Studies on the excess volume of mixing in blends of poly(methyl methacrylate) and poly(vinylidene fluoride)

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The excess volume of mixing ΔV_m of blends of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) was determined by dilatometry. This quantity turned out to be positive for all concentrations, in contradiction to expectations based on the equation-of-state theory. Computer simulations were performed within the framework of this theory to obtain conditions in terms of the equation-of-state variables p^* and T^*, for which the excess volume of mixing is predicted to be positive. The corresponding values are well beyond the range of those characteristic for PVDF and PMMA. The conclusion is that structural changes induced by strong interactions between the components may be the origin of positive values of ΔV_m.

(Keywords: blends; volume of mixing; poly(methyl methacrylate); poly(vinylidene fluoride))

INTRODUCTION

The mixing of chemically different species gives rise in general to volume changes. The free enthalpy of mixing thus contains a non-vanishing excess-volume-of-mixing term $p\Delta V_m$[1–5]:

$$\Delta G_m = \Delta H_m - T\Delta S_m = \Delta U - p\Delta V_m - T\Delta S_m$$

This aspect of the thermodynamics of mixing has been omitted in the lattice theories devised to describe the thermodynamic properties of mixtures of low-molar-mass systems, of polymer solutions and of polymer blends[6,7]. On the other hand, theories, such as the equation-of-state and the fluid-lattice theories, etc.[8–11], take this effect into account. It has frequently been pointed out that the equation-of-state theory predicts a negative excess volume of mixing, provided that one of the polymeric components is more expanded than the other, i.e. when the reduced volumes differ sufficiently[3].

We were recently able to report experimental evidence that seems to be in contradiction to this expectation[12]. We found positive volume changes on mixing for blends of both poly(methyl methacrylate) and poly(ethyl acrylate) with poly(vinylidene fluoride), despite the fact that the reduced volumes of the components differ substantially.

This finding motivated us to consider volume changes attending mixing of polymer compounds in more detail, both from an experimental and a theoretical point of view. A major problem we had to face was that reliable experimental values on the volume changes attending mixing are sparse. Density measurements, for instance, were performed on the glassy solid states of both the pure components as well as blends of different compositions[13,14]. The data were used to derive indirect information on the sign and the magnitude of the volume change on mixing. Zoller and Hoehn, for instance, reported room-temperature specific volumes for the binary system poly(propylene oxide)–polystyrene, displaying strong deviations towards smaller volumes relative to the values expected from linear mixing rules[13]. These results might be taken as indications for large negative excess volumes of mixing in these systems. However, the authors correctly point out that these data may not be totally conclusive, since they were obtained for the non-equilibrium glassy state. No deviations from the predictions of linear mixing rules were observed for the same system in the equilibrium molten state.

Information on the sign and the magnitude of the volume change on mixing is, of course, also available from studies on the pressure dependence of the critical solution temperature[15–17]. Walsh *et al.*[16,17], for instance, interpreted their results on the dependence of the critical temperature on the applied pressure in terms of the equation-of-state theory and concluded that binary blends composed of poly(ether sulphone) and poly(ethylene oxide) or blends of ethylene–vinyl acetate copolymers and chlorinated polyethylenes display negative excess volumes of mixing amounting to 0.48% and 0.02–0.08% respectively. A good agreement of these results with the predictions of the equation-of-state theory was reported in this paper. However, the authors point out that such good agreement is surprising in view of the fact that the blends considered display strong specific interactions and that the equation-of-state theory was not designed to take such strong interactions into account.

So it is apparent that our knowledge on volume changes attending mixing of polymer species is still very limited with regard both to experimental facts and to theoretical treatments. This is the topic of the present paper. It reports first of all systematic experimental studies on volume changes that occur in blends of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) due to mixing.

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Blends of PVDF and PMMA are thermodynamically stable up to temperatures well above their respective decomposition temperatures. Their lower critical solution temperature amounts to about 700 K[18]. The experimental method of choice for determining the volume changes during mixing was dilatometry, performed on samples in which interdiffusion processes occurred. The onset of such processes was independently checked by absolute small-angle X-ray studies[18–21].

It is a characteristic feature of these blends—and therefore we have selected them for the studies to be described in the following—that strongly negative values of the interaction parameter, large negative heats of mixing[19] as well as shifts of the frequency of specific i.r. absorption bands[22] occur, which have to be taken as indications of the occurrence of specific interactions in these blends.

This paper is furthermore concerned with an analysis of the volumetric data on the basis of the equation-of-state theory and finally with the simulation of volume effects taking place during mixing, based also on the equation-of-state approach.

EXPERIMENTAL

The PMMA samples were supplied by Röhm GmbH, Darmstadt, and the PVDF by Solvay, Solingen. The PMMA was characterized by an average molecular weight of $\bar{M}_n = 60\,000\,\mathrm{g\,mol^{-1}}$, and the ratio of the weight- to the number-average molecular weight $\bar{M}_w/\bar{M}_n$ was about 2. The PVDF was characterized by an average molecular weight of $\bar{M}_n = 38\,000$, and the ratio of the weight-average and the number-average molecular weight $\bar{M}_w/\bar{M}_n$ amounted to about 2.6. The experiment consisted of monitoring the volume changes attending the interdiffusion of the two polymers in mixtures of PMMA and PVDF powders[12]. Powder mixtures of given composition were filled into the dilatometer, which was then evacuated and filled with mercury at room temperature. The dilatometer was heated up to a temperature of 456 K, i.e. above the melting temperature of the PVDF. This resulted in the onset of an interdiffusion of PVDF and PMMA, as became apparent from small-angle X-ray studies reported previously[19–21] as well as from turbidity studies performed recently. The volume changes accompanying the interdiffusion and thus the mixing gave rise to variations of the mercury level at constant temperature.

EXPERIMENTAL RESULTS

A direct determination of the excess volume of mixing from the specific volumes of the pure components and of the blends meets with considerable difficulties if the volume changes are of the order 0.1% or below. Therefore we decided, as described in a previous communication[12], to take another approach, involving the direct determination of volume changes accompanying the mixing of the two components of binary blends. The results are reported in the following.

Figure 1 displays—in terms of the height of the mercury level within the capillary of the dilatometer—the variation of the total volume of powder mixtures of pure PVDF and PMMA as a function of the interdiffusion time at a constant temperature of 453 K. The variation of the volume with time differs somewhat from that reported previously for stacks of films of PMMA and PVDF which were placed in an alternating sequence within the stack, whereas the absolute values of the volume variations agree. The reason for these deviations is that the gross kinetics of interdiffusion is, of course, different in mixtures of powders and in stacks of films for geometric reasons.

The observation is that the volume of the composite systems, containing pure PVDF and PMMA regions in the molten state, increases as a function of time (i.e. interdiffusion time) for short times and that saturation effects occur at longer times. *Figure 1* also contains the corresponding volume–time curves for the pure components. It is apparent that neither PVDF, which is partially crystalline at lower temperatures, nor the amorphous PMMA show variations in volume as a function of time with the exception of the time interval comprising the first 2 min. The corresponding variations result from the temperature equilibration following the switch of the densitometer from a low- to a high-temperature bath.

The shape of the volumetric curve displayed in *Figure 1*, for the case of a mixture of 50 wt% PVDF in PMMA, is characteristic for all blends studied with the exception of those which contained large amounts of PVDF, i.e. more than 80%. *Figure 2* displays a characteristic trace

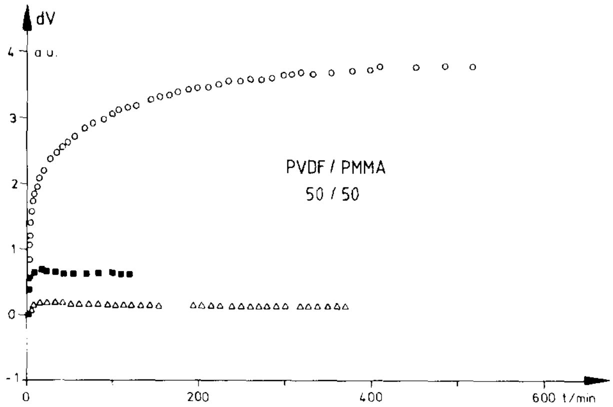

Figure 1 Variation of the mercury level dV of the dilatometer as a function of the interdiffusion time t, obtained for a powder mixture of 50% PMMA and 50% PVDF at 456 K as well as for the pure components: (○) mixture: (△) pure PMMA; (■) pure PVDF

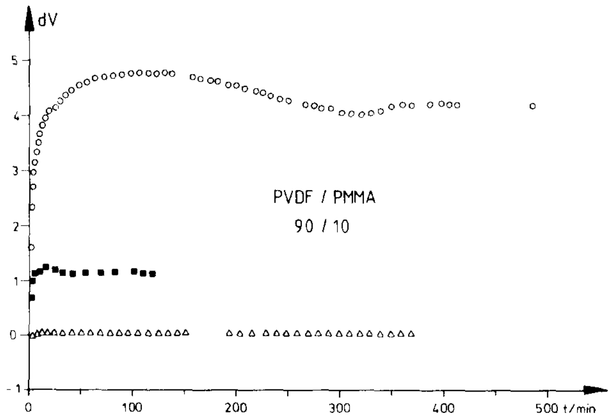

Figure 2 Variation of the mercury level dV of the dilatometer as a function of the interdiffusion time t, obtained for a powder mixture of 90% PVDF and 10% PMMA at 456 K: (○) mixture; (△) pure PMMA; (■) pure PVDF

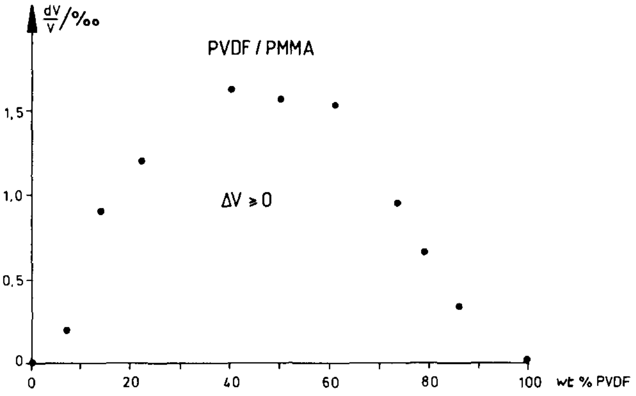

Figure 3 Concentration dependence of the excess volume dV/V of mixing of PVDF and PMMA at 456 K

for a blend containing about 90 wt% PVDF. The observation is that the trace consistently displays a maximum, decays again with increasing contact time and approaches a saturation value for long times. It seems that this peculiar behaviour results from the gross kinetics of the interdiffusion taking place in the powder mixtures and is related to the differences in the velocities of the interdiffusion process for PMMA into PVDF and vice versa[19–21]. This kinetic aspect will not be treated in this paper, we will consider just the saturation value of the volume in the following.

The really surprising finding—and this was already pointed out in a previous communication[12]—is that the volume of the composite system does not decrease as expected but increases due to the onset of the mixing process. Therefore we have to conclude that the binary system PVDF–PMMA is characterized by a positive excess volume of mixing.

The absolute value was found to be very small, of the order of 0.2%, as is obvious from the saturation value of the mixtures displayed in *Figure 1*. The results on the concentration dependence of the excess volume of mixing are displayed in *Figure 3*. A nearly symmetric variation of the excess volume of mixing is observed as a function of the concentration of the two components.

DISCUSSION

We thus have to conclude that the system PVDF–PMMA is characterized by positive values of the volume change on mixing, and that the absolute magnitudes amount to about 0.2% for the blends studied here. The results will be discussed within the framework of the equation-of-state approach for polymer blends.

The early theories of polymer mixing thermodynamics relied, as pointed out above, on the assumption of zero volume change on mixing[6,7]. More recently Flory and others have demonstrated that mixing thermodynamics depend also on the liquid structure and liquid-state properties[1–5,8–11]. Differences in these quantities, which may exist for the pure components of the blends, are expected to lead to a non-additivity of the volume. In the following we will briefly introduce the main features of the equation-of-state theory and the principal equations that will be used in the following.

The pure components and the mixture are described in terms of the reduced parameters $\tilde{T}, \tilde{p}, \tilde{v}$, which are defined as the ratio of the actual values and the so-called equation-of-state parameters:

$$\tilde{T} = T/T^*$$

$$\tilde{p} = p/p^*$$

$$\tilde{v} = v/v^*$$

where the asterisks denote the equation-of-state parameters. The reduced volume is connected to the thermal expansion coefficient α:

$$\tilde{v}^{1/3} - 1 = \alpha T/[3(1 + \alpha T)]$$

The reduced temperature $\tilde{T}$ can be calculated from the reduced volume as follows:

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}$$

The characteristic pressure parameter p^* is given by:

$$p^* = \gamma T \tilde{v}^2$$

where γ is the thermal pressure coefficient. If this quantity is not available one may obtain it from:

$$\gamma = -(dv/dT)/(dv/dp) = \alpha/\kappa$$

where $(1/v)\,dv/dt$ is the thermal expansion coefficient and $-(1/v)\,dv/dp$ is the compressibility of the material.

The values obtained on the basis of the equations given above are displayed in *Table 1* for the two components of the blends considered here, i.e. for PMMA and PVDF. It is apparent that the equation-of-state parameters p^* of the two components agree, whereas the parameters T^* and $\tilde{v}$ differ significantly.

Next one has to calculate the equation-of-state parameters for the mixtures. The pressure parameter p^* is obtained from the expression:

$$p^* = \varphi_1 p_1 + \varphi_2 p_2 - \theta_2^2 X_{12}$$

where X_{12} is the interaction parameter, θ_2 is the interaction site fraction, which is given by:

$$\theta_2 = \varphi_2/[(s_1/s_2)\varphi_1 + \varphi_2]$$

and φ_1 and φ_2 are given by:

$$\varphi_2 = 1 - \varphi_1 = r_2 N_2/(r_1 N_1 + r_2 N_2)$$

$$N = N_1 + N_2$$

The N_i are the number of molecules of species i, r_i are the number of segments in chain molecule i.

The characteristic temperature T^* can be calculated from the expression:

$$T = p^*/(\varphi_1 p_1^*/T_1^* + \varphi_2 p_2^*/T_2^*)$$

Using these parameters the equation of state:

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T}$$

has to be solved to yield, for instance, the required value for the volume change of mixing:

$$\Delta V/V_{mix} = 1 - (\varphi_1 \tilde{v}_1 + \varphi_2 \tilde{v}_2)$$

Table 1

	α (10^{-4} K^{-1})	γ (cal cm^{-3} K^{-1})	p^* (cal cm^{-3})	T^* (K)	$\tilde{v}$
PVDF[a]	7.61	0.190	141	7364	1.2808
PMMA[b]	5.8	0.209	141	8542	1.2229

[a] Values for PVDF were taken from ref. 23
[b] Values for PMMA were taken from ref. 12

This equation will now be transformed in such a way that one is able to solve it numerically:

$$\tilde{v} = 1/[1 - \tilde{T}\tilde{v}/(\tilde{p}\tilde{v}^2 + 1)]^3$$

and for the particular case of zero pressure:

$$\tilde{v} = 1/(1 - \tilde{T}\tilde{v})^3$$

The transformed equation can be solved iteratively to yield the reduced volume of the mixtures either at zero pressure or as a function of the applied pressure. These values are then used to calculate the excess volume of mixing.

The prediction is, as shown in *Figure 4*, that the volume change of mixing should be negative, in contrast to the experimental finding. In the absence of intermolecular interactions, i.e. for $X_{12} = 0$, the predicted values are very small, in the range of -0.03% for the 10/90 wt% PVDF-PMMA and -0.097% for the 50/50 wt% PVDF-PMMA blends. If the interaction parameter X_{12} is set to $-0.2\,\mathrm{cal\,cm^{-3}}$ (a moderate value for the PVDF-PMMA system) the absolute value for the volume change on mixing is increased to 0.18% and 0.53% respectively. It still remains negative. So a discrepancy between theoretical predictions and experimental findings seems to exist.

It is of course important to find out whether not only the sign of the predicted value of the volume change of mixing but also its magnitude depend sensitively on the values chosen for the thermal expansion coefficients and the isothermal compressibility and thus for the hard-core quantities of the components of the blends. In addition the influence of the magnitude and the sign of the interaction parameter X_{12} on the excess volume on mixing has to be investigated in some more detail, since first of all the values of the interaction parameter depend strongly on the temperature[17] and secondly since they are subject to some uncertainties.

RESULTS OF THE SIMULATIONS

Based on the experimental studies of the thermal expansion coefficient, the density and the thermal pressure coefficient (or the isothermal compressibility for that matter), one is able to obtain the characteristic values p^* and T^* for each of the components of a blend. We will, in the following, use these values, or more specifically the ratio of these values, in order to test the predictions of the equation-of-state theory with respect to the sign and the magnitude of the excess volume of mixing. Finally we will vary the interaction parameter X_{12} and investigate the corresponding effects on the volume change of mixing.

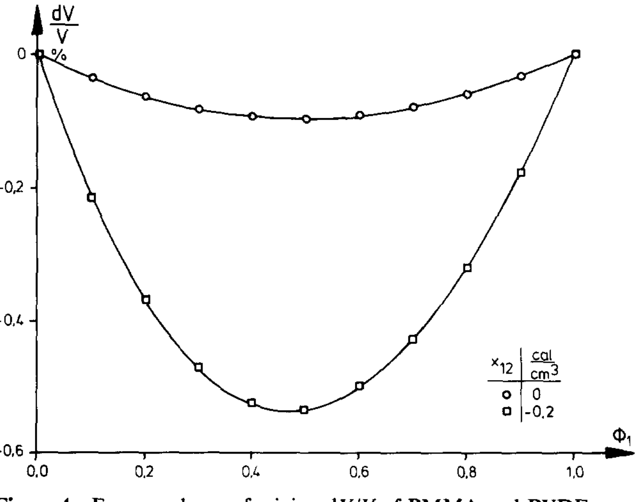

Figure 4 Excess volume of mixing dV/V of PMMA and PVDF as a function of the composition, as obtained from the predictions of the equation-of-state theory using the equation-of-state parameters given in *Table 1*

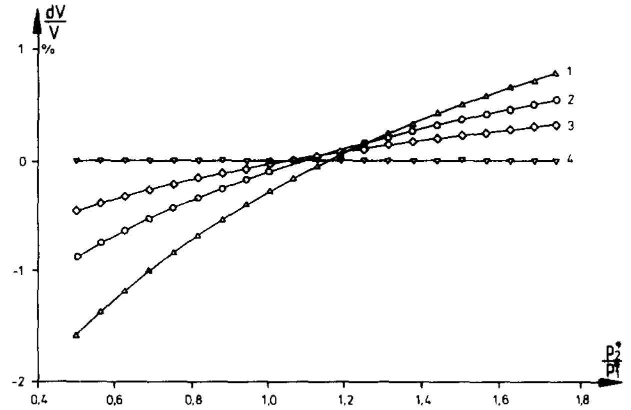

Figure 5 Dependence of the excess volume of mixing dV/V (50 wt% composition) on the ratio of the characteristic pressures p_2^*/p_1^* for various ratios of the characteristic temperatures T_2^*/T_1^*

Curve	p_1^* (bar)	T_1^* (K)	T_2^* (K)
1	8000	8000	6000
2	8000	7000	6000
3	8000	6500	6000
4	8000	6000	6000

To start with, we consider the influence of increasing the ratio of the characteristic pressures p_2^*/p_1^* at various values of T_2^*/T_1^* on the excess volume of mixing. The values of T_1^* and T_2^* are chosen in such a way that $T_2^* \leqslant T_1^*$. The results of the simulation are displayed in *Figure 5*. It is obvious that positive and negative volume changes occur, the size of which increases with increasing asymmetry of the characteristic temperatures. The volume change of mixing is zero, independent of the ratio of the characteristic pressures, provided that the characteristic temperatures are equal. The sign of the excess volume of mixing is negative for ratios of p_2^*/p_1^* smaller than about 1 and positive for values significantly larger than 1. (This result is, of course, independent of the particular choice of component A as 1 and B as 2 or vice versa.)

The absolute values obtained for the relative volume changes on mixing are of the order of 0.1 to 1% depending on the asymmetry of the characteristic temperatures. It should be pointed out that the results shown so far correspond to the case of a mixture of 50% of each of the components. A rather symmetric behaviour is predicted to occur for the variation of the volume of mixing with the concentration.

Figure 6 displays the dependence of the sign of the excess volume of mixing on the asymmetry of the characteristic pressures p_2^*/p_1^* and temperatures T_2^*/T_1^* of the two components. Displayed are the transition curves for various choices of the absolute value of the temperature T_1^*. The transition curves are characterized by the fact that the volume of mixing changes sign if one crosses the curves, i.e. the volume changes are zero on the curve. The finding is that the sign is negative both

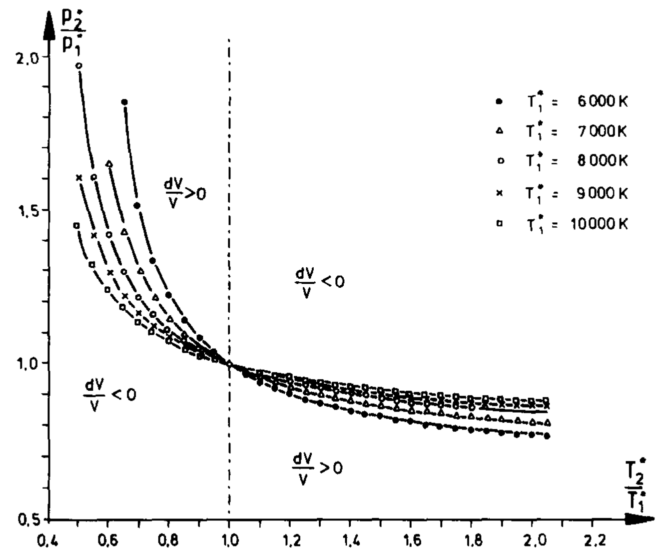

Figure 6 Dependence of the sign of the excess volume dV/V of mixing on the asymmetry of the ratios p_2^*/p_1^* and T_2^*/T_1^*. The curves shown represent the transition from positive to negative values and vice versa

for low values of the ratios p_2^*/p_1^* and T_2^*/T_1^* and for high values of both ratios whereas the volume changes become positive if the magnitudes of the ratios differ strongly. So the larger the asymmetry of the magnitudes of the ratios the larger the tendency towards positive volume changes of mixing.

Based on the equations given above, we have to conclude that the requirement for positive volume changes on mixing is a strong asymmetry in the thermal expansion coefficients:

$$\alpha_2 \ll \alpha_1$$

which leads to:

$$T_2^* \gg T_1^*$$

and at the same time a large asymmetry of the pressure coefficients:

$$\gamma_2 \ll \gamma_1$$

which causes:

$$p_2^* \ll p_1^*$$

Large differences in the thermal expansion coefficients of the components and thus in the reduced volumes $\tilde{v}$ give rise to negative values of the excess volume of mixing only for the case that the pressure coefficients are close to each other. This case was considered, for instance, by McMaster[3].

It has to be pointed out that we have not differentiated whether the simulated blends are actually compatible or not. Our justification is that one is able to obtain a homogeneous mixture by suitable solution techniques even for incompatible components, so that volume changes on demixing can be investigated for such blends.

Next we will consider the influence of non-zero values of the interaction parameter on the sign and magnitude of the excess volume of mixing. The results are displayed in *Figure 7* for a given set of parameters p_i^* and T_i^*, giving rise to either negative or positive values of the excess volume of mixing. The values are shifted linearly towards more positive or negative values, depending on the sign of the interaction parameter. The dependence of the volume change of mixing on the composition remains approximately symmetric even for strongly positive or negative values of the interaction parameter (*Figure 7*).

Negative interaction parameters, indicative of specific interactions between the components lead to shifts towards negative volume changes of mixing and positive interaction parameters to shifts in the reverse direction. So large interaction parameters may lead to a change of the sign of the excess volume of mixing, but only in the

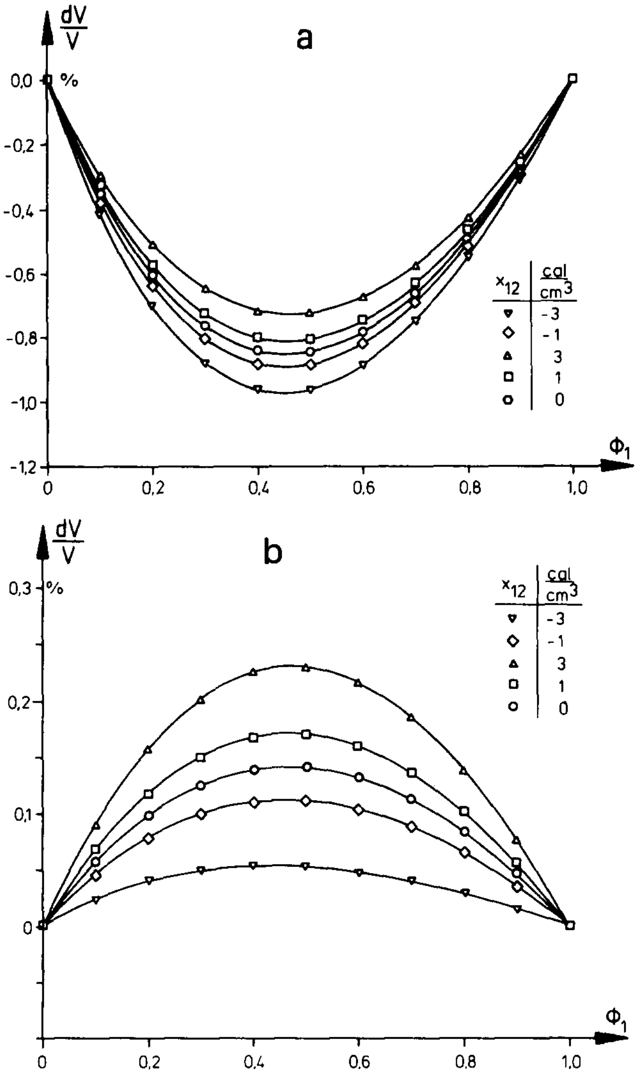

Figure 7 Influence of the sign and the magnitude of the interaction parameter X_{12} on the sign and the magnitude of the excess volume of mixing as a function of concentration. For all curves $T_1^*=T_2^*=8000$ K and $p_1^*=8000$ bar: (a) $p_2^*=6000$ bar, $X_{12}=0, 1, 3, -1, -3$; (b) $p_2^*=9000$ bar, $X_{12}=0, 1, 3, -1, -3$

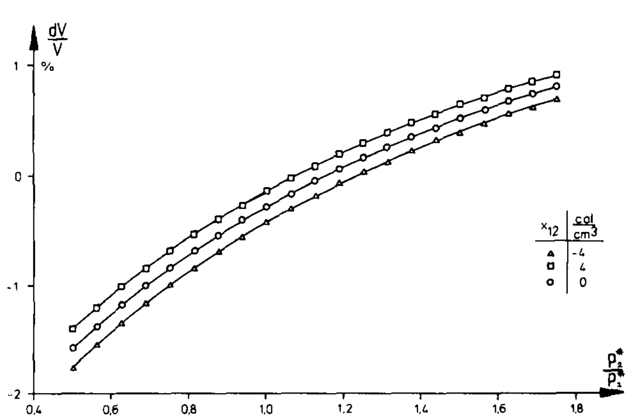

Figure 8 Variation of the excess volume of mixing dV/V as a function of the ratio of the characteristic pressures p_2^*/p_1^* for various values of the interaction parameter

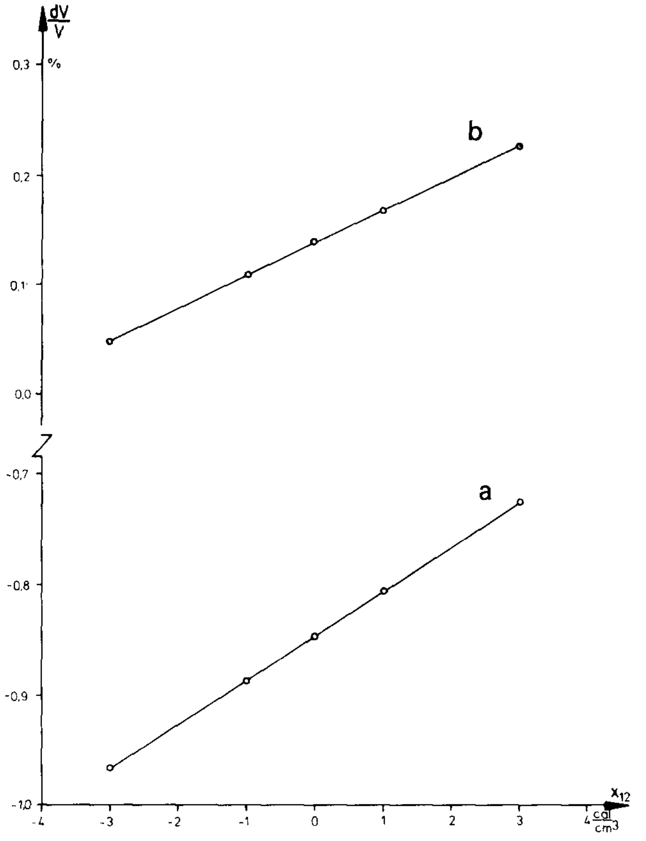

Figure 9 Dependence of the excess volume of mixing dV/V on the interaction parameter X_{12} for a given set of p_2^*/p_1^* at $T_1^* = T_2^*$ (for values see *Figure 7*)

direction of negative values. This is shown again in *Figure 8* where the volume change is displayed as a function of the ratio of the characteristic pressures for various values of the interaction parameter X_{12}. It is apparent that a variation of X_{12} leads to a parallel shift of curve characteristic for $X_{12} = 0$. Thus the excess volume of mixing varies approximately linearly with X_{12} (*Figure 9*).

So the general conclusion is that positive and negative volume changes of mixing may occur and that the sign depends strongly on the relative values of the quantities p_2^*/p_1^* and T_2^*/T_1^* as well as on the sign and the magnitude of the parameter X_{12}.

Returning to the problem of the positive volume change of mixing observed for the blends of PMMA and PVDF, it is apparent that the volume change should be negative on the basis of the equation-of-state approach and the corresponding values of the characteristic parameters p^* and T^*. Reasonable variations of the characteristic parameters p^* and T^* of the two components do not lead to a change in sign of the volume change of mixing. This should be even more the case in view of the strong interactions leading to negative values of the interaction parameter X_{12}.

Judging from the average value of the Flory–Huggins interaction parameter $\chi_{12} = -0.3$ reported in the literature for blends of PVDF and PMMA[18], a choice of $X_{12} = -2.5$ cal cm^{-3} is reasonable. It is apparent that such a value of X_{12} causes a further increase of the discrepancy between the predictions of the theory and the experimental findings.

Again it has to be pointed out, however, that the equation-of-state theory was originally not devised for blends in which strong specific interactions occur between the components, as is the case for the blends considered here. It seems that the strong interactions, i.e. hydrogen bonding, give rise to local variations of the structure, affecting, for instance, the configurations through alterations of bond rotational potentials. The strong effect of specific interactions on properties of blends has been manifested by i.r. spectroscopic results. It seems entirely possible—as in the case of the formation of ice from water—that strong interactions give rise to a very specific configuration characterized by a large free volume.

Recently thermodynamic properties of polymer solutions[23] were considered for the case that the strength of the local interactions is subjected to changes due to mixing. This case was treated within the framework of a modified equation-of-state approach. The predictions were:

(i) that the volume change of mixing depends on such local interactions;

(ii) that the predictions of the unmodified equation-of-state theory agree with the experimental values only for the case that the solutions are athermal and that the pure components obey the equation of state.

Nevertheless the variations predicted to occur in the presence of strong interactions are too small to be able to account for our experimental findings.

We are currently investigating the effects of pressure on the sign and the magnitude of the volume change of mixing, as well as on the location of the critical temperature. The expectation is that these studies will be helpful in unravelling the origin of the positive volume change of mixing observed experimentally for the blends considered here.

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