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Solvent Isotope Effect on Viscosity of Polystyrene-Benzene Solutions

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The concentration and temperature dependences of viscosity and density of solutions of nearly monodisperse polystyrene samples ($M_w/M_n < 1.06$) in benzene and deuterated benzene have been determined. The measurements were conducted with samples of different molecular weights (M_w) ranging from 4×10^3 to 4×10^5 between 293–313 K. Isotope H/D substitution in benzene causes visible changes in viscosity and density of solutions, however, its influence on intrinsic viscosities and Huggins constants, derived from the concentration dependences of viscosity, is negligible. No isotope effects on the exponents in the power law relationships have been detected. The viscosities of the solutions have been also correlated with the densities. The apparent close-packed volumes are practically constant for all solutions and seem to be determined by the properties of the solvent. The deuterium substitution visibly affects the close-packed volumes – they decrease by approximately 13%, both in pure solvent and in solutions.

Key words: polystyrene + benzene solutions, viscosity, deuterium isotope effect

The increasing importance of polymers in science and technology stimulates the study of their physicochemical properties. The strong interactions among the chains of polymers in the solid state make difficult to draw any conclusions on the properties of a polymer molecule itself and, therefore, to overcome this problem much interest has been focussed on polymer solutions. The study of such solutions provides with the valuable information on the molecular level. Viscosity seems to be one of the widely studied properties and the measurements of the viscosity coefficient η can provide us with a great deal of very useful information, especially about the dimension of polymer molecules (from intrinsic viscosity) and interactions between the polymer chains and molecules of solvent (from viscometric constant).

The effect of deuterium substitution on the viscosity of pure liquids is well known [1], but little effort has been made so far to study the influence of isotope substitution on the viscosity of solutions, in particular in solutions of polymers. Because it is known that the isotope effects can be a powerful tool in the study of various physicochemical properties, as well as the molecular structure and intermolecular interactions [2,3], we feel that the use of this isotope method can help to better understand the properties of polymer solutions.

Benzene is a very good solvent for polystyrene, and polystyrene + benzene solutions have been the subject of intensive studies [4–7]. Their hydrodynamic and thermodynamic properties are summarized in [8]. The primary interest was focussed on polystyrene samples of high molecular weight. In this work, the results of influence of H/D substitution on viscosity and density in dilute solutions of PS of rather low molecular weights, ranging from 4×10^3 to 4×10^5, in benzene between 293–313 K are reported.

EXPERIMENTAL

Materials: Polystyrene samples of molecular weights 4000 (PS4), 7500 (PS7), 25000 (PS25), 123000 (PS123), 400000 (PS400) and low polydispersity $M_w/M_n \le 1.06$ were obtained from Pressure Chemical Co. and used in experiments without further purification. Benzene (OBRPR, Poland) was carefully purified by column distillation. Molecular sieves A5 were used for drying. Benzene-d_6 (99.92%D, Polatom, Poland) was used without further purification. The molecular sieves used for drying deuterated benzene were previously treated by D_2O.

Measurements: Solutions used in viscosity and density measurements were made up gravimetrically and left stirring for several hours in sealed vials before being injected into the measuring cells. Concentrations varied from 8×10^{-4} gml^{-1} to 3×10^{-2} gml^{-1}. Kinematic viscosity was determined by using an optoelectronic capillary viscometer (Ubbelohde type) (Ecolab, Poland) with a precision of 10^{-4} cSt. This gauge was immersed into a bath controlled to ±0.01 K over the temperature range 273–313 K. Densities were measured in a vibrating tube densimeter (Ecolab, Poland) equipped with Peltier thermostat, with a precision of 10^{-5} gcm^{-3} in the same temperature range.

RESULTS AND DISCUSSION

The experimental results of the measurements of kinematic viscosities (ν) and densities (ρ) for PS4, PS7, PS25, PS123 and PS400 in benzene and benzene-d_6 were combined to calculate dynamic viscosities (η), according to the well known equation: $\eta = \nu\cdot\rho$. As expected, dynamic viscosities decrease with temperature and increase with concentration. A typical example of these variations is shown in Fig. 1. Temperature dependence can be described by Arrhenius relation, which gives the apparent activation energy of the viscous flow in the 12–14 kJ/mol range. As can be seen in Fig. 2, the activation energies increase with molecular weight of the polymer and with concentration. The latter dependence is much more pronounced for higher molecular weight. Let us note a visible isotope effect on activation energy, being the largest for pure solvent and slowly decreasing with concentration.

The analysis of the viscosity measurements shows that the isotope substitution in solvent affects the kinematic and dynamic viscosities in polystyrene solutions in a different way. Deuterium substitution decreases the kinematic viscosity of pure solvent, $\{(\nu_D-\nu_H)/\nu_H\} < 0$, and the same sign of the isotope effect is observed at very low concentrations for all polystyrene solutions studied. However, it appears that the isotope effect is dependent both on molecular weight and concentration of the polymer (Fig. 3). For low molecular weight no concentration dependence is observed and it becomes relatively strong for higher molecular weight, in particular for PS400. In the latter case the inversion of the sign of the isotope effect, $\{(\nu_D-\nu_H)/\nu_H\} > 0$, is already seen at very low concentration. The analysis of Fig. 3 shows that a similar behavior can be expected for PS123 and PS25 at higher concentration. We found also

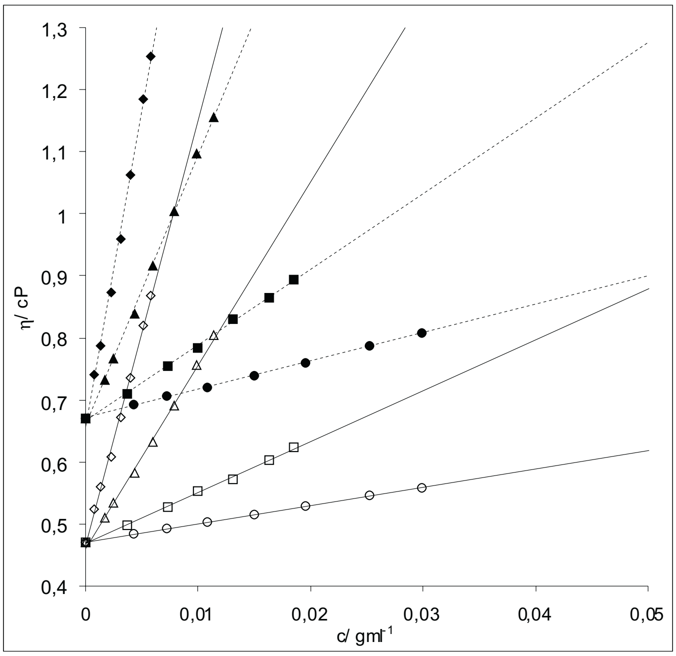

Figure 1. Concentration dependence of dynamic viscosity of polystyrene + benzene solutions at two temperatures: 293 K filled symbols, 313 K open symbols. ○ and ● PS4; □ and ■ PS25; △ and ▲ PS123; ◇ and ◆ PS400. Lines merely constitute the visual guides to data points.

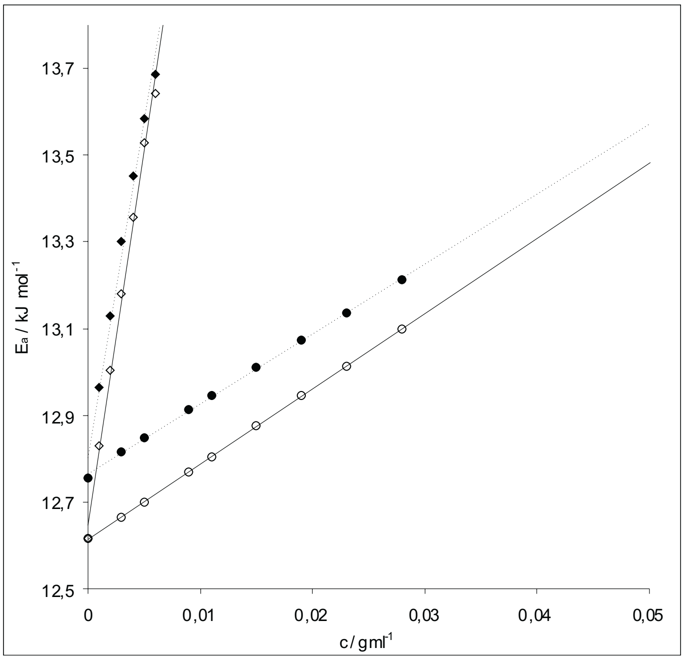

Figure 2. Concentration and molecular weight dependence of activation energy of the viscous flow for polystyrene + benzene solutions. Assignment of points: ○ (PS4 + B-h); ◇ (PS400 + B-h) and ● (PS4 + B-d); ◆ (PS400 + B-d). B-h and B-d refer to normal benzene and deuterated benzene, respectively.

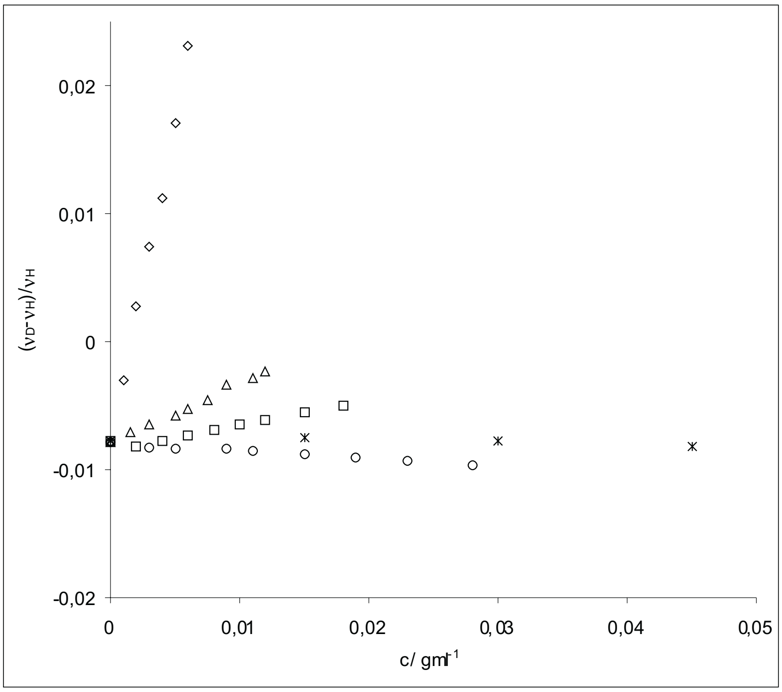

Figure 3. Isotope effect on kinematic viscosity in polystyrene + benzene solutions at 293 K. ○ PS4; ✱ PS7; □ PS25; △ PS123; ◇ PS400.

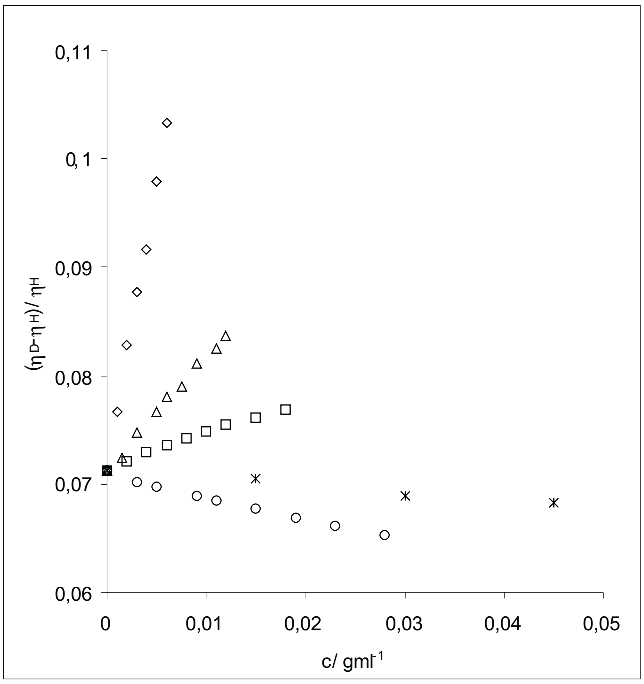

Figure 4. Isotope effect on dynamic viscosity in polystyrene + benzene solutions at 293 K. ○ PS4; ✱ PS7; □ PS25; △ PS123; ◇ PS400.

that the isotope effect on the kinematic viscosity is very weakly dependent on temperature. In the case of dynamic viscosity, deuterium substitution always leads to higher values of viscosity. The isotope effect on dynamic viscosity is also very weakly dependent on temperature, but visibly dependent on molecular weight of polymer and its concentration. For PS4 the isotope effect is found to be the largest for pure solvent and it decreases slowly with concentration. For higher molecular weight the concentration dependence is opposite and much stronger, especially for PS400 (Fig. 4). We think that the behavior of kinematic viscosity upon the isotope substitution reflects the pure isotope effect on the viscous flow, while in the case of dynamic viscosity we have to take into account the effect of density. Because in all known cases deuteration always increases the density [1], the observed isotope effect on dynamic viscosity is a result of the superposition of the opposing effects on kinematic viscosity and density. However, it is the dynamic viscosity, which has been used commonly in the literature and to our best knowledge deuterium substitution always increases the dynamic viscosity of pure liquids and mixtures [1]. The appearance of the isotope effect on viscosity in pure liquids can be explained in terms of mass ratio or better in terms of inertia moments ratio [9], although in some special cases, especially in solutions, some additional effects emerging from intermolecular interaction should be taken into account [1,10]. In the present case the concentration dependences suggest that intermolecular interactions play an important role in the appearance and magnitude of the viscosity isotope effect.

The concentration dependence of dynamic viscosity in polymer solutions is usually described by Huggins equation [11]:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + 0(c) \tag{1}$$

where: η_{sp} is specific viscosity defined as $\eta_{sp} = (\eta - \eta_0)/\eta_0$; and η, η_0 are the dynamic viscosities of solution and solvent, respectively; c is polymer concentration in g/ml; k_H is Huggins coefficient; $[\eta]$ is intrinsic viscosity; 0(c) are terms of higher power of c.

A typical graphical presentation of this dependence for PS4 between 293–313 K is shown in Fig. 5. The fitting procedure gives us very important viscometric parameters, *i.e.* intrinsic viscosity and Huggins constants. They are collected in Table 1. It is seen, that intrinsic viscosities are very weakly dependent on temperature. It implies the negligible influence of temperature on the sizes of dissolved coils of the polymer. Similar conclusions have been drawn by Berry for polystyrene + toluene system [12].

As expected, intrinsic viscosities increase with molecular weight. Fig. 6 presents a typical behavior of $[\eta]$ at 293 K. The data points first follow a slightly bent curve and above 2.5×10^4 they follow a straight line of slope 0.73 (corr. coeff. = 0.9994). Similar behavior had been observed by Einaga *et al.* [6] for polystyrene + benzene system for very large range of M_w ($4\times10^3 < M_w < 6\times10^7$), where the linear part of the plot was characterized by the slope 0.75. Their data are shown also in Fig. 5 for comparison. Analysis carried out by Fetters *et al.* [8] for a large number of polystyrene samples

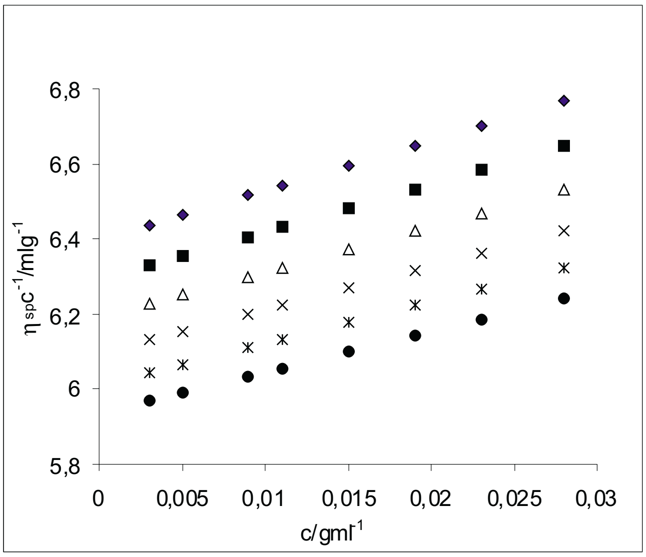

Figure 5. Dependence of reduced viscosity, η_{sp}/c, on polymer concentration for PS4 + benzene solution at given temperatures: ◆ 293 K; ■ 297 K; △301 K; × 305 K; ✱ 309 K; ● 313 K.

gives the power law equation in the following form: $[\eta] = 9.18\times10^{-3}\ M_w^{0.743}$. Kniewske and Kulicke [13] also observed a visible curvature for polystyrene + toluene system ($3\times10^4 < M_w < 24\times10^6$) for the low molecular weights of polystyrene. It is worth to mention, that within the experimental error no temperature effect and no isotope effect on the power law exponent was observed.

Table 1. Intrinsic viscosities $[\eta]$/mlg^{-1} and Huggins constants k_H obtained from fitting procedure (Eq. (1)) for PS + benzene and PS + deuterated benzene.

T/K	293		297		301		305		309	
	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
PS4	6.4_0	0.48	6.2_9	0.48	6.1_9	0.48	6.0_9	0.49	6.0_2	0.49
	6.1_9	0.47	6.1_0	0.47	6.0_1	0.47	5.9_3	0.48	5.8_5	0.48
PS7	9.4_5	0.42	9.3_4	0.42	9.2_3	0.42	9.2_0	0.43		
	9.3_5	0.42	9.2_6	0.42	9.1_8	0.42	9.1_0	0.42		
PS25	$15._9$	0.37	$15._7$	0.37	$15._5$	0.37	$15._3$	0.38	$15._2$	0.38
	$15._7$	0.37	$15._5$	0.37	$15._5$	0.37	$15._1$	0.37	$14._9$	0.37
PS123	$50._6$	0.33	$50._2$	0.33	$49._8$	0.33	$49._4$	0.33	$49._0$	0.33
	$50._1$	0.33	$49._7$	0.33	$49._3$	0.33	$49._1$	0.33	$48._9$	0.33
PS400	$123._5$	0.33	$122._7$	0.33	$121._8$	0.33	$121._1$	0.33	$120._1$	0.33
	$122._9$	0.33	$121._6$	0.33	$120._6$	0.33	$119._6$	0.33	$118._7$	0.33

The second row for each polystyrene sample refers to polystyrene solution in deuterated benzene.
The accuracy of the intrinsic viscosity is somewhat better than 1%.

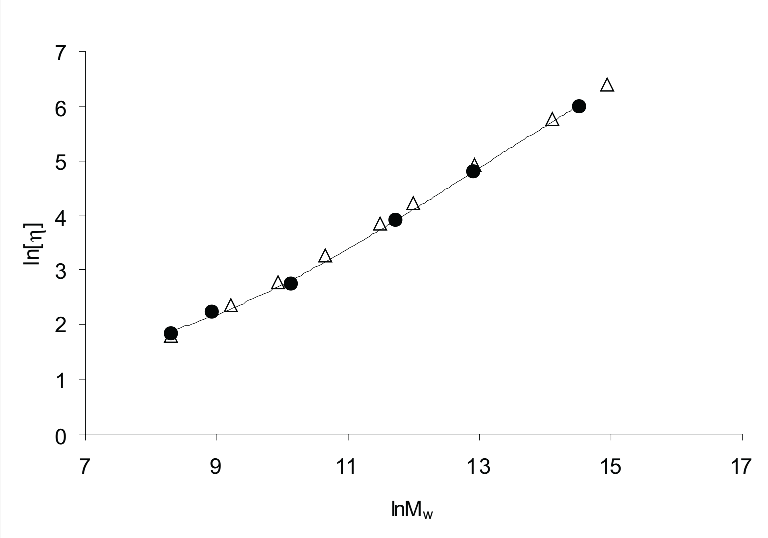

Figure 6. Molecular weight dependence of the intrinsic viscosity for polystyrene + benzene system at 293 K: ● – present data; △ data of Einaga *et al.* (ref. 6).

Deuteration of the solvent brings about a small decrease of the intrinsic viscosity. Actually this isotope effect is seen for the lowest molecular weights only. For the higher MW the isotope shift is comparable with the experimental error and, therefore, one can guess about some tendency only. Huggins constants presented in Table 1 are typical for a good solvent. They decrease with molecular weight and seem to approach the value of about 0.3, however, there is no simple correlation between Huggins constants and the molecular weight – we could not find any functional form describing this dependence. On the other hand, the reduced Huggins constants, $k_H/(M_w)^{1/2}$, are nicely correlated with M_w through the power law equation with the exponent equal to –0.442 (corr. coeff. = 0.995). Temperature has no visible effect on the Huggins constants. The effect of deuteration on k_H is not observed and eventual changes are obscured by the experimental error. From these results it becomes obvious that although viscosity itself is seriously affected by the isotope substitution, there is no direct transposition of this effect on the other viscometric parameters. In other words, deuteration of the solvent has practically no effect on the size of the dissolved coils and no effect on the interaction between polymer segments.

Continuing the analysis of various correlations it is worth to look at the relation of viscosity and density. In a number of polymer systems, density has been used quite successfully to scale and correlate the viscosity data, using the Doolittle relationship, based on the free volume consideration [14,15]:

$$\eta = A \exp[B/(1 - V_0 \rho)] \qquad (2)$$

where ρ is the density, A and B constants and V_0 is the close-packed volume. Fig. 7 presents the dependence of viscosity on density for concentration c = 0.005 g/ml for all PS samples and pure solvent. The fitting parameters are collected in Table 2. The apparent close-packed volumes appear to be practically constant for polymer solutions studied and slightly lower than that for the solvent. A similar situation is observed for deuterated systems and we can note a remarkable isotope effect on the apparent close-packed volume – it is practically independent of the MW of polymer and in fact equal to that observed for pure solvent: $V_0(H)/V_0(D) = 1.13$. It seems that for this low concentration, the properties of the solvent are a dominating factor and as a consequence we observe a large isotope effect upon deuterium substitution in benzene.

The measured densities themselves are also worth of a careful examination. From their temperature dependences one can obtain coefficients of thermal expansion (α) according to:

$$\alpha = -\frac{1}{\rho}\frac{\partial\rho}{\partial T} \tag{3}$$

Table 3 shows the coefficients of thermal expansion obtained at 293 K and 313 K for pure solvent and the solutions of the lowest and highest molecular weight of PS, at the lowest and highest concentrations used in experiments. The effect of deuteration is

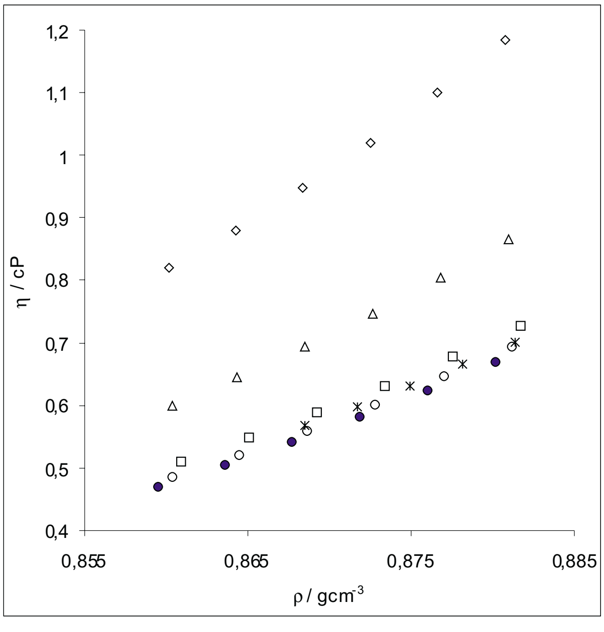

Figure 7. Variation of viscosity of polystyrene solutions (c = 0.005 gml^{-1}) in benzene with the solution density for different molecular weights: O PS4; ✱ PS7; □ PS25; △ PS123; ◇ PS400. The data for pure benzene are added for comparison (●).

also shown. The results obtained for pure benzene are in a good agreement with the literature data [1]. In the case of solutions, which are highly diluted, α seems to be very weakly depended on molecular weight of the polymer and its concentration, and its behavior is predominantly determined by the properties of the solvent, hence, the changes in α on transfer from pure solvent to a solution are insignificant. Let us note a weak influence of the isotope substitution in benzene on the thermal expansivity, both of pure solvent and solution. Although the isotope effect observed only slightly exceeds the experimental error, its direction and magnitude is in a good agreement with expectations [1].

Table 2. Fitting parameters of equation: $\eta = A\exp[B/(1 - V_0\rho)]$ for the density dependence of viscosity of benzene and polystyrene solutions in benzene ($c = 0.005$ gml^{-1}).

	A	B	V_0/cm^3 g^{-1}	$\sigma^2 \times 10^6$
benzene	0.00741	0.979	0.889	3.6
	0.00328	1.428	0.782	5.3
PS4	0.00339	1.330	0.852	2.4
	0.00138	1.762	0.757	4.9
PS7	0.00496	1.223	0.854	2.0
	0.00103	1.998	0.743	4.6
PS25	0.00350	1.331	0.851	2.1
	0.0021	1.774	0.759	4.7
PS123	0.00355	1.368	0.853	6.9
	0.00160	1.919	0.750	4.43
PS400	0.00389	1.452	0.847	3.7
	0.00126	2.041	0.741	4.08

The second row for each item refers to deuterated system; σ^2 is the variance of the fitting.

Table 3. Coefficients of thermal expansion for benzene/deuterated benzene and selected polystyrene solutions.

		α_H 10^3/K^{-1}		α_D 10^3/K^{-1}	
		293 K	313 K	293 K	313 K
benzene	c (g ml^{-1})	1.18_0	1.20_2	1.18_7	1.21_0
PS4	c = 0.004	1.18_1	1.21_0	1.19_1	1.22_4
	c = 0.033	1.17_7	1.20_2	1.19_0	1.21_5
PS400	c = 0.001	1.17_4	1.20_5	1.18_6	1.21_5
	c = 0.006	1.17_4	1.20_1	1.18_5	1.21_3

α_H and α_D refer to normal and deuterated systems, respectively; standard deviation of α is estimated to be $\pm 0.005 \times 10^{-3}$ K^{-1}.

Basing on density measurements, one can calculate molar volumes of polystyrene/benzene solutions. As expected, for these very low concentrations the molar volume of solution is totally dominated by the molar volume of benzene and the effect of the molecular weight of polystyrene is hardly seen (Fig. 8). A weak but detectable inverse isotope effect on molar volume, ($V_D/V_H < 1$), is also seen and is comparable to the isotope effect on molar volume for pure benzene ($V_D/V_H = 0.99$ at 293 K [1]).

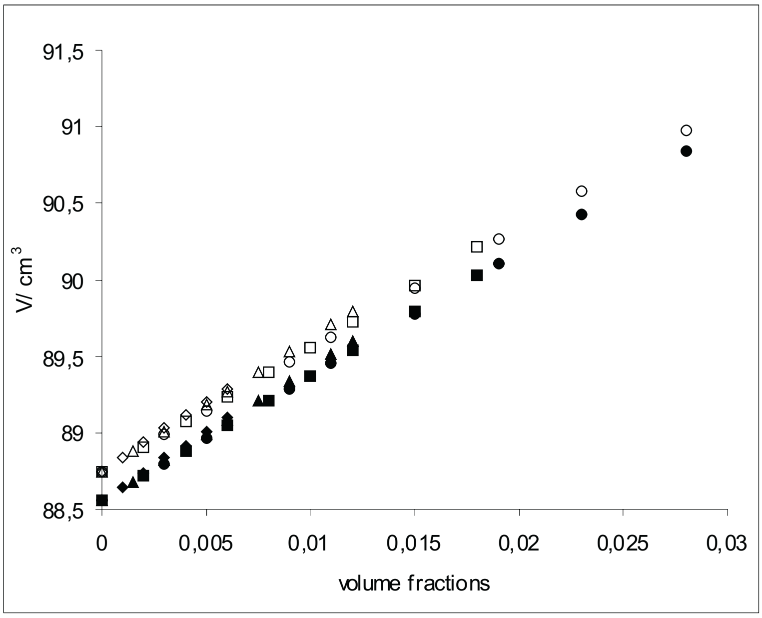

Figure 8. Dependence of the molar volume of polystyrene solutions in benzene on polymer concentration at 297 K. Filled symbols refer to solutions in deuterated benzene. ○ and ● PS4; □ and ■ PS25; △ and ▲ PS123; ◇ and ◆ PS400.

CONCLUSIONS

The experimental results presented in this work show that deuterium substitution in the solvent brings about visible changes in viscosity and density of the solution, however, the deuteration of the solvent negligibly affects the intrinsic viscosities. No isotope effect on Huggins constants could be observed. The dependence of viscosity on solution density reveals that apparent close-packed volumes remain essentially the same for all polystyrene solutions and are characterized by a remarkable isotope effect, $V_0(H)/V_0(D) = 1.13$, being the same for pure solvent and all solutions. We could also observe a very weak isotope effect on molar volume and thermal expansivity of the solutions. These thermodynamic properties seem to be predominantly determined by the property of the solvent and this conclusion refers to both volumetric properties and isotope effects thereon.

Acknowledgments

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