

A study on the parameters of exchange enthalpy, X_{12} , and entropy, Q_{12} , in the equation-of-state theory for some polymer–solvent pairs

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The parameters of exchange enthalpy, X_{12} , and entropy, Q_{12} have been determined for cyclopentane, tetrahydrofuran and 1,4-dioxane with poly(dimethyl siloxane) around room temperature using inverse gas chromatography technique. The parameters X_{12} were compared to the parameters calculated by means of the Berthelot relationship from characteristic pressures of the pure components in the mixtures. The parameters Q_{12} were compared to differences of thermal pressure coefficients of the pure components in the mixtures. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

Two exchange terms, the parameters of exchange enthalpy, X_{12} and entropy, Q_{12} were introduced into the equation-of-state theory by Flory and coworkers^{1–9}. These parameters were designed to quantify the magnitude of enthalpy and entropy required to exchange a polymer segment close to another polymer segment with a solvent molecule. Their values depend on the chemical nature of the components of a mixture. The exchange parameters were assumed to be independent of temperature and composition of the mixture in the theory. The X_{12} and Q_{12} parameters are chosen so that the thermodynamic features obtained from the measurements of heat of mixing, osmotic pressure, vapour sorption etc., are reproduced by the theory^{6–14}. The contact site ratio of the solvent to the polymer segment, s_1/s_2 is used as adjustable parameters to fit the theory to the experimental data. However, the magnitude of the ratio s_1/s_2 considerably affects the thermodynamic features calculated theoretically, as the polymer concentration decreases.

Recently, we have determined the exchange enthalpy and entropy parameters of poly(dimethyl siloxane)(PDMS) with some solvents by inverse gas chromatography (IGC) technique^{15–17}. The values of the parameters X_{12} and Q_{12} of these polymer–solvent systems are comparable with those determined earlier by other techniques at lower polymer concentrations^{12–14}. This implies that the parameters X_{12} and Q_{12} are almost independent of composition of a given polymer–solvent system.

IGC technique is a simple, rapid, reliable and inexpensive technique, as well as being one that allows study of solvents and non-solvents of a polymer under the same experimental conditions^{18–20}. At the same time, it is not necessary to know the value of s_2/s_1 in calculation of X_{12} and Q_{12} in the IGC technique.

In this study, we have determined the parameters X_{12} and Q_{12} of PDMS with cyclopentane as well as with tetrahydrofuran and 1,4-dioxane, which are its derivatives with etheric oxygen. PDMS is a suitable polymer because its densities and thermal pressure coefficients were previously determined with a high precision at a wide temperature

range and its low glass transition temperature (T_g , -42°C) permits us to study around room temperature, since IGC technique gives meaningful thermodynamic data related to solubility at temperatures at least 40°C higher than T_g . We have chosen the above-mentioned solvents, and also used previously published data¹⁵ on cyclohexane–PDMS system, because two of the solvents are nonpolar and two of them are moderately polar, having cohesive energies close to that of PDMS.

We expect a more accurate picture to appear from detailed investigations of a greater range of systems with comparison of intermolecular interactions of pure components and their exchange parameters.

Data reduction

The polymer–solvent interaction parameter, χ_1^∞ , at infinite dilution of the lower molecular weight component, is determined from the IGC measurements by the equation^{18–20}

$$\chi_1^\infty = \ln(273.2Rv_2^*/p_1^0V_g^0V_1^*) - (1 - V_1^*/M_2v_2^*) - p_1^0(B_{11} - V_1)/RT \quad (1)$$

where R is the universal gas constant; p_1^0 , V_1^* and B_{11} are saturated vapour pressure, molar hard-core volume and gaseous state second virial coefficient of the solvent, respectively, and v_2^* and M_2 are the specific hard-core volume and molecular weight of the polymer, respectively. Specific retention volume, V_g^0 is the net volume of the carrier gas required to move all solvent molecules through the column at 0°C , and is determined by applying the classical relation to the measurements of retention time difference of solvent and air as well as the flow rate of the carrier gas. The vapour pressure, p_1^0 , was calculated using Antoine's constants²¹. The molar volumes of the solvents were calculated from the empirical relations given in the literature^{22,23}. The B_{11} values of hydrocarbons were computed using the related equations given in the literature²⁴.

Under the gas chromatographic experimental condition the volume fraction of polymer approaches unity; equation-of-state theory estimates the χ_1^∞ interaction

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parameter as:

$$RT\chi_r^\infty = p_1^* V_1^* \{ 3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_2^{1/3} - 1)] + \tilde{v}_1^{-1} - \tilde{v}_2^{-1} \} + \bar{X}_{12} V_1^* \tilde{v}_2^{-1} \quad (2)$$

The reduced quantities in the above equation, i.e. reduced volume, \tilde{v} , temperature, \tilde{T} and pressure, \tilde{p} of a pure liquid or an amorphous polymer are defined as:

$$\tilde{v} = V/V^* \quad \tilde{T} = T/T^* \quad \tilde{p} = p/p^* \quad (3)$$

where V is the actual molar volume of the liquid at actual T , temperature in K, and p , pressure. The characteristic molar volume (or molar hard-core volume), V^* , characteristic temperature, T^* , and characteristic pressure, p^* , of a pure component can be calculated directly from experimental values of molar volume, V , thermal expansion coefficient, and thermal pressure coefficient, γ , of the pure component, by means of the following equations

$$\tilde{v}^{1/3} = [(\alpha T/3)/(1 + \alpha T)] + 1 \quad (4)$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (5)$$

$$\alpha = (1/V)(\partial V/\partial T)_{p=0} \quad (6)$$

$$p^* = \gamma \cdot T \cdot \tilde{v}^2 \quad (7)$$

$$\gamma = (\partial p/\partial T)_v \quad (8)$$

Generally, subscript 1 is used for lower molecular weight component, and subscript 2 for polymeric component. No subscript is used for their binary mixtures. The parameter \bar{X}_{12} in the last term of equation (2) combines the parameters X_{12} and Q_{12} .

$$\bar{X}_{12} = X_{12} - T\tilde{v}_2 Q_{12} \quad (9)$$

The enthalpic interaction parameter, χ_h^∞ , can be obtained from the slope of the plot χ_r^∞ vs $1/T$ from IGC measurements according to its definition

$$\chi_h^\infty = \Delta H_m^\infty/RT = [(\partial\chi_r^\infty)/(\partial(1/T))]/T \quad (10)$$

where ΔH_m^∞ is the enthalpy of mixing at infinite dilution of the solvent. According to the equation-of-state theory, the enthalpy interaction parameter, χ_h^∞ , is approximated as

$$\chi_h^\infty = (p_1^* V_1^*/RT)[(\tilde{v}_1^{-1} - \tilde{v}_2^{-1}) + (\alpha_2 T/\tilde{v}_2)(\tilde{T}_1 - \tilde{T}_2)/\tilde{T}_2] + V_1^*(1 + \alpha_2 T)X_{12}/(\tilde{v}_2 RT) \quad (11)$$

under the gas chromatographic conditions.

Experimental

PDMS was a Petrarch Inc. product with a number-average molecular weight of 2.8×10^4 . Cyclopentane, tetrahydrofuran and 1,4-dioxane were analytical reagent grade produced by Merck AG. Inc. and were used without further purification. The data of cyclohexane were reported in a previous work¹⁵. The gas chromatograph used was a Hewlett Packard model 5890, series II, equipped with thermal conductivity detector. The temperature of the column oven was checked by use of the Meter Digital thermometer, model D96M, and it varied within $\pm 0.1^\circ\text{C}$ of the control temperature at the studied temperature range. Other specifications and the experimental conditions were given in previous work¹⁵⁻¹⁷

Results and discussion

The parameters χ_r^∞ were found from equation (1) for the given polymer-solvent pairs using the values of V_g^0 determined experimentally. The effective exchange energy parameters, \bar{X}_{12} were obtained from equation (2) by using the parameters χ_r^∞ . The values of these parameters are given in Figure 1a and b. The required characteristic and reduced parameters are calculated by means of equations (3)–(8) from the molar volumes, V , thermal expansion coefficients, α and thermal pressure coefficients, γ of pure components of the given polymer-solvent pairs. The values of physical data used for the solvents are given in Table 1. The data required for pure PDMS were taken from the literature¹⁰. Data of cyclohexane were previously compared with data in the literature¹⁵. No data on χ_r^∞ of the PDMS-tetrahydrofuran system was found in the literature. The values of χ_r^∞ of the 1,4-dioxane-PDMS pair obtained in this work are comparable with those given in the literature, i.e. 1.26 and 1.17 at 40 and 70°C, respectively, in this study, compared with 1.27 and 1.18 at corresponding temperatures given by Lichtenthaler *et al.*²⁵. 1,4 Dioxane is a nonsolvent for PDMS²⁶ consequently χ_r^∞ parameters are considerably higher than those of others. Figure 1 shows a high effective exchange energy term as a consequence of high χ_r^∞ parameters of the PDMS-1,4 dioxane pair. The values of χ_r^∞ of the PDMS-cyclopentane pair are also comparable with data given by Lichtenthaler *et al.*²⁵, that is 0.47 and 0.48 in this study, compared with 0.43 and 0.46 at corresponding temperatures in the literature.

Later, the parameters X_{12} and Q_{12} were determined using equations (9)–(11), and were exhibited in Figure 2a and Figure 3a. The magnitude of X_{12} has varied as parallel to the variation of \bar{X}_{12} from cyclopentane to 1,4-dioxane. In Table 2, the obtained data with experimental errors in V_g^0 and apparent errors applied to the X_{12} and Q_{12} are listed at selected temperatures. The relative standard error in X_{12} is highest for the PDMS-cyclopentane pair.

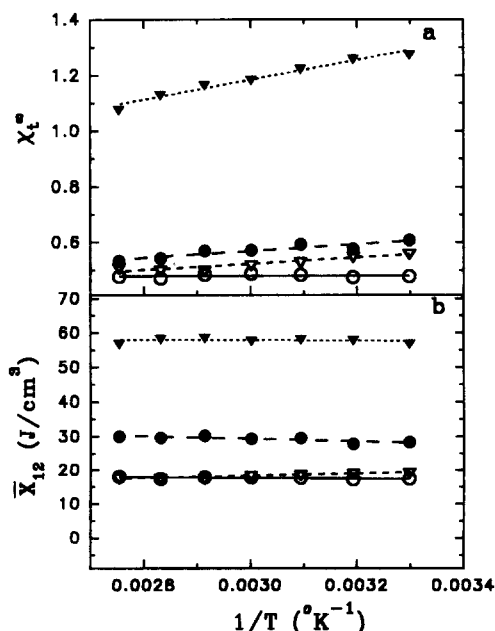


Figure 1 Polymer-solvent interaction parameters, χ_r^∞ (a), and effective exchange energy parameters, \bar{X} (b) related to the interactions of PDMS with the following solvents as a function of absolute column temperature. Hollow circles, cyclopentane; filled circles, tetrahydrofuran; hollow inverted triangles, cyclohexane; filled inverted triangles, 1,4-dioxane

Table 1 The values of molar volume, V , thermal expansion coefficient, α , and thermal pressure coefficient, γ , of pure solvents used in this study at selected temperatures

Solvent	V (cm ³ mol ⁻¹)			$\alpha \times 10^3$ (K ⁻¹)			γ (J cm ⁻³ K ⁻¹) ^a		
	$T = 30^\circ\text{C}$	$T = 60^\circ\text{C}$	$T = 90^\circ\text{C}$	$T = 30^\circ\text{C}$	$T = 60^\circ\text{C}$	$T = 90^\circ\text{C}$	$T = 30^\circ\text{C}$	$T = 60^\circ\text{C}$	$T = 90^\circ\text{C}$
cyclopentane ^b	95.6	99.8	104.8	1.354	1.540	1.726	0.980	0.792	0.633
cyclohexane ^b	109.3	113.4	118.2	1.189	1.322	1.439	1.000	0.825	0.677
tetrahydrofuran ^c	81.9	84.2	86.6	0.911	0.936	0.964	1.282	1.063	0.879
1,4-dioxane ^b	86.3	89.4	92.8	1.125	1.212	1.300	1.601	1.335	1.112

^a Calculated from enthalpy of vaporization of solvents²¹^b Ref. ²²^c Ref. ²³

In the theory, X_{12} is formally defined by^{3,4,6}

$$X_{12} = s_1 \Delta\eta / (2v^{*2}) \quad (12)$$

where

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \quad (13)$$

and η , being the energy for the pairs indicated. On the other hand, if it is adapted to the Bertholet relationship

$$\eta_{12} = (\eta_{11}\eta_{22})^{1/2} \quad (14)$$

for homopolar species whose interactions are dominated only by intermolecular dispersion energy, it can be written as

$$\Delta\eta = (\eta_{11}^{1/2} - \eta_{22}^{1/2})^2 \quad (15)$$

and

$$X_{12} = p_1^* [1 - (p_2^*/p_1^*)^{1/2} (s_1/s_2)^{1/2}]^2 \quad (16)$$

In Figure 2b, the right hand side of equation (16) calculated for the given polymer–solvent pairs is plotted at the temperatures studied. To calculate the characteristic pressures of the solvents, we assumed that the thermal pressure coefficients of them are equal to $1.1 \times$ their cohesive energy densities²⁷. In comparison of Figure 2a and b, it is seen that the magnitudes of X_{12} found experimentally are comparable to the magnitudes of $p_1^* [1 - (p_2^*/p_1^*)^{1/2} (s_1/s_2)^{1/2}]^2$ calculated

within the combined experimental error. However it should be noted that the magnitude of s_1/s_2 considerably affects the magnitude of the parameters in Figure 2b. In this study, the ratio s_1/s_2 was obtained as 1.30, 1.30, 1.33 and 1.35 for cyclopentane, cyclohexane, tetrahydrofuran and 1,4-dioxane in PDMS, respectively, by using Bondi's method²⁸.

The parameter Q_{12} is an entropy correction term introduced to overcome overestimation of ΔS in the theory, and therefore its physical meaning is unclear and used as an adjustable parameter in the treatments. However, the values of Q_{12} parameters may be compared to thermal pressure coefficients of the components since entropy change by volume of a substance at constant temperature is equal to thermal pressure coefficient of the substance, according to the Maxwell relation²⁹

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V = \gamma \quad (17)$$

In Figure 3b, $0.07 \times$ the difference of the thermal pressure coefficients of polymer and solvents, $0.07(\gamma_2 - \gamma_1)$, is plotted at the studied temperatures. We have no any theoretical explanation about the validity of the plots in Figure 3b, however the plots of the PDMS–cyclohexane and PDMS–tetrahydrofuran pairs are comparable to the experimental Q_{12} values of them in Figure 3a within combined experimental errors. The plots of PDMS–1,4-dioxane

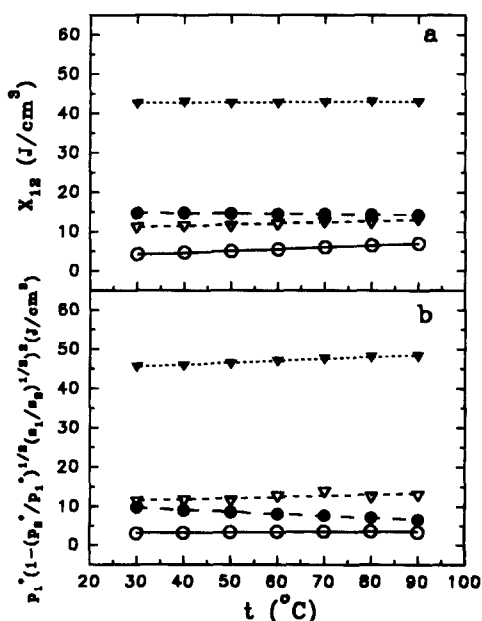


Figure 2 Comparison of the parameter exchange enthalpy, X_{12} (a), and the right hand side of equation (16) (b), at studied column temperatures. Symbols as in Figure 1

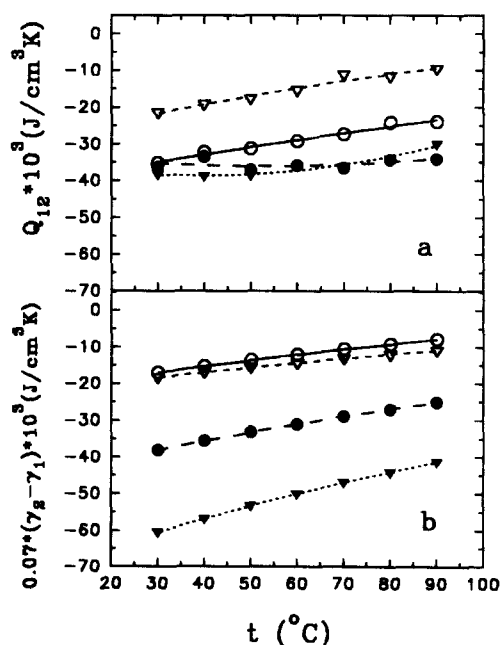


Figure 3 Comparison of the parameter exchange entropy, Q_{12} (a), and the parameter $0.07(\gamma_2 - \gamma_1)$ (b), at studied column temperatures. Symbols as in Figure 1

Table 2 The mean retention volumes, V_g^0 , polymer-solvent interaction parameters, χ_1^* , exchange enthalpy parameters, Q_{12} , and their standard errors for the given solvents with PDMS at selected temperatures

Solvent	$V_g^0 \pm S$ (cm ³ per gram polymer)			χ_1^*			Q_{12} (J cm ⁻³)			$-Q_{12} \times 10^3$ (J cm ⁻³ K ⁻¹)		
	T = 30°C	T = 60°C	T = 90°C	T = 30°C	T = 60°C	T = 90°C	T = 30°C	T = 60°C	T = 90°C	T = 30°C	T = 60°C	T = 90°C
Cyclopentane	119.9 ± 0.3	44.9 ± 0.1	20.6 ± 0.1	0.47 ± 0.01	0.48 ± 0.01	0.48 ± 0.01	4.2 ± 1.0	5.5 ± 1.0	7.0 ± 1.0	7.0 ± 1.0	29.2 ± 2.7	23.9 ± 2.8
Cyclohexane	297.2 ± 0.9	99.5 ± 0.2	41.1 ± 0.2	0.56 ± 0.01	0.52 ± 0.003	0.51 ± 0.01	11.2 ± 0.2	12.0 ± 0.2	13.2 ± 0.2	13.2 ± 0.2	15.4 ± 0.7	9.6 ± 0.9
Tetrahydrofuran	228.5 ± 1.0	76.1 ± 0.2	31.1 ± 0.1	0.61 ± 0.01	0.57 ± 0.01	0.53 ± 0.01	14.7 ± 0.4	14.4 ± 0.4	14.2 ± 0.4	14.2 ± 0.4	35.8 ± 1.1	34.1 ± 1.1
1,4-dioxane	489.5 ± 2.6	137.0 ± 0.4	52.2 ± 0.2	1.28 ± 0.01	1.18 ± 0.01	1.18 ± 0.01	42.6 ± 0.6	42.8 ± 0.6	43.0 ± 0.6	43.0 ± 0.6	36.0 ± 1.2	30.1 ± 1.0

Table 3 Comparison of the exchange entropy parameter, Q_{12} with the term $0.07(\gamma_2 - \gamma_1)$ of some polymer-solvent systems given in the literature

Polymer-solvent system	$Q_{12} \times 10^3$	$0.07(\gamma_2 - \gamma_1) \times 10^3$
Polystyrene-cyclohexane	23 ^{12a}	22
PDMS-methyl ethyl ketone	-32 ^{17b} , -42 ^{17c}	-27
PDMS-benzene	-37 ^{15b} , -42 ^{11a}	-29
PDMS-chlorobenzene	-44 ^{15b} , -59 ^{11a}	-39

^a Found by osmotic pressure

^b Found by inverse gas chromatography

^c Found by intrinsic viscosity

and PDMS-cyclopentane systems in Figure 3a and b are not in agreement. However it should be noted that PDMS is insoluble in 1,4-dioxane and the PDMS-cyclopentane system may exhibit a phase diagram with a lower critical solution temperature (LCST), since the parameter χ_1^* is an increasing function of temperature. Therefore, some repulsive forces lowering the Q_{12} may exist between unlike species in the PDMS-cyclopentane system. In Table 3, the quantity $0.07(\gamma_2 - \gamma_1)$ was calculated for some polymer-solvent systems whose Q_{12} are given in the literature. A reasonable agreement is present between two terms for the given systems.

Using experimental data in this study, it may be written that

$$Q_{12}/X_{12} \cong (-2.2 \pm 0.3) \times 10^{-3} (\text{K}^{-1}) \quad (18)$$

for PDMS-cyclohexane and PDMS-tetrahydrofuran systems around room temperature.

Consequently, this study suggests that the comparison of X_{12} experimentally found with the parameter calculated from pure substance properties by means of equation (16) may give qualitative and quantitative data about intermolecular forces between unlike components of a mixture. In addition, the parameter Q_{12} may be related to the difference of the thermal pressure coefficients of the components of a mixture.

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