

Thermodynamics of Poly(dimethylsiloxane)-Alkane Systems by Gas-Liquid Chromatography

Michal Roth* and Josef Novák

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 61142 Brno, Czechoslovakia. Received May 1, 1985

ABSTRACT: The specific retention volumes of five alkanes with eight poly(dimethylsiloxane) (PDMS) solvents of different mean chain lengths and with Apiezon K were measured at temperatures within 30–95 °C. The infinite-dilution Raoult-law activity coefficients of the alkanes were calculated from the specific retention volumes. From the temperature dependences of the activity coefficients, the partial molar excess thermodynamic functions were derived. The results were compared with the literature data obtained by both chromatographic and static methods.

Introduction

At present, gas-liquid chromatography can be looked upon as a rapid and fairly reliable method for the physicochemical studies of systems of nonelectrolytes of the type nonvolatile solvent-volatile solute.^{1,2} Some of these applications of gas chromatography have been concerned with the thermodynamics of polymeric solvent-low molecular weight solute systems, including poly(dimethylsiloxane) (PDMS)-hydrocarbon systems.³⁻¹¹ In the above-cited papers, the activity coefficients and/or Flory interaction parameters obtained were compared with theoretical calculations^{3,4,7,9,10} or with experimental data measured by static methods,¹¹ or they were used to calculate the partial molar excess thermodynamic functions of the solutes.⁸⁻¹⁰ About 10 years ago, significant differences were reported between activity coefficients measured by chromatographic and static methods⁵ and between activity coefficients measured independently by gas chromatography⁶ in PDMS-hydrocarbon systems. However, a recent straightforward comparison¹¹ of the activity coefficients of hydrocarbons at infinite dilution with PDMS indicated that the above differences apparently were due to artifacts.

PDMS solvents exhibit very low glass transition temperatures and considerable chain mobilities. Therefore, the viscosity of PDMS solvents is markedly lower as compared to hydrocarbons with the same chain length at the same temperature. It is due to these properties, together with good thermal stability, that PDMS solvents have found such a wide application as nonpolar stationary phases in analytical gas chromatography. In the past 25 years, PDMS solvents constituted 25% of all the stationary phases used in the papers quoted in "Gas Chromatography Abstracts".¹² The high frequency of use of PDMS solvents in analytical gas chromatography has led to extensive tabulations of retention data with these phases.^{13,14} The retention behavior of compounds with PDMS solvents, as compared to that with hydrocarbon-based stationary phases, is characterized by certain specific traits that manifest themselves markedly, e.g., when correlating absolute and relative retentions¹⁵ or when comparing different criteria of the polarity of chromatographic stationary phases.¹⁶

In this paper, the results are presented of a gas chromatographic investigation of the thermodynamics of solution of five hydrocarbons in eight PDMS solvents of different mean chain lengths and in Apiezon K. The activity coefficients of the solutes were calculated from the specific retention volumes, and from the temperature dependence of the activity coefficients were derived the partial molar excess thermodynamic functions of the solutes. A simple interpretation of the excess functions is suggested.

Table I
Producers and Number-Average and Weight-Average Molecular Weights of the Solvents

solvent	producer	\bar{M}_{2n}	\bar{M}_{2w}
MS 200	Midland Silicones, Barry, Great Britain	2 410	18 000
SF 96	Hewlett-Packard Co., Avondale, PA	3 480	8 810
DC 200	Packard-Becker B.V., Delft, The Netherlands	3 480	16 600
Lukoil M 500	East Bohemian Chemical Works "Synthesia", Kolín, Czechoslovakia	4 820	28 800
OV 101	Supelco, Inc., Bellefonte, PA	15 100	28 700
DC 200	Hewlett-Packard Co., Avondale, PA	20 700	95 300
JXR	Applied Science Laboratories, Inc., State College, PA	208 000	580 000
SE 30	Carlo Erba, Strumentazione SpA., Milano, Italy	218 000	480 000
Apiezon K	Edwards High Vacuum, Ltd., Crawley, Great Britain	1 210	

Experimental Section

Solutes and Stationary Phases. The solutes (*n*-pentane through *n*-octane and cyclohexane) were from two different producers (Lachema, Brno, Czechoslovakia, and VEB Laborchemie, Apolda, GDR) and were used as received. The stationary phases came from several suppliers (see Table I) and were also used without further treatment to prepare the column packings. The mean molecular weights of the stationary phases are quoted in Table I. In the case of the PDMS solvents the mean molecular weights have been derived from the positions and shapes of the elution curves obtained by size exclusion chromatography, employing the calibration method described by Mandík et al.¹⁷ The measurements were carried out with a GPC 200 chromatograph (Waters Associates, Inc., Milford, MA). The separation took place in toluene in a system of five columns packed with Styragel-type styrene-divinylbenzene gels of different pore diameters. The overall length and i.d. of the columns were 6 m and 9 mm, respectively. The columns were kept at 60 °C, and the toluene flow rate through the measuring part of the instrument was about 1 cm³ min⁻¹. The eluates were detected by a differential refractometer. The number-average molecular weight of Apiezon K was determined by cryoscopy in benzene solutions. The accuracy of both methods of molecular weight determination can be estimated to be ±5%.

Apparatus and Procedures. The gas chromatographic measurements were carried out on a Chrom 5 gas chromatograph (Laboratory apparatus, Prague, Czechoslovakia) equipped with a flame ionization detector and modified so as to yield high-precision retention data. Before entering the column, the nitrogen carrier gas passed through a pressure controller (Model 8286, Porter Instrument Co., Hatfield, PA), a mass-flow controller (Model S7, Chemoprojekt, Satalice, Czechoslovakia), and a homemade capillary flowmeter. The carrier gas flow rate did not exceed 9 cm³ min⁻¹. The column inlet pressure was measured by a mercury U manometer and was not higher than 4 psi above

atmospheric pressure. The specific retention volumes were measured within a temperature range of 30–95 °C in about 5 °C steps.¹⁸ Samples (10 μ L) of a gaseous mixture of the solute vapors with methane were injected. The measurements were repeated three times at each temperature. The scattering of the individual retention volumes did not exceed $\pm 0.5\%$ of the mean value. Glass columns 2.5 m long \times 3 mm i.d. were used in this work. The column temperature was controlled to ± 0.02 °C by means of a water thermostat. The packings were prepared by the slurry method, employing dichloromethane as a volatile solvent and 30/60 mesh Chromosorb G AW as the support. To determine the amount of the stationary phase in the packing, a weighed portion of the packing was extracted with toluene and/or dichloromethane in a Soxhlet extractor to a constant weight (at least 20 h). However, the amount of the stationary liquid in the packing found in this way was invariably lower than that calculated from the weights of the PDMS and the support taken to prepare the packing (cf. ref 11). The discrepancy between the two values increased with increasing chain length of the PDMS solvent, reaching about 8% with high molecular weight PDMS gums. Therefore, the theoretical values were used to calculate the specific retention volumes of the solutes (see Discussion).

Data Reduction. The infinite-dilution Raoult-law activity coefficients of the solutes at zero total pressure were computed from the equation¹⁹

$$\gamma_1^{\infty(0)} = 273.15R / (V_g^\circ P_1^0 \bar{M}_{2n}) \exp[(V_{1L}^\circ - B_{11})P_1^0 / (RT)] \exp[(2B_{13} - \bar{V}_{1L}^\infty)P_0 J_3^4 / (RT)] \quad (1)$$

where R is the gas constant, T the column temperature, V_g° the specific retention volume of the solute, P_1^0 the vapor pressure of the solute, V_{1L}° the molar volume of the pure liquid solute, \bar{V}_{1L}^∞ the infinite-dilution partial molar volume of the solute, B_{11} the second virial coefficient of the solute, and B_{13} the solute-carrier gas second cross-virial coefficient. P_0 denotes the column outlet pressure, which was equal to atmospheric pressure, and J_3^4 is given by²⁰

$$J_3^4 = (3/4)[(P_i/P_0)^4 - 1]/[(P_i/P_0)^3 - 1] \quad (2)$$

where P_i is the column inlet pressure. The quantities P_1^0 , V_{1L}° , B_{11} , and B_{13} were calculated from generalized correlating equations^{21–24} with critical constants from ref 21 and experimental B_{13} data from ref 25. The approximation $\bar{V}_{1L}^\infty \approx V_{1L}^\circ$ was made throughout the calculation.

From the temperature dependences of the activity coefficients the infinite dilution partial molar excess thermodynamic functions of the solutes were deduced according to the relations

$$\Delta \bar{G}_1^{\infty} = RT \ln \gamma_1^{\infty(0)} \quad (3)$$

$$\Delta \bar{H}_1^{\infty} = R \, d \ln \gamma_1^{\infty(0)} / d(1/T) = -RT^2 \, d \ln \gamma_1^{\infty(0)} / dT \quad (4)$$

$$\Delta \bar{S}_1^{\infty} = (R/T) \, d \ln \gamma_1^{\infty(0)} / d(1/T) - R \ln \gamma_1^{\infty(0)} = -RT \, d \ln \gamma_1^{\infty(0)} / dT - R \ln \gamma_1^{\infty(0)} \quad (5)$$

$$\Delta \bar{C}_{P1}^{\infty} = d\Delta \bar{H}_1^{\infty} / dT = -2RT \, d \ln \gamma_1^{\infty(0)} / dT - RT^2 \, d^2 \ln \gamma_1^{\infty(0)} / dT^2 \quad (6)$$

where $\Delta \bar{G}_1^{\infty}$, $\Delta \bar{H}_1^{\infty}$, $\Delta \bar{S}_1^{\infty}$, and $\Delta \bar{C}_{P1}^{\infty}$ denote the infinite-dilution solute partial molar excess Gibbs energy, enthalpy, entropy, and isobaric heat capacity, respectively. It is apparent from eq 4–6 that the excess functions can generally be calculated at several levels of approximation,²⁶ differing from each other by the extent of the temperature dependence attributed a priori to $\Delta \bar{H}_1^{\infty}$, $\Delta \bar{C}_{P1}^{\infty}$, and their temperature derivatives. Because the measurements have been carried out in a rather narrow temperature range (65 °C), the first two levels only are considered here, viz., (a) $\Delta \bar{C}_{P1}^{\infty} = 0$, i.e., $\Delta \bar{H}_1^{\infty}$ and $\Delta \bar{S}_1^{\infty}$ are assumed to be independent of temperature, and (b) $\Delta \bar{C}_{P1}^{\infty} = \text{constant} \neq 0$, i.e., $\Delta \bar{H}_1^{\infty}$ and $\Delta \bar{S}_1^{\infty}$ are dependent on temperature (in this case, the temperature dependence of $\Delta \bar{H}_1^{\infty}$ is linear). At level (a), the plot $\ln \gamma_1^{\infty(0)} - 1/T$ is supposed to be linear, i.e.

$$\ln \gamma_1^{\infty(0)} = k/T + q \quad (7)$$

Then, from eq 4 and 5 we have

$$\Delta \bar{H}_1^{\infty} = Rk \quad (8)$$

$$\Delta \bar{S}_1^{\infty} = -Rq \quad (9)$$

At level (b), the temperature dependence of $\ln \gamma_1^{\infty(0)}$ can be shown to have the form

$$\ln \gamma_1^{\infty(0)} = c \ln T + d/T + e \quad (10)$$

from which we obtain

$$\Delta \bar{C}_{P1}^{\infty} = -Rc \quad (11)$$

$$\Delta \bar{H}_1^{\infty} = Rd - RTc \quad (12)$$

$$\Delta \bar{S}_1^{\infty} = -R(c + e) - Rc \ln T \quad (13)$$

The constants k and q or c , d , and e were obtained by a robust regression analysis of the data sets with eq 7 and 10. For all the solute-solvent pairs, this was accomplished with the method of iteratively reweighted least squares.²⁷

Results and Discussion

Specific Retention Volumes. Rather than presenting an exhaustive list of our V_g° values, we concentrate on the comparison of our results with independent literature data. The specific retention volumes of the alkanes studied with several low- or medium-chain-length PDMS solvents are listed in Table II. A comparison of the respective second cross-virial coefficients²⁵ indicates that, for a given alkane, nitrogen constitutes a better “solvent” than helium at the same temperature. Therefore, our V_g° values, measured with nitrogen carrier gas, should invariably be lower than the literature data obtained with helium carrier gas. Taking account of this, the agreement between the literature data and our results can be considered to be satisfactory. With high molecular weight solvents, discrepancies amounting up to 4% are observed. These are apparently due to the uncertainty in the determination of the amount of the solvent in the column, which is a major source of the experimental error in the determination of V_g° .^{28,29} As it can be seen from eq 1 and 3–6, this kind of error manifests itself in the values of $\gamma_1^{\infty(0)}$, $\Delta \bar{G}_1^{\infty}$, and $\Delta \bar{S}_1^{\infty}$, whereas the values of $\Delta \bar{H}_1^{\infty}$ and $\Delta \bar{C}_{P1}^{\infty}$ as well as the differences between the $\Delta \bar{G}_1^{\infty}$ or $\Delta \bar{S}_1^{\infty}$ values of two solutes with a given solvent remain unimpaired.

One of the plots of $\ln V_g^\circ - 1/T$ is shown in Figure 1. The overall appearance of the plots with the other solvents is the same. With all the solutes studied, the plots are slightly nonlinear; i.e., their slopes are temperature-dependent. It can be proved that

$$[\partial \ln V_g^\circ / \partial (1/T)]_{\bar{P}} = -\Delta H_{\text{cond}}^\circ / R - \Delta \bar{H}_1^{\infty} / R + [\partial \ln \nu_1^\infty / \partial (1/T)]_{\bar{P}} \quad (14)$$

where \bar{P} is the mean column pressure, ν_1^∞ is the fugacity coefficient of the solute in the limit of infinite dilution with the carrier gas, and $\Delta H_{\text{cond}}^\circ$ is the standard enthalpy of condensation of 1 mol of the pure solute from an ideal-gas state at the temperature T to the liquid state at the temperature T and pressure \bar{P} . Generally, all the three right-hand-side terms of eq 14 are temperature-dependent. Therefore, the plot $\ln V_g^\circ - 1/T$ could be strictly linear only if the temperature dependences of the right-hand-side terms compensated each other.

Activity Coefficients. Figures 2 and 3 show the plots of $\ln \gamma_1^{\infty(0)}$ vs. t (°C) with DC 200 (HP) and Apiezon K solvents, respectively. As expected, the scattering of the data points around the regression lines (eq 7) in Figures 2 and 3 is much more pronounced as compared to the respective plots of $\ln V_g^\circ - 1/T$. The significance of the exponentials in eq 1 is illustrated in Figure 4. Table III shows a comparison of our values of infinite-dilution weight-fraction-based activity coefficients at 30 °C with the static and chromatographic data of Ashworth et al.¹¹

Table II
Specific Retention Volumes $V_g^\circ/(\text{cm}^3 \text{g}^{-1})$ of Alkanes with Several Low or Medium Molecular Weight PDMS Solvents

alkane	ref	$t/^\circ\text{C}$				
		40	50	60	70	80
<i>n</i> -pentane	<i>a</i>			24.76		
	<i>b</i>	48.08	35.42	26.57	20.26	15.70
	<i>c</i>	48.24	35.45	26.54	20.25	15.62
	<i>d</i>	46.9	34.3	25.6	20.0	15.3
	<i>e</i>	48.0	34.3	26.0	19.8	15.5
<i>n</i> -hexane	<i>a</i>			60.91		
	<i>b</i>	123.0	85.88	61.30	44.62	33.06
	<i>c</i>	123.2	85.97	61.32	44.60	33.03
	<i>d</i>	121.2	84.1	59.9	44.0	32.9
	<i>e</i>	122.2	84.9	60.6	44.3	33.1
	<i>f</i>	120.8		59.9		32.4
<i>n</i> -heptane	<i>a</i>			144.30		
	<i>b</i>	314.4	208.3	141.4	98.20	69.63
	<i>c</i>	314.6	208.5	141.6	98.45	69.84
	<i>d</i>	307.5	202.3	137.0	96.3	69.1
	<i>e</i>	309.7	204.0	138.8	97.0	69.6
	<i>f</i>			138.1		68.5
<i>n</i> -octane	<i>a</i>			332.14		
	<i>b</i>	803.9	505.0	326.3	216.2	146.6
	<i>c</i>	803.3	505.6	327.2	217.2	147.6
	<i>d</i>	771.2	481.7	310.6	208.9	143.8
	<i>e</i>	776.6	484.2	314.5	210.4	145.0
cyclohexane	<i>a</i>			106.14		
	<i>b</i>	211.8	146.5	103.6	74.74	54.94
	<i>c</i>	213.5	147.3	103.9	74.83	54.89
	<i>d</i>	209.8	144.0	101.4	73.8	54.7
	<i>e</i>	211.6	145.4	102.5	74.3	55.1
	<i>f</i>			101.2		52.9

^aReference 4 (molecular weight of PDMS was 3700). ^bReference 14 (OV 101). ^cReference 14 (SP-2100). ^dThis work, OV 101 (see Table I). ^eThis work, DC 200 HP (see Table I). ^fReference 10 ($M_{2n} = 30\,000$, $M_{2w} = 90\,000$).

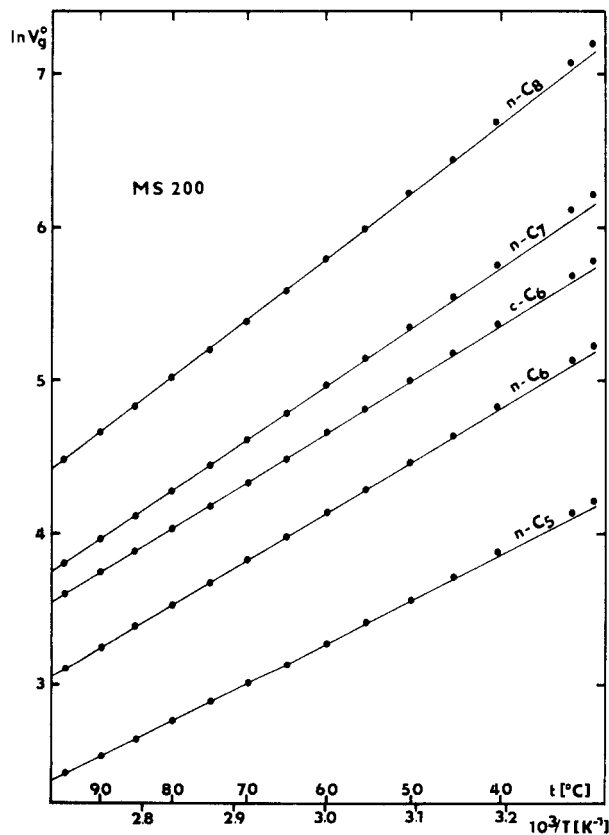


Figure 1. Temperature dependences of the specific retention volumes for the alkane-PDMS (MS 200) systems.

Partial Molar Excess Enthalpies. The values of $\Delta\bar{H}_1^{E\infty}$ were computed according to eq 4, 8, and 12. The extreme sensitivity of $\Delta\bar{H}_1^{E\infty}$ to errors in the temperature derivative of $\ln \gamma_1^{\infty(0)}$ is apparent from eq 4. At 60 $^\circ\text{C}$, the relative error of only 0.03% in the value of $d \ln \gamma_1^{\infty(0)}/dT$

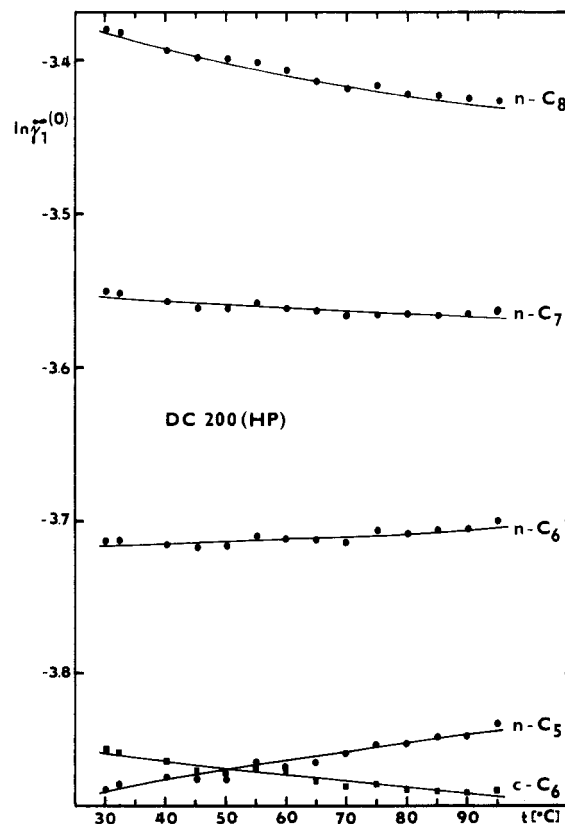


Figure 2. Temperature dependences of the activity coefficients for the alkane-PDMS (DC 200 HP) systems.

brings about an absolute error of 277 J mol⁻¹ in the value of $\Delta\bar{H}_1^{E\infty}$. With PDMS-alkane mixtures, the corresponding relative error amounts up to several tens or even hundreds of percent. Therefore, the calculation of $\Delta\bar{H}_1^{E\infty}$ by this method requires a careful correction³⁰ of the ac-

Table III
Weight-Fraction-Based Infinite-Dilution Activity Coefficients $\Omega_1^{\infty(0)}$ of Alkanes in Three PDMS Solvents at 30 °C

ref	condn	<i>n</i> -C ₅	<i>n</i> -C ₆	<i>n</i> -C ₇	<i>n</i> -C ₈	<i>c</i> -C ₆
Ashworth et al. ^a	static	6.066	6.003	6.109		5.363
	GLC	6.092	6.023	6.135	6.342	5.378
this work ^b	GLC	5.937	5.854	5.927	6.169	5.227
this work ^c	GLC	5.964	5.863	5.920	6.140	5.208

^a Reference 11, $\bar{M}_{2n} = 89\,000$. ^b DC 200 HP, $\bar{M}_{2n} = 20\,700$. ^c JXR, $\bar{M}_{2n} = 208\,000$.

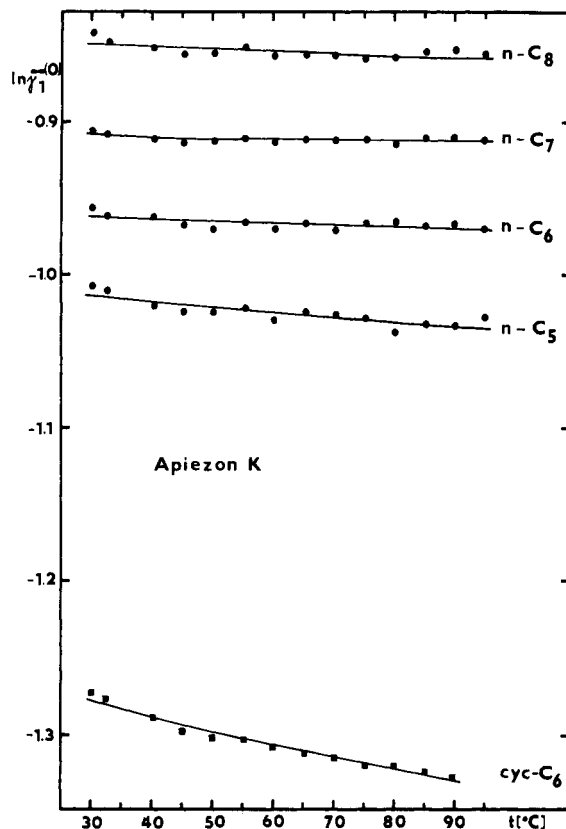


Figure 3. Temperature dependences of the activity coefficients for the alkane-Apiezon K systems.

tivity coefficients for both the nonideal behavior of the gas phase and the influence of pressure on the fugacity of the pure liquid solute and on the activity coefficient of the solute. From Figure 4 it can be seen that omitting the correction may even change the sign of $\Delta\bar{H}_1^{\infty}$. In Table IV, our $\Delta\bar{H}_1^{\infty}$ values (eq 10 and 12) are listed together with independent literature data obtained by gas-liquid chromatography. Our results differ considerably from those of Hammers and de Ligny.⁸ The difference is probably due to different methods of the calculation of the activity coefficients; Hammers and de Ligny dropped the second exponential term of eq 1 and used a different correlating equation for B_{11} .

The dependence of $\Delta\bar{H}_1^{\infty}$ on the mean chain length of the PDMS solvent may be assessed by using the calorimetric heat-of-mixing data on hydrocarbon-low molecular weight PDMS mixtures at 25 and 40 °C measured by Neff et al.³¹ At a constant composition of PDMS-alkane mixture, the heat of mixing decreases with increasing chain length of PDMS. The rate of decrease diminishes rapidly with increasing PDMS chain length, and at $\bar{M}_{2n} \approx 7000$ a constant value of the heat of mixing is attained. A similar tendency is apparent from Table IV. Delmas et al.³² reported calorimetric heat-of-mixing data on several PDMS solvents with C₅ to C₁₆ *n*-alkanes at 24.5 °C and at very low concentrations of PDMS. Except for *n*-pentane, heats of mixing of PDMS with *n*-alkanes were positive and in-

Table IV
Infinite-Dilution Partial Molar Excess Enthalpies $\Delta\bar{H}_1^{\infty}/(\text{J mol}^{-1})$ of Alkanes in PDMS Solvents

alkane	ref	<i>t</i> /°C		
		30	60	90
<i>n</i> -pentane	<i>a</i>	-37	-534	-1031
	<i>b</i>	-127	-478	-829
	<i>c</i>	-112	-607	-1102
	<i>d</i>	-278	-557	-836
	<i>e</i>	-303	-591	-879
	<i>f</i>	-152	-515	-878
<i>n</i> -hexane	<i>a</i>	493	-3	-499
	<i>b</i>	362	-40	-442
	<i>c</i>	328	-107	-542
	<i>d</i>	189	-162	-513
	<i>e</i>	152	-172	-496
	<i>f</i>	179	-112	-403
<i>n</i> -heptane	<i>g</i>		-332	
	<i>a</i>	508	191	-125
	<i>b</i>	563	335	107
	<i>c</i>	674	242	-190
	<i>d</i>	424	199	-26
	<i>e</i>	509	200	-109
<i>n</i> -octane	<i>f</i>	499	277	55
	<i>g</i>		111	
	<i>a</i>	656	384	111
	<i>b</i>	1057	797	536
	<i>c</i>	1122	708	294
	<i>d</i>	941	668	395
	<i>e</i>	929	683	437
	<i>f</i>	907	685	463

^a Reference 8, molecular weight of PDMS was 30 000. ^b This work, MS 200, $\bar{M}_{2n} = 2410$. ^c This work, SF 96, $\bar{M}_{2n} = 3480$. ^d This work, OV 101, $\bar{M}_{2n} = 15\,100$. ^e This work, DC 200 HP, $\bar{M}_2 = 20\,700$. ^f This work, SE 30, $\bar{M}_{2n} = 218\,000$. ^g Calculated from values given in ref 10, $\bar{M}_{2n} = 30\,000$, $\bar{M}_{2w} = 90\,000$.

creased gradually on increasing carbon number of the *n*-alkane. Our results are in accord with this finding, provided the heat of the mixing of PDMS with an alkane has the same sign throughout the composition range.

Partial Molar Excess Entropies. The $\Delta\bar{S}_1^{\infty}$ values computed by eq 9 are listed in Table V. The bracketed numbers indicate the standard deviations obtained by regression analysis.

If the mutual orientation of the molecules in the PDMS-alkane mixtures were entirely random and if no free volume change accompanied the mixing process, the excess entropy of the mixture should follow the Flory-Huggins expression³³ and the infinite-dilution partial molar excess entropy of the alkane should be given by the relation

$$\Delta\bar{S}_1^{\infty} = R[\ln m - (m - 1)/m] \quad (15)$$

The quantity *m* is often approximated by the ratio of the hard-core volumes of the polymer and the low molecular weight component, respectively. According to eq 15, $\Delta\bar{S}_1^{\infty}$ values should decrease systematically from *n*-pentane to *n*-octane with a given solvent. As it can be seen from Table V, this is the case with Apiezon K but not with PDMS solvents. Therefore, with PDMS-alkane mixtures the deviations from the randomness of the mutual position and orientation of the molecules seem to be more pronounced than with Apiezon K-alkane mixtures.

Table V
Infinite-Dilution Partial Molar Excess Entropies $\Delta\bar{S}_1^{E\infty}/(\text{J mol}^{-1} \text{K}^{-1})$ of Alkanes in PDMS Solvents and in Apiezon K^a

solvent	alkane				
	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane	<i>n</i> -octane	cyclohexane
MS 200	12.84 (0.16)	13.00 (0.17)	12.89 (0.11)	13.02 (0.12)	16.02 (0.10)
SF 96	15.85 (0.20)	15.94 (0.19)	15.95 (0.16)	16.17 (0.15)	18.97 (0.20)
DC 200 (Becker)	15.88 (0.08)	16.01 (0.08)	15.99 (0.08)	16.09 (0.13)	19.06 (0.06)
Lukoil M 500	18.62 (0.12)	18.58 (0.10)	18.31 (0.09)	18.25 (0.10)	21.25 (0.12)
OV 101	27.61 (0.09)	27.48 (0.18)	27.49 (0.08)	27.63 (0.10)	30.68 (0.10)
DC 200 (Hewlett-Packard)	30.32 (0.13)	30.34 (0.13)	30.20 (0.11)	30.32 (0.11)	33.38 (0.10)
JXR	49.35 (0.25)	49.37 (0.13)	49.04 (0.11)	49.16 (0.18)	52.13 (0.12)
SE 30	49.78 (0.14)	49.85 (0.10)	49.56 (0.12)	49.59 (0.11)	52.76 (0.14)
Apiezon K	9.44 (0.18)	8.32 (0.13)	7.68 (0.09)	7.39 (0.13)	12.91 (0.06)

^a The standard deviations refer to the scattering of data points around the regression lines only. They reflect neither the uncertainty of the amount of solvent in the column nor that of the gas-phase-imperfection correction.

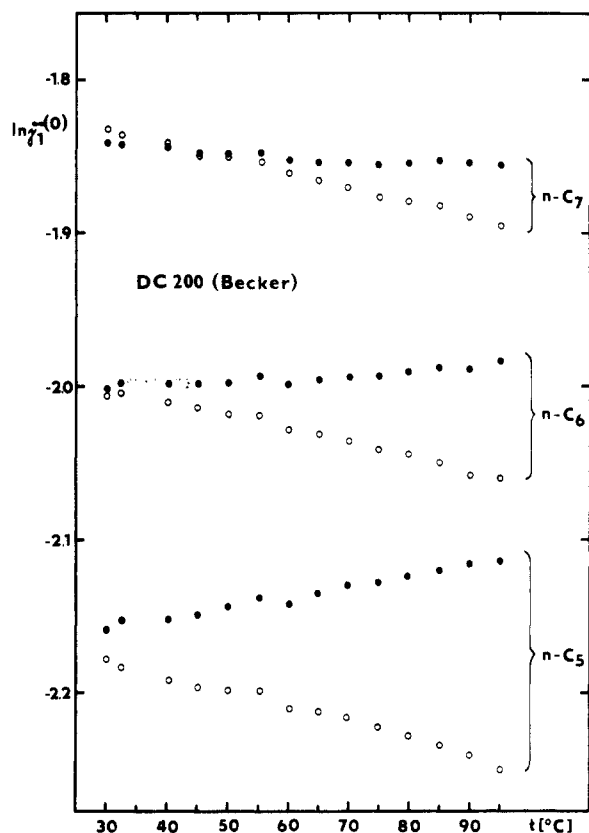


Figure 4. Infinite-dilution activity coefficients in the PDMS (DC 200 Becker) solvent, calculated with (●) and without (○) the exponential terms of eq 1.

Partial Molar Excess Heat Capacities. The $\Delta\bar{C}_{P1}^{E\infty}$ values of alkanes in the PDMS-alkane mixtures were estimated by eq 10 and 11 to fall within the range of -4 to $-20 \text{ J mol}^{-1} \text{K}^{-1}$. In view of the calculation method employed, $\Delta\bar{C}_{P1}^{E\infty}$ values should be treated as very rough estimates subject to relative errors of up to several hundreds of percent. The $\Delta\bar{C}_{P1}^{E\infty}$ values of C_5 - to C_8 *n*-alkanes in PDMS OV 101 (MW 30 000) calculated from the data of Hammers and de Ligny⁸ amount to -16.6 , -16.5 , -10.5 , and $-9.1 \text{ J mol}^{-1} \text{K}^{-1}$, respectively. This compares favorably with our results.

Conclusion

The most significant feature of our thermodynamic data obtained from the gas-liquid chromatographic retention volumes is the fact that the $\Delta\bar{S}_1^{E\infty}$ values in the Apiezon K-alkane mixtures conform to eq 15 while those in the PDMS-alkane mixtures do not. It should be pointed out that the observed pattern of behavior of the $\Delta\bar{S}_1^{E\infty}$ values cannot be due to the uncertainties in the exponential corrections applied when computing the activity coefficients of the solutes (eq 1). This is so because for a given solute the corrections do not depend on the solvent employed.

The classical Flory-Huggins formula for the partial molar combinatorial entropy of the solute (eq 15) thus does not provide a satisfactory description of the partial molar excess entropy of the alkane ($\Delta\bar{S}_1^{E\infty}$) in a PDMS-alkane mixture. Two alternative interpretations of this observation can be devised:

(1) The classical Flory-Huggins formula fails to give a satisfactory description of the combinatorial entropy in the PDMS-alkane mixtures.^{7,34-36}

(2) A significant change of the free volume occurs upon the mixing of a PDMS solvent with an *n*-alkane. This results in a significant residual entropy that manifests itself together with the combinatorial entropy in the experimental value of the excess entropy of the mixture. Our values of the infinite-dilution partial molar excess entropies of the solutes alone do not make it possible to prefer either one of the two interpretations.

The mixing of an *n*-alkane with PDMS becomes more and more endothermic (i.e., energetically unfavorable) on increasing the alkane carbon number. The probable reason for this is that the availability of the methyl groups in a PDMS molecule for interaction with an *n*-alkane decreases on raising the alkane carbon number. This interpretation is in accord with the conclusion of Lichtenthaler et al.⁷ that the surface area of the PDMS molecule available for interaction with the solute decreases on raising the molecular size of the solute.

Acknowledgment. Determination of the molecular weights of the PDMS solvents by Dr. Lumír Mandík (Research Institute of Synthetic Resins and Lacquers, Pardubice, Czechoslovakia) is gratefully acknowledged.

Registry No. *n*-Pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; cyclohexane, 110-82-7.

References and Notes

- Laub, R. J.; Pecsok, R. L. "Physicochemical Applications of Gas Chromatography"; Wiley-Interscience: New York, 1978.
- Conder, J. R.; Young, C. L. "Physicochemical Measurement by Gas Chromatography"; Wiley: Chichester, England, 1979.
- Summers, W. R.; Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 12.
- Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
- Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Macromolecules* **1974**, *7*, 565.
- Lichtenthaler, R. N.; Prausnitz, J. M.; Su, C. S.; Schreiber, H. P.; Patterson, D. *Macromolecules* **1974**, *7*, 136.
- Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Ber. Bunsen-Ges. Phys. Chem.* **1974**, *78*, 470.
- Hammers, W. E.; de Ligny, C. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2065.
- Hammers, W. E.; Bos, B. C.; Vaas, L. H.; Loomans, Y. J. W. A.; de Ligny, C. L. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 401.

- (10) Galin, M. *Macromolecules* 1977, 10, 1239.
- (11) Ashworth, A. J.; Chien, C.-F.; Furio, D. L.; Hooker, D. M.; Kopečni, M. M.; Laub, R. J.; Price, G. J. *Macromolecules* 1984, 17, 1090.
- (12) Haken, J. K. *J. Chromatogr.* 1984, 300, 1.
- (13) Chien, C.-F.; Kopečni, M. M.; Laub, R. J. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* 1981, 4, 539.
- (14) Chien, C.-F.; Furio, D. L.; Kopečni, M. M.; Laub, R. J. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* 1983, 6, 577.
- (15) Rohrschneider, L. *J. Chromatogr. Sci.* 1970, 8, 105.
- (16) Roth, M.; Novák, J. *J. Chromatogr.* 1982, 234, 337.
- (17) Mandík, L.; Foksová, A.; Foltýn, J. *J. Appl. Polym. Sci.* 1979, 24, 395.
- (18) After completing each run, replicate measurement at 30 °C was performed to check the significance of the bleeding of solvent from the column. With all the solvents studied, bleeding proved to be negligible.
- (19) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. *Proc. R. Soc. London, Ser. A* 1966, 295, 259.
- (20) Everett, D. H. *Trans. Faraday Soc.* 1965, 61, 1637.
- (21) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977; Appendix A, pp 629-665.
- (22) Spencer, C. F.; Adler, S. B. *J. Chem. Eng. Data* 1978, 23, 82.
- (23) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* 1975, 14, 209.
- (24) Tsonopoulos, C. *AIChE J.* 1974, 20, 263.
- (25) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Pure Gases and Mixtures. A Critical Compilation"; Clarendon Press: Oxford, England, 1980.
- (26) Clarke, E. C. W.; Glew, D. N. *Trans. Faraday Soc.* 1966, 62, 539.
- (27) Phillips, G. R.; Eyring, E. M. *Anal. Chem.* 1983, 55, 1134.
- (28) Wičarová, O.; Novák, J.; Janák, J. *J. Chromatogr.* 1970, 51, 3.
- (29) Laub, R. J.; Purnell, J. H.; Williams, P. S.; Harbison, M. W. P.; Martire, D. E. *J. Chromatogr.* 1978, 155, 233.
- (30) Wičarová, O.; Novák, J.; Janák, J. *J. Chromatogr.* 1972, 65, 241.
- (31) Neff, B.; Heintz, A.; Lichtenthaler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* 1983, 87, 1165.
- (32) Delmas, G.; Patterson, D.; Boehme, D. *Trans. Faraday Soc.* 1962, 58, 2116.
- (33) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969; p 293.
- (34) Lichtenthaler, R. N.; Abrams, D. S.; Prausnitz, J. M. *Can. J. Chem.* 1973, 51, 3071.
- (35) Heintz, A.; Neff, B.; Lichtenthaler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* 1983, 87, 1169.
- (36) Dolch, E.; Glaser, M.; Heintz, A.; Wagner, H.; Lichtenthaler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* 1984, 88, 479.

Determination of Binodal Compositions of Poly(methyl methacrylate)/Sulfolane Solutions with Pulsed-NMR Techniques

Gerard T. Caneba and David S. Soong*

*Department of Chemical Engineering, University of California, Berkeley, California 94720.
Received May 7, 1985*

ABSTRACT: Binodal compositions of a poly(methyl methacrylate)/sulfolane system have been determined with spin-lattice relaxation of ^{13}C nuclei. Relaxation data obtained from inversion-recovery experiments are fitted with a modified Bloch equation to isolate distribution coefficients and spin-lattice relaxation time constants of ^{13}C nuclei of the polymer and solvent in polymer-rich and solvent-rich phases. Binodal compositions as a function of temperature are then computed from the overall composition of the starting binary polymer solution and the distribution coefficients.

Introduction

Current techniques for the determination of binodal compositions of polymer solutions include cloud point¹⁻⁴ and sedimentation⁵ experiments. These methods have certain built-in disadvantages. Cloud point experiments require different samples for each point in the binodal curve; concentrated polymer samples take a very long time to equilibrate. As for sedimentation techniques, the main drawback is that phases in equilibrium need to be separated for subsequent analysis. Although all of the above-mentioned techniques have been successfully applied, they require a substantial amount of time and effort.

Pulsed-NMR techniques offer a potential solution to overcome the above difficulties in obtaining binodal compositions for polymer solutions. Experiments are done on samples in their mixed state; i.e., there is no need to separate the phases in equilibrium. Only one sample is needed to completely delineate the binodal curve if its overall composition is properly chosen. Magnetic field and/or radio-frequency perturbation are applied to alter the magnetic moments of certain nuclei in the mixed sample. When these perturbations are suddenly removed, the magnetic state of the affected nuclei will return to its unperturbed state with relaxation times that depend on the surrounding magnetic forces. If only two phases coexist, exactly two relaxation times can be resolved from the signal of a given type of nuclei. Certain perturbations or pulse sequences can be designed to maximize detection sensitivity by capitalizing on the differences in relaxation

times for the same nuclei in different phases. This superposition in relaxation processes has been shown to be accurate for polymer-polymer systems.^{6,7} In fact, the use of relaxation processes allows the analysis of a mixed system with overall compositions inside the phase envelope. Thus, compositions in the concentrated polymer phase are obtained from a system with a lower starting polymer concentration, greatly simplifying sample preparation.

In this work, we use the spin-lattice relaxation process to infer binodal compositions for a poly(methyl methacrylate)/sulfolane system. This is accomplished by using one sample for the entire procedure—one with an overall composition close to the critical or Θ point. This procedure is attempted in light of the successful use of spin-lattice and spin-spin relaxation by Kwei and his co-workers^{6,7} for obtaining phase diagrams of polymer-polymer systems. We have hereby extended their methods to polymer/solvent systems, particularly in the case where the solvent is viscous enough to cause significant difficulties with conventional phase diagram determination technique. Reasonable results have been obtained for relaxation of ^{13}C nuclei in the polymer and solvent without magic-angle spinning.⁸

Theory

NMR spectroscopy⁸ is based on the absorption of electromagnetic energy by nuclei at discrete frequencies or energy levels. Upon removal of the applied field, the nu-