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Solutions of Poly(dimethylsiloxane) in Supercritical CO_2: Viscometric and Volumetric Behavior

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ABSTRACT: Homogeneous mixtures of five poly(dimethylsiloxane) fractions [23–74 kg/mol] with CO_2 were studied (100–700 bar and 30–70 °C) in the entire range of composition. An antoclave, which allows the determination of densities, was used to prepare the solutions. Viscosities η were measured in a rolling-ball and in a Searle-type pressure apparatus, respectively, depending on the polymer content. For the lowest molar mass sample (the only one below the entanglement value) the viscosity of the mixtures is always less than that calculated on the basis of volume fractions from additivity of the η values of the pure components. With all other fractions this is only so for large polymer contents; as these solutions are diluted, the deviations become positive where the effects increase with rising M. This complex behavior can be described quantitatively by means of only one (physically meaningful and molecular weight independent) adjustable parameter, if one uses surface fractions as the composition variable instead of volume fractions. The evaluation of $\eta(T)$ at constant p with respect to activation energies $E^{\ddagger}$ and of $\eta(p)$ at constant T with respect to activation volumes $V^{\ddagger}$ reveals a pronounced sigmoidal dependence of these parameters on the composition of the mixtures. For the pure polymer one extrapolates the following values in the limit of infinitely long chains: $E^{\ddagger}_{\infty} = 75$ kJ/mol at 300 bar and $V^{\ddagger}_{\infty} = 43$ cm^3/mol at 30 °C. The measured densities yield maximum excess specific volumes on the order of -10 cm^3/kg; these effects are almost 10 times larger than predicted by the Flory–Orwoll–Vrij theory.

Introduction

Despite the great practical importance of reliable methods to predict the viscosities of mixtures from the data of their constituents, the state of the art in this field is rather disappointing. The behavior of liquid polymer blends is probably best understood; in the absence of large chemical differences between the components, the viscosities of the mixtures can be calculated,[1] subject to the condition that the molar masses of the constituents are all either below or above the entanglement value. At least eleven different mixing rules have been reported in the literature for Newtonian liquids;[2] the fact, however, that there are so many demonstrates the lack of generality. The common feature of all equations reported so far is the use of volume, weight, or mole fractions as variables of composition. A new approach[3] has recently been formulated for mixtures of low molecular weight liquids. It is—in contrast to the usual practice—based on surface fractions (in view of the conception that the dissipation of energy should mainly take place at the interfaces between molecules) and accounts for thermodynamic interactions.

Within the great variety of liquid mixtures the present type of systems, in which one component consists of a supercritical gas, is of particular interest.[4] For instance, the use of CO_2 as solvent enables the polymerization of perfluoro monomers in a very elegant manner.[5] Polymer solutions in supercritical gases are also well suited to study the effects of changes in free volume on the viscosities of mixtures. The present work is part of a larger experimental study which is presently being performed to broaden the basis for the testing of theoretical concepts.

Experimental Section

Materials. Poly(dimethylsiloxane) [PDMS] of different molar masses was purchased from Wacker GmbH (Munich). The numbers given in the abbreviation of the samples represent the weight average molar mass in kg/mol; except for PDMS 39 (which was obtained from a broadly distributed material by fractionation as described in the next paragraph). These substances were used without further treatment. The characteristic data for all polymers are collected in Table 1.

CO_2 was a technical grade product (>99.5 wt %) of Merck GmbH (Darmstadt); toluene and acetone, required for the fractionation, were also purchased with technical grade from Merck.

Fractionation. Continuous polymer fractionation (CPF), a comparatively new method that allows the production of large amounts of narrowly distributed material was applied to PDMS. The principles of that procedure and its theoretical background have already been described in detail.[6] Toluene was used as the solvent component and acetone as the nonsolvent component of the mixed solvent; the weight fractions at the working point were 0.065 for PDMS and 0.23 for toluene. A column of 3-m length and a diameter of 4.5 cm, filled with glass beads of 8-mm diameter, served as the apparatus. The feed (17.6 wt % polymer, 30 wt % toluene, and 52.4 wt % acetone) was pumped with a rate of 2 mL/min into the column at a height of 1.4 m, and the extracting agent (18.8 wt % toluene and 81.2 wt % methanol) with a rate of 6 mL/min at its lower end. The temperature within the lower part of the column amounted to 25 °C, and that within the upper (refluxing zone), to 15 °C.

The result of the single step CPF described above can be seen from Figure 1 where the differential molar mass distributions of the original product (feed) and of the two fractions (sol and gel) are shown. The lower molar mass fraction PDMS 39 has (according to GPC measurements) a weight average molar mass of 39.0 kg/mol and a number average of 28.0 kg/mol. The corresponding data for the higher molar mass fraction are 156.0 and 95.0 kg/mol, respectively.

Apparatus and Procedures. The densities of the pure polymers and of the mixtures of PDMS plus CO_2 were measured as a function of temperature and pressure in a Kratky apparatus (measuring cell DMA 512 and data processor DMA 60 of Fa. Paar Graz, Austria) as described.[7]

The central parts of the equipment used for the measurement of the viscosity η consist of two high pressure viscometers. The first one is a rolling-ball apparatus;[8] the second one, a rotational viscometer[9] of the Searle-type. Homogeneous mixtures were prepared in a so-called pvT cell (which also permits the determination of the volume of the liquids for given constant values of pressure and temperature). This cylindrical autoclave[10]

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Table 1. Abbreviations, Weight Average Molar Masses, and Molecular Nonuniformities $U = (M_w/M_n) - 1$ of the Polymer Samples

polymer	M_w (kg/mol)	U
PDMS 23	23	0.8
PDMS 30	30	0.5
PDMS 39	39	0.2
PDMS 42	42	0.5
PDMS 74	74	0.5

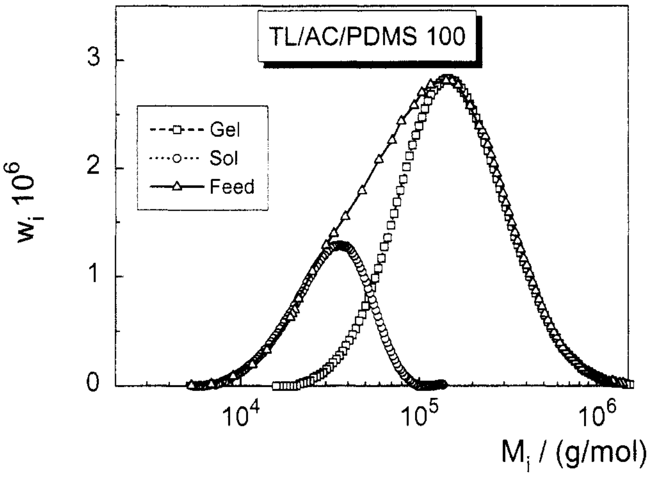

Figure 1. Differential molar mass distributions of a commercially available sample of poly(dimethylsiloxane) (feed) and of the sol and the gel fractions, respectively, as obtained by means of CPF[6] (continuous polymer fractionation) using toluene as solvent and acetone as nonsolvent.

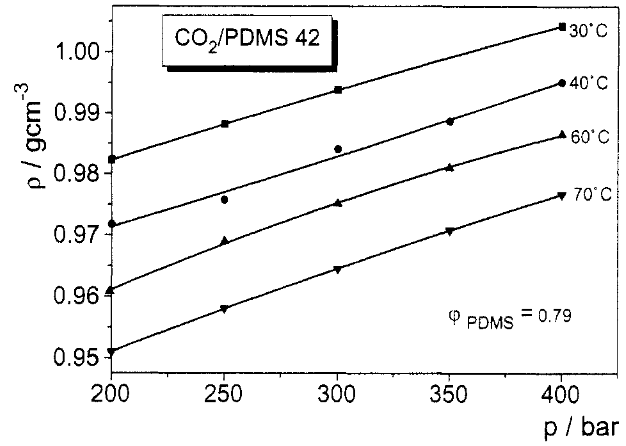

Figure 2. Pressure dependencies of the densities ρ of a solution of PDMS 42 in CO$_2$ ($\varphi_{\text{PDMS}}^{200\text{bar}} = 0.79$) at the indicated temperatures.

contains a gastight piston which moves freely and a stirrer that can be operated from outside by means of permanent magnets. Two sapphire windows allow the monitoring of the phase state. The homogeneous mixtures are transferred from the pvT cell into the evacuated viscometers by simultaneously opening the valve between them and reducing the total volume of the system rapidly by means of a hand pump.

Results and Discussion

Volumetric Behavior. A representative example of the results of the density measurements is shown in Figure 2. All primary data were evaluated according to the equation of state reported by Flory, Orwoll, and Vrij[11] using a nonlinear simplex fit[12] to determine the reduction parameters. Some data for the pure polymers are collected in Table 2.

How the specific hard-core volume v^* varies with composition for the system CO$_2$/PDMS 42 is shown in Figure 3. In this graph it is also indicated what one would expect according to a published mixing rule[13] (eq 1 with $\Delta_v = 0$) and to an extension of that expression[14] reading

Table 2. Reduction Pressures p^*, Specific Reduction Volumes v^*, and Reduction temperatures T^* of the Flory–Orwoll–Vrij Equation of State[11] for Some of the PDMS Samples

polymer	p^*/bar	v^*/cm^3 g^{-1}	T^*/K
PDMS 23	3673	0.8309	5312
PDMS 39	3785	0.8270	5254
PDMS 42	3468	0.8347	5397

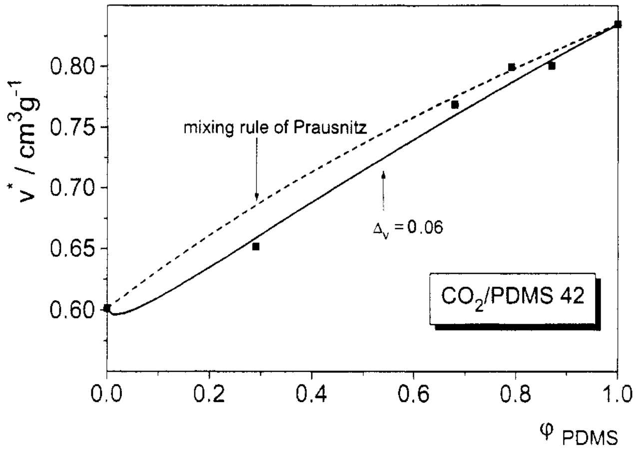

Figure 3. Concentration dependence of the specific hard-core volume v^* (as determined from the Flory–Orwoll–Vrij equation of state[11]). The broken line is calculated by means of eq 1 setting the parameter $\Delta_v = 0$; the value of this parameter for the full line is given in the graph.

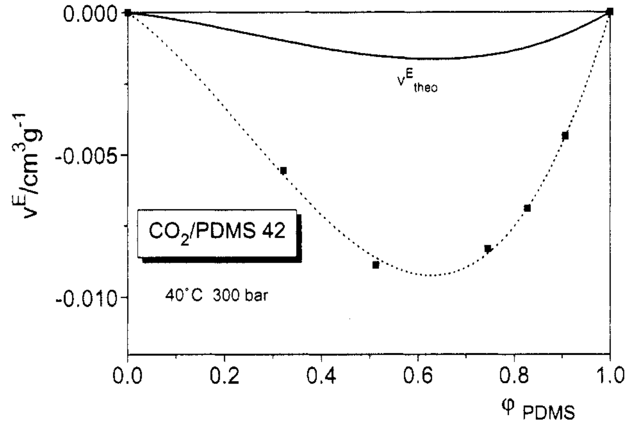

Figure 4. Excess specific volume v^E for the system CO$_2$/PDMS 42 at 40 °C and 300 bar. The curve can be well fitted by the empirical expression $v^E = (k_1\varphi_1 + k_2\varphi_2)\varphi_1\varphi_2$ in which k_1 and k_2 are adjustable parameters.

$$v^* = \psi_1^2 v_1^* + \psi_2^2 v_2^* + 2\psi_1 \psi_2 (v_1^* \cdot v_2^*)^{0.5}(1 - \Delta_v) \qquad (1)$$

ψ_i are the hard-core volume fractions (assuming additivity of the v_i^* values), and Δ_v is an adjustable parameter taking account of deviations from additivity.

For the system CO$_2$/PDMS 42 the densities were also evaluated with respect to excess volumes. The measured concentration dependence of the excess specific volume v^E is compared to that predicted[15] by the Flory–Orwoll–Vrij theory. As can be seen from Figure 4, the negative sign of the effect and the shape of the curve are very similar; the actual shrinking of the mixture upon mixing is, however, more than 5 times larger than anticipated by the corresponding states theory. Alternative equations of state have not been examined so far. It is worthwhile to note,

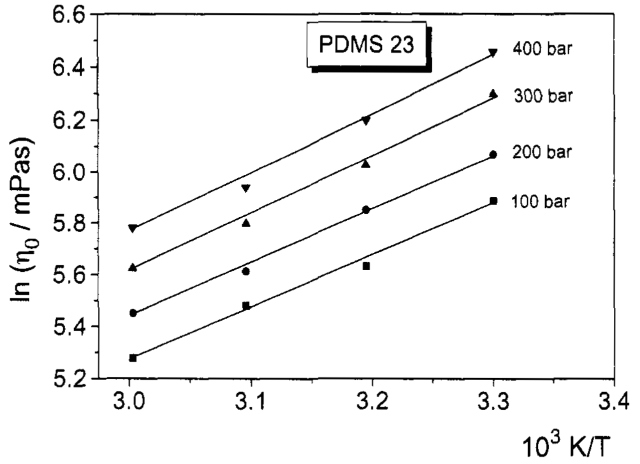

Figure 5. Arrhenius diagram for the zero shear viscosities η_0 of PDMS 23 at the indicated pressures.

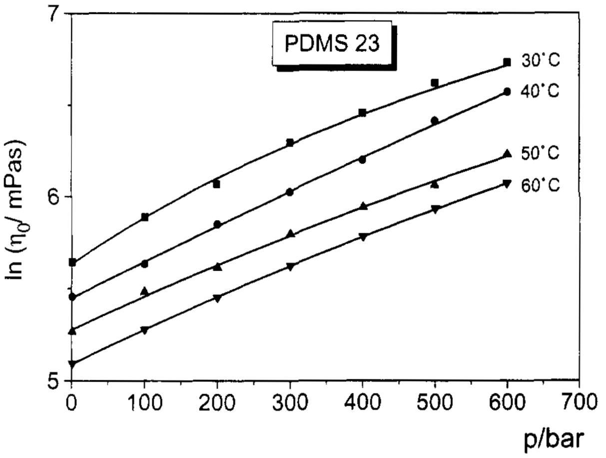

Figure 6. Pressure dependence of the zero shear viscosities η_0 of PDMS 23 at the indicated temperatures.

however, that the experimentally observed variation of *excess volumes* with φ_2 can be well described by a relation which has the same form as eq 4 discussed in the context of the *excess viscosities* (no theoretical interpretation of the parameters can presently be offered).

Melt Viscosities. As an example for the zero shear viscosities η_0 of the pure polymers and their temperature and pressure dependence, these data are shown in Figures 5 and 6 for PDMS 23. These plots yield the activation parameters of the viscous flow. The observed variation of the activation energies $E^{\ddagger}$ and activation volumes $V^{\ddagger}$ with chain length demonstrates that limiting values are approached as M goes to infinity. From Figure 7 it can be seen that $V^{\ddagger}$ increases—within experimental error—in a linear manner with $M^{-0.5}$ and that the extrapolated activation volume becomes 43 cm^3 mol^{-1} at 30 °C; the corresponding limiting value of the activation energy reads 75.0 kJ mol^{-1} at 300 bar. The reason for the above choice of the M dependence in the extrapolation of the activation parameters is the following: In the case of the present unperturbed chains, the fraction of contacts between polymer segments that belong to the *intra*molecular type is proportional to $M^{-0.5}$. This implies that the reported limiting values for infinite chain length are stripped of the contributions to the activation parameters stemming from *inter*molecular intersegmental contacts.

From the variation of η_0 with M, evaluated in the usual double logarithmic plots, one obtains critical molecular masses; Figure 8, giving the data for 30 °C, yields an M_c value of 24.0 kg/mol, which is in good agreement with literature data[16] (24.5). No pressure dependence is discernible within experimental error.

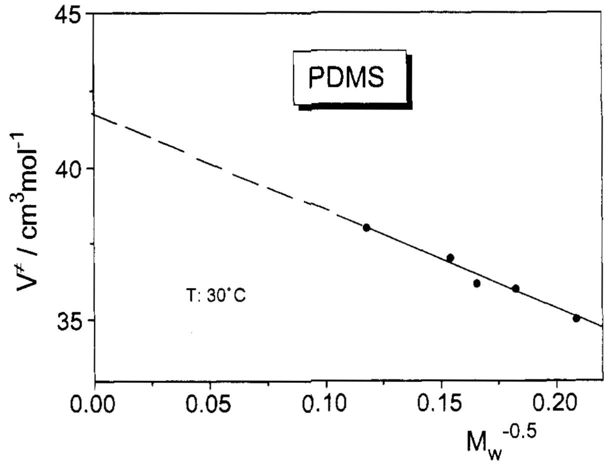

Figure 7. Molecular weight dependence of the activation volume of flow at 1 bar for PDMS at 30 °C.

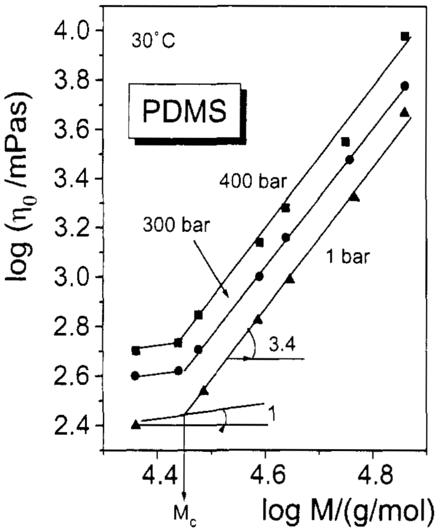

Figure 8. Molar mass dependence of the zero shear viscosity η_0 for melts of PDMS at 30 °C and the different indicated pressures. The data points are connected by lines with the theoretical slopes of 1 and 3.4, respectively.

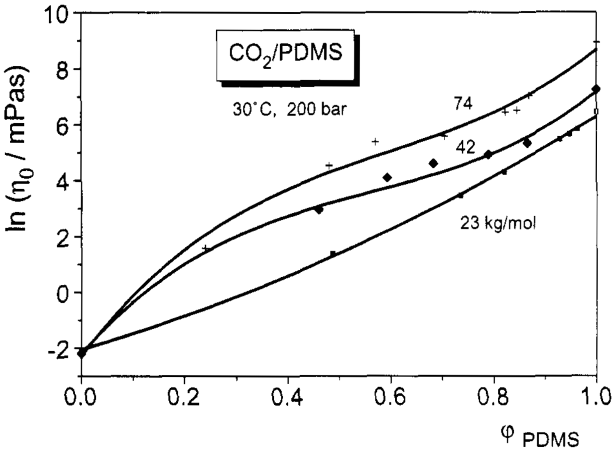

Figure 9. Zero shear viscosities η_0 of different representatives of the system CO$_2$/PDMS (the molar masses are given in the graph) as a function of φ_{PDMS}, the volume fraction of polymer, for the indicated fixed temperature and pressure.

Solution Viscosities. Typical examples of the concentration dependence of the zero shear viscosities are given in Figure 9 for 30 °C and 200 bar; for the sake of

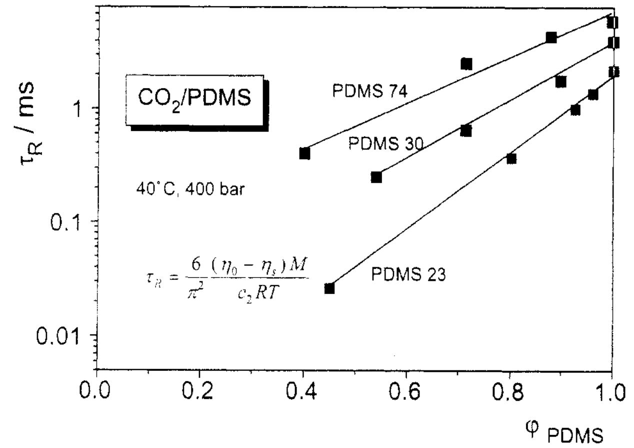

Figure 10. Concentration dependence of the Rouse relaxation times τ_R of PDMS in CO_2 calculated for 40 °C and 400 bar from their zero shear viscosities according to the equation given in this graph. η_s is the viscosity of the pure solvent.

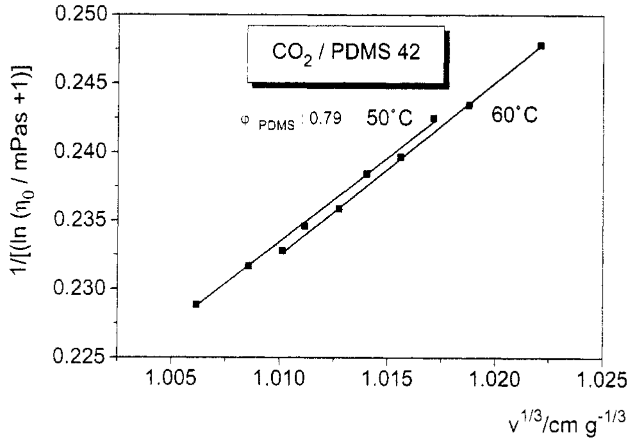

Figure 11. Example ($\varphi_{\mathrm{PDMS}}^{200\mathrm{bar}}$ = 0.79) for the evaluation of viscosities as a function of pressure at the indicated constant temperatures in terms of specific volume v of the liquid according to a generalized and modified Batschinski equation.[17]

clarity data are depicted for three of the five different molar mass samples only.

In the case of the shortest chains, η_0 is always less than calculated according to

$$\ln(\eta_0)_\varphi^{\mathrm{id}} = \varphi_1 \ln \eta_{0,1} + \varphi_2 \ln \eta_{0,2} \qquad (2)$$

from the viscosities of the pure components and the composition in terms of volume fractions φ_i. The other two representatives of the present system show an inversion of the effect; with increasing M the deviation becomes positive in the region of high CO_2 contents.

Rouse relaxation times τ_R were calculated to obtain information on the dynamic behavior of the solutions of PDMS in CO_2. Figure 10 shows how this quantity varies with composition. It is interesting to note that τ_R lessens approximately exponentially in all cases as the volume fraction of the solvent increases.

Furthermore it was tested whether the pressure and temperature dependence of the viscosities of the present system can be described by a generalized and modified Batschinski equation.[17] Figure 11, which is typical for the evaluation of the present data, demonstrates that this is indeed the case. Straight lines are obtained when $[\ln(\eta_0 + 1)]^{-1}$ is plotted as a function of $v^{1/3}$, where v is the specific volume of the liquid.

The evaluation of the T and p influences on the viscosities of the solutions of PDMS in CO_2 yields the activation parameters $E^\ne$ and $V^\ne$ and their variation with composition (for examples see Figures 12 and 13). One observes a pronounced sigmoidal transition from the low values of the condensed gas to the high values of the polymer.

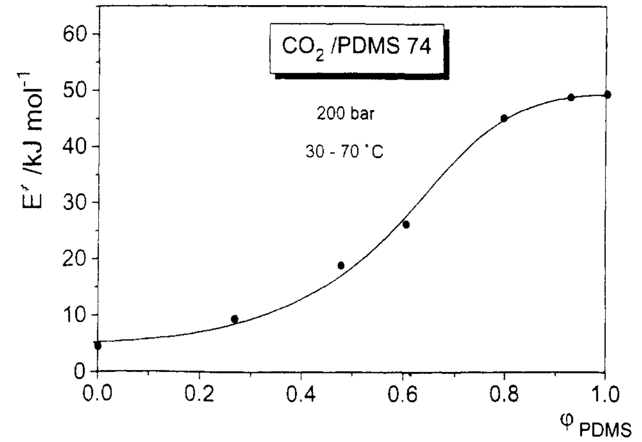

Figure 12. Activation energy of viscous flow, $E^\ne$, at 200 bar as a function of φ_{PDMS}, the volume fraction of polymer, obtained from data within the temperature range from 30 to 70 °C.

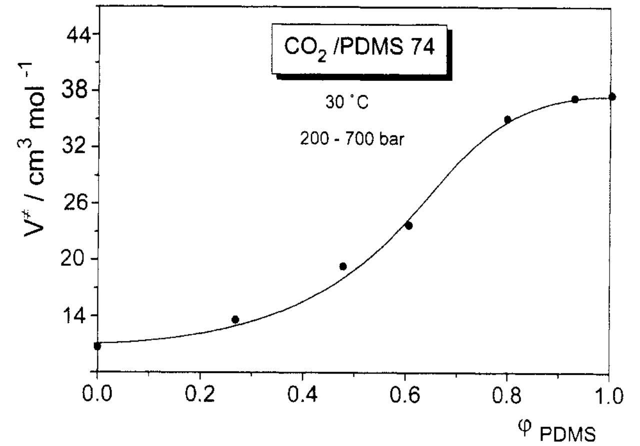

Figure 13. Activation volume of viscous flow, $V^\ne$, at 30 °C as a function of φ_{PDMS}, the volume fraction of polymer, obtained from data within the pressure range from 200 to 700 bar.

Excess Viscosities. The viscosities of mixtures are often discussed theoretically in terms of the excess viscosity defined by eq 2 and

$$\Delta \ln \eta_0 = \ln \eta_0^{\mathrm{exp}} - \ln(\eta_0)_\varphi^{\mathrm{id}} \qquad (3)$$

Figure 14 shows the results of an evaluation according to the above relation for one pair of values of temperature and pressure and the different samples of PDMS under investigation.

The most striking features of this diagram are the change in the sign of the effects from negative to positive within the region of high CO_2 content as the molar mass of the polymer becomes higher and the shift in the composition of inversion toward higher polymer contents as M goes up.

The curves combining the individual data points in Figure 14 were calculated by means of

$$\Delta \ln \eta_0 = (k_1\varphi_1 + k_2\varphi_2)\varphi_1\varphi_2 \qquad (4)$$

in which k_1 and k_2 are parameters that can be theoretically interpreted in the following manner.

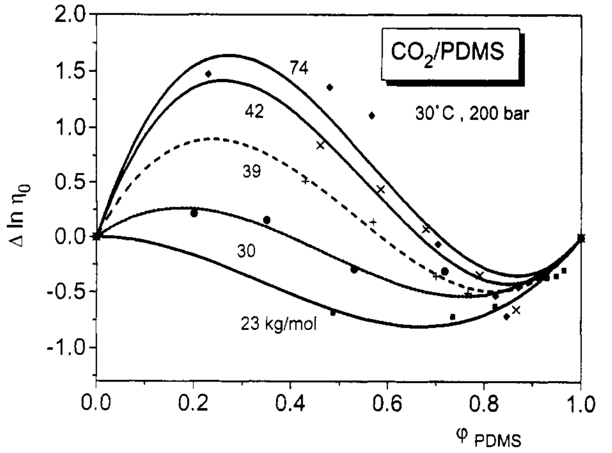

Figure 14. Excess viscosities $\Delta \ln \eta_0$ (defined by eq 3) as a function of φ_{PDMS}, the volume fraction of polymer, for the indicated samples of different molar mass at 30 °C and 200 bar. The curves are calculated by means of eq 4, and the parameters are collected in Table 2.

k_1: The comparison of the phenomenological relation[18]

$$\lim_{\varphi_2 \to 0} \frac{\partial \ln \eta_0}{\partial \varphi_2} = [\eta]\rho_2 \tag{5}$$

in which ρ_2 is the density of the polymer, with the corresponding expression resulting from eqs 2–4 [$\lim_{\varphi_2 \to 0} \partial \ln \eta_0/\partial \varphi_2 = k_1 + \delta$] leads to

$$k_1 = [\eta]\rho_2 - \delta \tag{6}$$

where δ, measuring the differences in the viscosities of the pure components, is defined as

$$\delta = \ln \eta_{0,2} - \ln \eta_{0,1} \tag{7}$$

k_2: The interpretation of this parameter is based on the results of a study on the excess viscosities of low molecular weight liquids.[3] According to that approach—which replaces volume fractions by surface fractions—the following expression should hold true

$$\Delta \ln \eta = \frac{\gamma\delta}{1 + \gamma\varphi_2}\varphi_2(1 - \varphi_2) + 2g\frac{(1 + \gamma)}{(1 + \gamma\varphi_2)^2}\varphi_2(1 - \varphi_2) \tag{8}$$

γ—a geometrical factor characterizing the differences between *volume* and *surface* fractions in terms of the molar surfaces F_i and the molar volumes V_i—is given by

$$\gamma = \frac{F_2/V_2}{F_1/V_1} - 1 \tag{9}$$

and g represents the (integral) Flory–Huggins parameter.

An analysis of the applicability of eq 8 to low molecular weight liquids (using published experimental data on $\Delta \ln \eta$ and g) has demonstrated that the influence of g needs only to be taken into account for strongly interacting systems, like mixtures of alcohols and water.

In order to assign a physical meaning to k_2, it is again useful to discuss the limiting case of an infinitely large excess of one component; from eq 8 it follows that

$$\lim_{\varphi_2 \to 1} \frac{\partial \ln \eta_0}{\partial \varphi_2} = \frac{\delta - 2g}{1 + \gamma} \tag{10}$$

so that a comparison of eq 10 with the corresponding relation resulting from eq 4 yields

Table 3. Parameters of Eqs 4–11 Used for the Calculation of the Concentration Dependence of the Excess Viscosities Shown in Figure 14

Polymer	$[\eta]_\Theta$	δ	k_1	k_2
PDMS 23	9.0	8.4	−0.03	−5.4
PDMS 30	12.4	8.5	3.8	−5.4
PDMS 39	15.5	9.0	6.0	−5.9
PDMS 42	17.0	9.4	12.0	−6.0
PDMS 74	24.0	11.1	13.0	−5.4

$$k_2 = \frac{\gamma\delta + 2g}{1 + \gamma} \tag{11}$$

The curves shown in Figure 14 were calculated according to eq 4 using k_1 and k_2 values which were obtained in the following way: The intrinsic viscosities of eq 6—required for the prediction of k_1—were approximated by calculating $[\eta]$ from the known M values of the polymers using an $[\eta]$ – M relationship reported for a Θ solvent[19] (bromocyclohexane) in view of the fact that the present condensed gases should be marginal solvents only; k_2 was adjusted. The parameters used to calculate the curves of Figure 14 are collected in Table 3.

For a discussion of k_2 (eq 11), the thermodynamic interaction parameter g was set to zero in view of the results with low molecular weight liquids and the geometric factor γ was calculated. This procedure yields—within experimental error—the same value of $\gamma_{adj}^{g=0} = -0.39$, irrespective of the molar mass of PDMS. It is interesting to compare this result with the γ value calculated theoretically from the group contributions tabulated by Bondi.[20] The considerable discrepancy between $\gamma_{Bondi} = -0.12$ and $\gamma_{adj}^{g=0} = -0.39$ cannot be explained in terms of the neglect of the thermodynamic parameter g (since negative and unrealistically large values would be required). The mismatch is more likely due to the fact that the increments of Bondi—which were obtained from information on *low molecular weight compounds*—cannot be directly applied to *polymers*.

In view of the different approximations described it is remarkable how well the present data can be reproduced analytically by means of only one adjustable parameter. Furthermore it is interesting to note that the occurrence of inversions in $\Delta \ln \eta$ as a function of composition might be bound to molar masses of the polymer that are larger than the entanglement value. However, at the moment it cannot be decided whether this finding is general or only a coincidence.

Conclusions

The present results on the volumetric and the viscometric behavior of polymer solutions in condensed gases demonstrate that the solutions of polymers in condensed gases behave very much like that in ordinary low molecular weight liquids. However, large negative excess volumes appear characteristic for highly volatile solvents. The concentration dependence of both excess volumes and excess viscosities can be described quantitatively by a simple relation of the form $(k_1\varphi_1 + k_2\varphi_2)\varphi_1\varphi_2$. In the case of $\Delta \ln \eta_0$ the parameters of this equation—which covers all details of a complex and strongly molecular weight dependent behavior by means of only one (M-independent) adjustable parameter—can be given a well-defined physical meaning. Other interesting features of the present system concern the concentration dependence of the activation energies and volumes, which exhibit pronounced sigmoidal shapes, and indications that chain entanglements could play an important role for the occurrence of inversions in the excess viscosities. Further experimental and theoretical work is, however, required to clarify this item.

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