Study of the apparent specific volume of polystyrene in binary solvent

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The variation of apparent specific volume of polystyrene in benzene–methanol mixture has been studied as a function of the composition of the solvent, for polymers of various molecular weight and structure. These experiments allow us to confirm the simultaneous influences of the intramolecular segment density and of the molar volume of the solvent on the apparent specific volume of the polymers in solution.

INTRODUCTION

A model has recently been suggested[1] to explain the variation of the partial specific volume of polystyrenes in solution. It is assumed that the packing of solvent molecules in the macromolecular coil depends on two fundamental parameters: (a) the intramolecular density of the macromolecule segments inside the coil; (b) the size of the solvent molecules (molar volume).

This model seems likely to explain qualitatively some experimental results obtained with linear and grafted polystyrenes in pure solvents (i.e. theta or good solvents, or solvents of intermediate power) and at a given temperature.

Unfortunately, under these conditions, it is difficult to obtain large variations of the molar volume of the solvents. It was tempting to study the variation of ϕ_2 when methanol is added to polystyrene–benzene solutions, the molar volume of methanol being half that of benzene. However, in this case, the methanol addition leads equally to a decrease in the expansion of the macromolecular coil. The simultaneity of the variations of the two parameters, intramolecular segment density and mean molar volume of the solvent, allow us to verify the hypothesis formulated by François *et al.*

We have chosen the benzene–methanol system for which the phenomenon of preferential adsorption has been extensively studied[2–7].

EXPERIMENTAL

By making very precise density measurements (Kratky densimeter[11,12]), it is possible to determine the apparent specific volume ϕ_2 of a polymer at infinite dilution, with an accuracy of $\pm 10^{-3}$ cm^3/g.

The characteristics of the polystyrene samples, prepared by anionic polymerization, are reported in *Table 1*[14–16].

The value of ϕ_2, as a function of the volume fraction of methanol, u_2, are given in *Table 2* and *Figure 1*. We can note for u_2 in the range between 0 and 22%, that the apparent specific volume varies almost linearly, and that the slope of the straight line depends on the molecular weight and on the structure of the polymer. This slope is positive for the polymer 1749 ($M_w = 1.8 \times 10^6$), negative for the other linear polymers, and presents for the polymer 1278 ($M_w = 74\,000$) a minimum which corresponds also to the value obtained for some branched polymers (PS 4A and P3). This suggests behaviour similar to that observed by François *et al.*[1], for the specific volume in a single solvent and by Hert and Strazielle for the preferential adsorption[6], the segment density inside the macromolecular coil seeming to be the fundamental parameter. In order to verify this fact, we have plotted (*Figure 2*) the slope $d\phi_2/du_2$ as a function of $\langle v_3 \rangle$ (equation 7), the mean volume fraction of polymer in the coil. Thus we obtain a single curve of ϕ_2 *versus* $\langle v_3 \rangle$, whatever the structure of the polymer is; we can remark for example that the comb-like polystyrene 4A ($M_w = 8.5 \times 10^6$) presents the behaviour not of its linear homologue polystyrene but of a linear polymer with a very low molecular weight and with the same intramolecular segment density.

INTERPRETATION MODEL

The previous work of François *et al.*[1,13] has shown that the apparent specific volume of polystyrene in dilute solution depends on the molecular weight and on the structure of the polymer, the intramolecular segment density being the fundamental parameter. They proposed the following empirical relation, for a given solvent:

$$\phi_2 = \phi_{2m} - B\exp(-C\langle v_3 \rangle) \qquad (1)$$

(see *Figure 3*), where $\langle v_3 \rangle$ is the mean volume fraction of polymer inside the coil and B and C are constants equal to 1.4×10^{-2} and 1.02×10^2, respectively. ϕ_{2m} is the value of the plateau obtained for $M < 2 \times 10^4$. This equation can be transformed into a linear relation when $\langle v_3 \rangle$ tends to zero:

$$\phi_2 = \phi_{2m} - B + BC\langle v_3 \rangle$$

The apparent specific volume of the polymers depends strongly on the form and size of the solvent molecules. This fact suggested by Heller[8,9] has been confirmed by the investiations of Eskin *et al.*[10] on polyisobutylene and more recently by the work of François *et al.*[1] on the polystyrene. The term ϕ_{2m} of the apparent specific volume can be related to the molar volume of the solvent by a linear law[1]:

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Table 1 Parameters of polystyrenes in solution in benzene at 25°C
(a) Linear polystyrenes

Polymer	Initiator	M_n*	M_w†	ϕ_2 (cm^3/g)	$\langle v_3 \rangle \times 10^2$
1770	Sodium naphthalene		14 000	$0\ 926_3$	6.55
1749	Butyl lithium		1.4×10^6	0.908_4	0.17
1811	Butyl lithium	2000	–	0.938_3	30.56
PE 2	Butyl lithium	15 600	16 000	0.923_5	5.88
1753	Butyl lithium	23 900	25 000	0.921_7	4.13
31	α-Methylstyrene tetramer	7300	–	0.919_3	10.84
1903	α-Methylstyrene tetramer	4150	4990	0.920_4	17.09
1278	α-Methylstyrene tetramer	53 000	74 000	0.917_2	1.76
1	Potassium cumyl	1.35×10^5	1.4×10^5	0.911_5	1.06
3	Potassium cumyl	6.6×10^5	7×10^5	0.906_6	0.30

(b) Star polystyrenes

Polymer	r	g^{th}	p	M_w*	ϕ_2 (cm^3/g)	$\langle v_3 \rangle 10^2$
P3	–	0.224	11	8.28×10^5	0.917_4	2.48
M7A	–	0.388	7	1.8×10^5	0.918_0	3.62

(c) Comb-like polystyrenes

Polymer	r	g^{th}	p	M_w*	ϕ_2 (cm^3/g)	$\langle v_3 \rangle \times 10^2$
1752f3	5	0.241	28	1.57×10^5	0.918_2	8.23
1752f4	5	0.289	17	98 000	0.917_2	9.22
1A	0.27	0.814	5	9×10^5	0.908_2	0.33
2A	1.12	0.53	20	1.5×10^6	0.912_6	0.45
4A	10.70	0.098	195	8.5×10^6	0.917_7	1.35

* Molecular weight determined from light scattering measurements; † molecular weight determined from vapour pressure, osmotic pressure or gel permeation chromatography measurements

Table 2 Partial specific volume of polystyrenes in benzene–methanol mixtures as a function of the volume fraction of methanol u_2

	u_2*										
Polymer	0	0.07	0.10	0.14	0.18	0.20	0.21	0.22	0.23	0.24	$d\phi_2/du_2$ $\times 10^2$cm^3/g)
(a) Linear polystyrenes											
PS 1811	0.938_3					0.936_6		0.934_5			−1.31
PS 1903	0.920_4	0.919_0	0.919_8	0.925_2				0.914_6		0.920_1	−1.33
PS 31	0.919_3					0.910_2		0.914_2			−2.32
PS 1770	0.926_3					0.918_4		0.920_7			−2.65
PS 1753	0.921_7					0.917_1		0.916_4			−2.40
PS 1278	0.917_2	0.914_1	0.914_2		0.912_7		0.910_0	0.908_0	0.907_8	0.900_3	−3.50
PS 1	0.911_5	0.917_4	0.910_0	0.906_5				0.906_1		0.895_0	−2.50
PS 1749	0.905_0	0.907_5		0.911_4	0.908_9		0.907_0	0.906_9	0.901_9	0.886_3	+0.86
(b) Star polystyrenes											
PS P3	0.917_4	0.914_0	0.905_4	0.904_0				0.911_0		0.902_5	−2.91
PS M7A	0.918_0	0.913_3		0.905_0				0.911_7		0.902_6	−2.86
(c) Comb-like polystyrenes											
PS 1752f3	0.918_2					0.913_0		0.912_3			−2.69
PS 1752f4	0.917_2					0.910_9		0.913_4			−2.63
PS 1A	0.908_2					0.905_4		0.908_0			−1.00
PS 2A	0.912_6					0.907_2					−2.80
PS 4A	0.917_7					0.906_1					−3.70

$$\phi_{2m} = \phi_{2m,0} + DV_0 \tag{2}$$

which leads to the complete definition of ϕ_2:

$$\phi_2 = \phi_{2m,0} + DV - B\exp(-C\langle v_3 \rangle) \tag{3}$$

Starting from this relationship, we have attempted to calculate the expected variations of ϕ_2 with the concentration of methanol u_2, in order to compare them with our experimental results. The following had to be evaluated.

Mean molar volume of the solvent inside the coil

This depends on the real volume fraction of methanol inside the coil and varies, for the different samples, with the

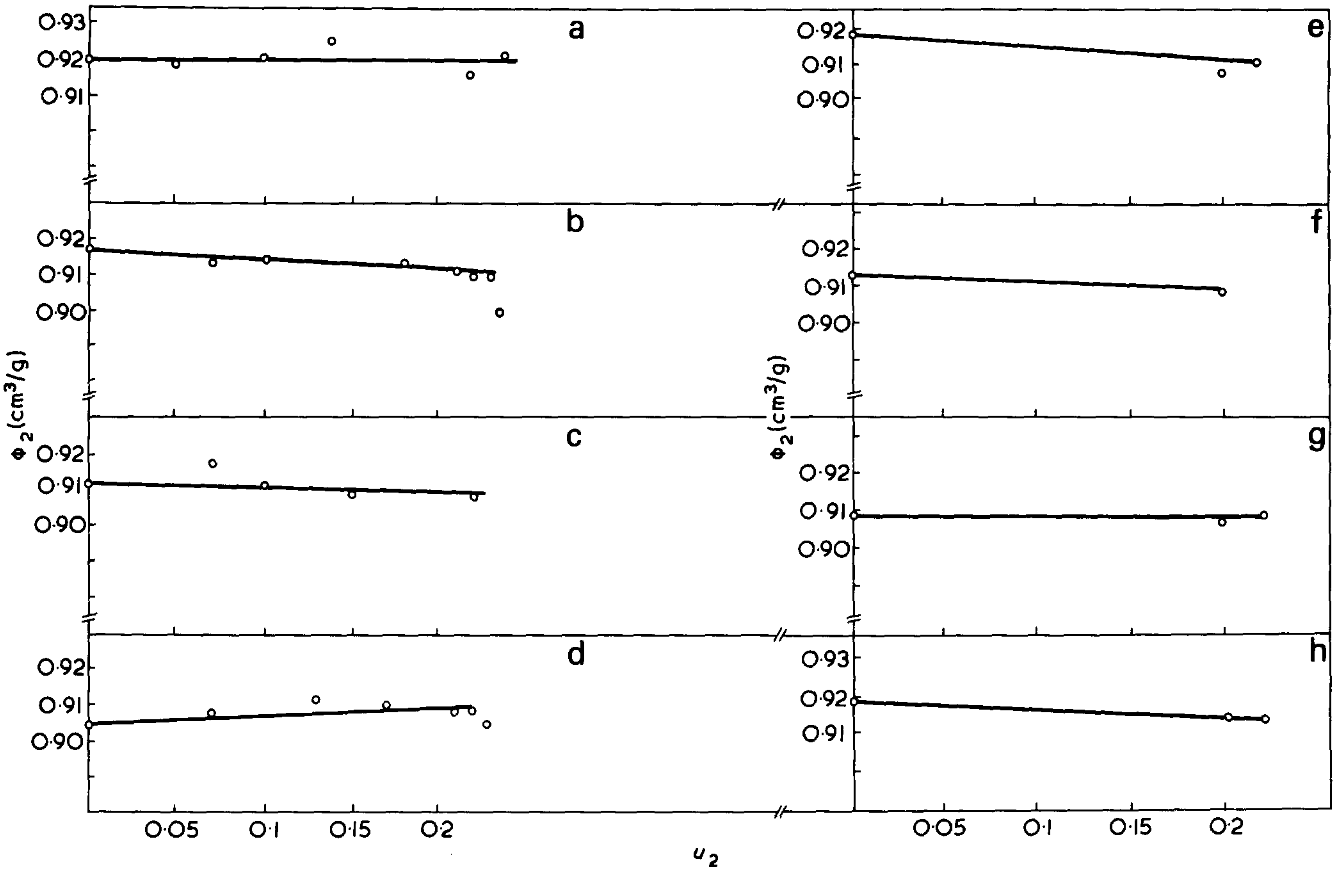

Figure 1 Apparent specific volume ϕ_2 against u_2 the volume fraction of methanol. Linear polystyrenes: (a) PS 1903; (b) PS 1278; (c) PS 1; (d) PS 1749. Graft polystyrenes: (e) PS 4A; (f) PS 2A; (g) PS 1A; (h) PS 1752f3

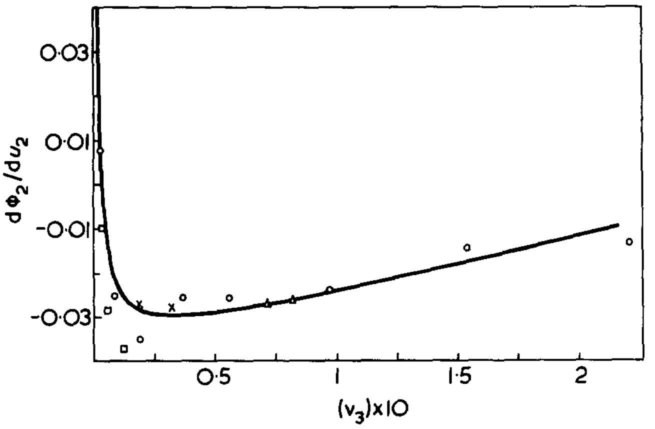

Figure 2 Plot of the $d\phi_2/du_2$ slope for different structure polystyrenes *versus* the polymer volume fraction $\langle v_3\rangle$ inside the coil: ○, linear PS; X, star PS; △, comb-like polystyrenes

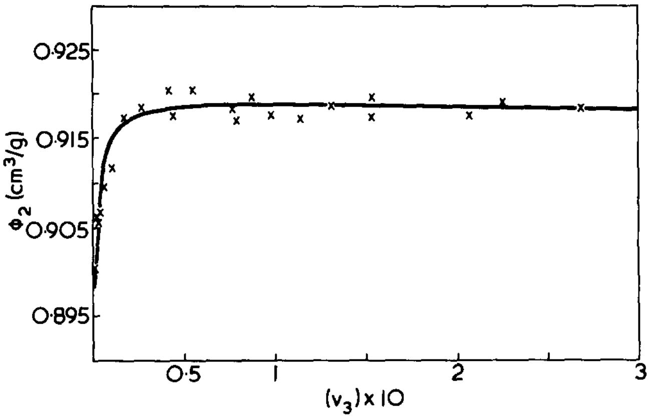

Figure 3 Plot of the apparent specific volume ϕ_2 for different structure polystyrenes in benzene *versus* the polymer volume fraction $\langle v_3\rangle$ inside the coil

preferential absorption coefficient.

The experimental work of Dondos *et al.*[5] and Hert *et al.*[6] has shown that the coefficient of preferential absorption λ, defined as the volume of benzene in millilitre absorbed per gram of polymer, can be related, whatever the structure of the sample, to the mean volume fraction inside the macromolecular coil by:

$$\lambda = \lambda_\infty + A'\langle v_3\rangle + B'\langle v_3\rangle^2 \qquad (4)$$

λ_∞ is the preferential absorption coefficient of a polymer of infinite molecular weight and segment density equal to zero. λ_∞ and the A' and B' constants vary with the concentration of methanol u_2 and we have used the experimental data of Hert *et al.*[6].

Experimentally, λ is determined from light scattering measurements in benzene–methanol mixtures[6]. From a theoretical point of view, these authors explain their results on the basis of the theory of thermodynamical equilibrium between the solvent inside the coil and the external liquid without polymer.

If we know λ, we can easily deduce, for each sample and each u_2 concentration, the real volume fraction of methanol inside the coil:

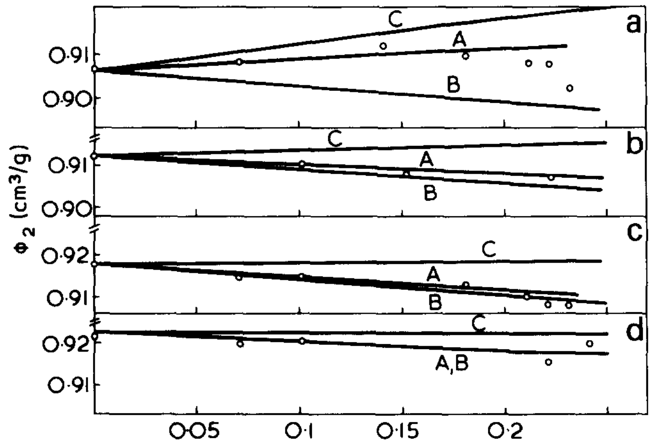

Figure 4 A, Theoretical variation of ϕ_2 against u_2 for different polystyrenes; B, effect of solvent molar volume; C, effect of segments density inside the coil; D, corresponding experimental values. (a) PS 1749; (b) PS 1; PS 1278; (d) PS 1903

$$u_2' = u_2 - \epsilon = u_2 - \frac{\lambda\langle v_3\rangle}{(1 - \langle v_3\rangle\phi_2)} \tag{5}$$

and the mean molar volume of the solvent:

$$V_0 = V_1 + u_2'(V_2 - V_1) \tag{6}$$

where V_1 and V_2 represent the molar volumes of benzene and methanol and equal 89.43 and 40.68 ml, respectively.

Mean volume fraction of polymer inside the coil $\langle v_3\rangle$ *and the gyration radius* R_{u2}

It is well known[6] that:

$$\langle v_3\rangle = 2C_M V_0/\phi_2 M^{0.5}\alpha^3 g^{3/2} \tag{7}$$

where, C_M is the Flory constant $27\phi_2^2/2^{2.5}6M^{1.5} \times N_A V_0(R^2/M)^{1.5}$; α is the Flory expansion coefficient of the macromolecular coil; V_0 is the molar volume of the solvent; g is the structure parameter for grafted polymers and R is the radius of gyration.

The values of ϕ_2 used here are those of the polystyrene dissolved in benzene; the variations of ϕ_2 *versus* u_2, being neglected.

The variation of the radius of gyration *versus* the composition of the solvent mixture has rarely been studied in work concerned with the preferential absorption. The mixture containing 22% of methanol is considered as a 'theta' solvent at 25°C since the second virial coefficient becomes zero. Nevertheless, we did not know if the macromolecule really adopts unperturbed dimensions. The work of Dondos[5] and that more recently of Yamakawa[17] show, for other systems the existence of two 'theta' compositions, one for which the dimensions are unperturbed and the second for which the second virial coefficient equals zero. In the case of a polystyrene–benzene–methanol mixture, no results have clearly established the validity of these assumptions. Therefore, we assume, in the first approximation, that the radius of gyration, at 25°C and for 22% of methanol, is equal to that obtained in cyclohexane at 35°C, a well known 'theta' solvent for polystyrene. This supposes that the unperturbed dimensions vary only slightly with temperature as shown by Rossi *et al.*[18].

We assume moreover that R changes linearly with u_2, between the value R_{bz}, found in benzene and the theta value R:

$$R_{u_2} = R_{b_z} - u_2\,(R_{b_z} - R_\theta)/0.22 \tag{8}$$

In order to determine the radius of gyration R_{b_z} and R_θ, we use the empirical laws established by Decker[19]:

$$R_{b_z} = 0.145 M_w^{0.595} \text{ at } 25°\text{C} \tag{9}$$

$$R_\theta = R_{0,u_2 = 0.22} = 0.347 M_w^{0.5} \tag{10}$$

In the case of grafted polymers we have calculated R_b^2 using the Stockmayer[20] formula:

$$R_b^2 = gR^2{}_{\text{linear}} \tag{11}$$

This gives R_b^2 against $R^2{}_{\text{linear}}$ which is the mean square radius of gyration of their linear homologues calculated from formula (18), with the g factor determined by Orofino *et al.*[21]:

$$g = (3/\rho)\,[R/(1 + r)]^2 + 1/(1 + r) \tag{12}$$

This can be applied to a comb-like polymer characterized by these structure parameters: ρ, the graft number and r, the ratio of the graft length on the mean length between two successive grafts.

$$g = (3\rho - 2)/\rho^2 \tag{13}$$

for a star-like polymer.

Combining equations (3) to (13), we have obtained the variations of ϕ_2 *versus* u_2, according to the proposed model, for each studied sample.

COMPARISON BETWEEN OUR EXPERIMENTAL AND THEORETICAL RESULTS

We have plotted on *Figure 4* the variation of the calculated apparent specific volume ϕ_2 (curve A) *versus* u_2 for some linear polymer with extreme limiting behaviour. We see in all cases quite good agreement between the calculated and experimental values. We have also plotted the variation of the apparent specific volume ϕ_2 due to either effect separately, in order to give an idea of the relative importance of the two effects taken into consideration. For high molecular weights ($M > 2 \times 10^4$) curve B which corresponds to the influence of the molar volume of solvent lies beyond the experimental points whereas curve C relative to the second effect lies on the other hand, widely above.

The effect of segment density can as we saw be neglected for low molecular weight polymers and consequently the volume effect is enough to explain the results.

One can deduce from these comparisons between calculated and experimental values that both effects are of comparable importance on apparent specific volume and the volume fraction of a chain in solution and that ϕ_2 variations are well defined by the superposition of these two effects.

Curve A on *Figure 5* shows the calculated change of $d\phi_2/du_2$ against the intramolecular segment density $\langle v_3\rangle$ determined for polymers in benzene. We also see clearly on this plot a good fit between experimental and theoretical

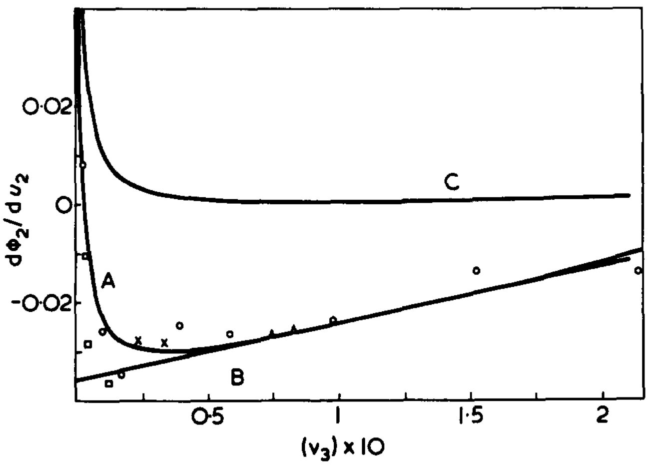

Figure 5 Plot of the theoretical variation of the slope $d\phi_2/du_2$ against the polymer volume fraction $\langle v_3 \rangle$ inside the coil. A, Both effects; B, effect of molar volume solvent mixture; C, segment density effect

values. We have also plotted curves B and C which correspond respectively to the molar volume and the segment density effects. It is clear that the entire explanation of our results is obtained by the additivity of both effects; if we do not consider the preferential absorption phenomenon λ in the calculation of the mean molar volume of the solvent we notice that the influence of the size of the solvent molecule would be constant over the whole range of $\langle v_3 \rangle$.

The good agreement between the calculated curve and the experimental values for low molecular weight polymer provides a good check of our interpretation.

CONCLUSION

These calculations give good confirmation of the two influences of the polymer volume fraction inside the macromolecular coil and of the mean molar volume of the solvent on the apparent specific volume of polystyrene.

The excellent agreement between experimental and theoretical values shows the validity of our assumptions, especially those which identify a macromolecular coil with a well defined thermodynamic system.

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