

A Study of Some Equation-of-State Parameters of Poly(methylhydrosiloxane-*co*-dimethylsiloxane) with Some Solvents by Gas Chromatography

Selin Coskun, Özlem Cankurtaran, Belkis B. Eran, Ayfer Sarac

Department of Chemistry, Yildiz Technical University, Davutpasa Campus, 34220 Esenler, Istanbul, Turkey

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ABSTRACT: Trace amount of methyl acetate, ethyl acetate, *tert*-butyl acetate, pentane, hexane, and heptane were passed through the chromatographic column loaded with poly(methylhydrosiloxane-*co*-dimethylsiloxane) coated on Chromosorb W. The retention diagrams of the solvents on the copolymer were plotted by means of specific retention volumes at temperatures between 40 and 80°C by inverse gas chromatography technique. In this study, some thermodynamic interaction parameters such as Flory–Huggins polymer–solvent interaction parameter, equation-of-state polymer–solvent interaction parameter, effective exchange energy parameter, and weight fraction activity coefficients at infinite dilution of the

solvent were determined. Then, the exchange enthalpy parameter and entropy parameter were determined by using a relation for the enthalpy interaction parameter of the equation-of-state theory, which is arranged for the inverse gas chromatography conditions. Later, the partial molar heat of sorption and the partial molar heat of mixing were obtained. The solubility parameter of this copolymer was determined as 6.64 (cal/cm³)^{1/2} at room temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1627–1631, 2007

Key words: chromatography; thermodynamics; polysiloxanes; solution properties; solubility parameter

INTRODUCTION

Siloxane polymers are also well known because of their highly flexible backbone. One of the important features of siloxane polymers is their unusually high gas permeability. Poly(dimethylsiloxane) and other silicon polymer were used as gas separation membranes.^{1,2} The hydrosilylation of vinyl functional siloxanes by hydride functional siloxanes is the based of addition cure chemistry. The most widely used materials for these applications are methylhydrosiloxane–dimethylsiloxane copolymers, which have more readily controlled reactivity than do the homopolymers and result in tougher polymers. Solubility behavior and thermodynamic interactions of methylhydrosiloxane–dimethylsiloxane copolymers with solvents are important to use them but there are not any data about the solvent resistance in the literature.

Inverse gas chromatography (IGC) method, which is simple, fast, and economical has been used extensively to study the structure of polymers, to predict the thermodynamic properties and the interactions of many polymer–solvent mixtures and the solubility of solvents in polymers. Knowledge of the solubility of solvents in polymers is essential for many high-

molecular-weight compound technologies. Advantage of the IGC technique is the possibility of working with both solvent and nonsolvent of the polymer under the same experimental conditions. IGC data may be collected quite rapidly over extended temperature ranges.^{3–5}

In this study, the retention diagrams of some solvents on the poly(methylhydrosiloxane-*co*-dimethylsiloxane) (HMS-013) were obtained by IGC. Then, some thermodynamic parameters in the Flory–Huggins theory and equation-of-state theory and solubility parameter of the copolymer were determined in the range of 40–80°C. The exchange enthalpy parameters, X_{12} , and entropy parameters, Q_{12} , in the equation-of-state theory are assumed to be independent of temperature and composition of the mixture, but this situation is not confirmed yet. For the first time, we have determined exchange enthalpy and entropy parameters of poly(dimethylsiloxane) and poly(methylmethacrylate) with some solvents directly from IGC measurements earlier.^{6–10} X_{12} and Q_{12} parameters of these polymer–solvent systems were comparable with those determined earlier by other techniques at lower polymer concentrations. There are not any other data in the literature related to the determination of X_{12} and Q_{12} parameters of methylhydrosiloxane–dimethylsiloxane copolymers. In this study, we determined X_{12} and Q_{12} parameters by IGC measurements and we also investigated the dependence of X_{12} and Q_{12} parameters on temperature for HMS-013.

Correspondence to: Ö. Cankurtaran (kurtaran@yildiz.edu.tr).

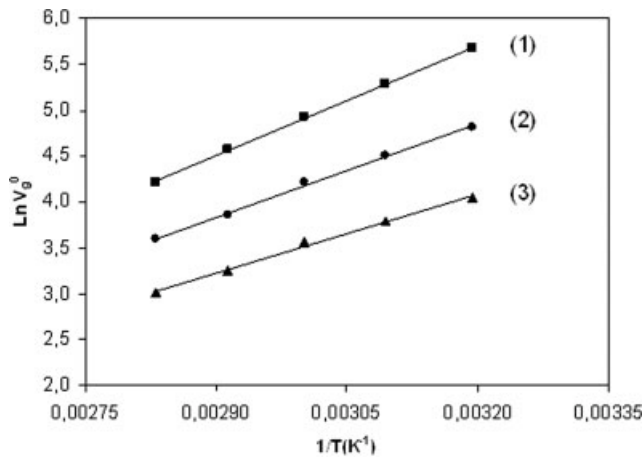


Figure 1 The retention diagram of tBA (1), EA (2), and MA (3) on HMS-013.

Theoretical background

The specific retention volume, V_g^0 , is determined experimentally from IGC measurements as follows.^{11–16}

$$V_g^0 = \frac{Q(t_R - t_A) J 273.2}{(T_r w)} \quad (1)$$

where Q is carrier gas flow rate measured at the room temperature T_r ; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor, and w is weight of polymer in the column.

According to the theories of Flory–Huggins and equation-of-state interaction parameters, χ_{12}^* and χ_{12}^∞ are defined in eqs. (2) and (3) respectively:

$$\chi_{12}^\infty = \ln \left(\frac{273.2 R v_2}{p_1^0 V_g^0 V_1^0} \right) - 1 - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (2)$$

where R is the universal gas constant; p_1^0 , B_{11} , and V_1^0 , respectively, are saturated vapor pressure, gaseous state second virial coefficient, and molar volume of the solvent at temperature T , and v_2 is the specific volume of the polymer.

$$\chi_{12}^* = \ln \left(\frac{273.2 R v_2^*}{p_1^0 V_g^0 V_1^*} \right) - 1 - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (3)$$

where v_2^* is the specific hard-core volume of the polymer and V_1^* is the molar hard-core volume of the solvent.

The effective exchange energy parameter, X_{eff} , in the equation-of-state theory is defined as follows:

$$RT \chi_{12}^* = p_1^* V_1^* \left\{ 3 T_{1r} \ln \left[\frac{(v_{1r}^{1/3} - 1)}{(v_{2r}^{1/3} - 1)} \right] + v_{1r}^{-1} - v_{2r}^{-1} + X_{\text{eff}} V_1^* v_{2r}^{-1} \right\} \quad (4)$$

where p_1^* is the characteristic pressure, v_{1r} and v_{2r} are reduced volume of the solvent and polymer, respectively. T_{1r} is the reduced temperature of the solvent. Reduced quantities in the above equation are defined as

$$v_r = \frac{V}{V^*}, T_r = \frac{T}{T^*}, p_r = \frac{p}{p^*} \quad (5)$$

where V is the actual molar volume of the liquid at actual T , temperature in kelvin, and p , pressure. The characteristic molar volume, V^* , and the characteristic pressure, p^* , of a pure component can be calculated directly from experimental values of molar volume, V . Thermal expansion coefficient, α , and thermal pressure coefficient, γ , of the pure component, can be calculated by means of the following equations:

$$v_r^{1/3} = \left[\frac{(\alpha T/3)}{1 + \alpha T} \right] + 1 \quad (6)$$

$$T_r = \frac{(v_r^{1/3} - 1)}{v_r^{4/3}} \quad (7)$$

$$\alpha = \left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial T} \right)_{p=0} \quad (8)$$

$$P^* = \gamma T v_r^2 \quad (9)$$

$$\gamma = \left(\frac{\partial p}{\partial T} \right)_V \quad (10)$$

The enthalpic interaction parameter χ_h^* can be obtained from the slope of the plot χ_h^* versus $1/T$ from IGC measurements according to its definition^{6–10}

$$\chi_h^* = \frac{[\partial \chi_{12}^* / \partial (1/T)]}{T} \quad (11)$$

According to the equation-of-state theory, χ_h^* is approximated as under the gas chromatographic conditions.

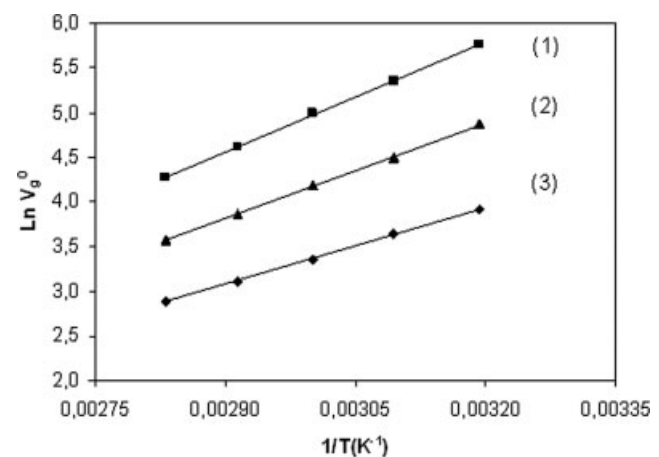


Figure 2 The retention diagram of Hp (1), Hx (2), and P (3) on HMS-013.

TABLE I
Flory–Huggins Polymer–Solvent Interaction Parameters,
 χ_{12}^{∞} with HMS-013

Solvent	T (K)				
	313	323	333	343	353
MA	1.23	1.11	0.98	0.96	0.90
EA	1.00	0.90	0.81	0.82	0.74
tBA	0.76	0.50	0.38	0.41	0.56
P	0.24	0.20	0.19	0.15	0.12
Hx	0.28	0.28	0.24	0.25	0.23
Hp	0.37	0.36	0.32	0.33	0.32

$$\chi_{12}^* = \left(\frac{p_1^* V_1^*}{RT} \right) \left[(v_{1r}^{-1} - v_{2r}^{-1}) + \frac{(\alpha_2 T / v_{2r})(T_{1r} - T_{2r})}{T_{2r}} \right] + \frac{V_1^*(1 + \alpha_2 T)X_{12}}{v_{2r}RT} \quad (12)$$

where X_{12} is the exchange enthalpy parameter.

X_{eff} combines the exchange enthalpy parameter X_{12} and the exchange entropy parameter Q_{12} as follows:

$$X_{\text{eff}} = X_{12} - T v_{2r} Q_{12} \quad (13)$$

The partial molar heat of sorption, $\Delta H_{1,\text{sorp}}$, of the solvent sorbed by the polymer is given as^{14,17}

$$\Delta H_{1,\text{sorp}} = -R \left[\frac{\partial(\ln V_g^0)}{\partial(1/T)} \right] \quad (14)$$

where T is the column temperature (in kelvin) and the partial molar heat of mixing, ΔH_1^{∞} , at infinite dilution of the solvent is given as

$$\Delta H_1^{\infty} = R \left[\frac{\partial(\ln \Omega_1^{\infty})}{\partial(1/T)} \right] \quad (15)$$

where Ω_1^{∞} is the weight fraction activity coefficient of solvent at infinite dilution, defined by the following equation:

$$\ln \Omega_1^{\infty} = \ln \left(\frac{273.2R}{V_g^0 p_1^0 M_1} \right) - p_1^0 \frac{(B_{11} - V_1^0)}{RT} \quad (16)$$

where M_1 is the molecular weight of solvent.

TABLE II
Equation of State Polymer–Solvent Interaction
Parameters, χ_{12}^* , with HMS-013

Solvent	T (K)				
	313	323	333	343	353
MA	1.37	1.27	1.14	1.13	1.09
EA	1.15	1.06	0.97	0.99	0.92
tBA	0.89	0.65	0.53	0.59	0.73
P	0.43	0.39	0.39	0.38	0.36
Hx	0.43	0.44	0.42	0.43	0.43
Hp	0.50	0.49	0.46	0.48	0.48

TABLE III
Effective Exchange Energy Parameters, X_{eff} (J/cm³), of
HMS-013 with Studied Solvents at Various Column
Temperatures

Solvent	T (K)				
	313	323	333	343	353
MA	43.50	38.74	33.13	33.57	32.19
EA	23.43	20.04	16.63	17.95	15.45
tBA	11.74	3.20	-1.51	-0.34	4.22
P	-5.32	-6.39	-7.17	-8.52	-9.37
Hx	-2.46	-2.29	-4.63	-4.08	-5.02
Hp	0.92	0.35	-0.69	-0.37	-0.24

Molar heat of vaporization, ΔH_{v_r} , of the solvent is related to $\Delta H_{1,\text{sorp}}$ and ΔH_1^{∞} as follows:

$$\Delta H_{v_r} = \Delta H_1^{\infty} - \Delta H_{1,\text{sorp}} \quad (17)$$

The solubility parameter of the polymer, δ_2 , is found by combining of the theories Flory–Huggins and Hildebrand–Scathard:¹¹

$$\left[\left(\frac{\delta_1^2}{RT} \right) - \left(\frac{\chi_{12}^{\infty}}{V_1^0} \right) \right] = \left(\frac{2\delta_2}{RT} \right) \delta_1 - \frac{\delta_2^2}{RT} \quad (18)$$

where δ_1 is the solubility parameter of the solvent.

EXPERIMENTAL

Poly(methylhydrosiloxane-*co*-dimethylsiloxane) (HMS-013) was a product of ABCR. Methyl acetate (MA), ethyl acetate (EA), *tert*-butyl acetate (tBA), pentane (P), hexane (Hx), and heptane (Hp) were of analytical reagent grade and used without further purification. The solvents and support material being Chromosorb W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Silane-treated glass wool used to plug the ends of the column was obtained from Alltech Associates. A Hewlett–Packard 5890 model, series II gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents in this study. Data acquisition and analysis were performed by means of HP-3365 software. The column was a stainless steel tubing with 3.2 mm o.d. and 1 m in length. The polymer was coated on the support by slow evaporation of chloroform by stirring the Chromosorb W in the polymer solution.

RESULTS AND DISCUSSION

The specific retention volumes V_g^0 of MA, EA, tBA, P, Hx, and Hp were obtained experimentally from IGC measurements between 40 and 80°C using eq. (1). The percent error in V_g^0 was calculated as less than ± 0.5 by using four or five successive mea-

TABLE IV
Exchange Enthalpy Parameters, X_{12} (J/cm³), of HMS-013 with Studied Solvents at Various Column Temperatures

Solvent	T (K)				
	313	323	333	343	353
MA	115.77	116.70	117.40	114.88	115.22
EA	73.26	74.05	74.76	75.26	75.61
tBA	41.62	42.74	43.77	44.74	45.52
P	24.52	24.83	26.08	27.10	27.86
Hx	6.67	7.20	8.50	8.89	10.02
Hp	8.21	8.71	9.18	9.64	10.02

measurements of each datum. Results are given in Figures 1 and 2, respectively.

The polymer–solvent interaction parameters, χ_{12}^{∞} and χ_{12}^* , were determined from eqs. (2) and (3) between 40 and 80°C and the values of χ_{12}^{∞} and χ_{12}^* are given in Tables I and II, respectively. The apparent standard errors in the values of χ_{12}^{∞} and χ_{12}^* were less than ± 0.01 . The values of χ_{12}^{∞} greater than 0.5 represent unfavorable polymer–solvent interactions while the values lower than 0.5 indicate favorable interactions in dilute polymer solutions.¹⁸ The values of them suggest that MA and EA are poor, and tBA is moderately poor; however P, Hx, and Hp are good solvents for HMS-013.

The effective exchange energy parameters, X_{eff} , in the equation-of-state theory were obtained from eq. (4) and the results are given in Table III. It was determined that X_{eff} of HMS-013 in all solvents is dependent on temperature.

The parameters X_{12} were obtained by means of the eq. (12) using the values of χ_i^* found from slopes of the plots according to eq. (11). Then, parameters Q_{12} were calculated from eq. (13). Results are given in Tables IV and V, respectively. The apparent standard errors calculated are better than ± 1 in the values of X_{12} and Q_{12} . Although the parameters X_{12} and Q_{12} are found to be slightly increased for studied solvents, the temperature dependences of X_{12} and Q_{12} are negligible.

In theory, it was assumed that their magnitude depends on chemical nature of the polymer and sol-

TABLE V
Exchange Entropy Parameters, Q_{12} (10² J/cm³ K⁻¹), of HMS-013 with Studied Solvents at Various Column Temperatures

Solvent	T (K)				
	313	323	333	343	353
MA	19.83	20.64	21.60	20.12	19.89
EA	13.67	14.30	14.88	14.18	14.41
tBA	8.20	8.27	8.51	8.82	8.92
P	8.19	8.27	8.51	8.82	8.92
Hx	2.50	2.51	3.36	3.21	3.60
Hp	2.00	2.21	2.52	2.48	2.46

TABLE VI
Weight Fraction Activity Coefficient at Infinite Dilution of the Solvents, Ω_1^{∞} , with HMS-013

Solvent	T (K)				
	313	323	333	343	353
MA	10.18	9.13	8.08	7.99	7.64
EA	8.42	7.71	7.06	7.19	6.71
tBA	6.71	5.22	4.62	4.88	5.64
P	5.72	5.52	5.54	5.42	5.32
Hx	5.60	5.68	5.51	5.57	5.56
Hp	5.90	5.85	5.68	5.77	5.80

vent and is independent on composition of the mixture. It is expected that the exchange parameters of a polymer with solvents in a homologue series should be close each other. It was found earlier that the magnitudes of the exchange parameters of the poly(dimethylsiloxane) with some solvent system were close^{6–9} to each other, while those of the poly(methylmethacrylate) were not.¹⁰ In this study, the magnitudes of the exchange parameters of poly(methylhydrosilane-co-dimethylsiloxane)–solvent systems are not close to each other, although their chemical natures are similar.

$\Delta H_{1,\text{sorp}}$ and ΔH_1^{∞} were calculated from the slopes of the plots of V_g^0 versus $1/T$ and $\ln \Omega_1^{\infty}$ versus $1/T$ in the temperature range 40–80°C using eqs. (14) and (15), respectively. The weight fraction activity coefficient of solvents at infinite dilution, Ω_1^{∞} , were calculated from eq. (16). Ω_1^{∞} values are given in Table VI.

The values of ΔH_v obtained from eq. (17) were compared to the values of ΔH_v calculated according to the related reference¹⁹ and the results are given in Table VII. It is shown that the agreement is good for the solvents.

The solubility parameter of HMS-013, δ_2 , was determined from the slope and intercept of the plots drawn according to eq. (18). The magnitudes of δ_2 were found by averaging the values obtained from slope and intercept at studied temperatures.^{20,21} δ_2 at room temperature was estimated approximately as 6.64 (cal/cm³)^{1/2} by extrapolating the average values

TABLE VII
Partial Molar Heat of Sorption, $-\Delta H_{1,\text{sorp}}$ (kcal/mol), Partial Molar Heat of Mixing, ΔH_1^{∞} (kcal/mol), Molar Heat of Vaporization, ΔH_v (kcal/mol), Obtained by eq. (8) in the Temperature Range 40–80°C and Molar Heat of Vaporization, ΔH_v^{19} (kcal/mol)

Solvent	$-\Delta H_{1,\text{sorp}}$	ΔH_1^{∞}	ΔH_v	ΔH_v^{19}
MA	5.7	1.6	7.3	7.2
EA	6.8	1.2	8.0	7.7
tBA	7.9	0.97	8.9	8.0
P	5.7	0.36	6.1	6.2
Hx	7.1	0.08	7.2	6.9
Hp	8.1	0.11	8.2	7.6

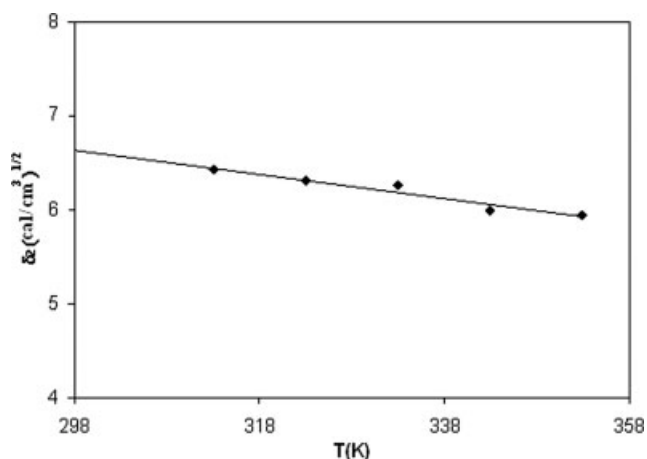


Figure 3 Extrapolation of the solubility parameters of HMS-013, δ_2 , from studied temperatures to 25°C.

of δ_2 obtained at studied temperatures to 25°C in Figure 3.

CONCLUSIONS

This study suggests that studied *n*-alkanes are good solvents and tBA is a moderately good solvent, but EA and MA are nonsolvents for HMS-013 between 40 and 80°C. It is shown that solvent quality of MA, EA, and P increase and Hx and Hp slightly increase with temperature, but it does not almost change in tBA. It was seen that X_{eff} of HMS-013 in all studied solvents are dependent on temperature while the temperature dependences of X_{12} and Q_{12} are negligible. Solubility parameter of HMS-013 was determined to be $6.64 \text{ (cal/cm}^3\text{)}^{1/2}$ at 25°C.

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