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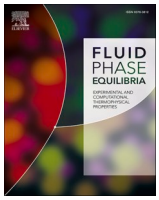

Polymer solutions in supercritical fluids: Their flow behavior compared to that in normal solvents

Rüdiger Mertsch [a], Bernhard A. Wolf [b,*]

[a] Evonik Operations GmbH, Research, Development & Innovation, Goldschmidtstraße 100, D-55099, Essen, Germany
[b] Johannes Gutenberg-Universität Mainz, Department Chemie, Jakob Welder-Weg 11, D-55099, Universität Mainz, Germany

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ABSTRACT

The dissimilar flow behavior of polymer solutions in super critical fluids, as compared with that in normal solvents, are primarily resulting from the great differences in the free volume of the pure solvents. The present analysis compares the generalized intrinsic viscosities $\{\eta\}$ and the average shear overlap parameters for the two types of solvent. $\{\eta\}$ depends on the polymer concentration c; it starts from the intrinsic viscosity $[\eta]$ at infinite dilution and ends at the intrinsic bulkiness in the limit of the pure polymer. The overlap parameter states the average number of polymer molecules that flow together under given conditions. With regard to these parameters, super critical fluids differ from normal solvents in the following manner: $[\eta]$ is much less, the intrinsic bulkiness much larger and $\{\eta\}$ (c) runs through a deep minimum; in addition the cross-over concentration, separating the solvent dominated from the polymer dominated flow regime, is much higher. Another fundamental dissimilarity is the change in the enthalpy of mixing with increasing c from exothermic to endothermic. The above features explain, why super critical fluids have numerous advantages (like viscosities that remain very low even at high polymer concentrations) over conventional solvents and why they are used for the modification and synthesis of high-molecular substances.

1. Introduction

This article examines the differences and similarities between normal solvents and supercritical fluids with respect to the flow properties of polymers dissolved in them. In view of the importance of such systems in many technical and medical fields as well as for environmental issues, there is great interest in a better theoretical understanding of their behavior, as the numerous review articles listed below demonstrate.

The value of carbon dioxide for eco-friendly chemical processes, especially for minimizing hazardous waste and coping with the solvent recovery challenges is one central topic [1]. Another contribution [2] demonstrates that supercritical gases have become important for drug delivery and related biomedical processes, particularly for improving the bioavailability of active pharmaceutical ingredients and producing advanced drug delivery systems. Reference [3] offers a critical analysis of current research directions and discusses foaming processes for different polymer types, including amorphous, semi-crystalline, polymer blends, copolymers, and thermosetting polymers. Another contribution [4] explores the use of supercritical fluids, especially supercritical carbon dioxide, in pharmaceutical applications like microencapsulation and nanoencapsulation for drug delivery and discusses strategies for optimizing particle morphology, drug loading, and yield. Reference [5], finally, focuses on the use of supercritical gases in the oil and gas sector for refining, enhancing heavy oil recovery, hydraulic fracturing, and managing oil sludge and asphaltenes and discusses its pros and cons.

The above review articles demonstrate that super critical fluids technologies are almost exclusively applied in the area of high solute concentrations. In order to provide information on the entire composition range, this article only studies systems for which the viscous behavior has been measured from the compressed gas up to the pure polymer. A prerequisite for the theoretical evaluation of this experimental information is the introduction of the generalized intrinsic viscosity $\{\eta\}$ and of a viscometric degree of overlap Σ. The former variable measures the hydrodynamic specific volume and the latter states how many dissolved molecules flow together under given conditions.

* Corresponding author.
E-mail addresses: ruediger.mertsch@evonik.com (R. Mertsch), bernhard.wolf@uni-mainz.de (B.A. Wolf).

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2. Theoretical background

This section collects all mathematical relations required for the analysis of the experimental data with respect to shear clusters, which is an entity that contains a minimum of two solute molecules that flow together. The driving force for establishment of such aggregations consists first and foremost in the minimization of the entropy production of the system. Since all experiments were performed under Newtonian conditions, shear rate effects need not be considered here.

The generalized intrinsic viscosity [6] $\{\eta\}$, i.e. the hydrodynamic specific volume of the solute at arbitrary composition c (expressed in terms of mass/volume), represents the pivotal quantity

$$\{\eta\} = \left(\frac{\partial \ln \eta}{\partial c}\right) = \left(\frac{\partial \ln \eta_{\mathrm{rel}}}{\partial c}\right) \tag{1}$$

where η_{rel} stands for the viscosity, normalized to that of the pure solvent. The limiting values of $\{\eta\}$ at the two ends of the composition scale are the intrinsic viscosity $[\eta]$ and the intrinsic bulkiness $[\![\eta]\!]$ as defined below

$$[\eta] = \lim_{c\to 0}\left(\frac{\partial \ln \eta_{\mathrm{rel}}}{\partial c}\right) \tag{2}$$

and

$$[\![\eta]\!] = \lim_{c\to \rho}\left(\frac{\partial \ln \eta_{\mathrm{rel}}}{\partial c}\right) \tag{3}$$

where ρ stands for the density of the polymers.

Physically the generalized intrinsic viscosity stand for the inverse of $c_{\mathrm{shear\ cluster}}$, the concentration of an *individual* solute molecule within the shear cluster [7,8], according to

$$c_{\mathrm{shear\ cluster}} = \frac{1}{\{\eta\}} \tag{4}$$

The following relation[7, 8] holds true for the shear overlap parameter Σ, the number of solute molecules a selected solute molecule is flowing together with,

$$\Sigma = c\{\eta\} \tag{5}$$

Studies of the present type also provide information on the so-called cross-over concentration[7, 8], c_{crov}, which subdivides the concentration regime in a dilute region, within which the solvent dominates the flow behavior and a concentrated regime, where the polymer dominates. The condition that needs to be fulfilled at this characteristic point reads

$$\frac{\partial^2 \Sigma}{\partial c^2} = 0 \tag{6}$$

The measured composition dependence of ln η_{rel} can usually be modeled quantitatively by the following, largely universal relationship [7] between ln η_{rel} and $\tilde{c}$

$$\ln\eta_{\mathrm{rel}} = \frac{\tilde{c} + \alpha\tilde{c}^2}{1 + \beta\tilde{c} + \gamma\tilde{c}^2} \tag{7}$$

where α, β and γ are hydrodynamic interaction parameters and $\tilde{c}$ stands for the reduced polymer concentration

$$\tilde{c} = c[\eta] \tag{8}$$

One or even two of the interaction parameters of Eq (7) can in most cases be set equal to zero.

All previous explanations have been of a purely phenomenological nature. In order to also cover some minimal molecular aspects [9], the molecular significance of the viscometric interaction parameters will be discussed below.

Rewriting ln η_{rel} (Eq (7)) as a series with respect to the reduced concentration $\tilde{c}$ up to the third power gives

$$\ln\eta_{rel} = \tilde{c} + M_2\tilde{c}^2 + M_3\tilde{c}^3 \tag{9}$$

where the parameter M_2 measures the contribution of binary solute contacts and M_3 that of ternary ones. The corresponding series expansion for eq (7) yields

$$\ln\eta_{rel} = \tilde{c} + (\alpha-\beta)\tilde{c}^2 + (\beta^2 - \alpha\beta - \gamma)\tilde{c}^3 \tag{10}$$

By comparison of these two expressions, one obtains

$$M_2 = \alpha - \beta \tag{11}$$

and

$$M_3 = \beta^2 - \alpha\beta - \gamma \tag{12}$$

3. Materials and procedures

The polymer samples under investigation were of industrial origin and fractionated [10] prior to their use. Poly(dimethyl siloxane) (PDMS) of different molar mass was purchased from the Wacker GmbH, Munich [11] and poly(isobutene) (PIB) was donated by the Bayer AG, Leverkusen, Germany [12].

The densities of the polymer solutions were measured by means of a Kratky apparatus (measuring cell DMA 5 12 and data processor DMA 60, of Fa. Paar Graz, Austria). A U-tube that can sustain elevated pressures was filled and the resonance frequency was determined, calibrating the apparatus with liquids of known density [12].

Viscosities were determined by means of two high-pressure viscometers, a rolling-ball apparatus and a viscometer of the Searle type. The latter device consists of a cylindrical rotor containing four powerful Co-Sm magnets which is driven by a similar cylinder situated outside the cell [12]. Homogeneous mixtures were prepared in the 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 contains a gas-tight piston which moves freely and a stirrer that can be operated 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 viscometer by simultaneously opening the valve between them and reducing the total volume of the system rapidly by means of a hand pump.

4. Results and discussion

The presentation of the experimental results is organized in the following way: It starts with the composition dependence of the viscosities, which can in the present case be measured from the pure solvent up to the pure melt. This evaluation yields data for the intrinsic viscosities $[\eta]$ and for the intrinsic bulkiness $[\![\eta]\!]$, to be discussed in the next section. Topic of the following part is the general hydrodynamic specific volumes at arbitrary concentration, $\{\eta\}$, as a function of c. Finally, the last section deals with the shear overlap parameter Σ, quantifying the number of solute molecules that flow together at different concentrations.

4.1. Viscosities as a function of polymer concentration

All experimental data are modeled according to Eq (6) and the obtained viscometric interaction parameters are collected in Table 1.

Fig. 1 shows the results obtained at 30 °C and 200 bar for solutions of the PDMS in CO_2. For comparison this graph also contains the results for a solution of PDMS with comparable molar mass in its pentamer at the same temperature but at 1 bar.

For the PDMS solution in CO_2 at 200 bar the common feature of the composition dependencies of ln η_{rel} lies in a more than linear increase of

Table 1
Systems, characterization of the components, plus temperatures and pressures of the experiments [η]: intrinsic viscosity, $[\![\eta]\!]$: intrinsic bulkiness, α β and γ: parameters of eq (8), $c_{\text{cross-over}}$ and Σ_{crov}: cross-over concentration and shear overlap.

solvent	Polymer	M kg/mol	°C	bar	[η] mL/g	±	α	±	β	±	1000 g	±	$[\![\eta]\!]$ mL/g	C_{crov}	Σ_{crov}
CO_2	PDMS	23	30	200	6.88	0.24	0		−0.048	0.006	0		13.40	$\partial^2\Sigma/\partial c^2 > 0$	
CO_2	PDMS	42	30	200	26.16	4.62	−0.042	0.016	0.046	0.035	−3.74	0.05	40.00	0.428	2.98
CO_2	PDMS	74	30	200	31.37	3.66	−0.034	0.008	0.044	0.019	−2.72	0.02	49.00	0.418	3.38
DMS 5	PDMS	36	30	1	19.00	0.38	0		0.048	0.0016	0		5.95	$\partial^2\Sigma/\partial c^2 < 0$	
Ethylene	PIB	3.9	40	600	5.55	0.14	0		−0.115	0.005	0		27.50	$\partial^2\Sigma/\partial c^2 > 0$	
Ethylene	PIB	3.9	40	400	5.41	0.18	0		−0.124	0.008	0		30.50	$\partial^2\Sigma/\partial c^2 > 0$	
Ethylene	PIB	3.9	70	400	3.36	0.11	0		−0.490	0.012	0		46.40	$\partial^2\Sigma/\partial c^2 > 0$	
Ethylene	PIB	1.4	40	600	5.26	0.32	0		−0.121	0.014	0		25.90	$\partial^2\Sigma/\partial c^2 > 0$	

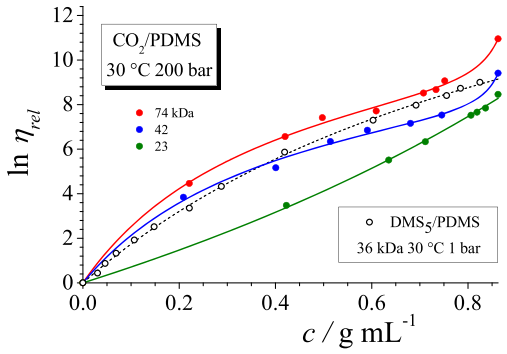

Fig. 1. Concentration dependence of ln η_{rel} for PDMS solutions in CO_2 or in its pentamer under the conditions specified in the graph. The curves are modeled according to Eq (7).

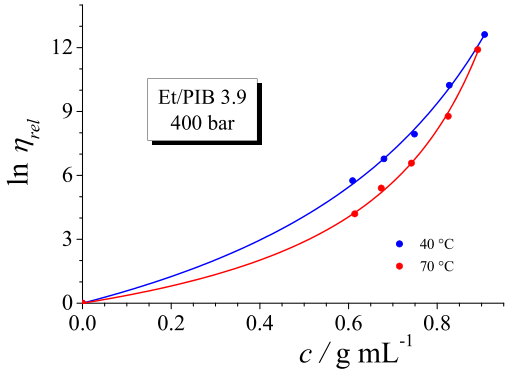

Fig. 3. Concentration dependence of ln η_{rel} for PIB solutions in ethylene at different temperatures.

the curves on the approach of the pure melt, where the size this effect becomes larger with rising molar mass of the solute. In contrast, the dependence for the solution of PDMS in its pentamer under atmospheric pressure decreases monotonously over the entire composition range.

Fig. 2 shows the analogous results for solutions of PIB in ethylene at two pressures and two different molar masses, both being considerably lower than that of PDMS. For the higher molecular weight sample, the viscosities are expectedly larger than for the lower at both pressures. However, the observation that all viscosities in the range of large polymer concentrations are at 400 bar higher than at 600 bar surprises. Presently it is unclear whether this discrepancy is due to a systematic experimental error or caused by the different compressibility of the components.

Fig. 3 documents that the temperature influences are much larger than the pressure effects. All dependencies for the solutions of PIB lack points of inflection, in contrast to PDMS. This behavior is likely caused by their much lower molar masses, i.e. by the lower number of entanglements per molecule.

In conclusion of this section, we check whether the coefficients of the series expansion of the viscosityEqs (11) and (12)) differ for the solutions of PDMS and PIB. The parameter M_2, quantifying the effect of the formation of binary interpolymer contacts, is only negative for the solutions of the two higher molecular weight samples of PDMS in CO_2 and for the system DMS_5/PDMS at atmospheric pressure. This means that the ln η_{rel} values increase less than linearly with c *within the dilute regime*, where the binary interactions dominate; in all other cases the opposite is true. M_3, on the other hand is always positive, which indicates that the formation of ternary contacts always increases ln η_{rel}. Remarkably and unexpectedly, both M_2 and M_3 are for PIB solutions in ethylene at 70 °C significantly larger than at 40 °C.

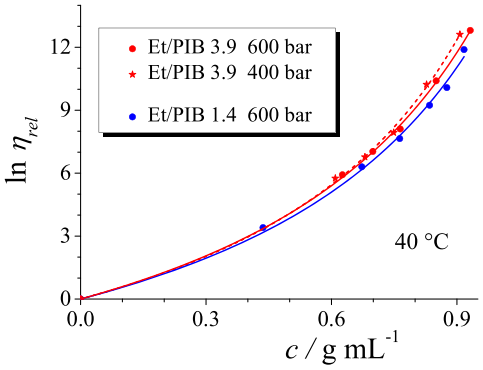

Fig. 2. Concentration dependence of ln η_{rel} for PIB solutions in ethylene at different pressures.

4.2. *Intrinsic viscosities and intrinsic bulkiness*

Initial and final slopes of ln η_{rel} vs c yield information on [η] (the hydrodynamic specific volume at infinite dilution) and on $[\![\eta]\!]$ (the hydrodynamic specific volume in the limit of the pure polymer). Fig. 4 displays these data for the system CO_2/PDMS as a function of the polymer molar mass in form of Kuhn-Mark-Houwink plots, i.e. on a double logarithmic scale.

For the two higher molecular samples shown in Fig. 4 the slope equals 0.5, documenting a close to theta behavior for [η] as well as for $[\![\eta]\!]$. The corresponding values for the lowest molecular weight sample on the other hand are much less. This observation is probably due to the low molar mass of this sample, which is too small to exhibit the typical polymer behavior. For comparison Fig. 4 also shows the result for a PDMS sample with a molar mass in the range of present interest and atmospheric pressure, which is not dissolved in a supercritical gas, but in its pentamer. It is interesting to note that the value for the intrinsic

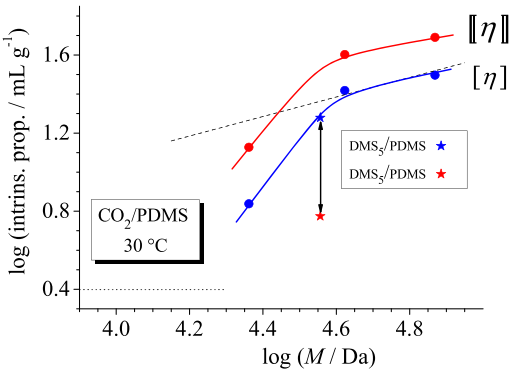

Fig. 4. log $[\eta]$ and log $[\![\eta]\!]$ as a function of log M for solutions of different poly (dimethyl siloxane) samples in CO_2; the slope of the broken line is 0.5; the dotted line indicates $[\eta] = 2.5$ mL/g.

viscosity agrees well with that for the CO_2 solutions, whereas the corresponding value for the intrinsic bulkiness amounts to only approximately one sixth. This observation is a clear indication that the large values of $[\![\eta]\!]$ are typical for solutions in supercritical gases as can also be seen from Fig. 5, showing the results for the system Et/PIB/PIB.

The little variation of the intrinsic viscosities and of the intrinsic bulkiness with molar mass displayed in Figs. 4 and 5 can again be rationalized by the assumption that these chains are too short to exhibit the characteristic features of polymers.

4.3. Generalized intrinsic viscosities

This section deals with $\{\eta\}(c)$, the hydrodynamic specific volume of the solute as a function of composition. Fig. 6 shows the results for the solutions of PDMS in CO_2.

The most outstanding information of this graph consists in a marked increase of $\{\eta\}$ for all PDMS solutions in CO_2 – except for the lowest molecular weight sample - upon the approach of the pure polymer where the effect become the larger the higher the molar mass of the polymer becomes. This behavior differs fundamentally from that of the PDMS solution in its pentamer, for which the hydrodynamic specific volume decreases monotonously with concentration. The question that arises is, why $\{\eta\}$ as a function of c runs through such a deep minimum for the solutions of the higher molecular weight PDMS samples in CO_2, in contrast to most polymer solutions in normal solvents.

To be able to answer it, one has to realize that the structures that form during stationary flow evolve from equilibrium structures. A decisive element in this context is the fact that polymer solutions within the dilute and moderately concentrated regime are in any case two-phase on a mesoscopic level, i.e. volume elements of pure solvent coexist with regions within which the components are homogeneously mixed. To account for this situation, the Flory-Huggins interaction

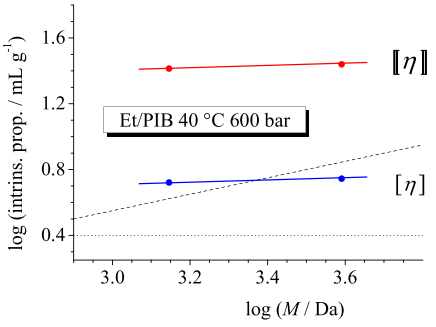

Fig. 5. As Fig. 3 but for solutions of polyisobutylene in ethylene.

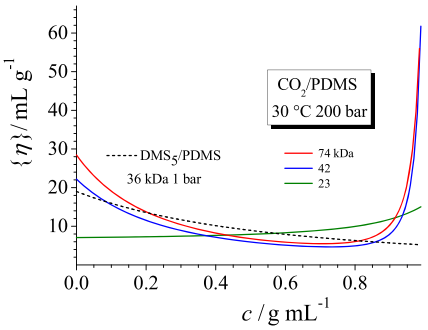

Fig. 6. Concentration dependence of the generalized intrinsic viscosity for the solutions of different PDMS samples under the conditions specified in the graph.

parameter χ, determining the equilibrium structure, needs to be split into *inter*-molecular and an *intra*-molecular contributions, respectively [13]. In view of the fact that the application of that concept to solutions in supercritical gases would require extra studies, the following discussion is limited to some basic phenomenological considerations.

In the limit of infinite dilution, the isolated polymer coils will take up considerable amounts of solvent because of the large gain in mixing entropy. For this reason, the hydrodynamic specific volume, i.e. $\{\eta\}$ should assume relatively large values. It is also to be expected that $\{\eta\}$ values decrease pronouncedly as c rises, because the polymer coils can now very favorable overlap of other coils to avoid the neighborhood of voids. Up to this point, we have limited ourselves to equilibrium considerations in view of the observation that the contributions of clustering become actually significant at larger c values only [7]. Once the coils overlap considerably, however, cluster formation can no longer be neglected. This effect, primarily based on the minimization of the entropy production leads to an increase in $\{\eta\}$ that becomes the more pronounced the closer one gets to the pure polymer and reaches its supremum as the solvent concentration approaches zero. In summary, it can be therefore be concluded that the unusually deep minimum in $\{\eta\}$ versus c results from the extremely low solvent power of the condensed gases under consideration. The results shown in Fig. 7 for the PIB solutions in ethylene seemingly contradict the above-said, since the generalized intrinsic viscosity rises steadily within the entire composition range. However, this finding simply means that the PIB chains are too short to exhibit the typical polymer behavior. The observation that the generalized intrinsic viscosities are at 400 bar higher than at 600 bar has already been discussed in the context of the corresponding uncommon ln η_{rel} behavior.

Fig. 8 shows the concentration dependence of the hydrodynamic specific volume for two temperatures at constant values of M and p. The curves for 40 and 70 °C intersect at $c_{is} = 0.69$; g/mL; for $c < c_{is}$ $\{\eta\}$

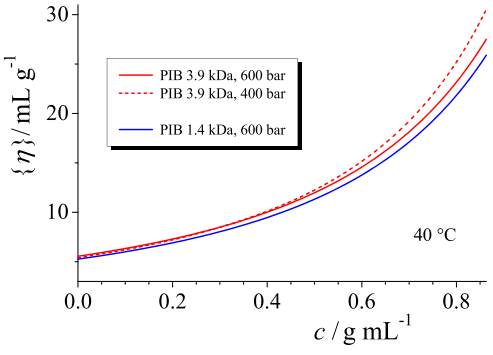

Fig. 7. As Fig. 6 but for solutions of PIB in ethylene.

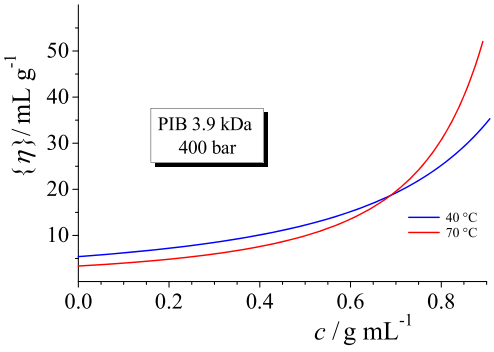

Fig. 8. Concentration dependence of the generalized intrinsic viscosity at 40 and 70 °C, respectively.

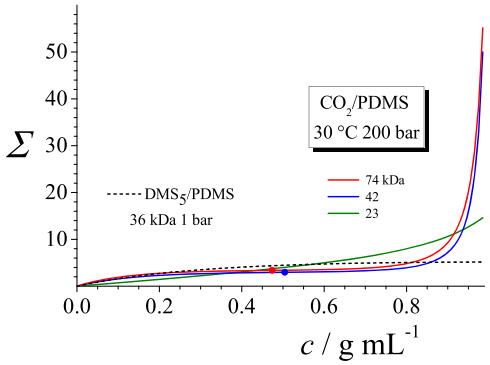

Fig. 9. Concentration dependence of the shear overlap parameter Σ and cross-over conditions (points) for solutions of PDMS in either CO_2 or in its pentamer.

decreases with rising T, whereas it increases for $c < c_{is}$.[1] A phenomenological thermodynamic interpretation of this observation leads to the conclusion that the formation of shear clusters from the solvent and the polymer is exothermic in the dilute range, but endothermic in the highly concentrated range. To gain some molecular understanding, it is helpful to account for the differences in the mixing processes leading to dilute or concentrated polymer solutions. In the former case, the mixing procedure will be dominated by exothermic filling the abundant holes of the supercritical gas; in the latter case most of these holes are already filled and the endothermic contact formation between the supercritical gas and polymer segments prevails. The analogous results concerning the pressure influences (Fig. 7) corroborate the present interpretation. In this case the intersection is not as obvious due to the smaller effects of pressure as compared with temperature. In this case $c_{is} = 0.31$ g/mL and the generalized intrinsic viscosities are in the dilute range at 400 bar lower than at 600 bar, whereas the opposite is true for high polymer concentrations.

4.4. Shear overlap parameters

This section deals with the number of polymer molecules that flow together as a function of concentration at different pressures and temperatures. The boundaries between the solvent dominated and the polymer dominated flow regimes, the so called cross-over conditions determined in this context are of particular interest. In diagrams Σ vs c they manifest themselves by the second derivative becoming zero (Eq (6)).

Fig. 9 gives an overview for the behavior of the PDMS solutions in CO_2. One recognizes that cross-over concentrations are only observed for the two higher molecular weight samples, where the c_{crov} value for PDMS 74 is lower than for PDMS 42, in accordance with the fact that the concentration required for the establishment of a fully developed entanglement network is reached the earlier the lower the molar mass of the polymer. Cross-over conditions are absent for the solution of lowest molecular weight of PDMS in CO_2 and for the solution of PDMS in its pentamer, where the causes of this behavior are different. For the system DMS_5/PDMS it can be explained by the molar mass of the solute, which is too low to establish the entanglement network. Accordingly, Σ rises less than linearly with c. For CO_2/PDMS, on the other hand, the reason lies in the extremely dissimilar viscosities of the pure components. In this case the solution segregates increasing amounts of the polymer into clusters as the concentration rises, which means that Σ increases more than linearly with c. Accordingly in Σ approaches suprema for vanishing solvent content of the mixtures, which are the larger the higher the molar mass of the polymer as demonstrated in Fig. 9.

If one compares the maximum number of polymer molecules that flow together with solutions in supercritical gases at comparable molar masses with those in the normal solvents (Fig. 6 of reference [7]), one recognizes that this number is more than a factor ten higher. The reason lies in the low solvent quality and low viscosity of CO_2 leading to a larger segregation of the solute into clusters. Another particularity of supercritical gases as solvents lies in the pronouncedly higher cross-over concentrations, which means that the composition region within which the solvent dominates the flow behavior becomes larger.

Fig. 10 shows the analogous results for the system Et/PIB at different pressures. As already mentioned earlier, the viscosities at high polymer concentration resulted larger at 400 than 600 bar, which means that the shear overlap parameters are higher. Presently it is unclear, whether this a systematic error or a real phenomenon.

Fig. 11 shows how different temperatures affect the clustering behavior of PIB solutions in ethylene. As in Fig. 8, the curves for the different temperatures intersect at the concentration at which athermal mixing conditions prevail. Within the exothermal composition range the solute clusters less at 70 °C, within the endothermal range at 40 °C.

Last but not least it is important to note that the information on the number of polymer molecules that are contained in the clusters in cases where supercritical gases serve as solvents should be helpful for the tailored synthesis of polymers and their modification in supercritical solutions.

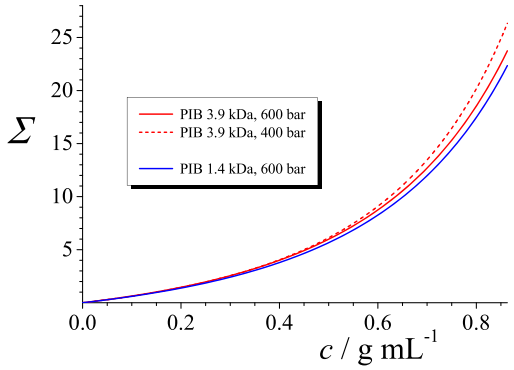

Fig. 10. Concentration dependence of the shear overlap parameter Σ for solutions of PIB of the indicated molar mass in ethylene at 40 °C and different pressures.

[1] To avoid misunderstandings, it should be noted that the described behavior does not mean that the viscosity is for large c values at 70 °C higher than at 40 °C (cf. Fig. 3), it only means that the hydrodynamic specific volume of the solute is larger under these conditions.

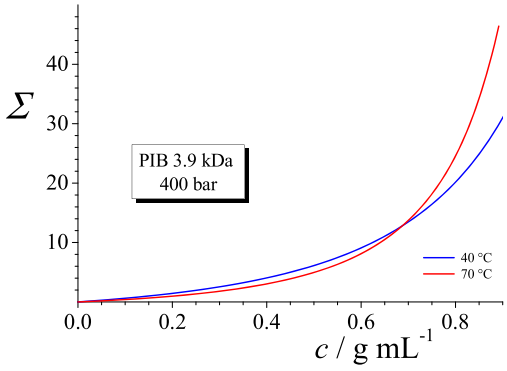

Fig. 11. Concentration dependence of the shear overlap parameter Σ for a PIB solution in ethylene at 400 bar and the indicated temperatures.

5. Conclusions/outlook

The present analysis - based on the generalized intrinsic viscosity $\{\eta\}$ and on the quantitative modeling of η (c) – has made it possible to compare the flow behavior of polymer solutions in supercritical gases with that in normal solvents. In the course of these investigations, very low molecular weight samples were also examined, they exhibit a number of special features.

With respect to the composition dependence of ln η_{rel}, qualitative differences between supercritical gases and normal solvents are absent. The quantitative values of the generalized intrinsic viscosities $\{\eta\}$, of the intrinsic viscosities $[\eta]$ and of the intrinsic bulkiness $[\![\eta]\!]$ derived therefrom, on the other hand, differ markedly. For supercritical gases $\{\eta\}$ (c) passes deep minima due to their marginal solvent power resulting from the high volume fraction of voids. Such dependences are also known for normal solvents. In these cases, however, they are caused by the proximity of the measuring temperature to the glass transition temperature of the polymer. The intrinsic viscosities of the polymers in supercritical gases are typically much lower and close to their theta values in normal solvents, again because of the marginal solvent power. In contrast to this, the intrinsic bulkiness is much larger due to the pronounced reduction of entropy dissipation, resulting from the transfer of polymer molecules into shear clusters.

Another quantity that needs to be discussed when comparing supercritical gases with normal solvents, is the shear overlap parameter. The dependence Σ (c) shows inflection points for both, supercritical gases and normal solvents. At these characteristic compositions, c_{crov}, the flow behavior changes from solvent dominated on the dilute side to polymer dominated on the concentrated side. Due to the large fraction of free volume, the c_{crov} values are significantly higher for the supercritical liquids than for normal solvents. At very high polymer concentrations, shear clusters are formed in which forty to fifty polymer molecules flow conjointly, even in the case of relatively low molar masses.

The viscous behavior of uncommonly low-molecular weight polymers in supercritical gases is primarily determined by the fading polymer character. The composition dependence of ln η_{rel} does no longer exhibit points of inflection and extrema in $\{\eta\}$ (c) are absent. The intrinsic viscosities become very small - on the order of the Einstein value - and their molecular weight dependences do no longer follow the usual Kuhn-Mark-Houwink relation; log $[\![\eta]\!]$ as a function of log M runs approximately parallel to that of the intrinsic viscosities but at markedly larger values. Due to the lack of points of inflection in Σ (c), cross-over conditions cannot be observed.

One finding that deserves special mentioning is the intersection of $\{\eta\}$ (c) for different temperatures at constant pressure, as well as for different pressures at constant temperature. This observation implies that enthalpies and probably also volumes of mixing change their sign as a function of composition. On the solvent side the mixing process is exothermic and the excess volumes are negative, whereas it is endothermic on the polymer side and the excess volumes are positive. This behavior is due to the dominance of different effects: At low c values, the solute preferentially enters the voids of the solvent, leading to the evolution of heat and a reduction of volume. At sufficiently high c values most of these holes are already filled and the enthalpically unfavorable contact formation between the supercritical gas and polymer segments prevails. Based on the general nature of the described phenomena, it is not unreasonable to conclude that the observed behavior is typical for the solutions of polymers in supercritical gases.

Finally, it should not go unmentioned that polymer solutions in supercritical gases offer considerable advantages in the fields of modification and synthesis of high-molecular substances, because the viscosity of the mixtures remains very low even at high polymer concentrations.

CRediT authorship contribution statement

Rüdiger Mertsch: Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Bernhard A. Wolf:** Writing – review & editing, Writing – original draft, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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