes at 65 °C are used for $\text{C}_6\text{H}_6 + \text{PIB}$ solution with $\phi_2 = 0.4355$.

When judging the performance of the theory for solutions at elevated pressures, it should be emphasized that these results are true predictions without any

adjustments or variations in the scaling parameters. One might wish to explore a simultaneous fit [15] of the scaling parameters to the *PVT* surface in order to derive more accurate results for the isotherms.

It will be noted that the two PIB solutions represent examples of a comparatively good (*c*-C₆H₁₂) and a poor (C₆H₆) solvent. A comparison of the compression ratios V/V_o does not indicate significant differences. However, the coefficients D (see table 2) and hence the thermal expansivities at a given temperature are higher in the better solvent, in accord with expectation. A more detailed comparison in terms of the ϵ_{ii}^* and ϵ_{ik}^* in equation (5) does not result in further conclusions. Evaluations of the free energies of mixing and of the chemical potentials [16] would be required.

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Authors' address:

Robert Simha
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106, U.S.A.