A more accurate corresponding states reduced equation for solvent/polymer systems

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Values of the polymer/solvent interaction energy parameter were obtained within the Flory and Fujisawa–Hamada–Nakajima (FHN) corresponding states frameworks for the system carbon tetrachloride/poly(vinyl methyl ether). The FHN theory follows more closely the free-volume variation with temperature and accordingly, one is better able to correct for these free volume effects, obtaining a polymer/solvent interaction energy parameter independent of temperature. The scaling is also such, with FHN, that it results in lower, i.e. more negative, interaction energy parameters.

(Keywords: corresponding states; poly(vinyl methyl ether); interaction parameter; free volume; inverse gas chromatography)

Introduction

Several approaches in the literature try to improve on Flory's theory as to the characterization of polymer/solvent or polymer/polymer interactions[1]. One approach is to use a different equation of state to that used by Flory[2–5]. Fujisawa *et al.*[4,5] have successfully used a different equation of state for free volume evaluation and have applied it to excess volume interpretation. We wish to use the same approach, but to obtain the polymer/solvent interaction energy parameter, X_{12}. This has been done for the system carbon tetrachloride/poly(vinyl methyl ether), CCl_4/PVME, with experimental results taken from a previous publication[6].

Theory

In this paper, two procedures have been used to obtain X_{12}. The first makes use of Flory's classical theory, which is based on the following reduced equation of state:

$$\tilde{P}\tilde{V}/\tilde{T} = [\tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1)] - 1/\tilde{V}\tilde{T} \qquad (1)$$

where the reduced variables $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are given by, respectively, $\tilde{P} = P/P^*$, $\tilde{V} = V/V^* = v/v^*$ and $\tilde{T} = T/T^*$, where the parameters with asterisks are solvent or polymer characteristic parameters. Those can be related to the thermal expansion coefficients, α, and thermal pressure coefficients, γ, as follows:

$$\tilde{V}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \qquad (2)$$

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

$$P^* = \gamma T\tilde{v}^2 \qquad (4)$$

The X_{12} can be obtained from the polymer interaction parameter, χ_{12}, with[2]:

$$\chi_{12} = (P_1^* V_1^* / \tilde{v}_1 RT)(A^2 \alpha_1 T/2 + Y_{12}) \qquad (5)$$

where

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (s_2/s_1)(X_{12}/P_1^*)$$

and

$$Y_{12} = (s_2/s_1)^2 (X_{12}/P_1^*)$$

The Fujisawa–Hamada–Nakajima (FHN) approach is similar, but uses a different reduced equation of state:

$$\tilde{P}\tilde{V}/\tilde{T} = [\tilde{V}^2/(\tilde{V} - 1)^2] - 1/\tilde{V}\tilde{T} \qquad (6)$$

from which one can relate the characteristic parameters to α and γ by[4,5]:

$$\tilde{V} = [2\alpha T/(1 + \alpha T)] \qquad (7)$$

$$\tilde{T} = (\tilde{V} - 1)^2/\tilde{V}^3 \qquad (8)$$

while P^* is as in equation (4). From equations (2)–(4), (7) and (8), one can obtain the characteristic temperature for the solvent and polymer, as shown in *Table 1*.

Results and discussion

Variation of the parameters with asterisks as a function of temperature. If the value of α is calculated from equations (2), (3), (7) and (8) and constant characteristic parameters over a range of temperatures, it should match the experimental temperature variation, if the equation of state corrects for $d\alpha/dt$. The experimental variation of α is shown in *Figure 1*, as well as that calculated from the Flory and FHN procedures, with characteristic temperatures as in *Table 1*. This is for CCl_4, over the 120–180°C range, also expressed as a function of the ratio of temperature over the critical temperature, T_c, of CCl_4. It is apparent that the FHN theory gives better agreement with the experimental variation over the temperature range considered. This is due to the different equation of state used.

One can also use the reverse procedure. That is, calculate at each temperature the value of the characteristic parameters from the experimental α and γ values. A true corresponding states theory should give constant values of the characteristic parameters over a temperature range. This was done, using precise expansibility and compressibility data[7,8], and the result is shown in *Figure 2*. It is apparent that, again, the FHN framework gives a better performance in modelling the variation of reduced volumes, temperatures and pressures.

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Table 1 Thermal expansion and pressure coefficients and characteristic parameters for CCl_4 and PVME at 120°C with the Flory and FHN equations of state

	$\alpha \times 10^3$ (K^{-1})	γ (bar K^{-1})	T^* (K)	V^* ($cm^3\ g^{-1}$)	P^* (J cm^{-3})	$s/v \times 10$ (nm^{-1})
CCl_4						
Flory	1.604[a]	6.99[b]	4954	0.500	490	1.0
FHN	1.604[a]	6.99[b]	3666	0.406	743	1.0
PVME						
Flory	0.723[c]	7.24[d]	7201	-	438	1.47
FHN	0.723[c]	7.24[d]	6090	-	596	1.47

[a] From volumetric data[10]
[b] From compressibility data[11]
[c] From ref. 9
[d] From ref. 12

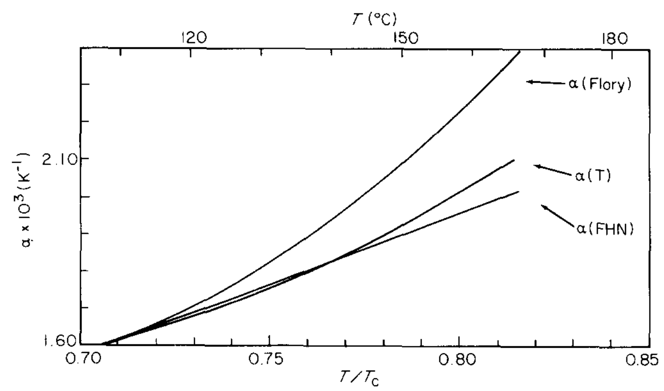

Figure 1 Variation of α for CCl_4 as obtained experimentally[10] calculated assuming a characteristic temperature of 4954 K and using the reduced equation of state of Flory, and calculated assuming a characteristic temperature of 3666 K and using the FHN reduced equation of state

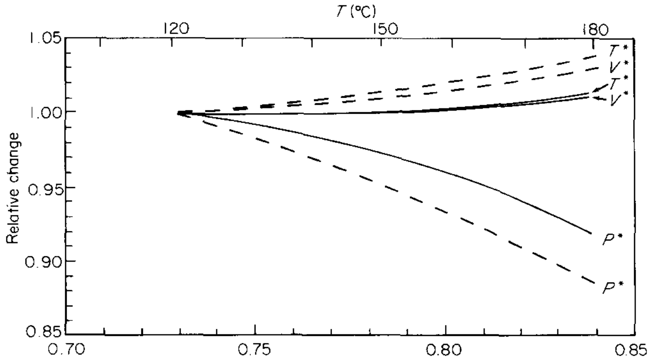

Figure 2 Relative change with respect to the values at 120°C of the characteristic parameters T^*, V^* and P^*, for CCl_4, over the 120–180°C temperature range, if calculated (1) from Flory's theory and experimental α and γ values[10,11] (– – –) and (2) from the FHN theory and experimental α and γ values[10,11] (——)

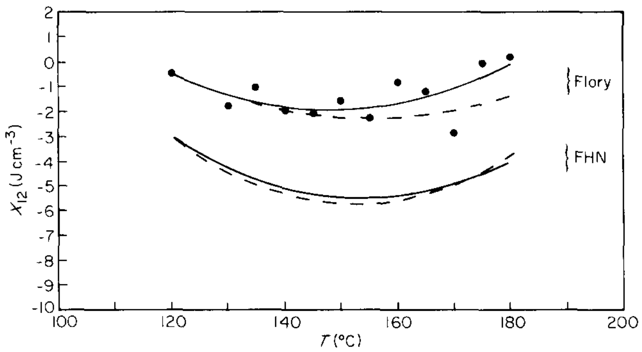

Figure 3 Values of X_{12} as calculated from χ_{12} data[6] over the 120–180°C temperature range, for the CCl_4/PVME system, at infinite dilution of CCl_4, with (1) Flory's theory, using the values of the characteristic parameters P^*, V^* and T^* at 120°C, i.e. constant values of reduced parameters (——), (2) from Flory's theory, using the values of characteristic parameters P^*, V^* and T^* calculated from α and γ values calculated at each temperature (– – –), (3) FHN theory, using the values of the characteristic parameters P^*, V^* and T^* at 120°C, i.e. constant values of reduced parameters (——) and (4) FHN theory, using the values of the characteristic parameters P^*, V^* and T^* calculated from α and γ values at each temperature (– – –)

Comparison of the interaction energy parameters obtained from both theories. One can use the preceding results to compare both frameworks. We will follow the same procedure as in the preceding paper[6], where inverse gas chromatography results were used to obtain interaction energy parameters. In *Figure 3*, results are shown, using either constant characteristic parameters (solid lines) or temperature drift-corrected characteristic parameters (broken lines). The experimental points are shown only for the uppermost curves, since the dispersion of the data is the same for the other curves, the source data being the same. First it is apparent that the curves obtained from the FHN framework give better agreement between the values obtained from both constant and temperature dependent parameters. This confirms that the FHN equation of state takes better account of the state behaviour of the probe molecule, CCl_4. Second, the scaling of the FHN reduced equation of state is such that it gives interaction energy parameters more negative than those obtained using Flory's theory. This is due to the fact that the latter underestimates the equation of state contribution to χ_{12}, as mentioned by Flory[13]

Conclusions

The FHN corresponding states theory, based on a different equation of state than Flory's, gives better agreement, over a wide temperature scale, with state data. The FHN theory also gives distinctly different results, as to the estimation of the interaction energy parameters, than Flory's theory. The different results are due partly to the more accurate representation of free volume differences with the FHN theory, which does not overestimate the solvent/polymer free volume difference, as the Flory theory, through its equation of state, does. The scaling is then such, with FHN, that it results in lower, i.e. more negative, interaction energy parameters.

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