Determination of the equation-of-state parameters of poly(methyl acrylate)

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The specific volume and thermal pressure coefficient for poly(methyl acrylate) of $M_w = 30\,600$ have been accurately determined. Results are compared with the Prigogine–Flory reduced equation of state employed in the theory of solutions. The characteristic parameters v^*, T^* and p^* required for the treatment of poly(methyl acrylate) solutions and blends are obtained from the experimental results.

(Keywords: poly(methyl acrylate); specific volume; thermal expansion coefficient; thermal pressure coefficient; reduced equation of state)

Introduction

During the last decade an increasing interest in the theoretical prediction of phase equilibria in polymer blends has given incentive to study the more versatile Prigogine–Flory equation-of-state theory[1,2]. On the other hand, it requires more information about the thermodynamic properties of pure components in their liquid state, i.e. the thermal expansion and the thermal pressure coefficients, to be fully applied. For well-known polymers these data are readily available from the literature. Now the investigation of polymer miscibility has moved to systems comprising less conventional polymers in order to test more widely any possible interactions between molecular chains, and this has prompted the need for data on a larger number of compounds. Moreover, an investigation on the agreement between theoretical predictions and experimental values of pure component properties may be useful to increase the degree of accuracy of the theory itself.

An experimental obstacle for having thermodynamic data suitable for this purpose relies upon the fact that many polymers are below their glass transition temperature (T_g) near room temperature and therefore data extrapolated to high temperatures are needed. A quick procedure used to calculate these coefficients theoretically is the group additivity method[3], which can give reasonable but approximate results. However, both these methods may not be entirely suitable.

Being in the liquid state for a wide temperature range because of its low T_g, poly(methyl acrylate) (PMA) seems to be an ideal polymer for an accurate analysis of the equation-of-state theory predictions of pure component properties and for determining the equation-of-state parameters. The present work has the primary aim of providing a full description of such properties and a comparison between experiment and theory is carried out to check the foundation of this approach.

Experimental

PMA, having nominal $M_w = 30\,700\,\mathrm{g\,mol^{-1}}$ and $M_n = 10\,600\,\mathrm{g\,mol^{-1}}$, was purchased from Aldrich as a 40 wt% toluene solution. A g.p.c. run based on polystyrene standards gave $M_w = 30\,600\,\mathrm{g\,mol^{-1}}$ but $M_w/M_n = 1.75$.

Since dilatometry and thermal pressure coefficient measurements require a sample completely free from gases, the following procedure was adopted. The solvent was removed leaving the solution under aspiration for 5 days. The samples were solidified with liquid nitrogen to allow an easy transfer into the vacuum line cell. All the gases were removed after having kept the sample at 363 K under vacuum for 12 h. After this treatment the polymer was suitable for both dilatometric and thermal pressure coefficient measurements.

The dilatometer was joined to a capillary tubing having a known internal diameter. The device was calibrated by measuring the height of a weighed quantity of mercury inside the capillary tubing at 300 K (± 0.05 K) with a cathetometer having a precision of ± 0.005 cm. This height determined the volume of the dilatometer and a visible mark was made on the dilatometer itself to act as a constant reference during the measurements.

A known amount of sample was introduced into the dilatometer, which was kept under vacuum to remove moisture and to fill with mercury. A water bath was used to regulate temperature from 283 to 368 K (± 0.05 K).

The volume of the cell at a given temperature was determined by the difference of the heights of mercury and of the calibration mark, having taken into account the effects of glass expansion. Data were taken every 5 K from 283 to 368 K, heating and cooling the system. The equilibrium time after the temperature change was estimated to be 1 h. With the quantity of mercury being known, and consequently the volume occupied by it, the sample volume was determined by difference.

Thermal pressure coefficients, γ, were determined according to the method developed by Allen *et al.*[4] and largely used some years ago in our laboratories[5,6]. A weighed quantity of PMA was solidified with liquid nitrogen and inserted into the cell (*Figure 1*). Maintaining the polymer in the glassy state, the cell was sealed by flame and kept under vacuum to remove air and moisture. The cell was filled under vacuum with a known quantity of mercury and put in an autoclave which was

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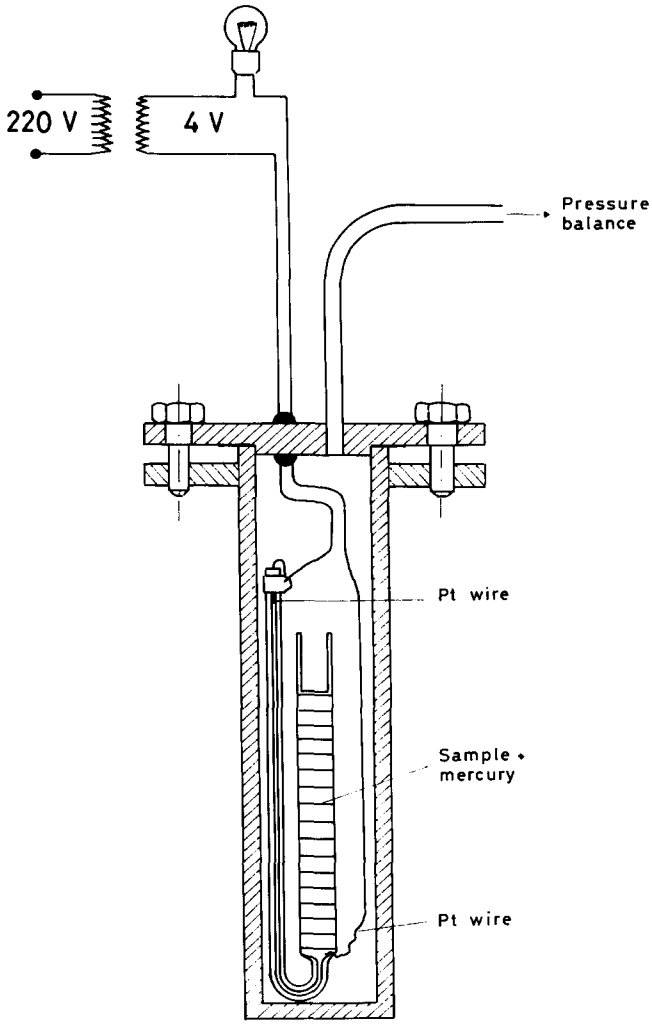

Figure 1 Pressure device

carefully sealed (*Figure 1*). The system was attached to a pressure balance (Budenberg balance) for measuring pressures working with oil as the force transmission fluid.

The volume in the cell was maintained constant through adjustment of the weights on the balance until equilibrium at a given temperature was reached. On heating the system, the volume expansion of the sample produced a pressure which increased the mercury in the capillary tubing and allowed an electrical contact to be switched on. This pressure was counteracted by adding weights on the balance until the contact was switched off. As the system was cooled, the reverse was carried out: weights were taken away from the balance until the electrical contact was switched on. The average pressure of measurements was $\sim 15 \times 10^5$ Pa; at a given equilibrium temperature, the corresponding pressure to keep the volume constant was estimated with very high sensitivity to be $\pm \sim 7$ kPa.

Temperature was regulated electrically to within ± 0.002 K in an oil bath operating from 313 to 353 K. By heating and cooling the system in a narrow range of temperatures (± 0.3 K) a curve of pressure as a function of temperature could be constructed, with a slope of γ at the average temperature. A Beckman thermometer was used to check the thermal equilibrium of the oil bath.

The resulting γ values have to be corrected for the glass and mercury thermal expansion and compression effects. The mathematical treatment[4] uses a correction factor f defined by:

$$f = \frac{\gamma_{corr}}{\gamma_{exp}} \tag{1}$$

which is also a function of different contributions:

$$f = 1 + \frac{v_g\alpha_g - v_{Hg}\alpha_{Hg}}{v_p\alpha_p} + \frac{(v_{Hg}\beta_{Hg} - v_g\beta_g)\gamma}{v_p\alpha_p} \tag{2}$$

where v_i, α_i and β_i are the volume, the thermal expansion coefficient and the isothermal compression coefficient of the ith component, respectively, and the subscripts g, Hg and p correspond to glass, mercury and polymer, respectively. An iterative process is used to calculate a corrected value for each experimental temperature. The process is repeated until the coefficient does not show significant variation. In this case the corrected values became constant after the third step.

Results

The best curve for the specific volume, determined as described previously, is given by equation (3) in which v and T are in units of $cm^3\,g^{-1}$ and K, respectively:

$$v = 0.8363 + 5.34 \times 10^{-4}(T-273) + 3.52 \times 10^{-7}(T-273)^2 \tag{3}$$

This equation reproduces the experimental results within $\pm 2.7 \times 10^{-4}\,cm^3\,g^{-1}$. According to the definition of α, its expression is determined from the derivative of the logarithm of equation (3). Because of the complexity of this analytical function, α is given by the following second order polynomial:

$$\alpha = 4.90 \times 10^{-4} + 6.64 \times 10^{-7}T - 4.4 \times 10^{-10}T^2 \tag{4}$$

which has a standard deviation of fit from the analytical expression of $2.3 \times 10^{-7}\,K^{-1}$.

The determination of an expression for γ presents some difficulties. Experimental uncertainty of $\pm 4\%$ is evident, because of the iterative process correction. The experiments suggest a non-linear relationship between γ and temperature. Thus, the experimental points give (in $J\,cm^{-3}$):

$$\gamma = 2.359 - 0.0298\,(T-273) + 1.96 \times 10^{-4}\,(T-273)^2 \tag{5}$$

but the resulting parabola has its minimum within the temperature range studied. This means that the theoretical formula predicts an increase of γ with increasing temperature after 349 K, which is a non-physical behaviour. Since the standard deviation of the fit of this parabola from experiments is less than the experimental uncertainty, one may assume that after the minimum, γ practically becomes constant and therefore temperature independent.

Treatment of data and discussion

The present paper uses the notation introduced by Flory *et al.*[2,7], and therefore the necessary equations are quoted as required without proof. From the Prigogine–Flory reduced equation of state:

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \tag{6}$$

At $p = 0$, we have

$$\tilde{v} = 1 + \alpha T/3(1 + \alpha T) \tag{7}$$

Table 1 Equation-of-state data and characteristic parameters of PMA interpolated to rounded temperatures

T (K)	$\alpha \times 10^4$ (K^{-1})	γ ($J K^{-1} cm^{-3}$)	$\tilde{v}$	v^* ($cm^3 g^{-1}$)	T^* (K)	p^* ($J cm^{-3}$)
273	6.3853	2.359[a]	1.1559	0.7235	6693	860
293	6.4699	1.842[a]	1.1680	0.7253	6785	736
313	6.5503	1.482	1.1800	0.7273	6857	646
333	6.6264	1.279	1.1919	0.7290	6984	604
353	6.6985	1.232	1.2037	0.7328	7090	629
373	6.7665	1.229[b]	1.2154	0.7349	7202	677

[a] Values extrapolated from experimental data
[b] Value obtained assuming temperature independence

and consequently

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (8)$$

Further, from equation (6) under the same conditions

$$\tilde{p} = p/\gamma T \tilde{v}^2 \quad (9)$$

We are thus able to calculate v^*, T^* and p^* from v, α and γ (refs 2 and 7).

Values of equation-of-state parameters for liquid PMA from these experimental relations are presented in *Table 1* with the experimental results of α and γ. As observed previously for other polymers[8,9], these parameters vary with temperature, although the theory defines them as temperature independent. Comparing the theoretical and experimental values of the derivatives of α and γ, that discrepancy may be better quantified.

From equation (7) it follows that:

$$d\alpha/dT = (7 + 4\alpha T)\alpha^2/3 \quad (10)$$

Equation (10), which yields $(d\alpha/dT)_{theor}$, may be compared with the derivative of equation (4), $(d\alpha/dT)_{exp}$. As *Figure 2* shows, the experimental curve is significantly lower than the theoretical one. Moreover the two curves have conflicting behaviours, the latter increasing slightly with temperature and the former decreasing. This means that some conditions assumed to develop the partition function are true at lower temperatures than those verified here.

A few words on this point are appropriate, albeit theoretical improvements are beyond the aim of the present work. One of the most intuitive rather than rigorous points of the theory seems to be the designation of the factor c, where $3c$ represent the number of external degrees of freedom per segment. Although introduced[1,2] to take into account the effects of polymeric structures, it was assumed temperature independent. This condition may be true at low temperature when there is a small free volume fraction, but c should increase when segments have a wider free volume available. The fact that low molecular weight liquids show a smaller discrepancy[10,11] may support the accuracy of this criticism.

According to the definition of the reduced and star pressure:

$$(d\gamma/dT)_{p=0} = -(\gamma/T)(1 + 2\alpha T) \quad (11)$$

with p^* and v^* treated as constants. As shown in *Figure 3*, the agreement between theoretical and experimental values is fairly good considering the uncertainty in these experiments. The assumption of having a constant γ for $T \geqslant 349$ K made in the previous section appears to be in agreement with the theoretical curve, even though a quantitative discrepancy is exhibited. This behaviour may support the chosen formulation of the mean intermolecular energy and the energy of interaction for a pair of neighbouring sites[2,7,12], on which the definition of p^* is based.

Although not entirely successful from a quantitative point of view, use of such an approach nevertheless represents an improvement in understanding and in predicting polymer blend miscibility. The theoretical ability to predict thermodynamic phenomena such as the change in volume on mixing and lower critical solution temperature behaviour is a step forward in the knowledge of mixing properties. In order to avoid the above-mentioned imperfections, two methods are generally suggested.

The first assumes that for best results the star parameters, which are the very essence of every equation-of-state theory, must be chosen as close as possible to those experimentally determined at the given temperature. This assumption actually overrules a basic hypothesis of the theory, because it implies that star parameters vary with temperature.

The second way to bypass such a problem is to choose average star parameters within the range of temperature studied. This yields a degree of uncertainty in these values which will affect the final results. In the case of PMA, star parameters are evaluated using a 'trial-and-error' method which minimizes the deviation of thermodynamic coefficients calculated with a constant star parameter from the experimental ones when temperature is varying. The resulting v^* is $0.729 \pm 0.007\ cm^3 g^{-1}$, which means a prediction of α values with a precision of $\pm 6\%$. T^* calculated with this fixed value is 6978 ± 22 K. According to equation (9) and using the constant value of v^*, p^* is

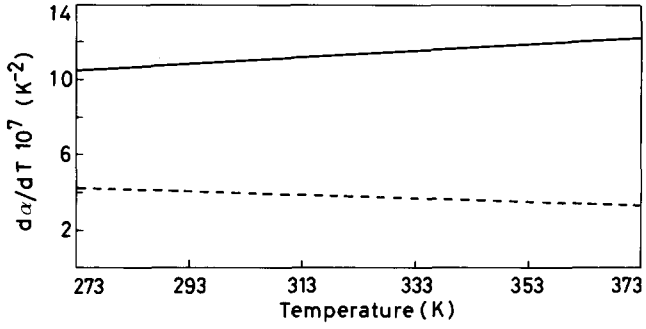

Figure 2 Comparison between the theoretical (——) and experimental (– – –) derivative of the thermal expansion coefficient

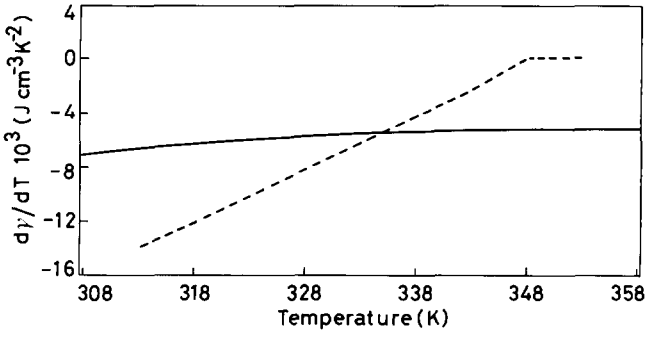

Figure 3 Comparison between the theoretical (——) and experimental (– – –) derivative of the thermal pressure coefficient

$623 \pm 19\ J\ cm^{-3}$. These two parameters together are able to reproduce the experimental γ value to within $\pm 4\%$.

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