# SOLUTION PROPERTIES OF POLY(DIMETHYLSILOXANES) IN TOLUENE

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*Abstract:* A commercial sample of liquid poly(dimethylsiloxanes) [PDMS] was fractionated, yielding five fractions of $M_n$ ranging from 480 to 1130 g/mol and of $M_w$ ranging from 500 to 1175 g/mol. The fractions were dissolved in toluene and characterized by vapour pressure osmometry, viscometry, differential refractometer and light scattering. Light scattering and vapour pressure measurements reveal that the fractions are monodisperse. The viscosity measurements along with vapour pressure osmometer and light scattering give the Mark-Houwink constants in toluene at 25 °C as $\nu = 1.01$ and $K' = 1.35 \times 10^{-3}$. Others parameters, e.g. second virial coefficient, radius of gyration, unperturbed dimension, density, refractive index, coefficient of isothermal compressibility, light scattering depolarization ratio and Rayleigh ratio have also been evaluated at different temperatures.

Keywords: Poly(dimethylsilohexanes) solution, Intrinsic viscosity, Mark-Houwink constants, Second virial coefficient

## INTRODUCTION

Light Scattering techniques are among the methods available for investigating polymer characterization [1,2,5]. It was used to investigated the characterization of poly(dimethylsiloxanes),PDMS solutions. With the aim of investigating the compatibility of poly(dimethyl siloxanes) and other polymer, poly(dimethylsiloxanes) solution in toluene were used as model systems for characterization studies [8].

## EXPERIMENTAL

### *Materials*

Poly(dimethylsiloxanes), PDMS was a Dow Corning fluid DC200/5 of nominal bulk viscosity 5 centistokes, which possesses trimethylsilyl end-group, viz:

$$(CH_3)_3\text{-Si-O}\text{—}[\text{— Si}(CH_3)_2\text{-O —}]_n\text{—Si}(CH_3)_3$$

Separation into five fractions (A,B,C,D,and E) was effected by vacuum distilllation (1-1.5 mm Hg), the distillate within discrete temperature intervals being collected at ~1 $cm^3$ $min^{-1}$.

Toluene was dried with anhydrous $MgSO_4$ and distilled at atmospheric pressure. The boiling point, refractive index (25°C, $\lambda_o$ = 436 nm) and density (25 °C) were 110 °C. 1.5152 and 0.8623 g $cm^{-3}$, respectively.

### *Refractive Index, $\tilde{n}$*

Refractive indices of all samples were measured with a Pulfrich refractometer at wavelength in vacuo, $\lambda_o$= 436 nm and temperatures of 25 °C, 35 °C and 50 °C were used. For a particular composition, linearity between refractive index and temperature allowed interpolation to additional temperature of 70 °C.

*Refractive Increment, $d\tilde{n}/dc_2$*

A differential refractometer accommodates a pair of liquids differing in refractive index by not more than ~0.01. Consequently, it is suitable for a solvent/dilute solution pair in order to obtain $(d\tilde{n}/dc)_{c2\rightarrow 0}$. However, we are concerned here and in future work on these systems with whole composition range. Moreover, the refractive index, ñ of PDMS is much smaller than that of toluene. Hence, it proved much more convenient to derive dñ/dc from directly measured refractive indices of solution, covering the whole range of composition. The refractive index of the solution was fitted to polynomial in composition, c. At fixed temperature, the best fit of experimental data was one of the second degree invoking concentration c (mass/volume), and in accord with

$$\tilde{n} = a + bc_2 + e\,c_2^2 \qquad (1)$$

Thus enabling $d\tilde{n}/dc_2$ to be calculated at any particular concentration, $c_2$. Where a, b, and e are the constant for polynomial and reported elsewhere [7].

*Intrinsic Viscosity, $[\eta]$*

Values of $[\eta]$ for A,B, C, D, and E were determined in toluene at 25 °C in Ubbelohde suspended level viscometer. Because of the low molecular weights, the concentration used were rather high, viz.~0.08 g $cm^{-3}$ to 0.20 g $cm^{-3}$. Good agreement was obtained by extrapolations according to the Huggins and Kreamer equations (7)

*Vapor Pressure Osmometry*

Values of number average molecular weight, $M_n$ of all samples were determined in toluene at 55 °C with a Hitachi-perkin Elmer vapour pressure osmometer using concentrations up to ~26g $(kg\ solvent)^{-1}$.

*Light Scattering*

Light scattering experiments were performed with a Sofica photometer (Model 42000) calibrated with the makers glass standard in conjunction with the total Rayleigh ratio of benzene, $R_B$ at different temperature T(K). The following dependence of $R_B$ on T was employed [9]

$$R_B\,(cm^{-1}) = 10^{-6}\,\{45.4 + 0.109\,(T - 273)\} \qquad (2)$$

Scattering at an angle of 90 °C was measured with unpolarized incident light ($\lambda_o$ = 436 nm). The light scattering depolarisation ratio, $\sigma_u$ (denoted thus rather than by the more customary $\rho_u$ to avoid confusion with density ρ) was measured from the ratio horizontal: vertical components of the incident light.

Temperatures were controlled by circulating water from an external thermostat and the internal thermostat of the instrument. Solutions and solvent were clarified by filtrations (usually three times) at room temperature through a very fine porosity glass sinter filter.

With regard to the total Rayleigh ratio, $R_T$ values were obtained via

$$R_T = (R_B \times 1.19I/I_G)(\tilde{n}/\tilde{n}_B)^2 \qquad (3)$$

Where I and $I_G$ are the digital voltmeter readings for the substance and glass standard, respectively, ñ and $\tilde{n}_B$ are the refractive indices of substance and benzene respectively, and the factor 1.19 is the glass standard calibration factor with respect to benzene [7].

The isotropic Rayleigh ratio, $R_{iso}$ is given by:

$$R_{iso} = R_T\,(6 - 7\sigma_u)/(6 + 6\sigma_u) \qquad (4)$$

The density fluctuation scattering, $R_d$ in pure liquid as well as in a mixture is given by

$$R_d = (\pi^2/2\lambda_o^4)kT\beta[\rho(\delta\varepsilon/\delta\rho)_T]^2 \qquad (5)$$

Where $\lambda_0$ is the wavelength in vacuo, k is Boltzmann constant, $\varepsilon$ is the optical dielectric constant ($= \tilde{n}^2$) and $\beta$ is the coefficient of isothermal compressibility. With regard to the factor $\rho(\delta\varepsilon/\delta\rho)_T$ in equation (5), We have used the following Eykman expression [7].

$$\rho(\delta\varepsilon/\delta\rho)_T = \{2\tilde{n}(\tilde{n}^2 - 1)(\tilde{n} - 0.8)\}/\{\tilde{n}^2 + 0.4\tilde{n} + 1\} \qquad (6)$$

For a pure liquid $R_d \equiv R_{iso}$ and combination of equations (5) and (6) yield $\beta$.

## RESULTS AND DISCUSSIONS

### *Coefficient of Isothermal Compressibility, $\beta$*

The values of coefficient of isothermal compressibility, $\beta$ of the solutions were obtained from the values for the pure PDMS and toluene [6, 7] using equation (7), in which X and V denote mol fraction and molar volume respectively;

$$\beta = (1/V)\{(\beta_1 V_1 X_1) + (\beta_2 V_2 X_2)\} \qquad (7)$$

### *Weight Aerage Molecular Weights, $M_w$*

The values of $M_w$ in Table 1 and 2 were obtained from equation (8) in which $M_w$ is denoted by $M_2$:

$$(Kc_2/R_c) = (1/M_2) + 2A_2 c_2 + 3A_3 c_2^2 \qquad (8)$$

Here $A_2$ and $A_3$ are the second and third virial coefficients. The factor K is a constant that varies with concentration. Its values were calculated from;

$$K = \{2\pi^2/(N_A \lambda_o^4)\}\{(\tilde{n})(d\tilde{n}/dc_2)\}^2_{T,P} \qquad (9)$$

Here $N_A$ is the Avogadro number and $\tilde{n}$ is the refractive index of the solutions. The concentration fluctuation Rayleigh ratio $R_c$ was obtained from

$$R_c = R_{iso} - R_d(1 + 4Y) \qquad (10)$$

$R_{iso}$ for a solution was calculated from equations (4). The density fluctuation Rayleigh ratio $R_d$ was obtained by calculation via equations (5), (6), and (7).Use of the Eykmann equation (Equation (6)) enabled Y to be calculated

$$Y = \{c_2\, \tilde{n}(d\tilde{n}/dc_2)_{T,P}\}/\{\rho(\delta\varepsilon/\delta\rho)_T\} \qquad (11)$$

The second and third virial coefficients are interrelated by;

$$(A_3)/(A_2^2 M_2) = (1/3) \qquad (12)$$

Binomial expansion of Equation (8) gives;

$$(Kc_2/R_c)^{1/2} = (1/M_2)^{1/2}\{1 + M_2 A_2 c_2 + \{(3/2)A_3 M_2 - (1/2)A_2^2 M_2^2\}c_2 + \ldots\ldots\}(13)$$

and truncation at squared and higher powers of c reduces Equation (13) to Equation (14). Empirically, such square root plots are considered to be sensibly linear up to higher concentrations than Equation (8) and hence may permit a better means of estimating $M_2$ and $A_2$. A plot of the left-hand side of Equation (13) versus c should be linear, with intercept = $(1/M_2)^{1/2}$ and (slope x intercept) = $A_2$.

$$(Kc_2/R_c)^{1/2} = (1/M_2)^{1/2}[1 + 2M_2 A_2 c_2] \qquad (14)$$

We have examined this possibility with regard to solutions of five PDMS samples, each at three different temperatures. *Figure 1*, curves A and B, display a similar behaviour over the whole composition range for both types of plot. The linear regions are shown on larger scale in *Figure 2a* and *2b*. It is seen that $M_2$ and $A_2$ can be evaluated from data relating to concentrations not exceeding ~0.2 g cm$^{-3}$. This approximate limiting concentration applies to all the samples, i.e. it is not dependent on the molecular weight of the PDMS for the range of $M_2$ studied. Consistency of the molecular weights is evident by the fact that plots at different temperatures yielded a common intercept. Thus, for samples B at 25 °C, 50 °C, and 70 °C, the plots yielded $M_2$= 610, 608 and 609 respectively. Plots covering the linear region according to equations (8) and (13) afforded values of $A_2$ differing by no more than 0.5%. The data are listed in Table 1.

*Intrinsic Viscosity, [η]*

The variation of intrinsic viscosity with weight average molecular weight for PDMS fractions in toluene at 25 °C is shown in *Figure* 3, from which the Mark-Houwink relationship is derived as;

$$[\eta]\ (\text{cm}^3\ \text{g}^{-1}) = 1.35 \times 10^{-3}\ M_w^{1.01} \tag{15}$$

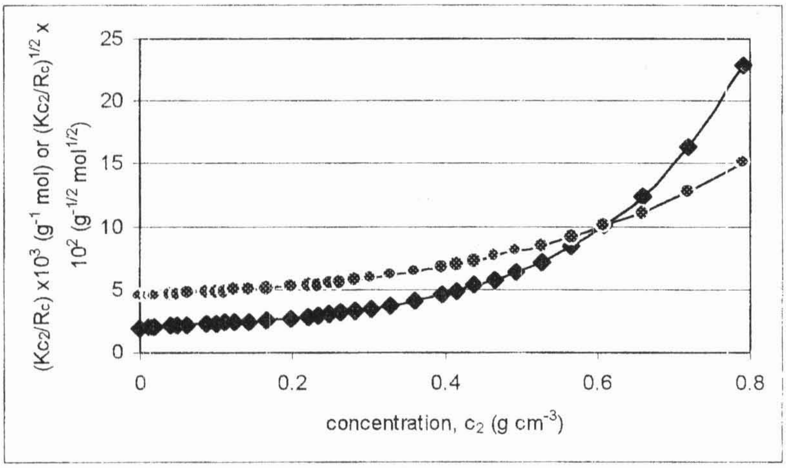

Figure 1: Reduced light scattering versus concentration, $c_2$ for fraction A dissolved in toluene at 50 °C

Plot A = ◆ = normal plot according to Equation (8); Plot B = ● = square root plot according to equation (13).

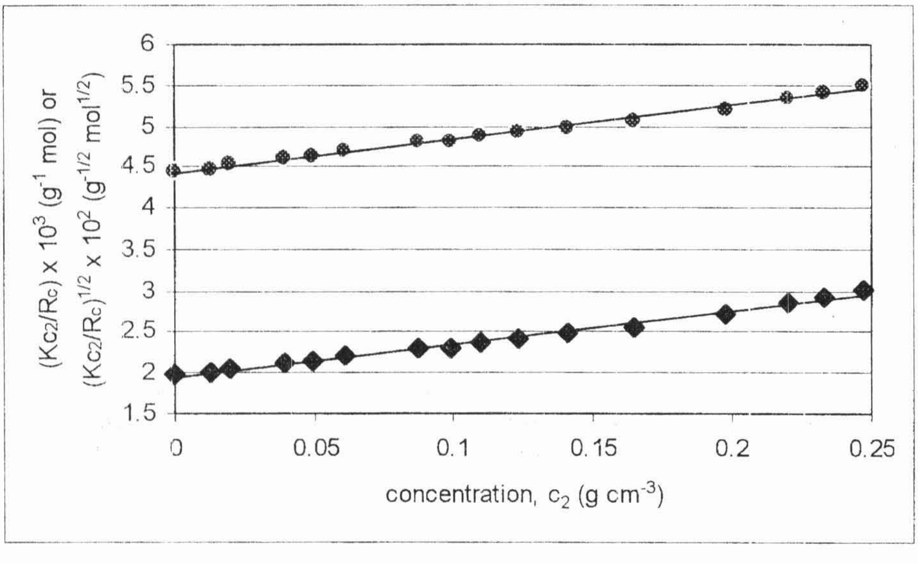

Figure 2: Plot a = ◆ = dilute region of *Figure 1*, curve A; Plot b = ● = dilute region of *Figure 1*, curve B

Table 1: Second virial coefficients of PDMS solutions in toluene

| PDMS fractions | Temperature (K) | $M_w$ (g mol$^{-1}$) | | | | $M_n$ (g mol$^{-1}$) | $A_2$ x $10^3$ (cm$^3$ g$^{-2}$ mol) |
|---|---|---|---|---|---|---|---|
| | | Eq (8); if Y=0 | Eq(8) | Eq(13) | Average | | |
| A | 298 | 487 | 504 | 506 | 500 | 481 | 1.68 |
| | 323 | 479 | 507 | 506 | | | 1.94 |
| | 343 | 475 | 504 | 502 | | | 2.05 |
| B | 298 | 590 | 612 | 610 | 606 | 598 | 1.62 |
| | 323 | 583 | 608 | 608 | | | 1.89 |
| | 343 | 593 | 614 | 609 | | | 1.97 |
| C | 298 | 695 | 718 | 717 | 714 | 677 | 1.55 |
| | 323 | 682 | 712 | 710 | | | 1.75 |
| | 343 | 691 | 716 | 714 | | | 1.87 |
| D | 298 | 910 | 926 | 938 | 930 | 893 | 1.40 |
| | 323 | 906 | 927 | 917 | | | 1.66 |
| | 343 | 893 | 926 | 917 | | | 1.83 |
| E | 298 | 1156 | 1180 | 1173 | 1176 | 1132 | 1.37 |
| | 323 | 1155 | 1182 | 1183 | | | 1.58 |
| | 343 | 1173 | 1174 | 1177 | | | 1.72 |

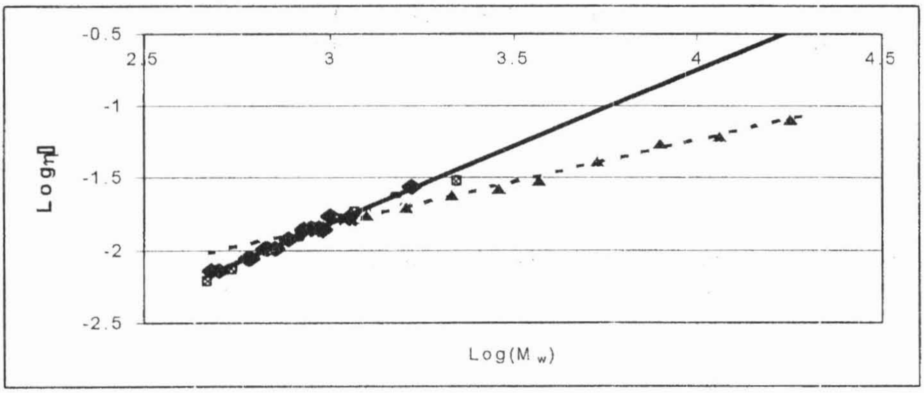

Figure 3: Dependence of [η] on $M$ for PDMS in toluene at 25 °C

◆- present data; ▨ - Barry , 1946; ▲ - Kuntman and Yilmaz, 1995.

Table 2 gives the boiling point range over which the fractions were collected, number average molecular weight, $M_n$ (via vapour pressure osmometry), weight average molecular weight, $M_w$ (via light scattering), polydispersity index and intrinsic viscosities, [η].

Table 2: Molecular characteristics of PDMS fractions

| PDMS Fraction | b.p. at 1 mm Hg pressure (°C) | Yield (% volume of original) | $M_w$ (g/mol) | $M_n$ (g/mol) | Polydispersity index | [η] (cm$^3$ g$^{-1}$) |
|---|---|---|---|---|---|---|
| A | 60-120 | 20.0 | 500 | 481 | 1.040 | 0.723 |
| B | 120-140 | 22.5 | 606 | 598 | 1.013 | 0.871 |
| C | 140-170 | 25.0 | 714 | 677 | 1.055 | 1.02 |
| D | 170-200 | 17.0 | 930 | 893 | 1.041 | 1.40 |
| E | 200-270 | 15.0 | 1176 | 1132 | 1.039 | 1.66 |

### *Refractie Index Increment, dñ/dc₂*

We have varified that dñ/$dc_2$ at $c_2 = 0$, obtained by differentiation of the polynomial in $c_2$, agrees well with the value obtained by using experimental values of ñ at different concentrations and taking the value of Δñ/$c_2 = 0$ in the corresponding linear plot. Values of dñ/$dc_2$ versus $(1/M_n)$ thus yield at each T the refractive index increments in the limit of $c_2 = 0$ and $(1/M_n) = 0$. The temperature coefficient of these is found to be 5.26 x $10^{-5}$ $cm^3g^{-1}deg^{-1}$ as compared to the liturature value of 9.5 x $10^{-5}$ $cm^3$ $g^{-1}deg^{-1}$ found for high molecular weight polymer.

### *Intrinsic Viscosity/Molecular Weight Relationship*

In view of the near monodispersity of the samples, the Mark-Houwink constant on the basis of $M_n$ are practically the same as those already presented in equation (15) which related to $M_w$. The data of Barry (1946) also give an exponent $\nu = 1.0$ within the molecular weight region of 458 to 840, but a falls to 0.66 at high molecular weight. The reported value of $\nu = 0.50$ under the same conditions for low molecular weight PDMS constitute an exceptional finding for this polymer.

We have reported previously [3] that $\nu = 0.50$ for oligomeric nylon-6, a higher value of a holding for medium to high molecular weight polymer. In other systems a normal (0.7 – 0.8) value of ν extends down even to low molecular weights. Hence the contention that oligomers in good solvents behave as if they were under θ - condition (i.e. $\nu = 0.50$) does not seem to be of universal applicability. In particular, the present oligomeric PDMS is unusual in that in the low molecular weight region ν increases to a high value (1.01) rather than exhibiting a change to low value (0.50). This high value of ν lends support to the view that oligo-PDMS is helical. Although this view is based on light scattering plots indicative of association, our present light scattering data actually give no indication of association. A rod like form for oligo-PDMS is an unverified assumption, which has been adopted in Corresponding States Theory calculations.

### *Second Virial Coefficient, $A_2$*

The dependence of $A_2$ on $M_w$ for PDMS solutions in toluene at 25 °C is shown in *Figure 4*. The four literature values included do not exhibit alone any regular dependence among them, but one of the values relating to a sample of $M_w$= 3.53 x $10^5$ has an $A_2$ value which agrees well with that interpolated from the present data for oligomers. The present data at three different temperatures may be represented as:

$$A_2 \propto M_w^{\gamma} \qquad (16)$$

The value of γ are found to be – 0.25, - 0.22, and – 0.20 at 25 °C, 50 °C, and 70 °C respectively and are unchanged, when the dependence is expressed in terms of $M_n$. As seen in Table 1, $A_2$ increases with T at any fixed molecular weight. The system are thus above the upper critical solution temperature, but are not yet approaching the lower critical solution temperature, since $A_2$ would decrease with T if the latter were the situation.

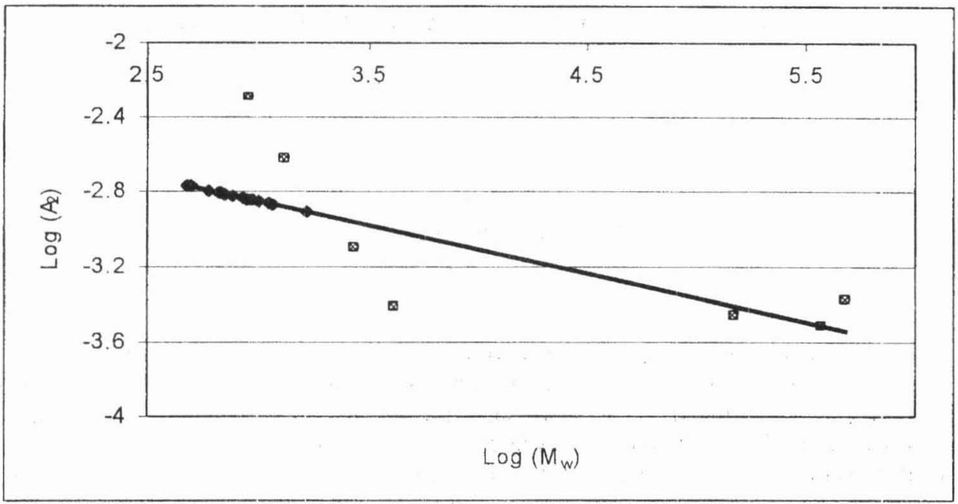

Figure 4. Dependence of $A_2$ on $M_w$ for PDMS fractions in toluene at 25 °C.
◆-present data; ■ - Kuntman and Yilmaz, 1995.

At a particular temperature, any enhancement of polymer-polymer interaction must occur at the expense of reduced polymer-solvent contacts. Since the letter are reflected in the magnitude of $A_2$, the increased polymer-polymer interaction associated with increasing chain length of polymer, causes a reduction in $A_2$ and a resultant negative value of $\gamma$ in equation (16).

The three quoted values of $\gamma$ show that the fall in $A_2$ with $M_w$ is less pronounced at high temperature than at a lower temperature. Qualitatively, this is explicable as follows. At a fixed temperature, $\gamma$ manifests the decrease in polymer-solvent interaction accompanying an increase in $M_w$. At a high temperature this decrease, whilst still obtaining, is less marked, because it is offset partially by the effect of temperature in increasing independently polymer – solvent interaction. Consequently, the value of $-\gamma$ at 70 °C is less than that at 25 °C. Accordingly, one would predict that at temperature approaching the upper critical solution temperature the reverse situation could hold with regard to the change in $\gamma$.

## REFERENCES

1. Ghazy, R., El-Baradie, B., El-Shaer, A., and El-Mekawey, F.1999. *Optic & Laser Technology. 31 (6)*, 447

2. Huglin, M.B. 1972. *Light scattering from polymer solution.* Acadamic press. London.

3. Huglin, M. B. and Maimunah Sokro. 1980. *Polymer*, **21** (6):651

4. Kuntman, A. and Yilmaz, F. 1995. *Polymer,* **36** (10), 2107

5. Lee, E.C. and Muller, S.J. 1999. *Polymer,* **40** (10): 2501

6. Maimunah Sokro. 2003. SKAM – 16. 99

7. Maimunah Sokro. 1980. *Compatibility studies on oligomeric poly (dimethylsiloxanes).* Unpublished doctoral thesis. University of Salford. United Kingdom.

8. Roovers, J. 1979. *Polymer,* **20**: 843

9. Scornaux, J and Van Leemput, P. 1976. *Makromol. Chem,* **177**: 2721