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Tejraj M. Aminabhavi^a

^a Department of Chemistry, Karnatak University, Dharwad, India

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Concentration Dependence of Translational Diffusion Coefficient of Polystyrene in Toluene Using an Ultracentrifuge

TEJRAJ M. AMINABHAVI

Department of Chemistry
Karnatak University
Dharwad, 580003, India

ABSTRACT

The concentration dependence of translational diffusion coefficient D of a narrow fraction polystyrene in toluene has been studied using an ultracentrifuge at 25°C. Over a somewhat broader range of concentrations, a linear dependence of D with concentration was observed. Further, from the experimental results, an attempt was made to assess the magnitude of the hydrodynamic interaction parameter K_D .

INTRODUCTION

Of late, the analytical ultracentrifuge has emerged as a versatile tool for studying the nonequilibrium properties of dilute polymer solutions, micelles, and solvent mixtures [1-5]. In this paper as a part of an ongoing research program, we report the results of the translational diffusion coefficients D of a narrow fraction polystyrene in toluene at 25°C using an ultracentrifuge. The values of D were obtained from spreading the boundary between two polymer solutions in a synthetic boundary cell of the centrifuge.

EXPERIMENTAL

A Beckman Model E analytical ultracentrifuge with the schlieren optical system and the heavy rotor ANJ at 4900 rpm was employed. The boundary between two solutions was formed in a 12-mm aluminum-filled Epon capillary type double sector synthetic boundary cell with quartz windows. For each experiment the concentration difference across the boundary was maintained around 0.005 g/cm^3 . The values of D were evaluated from the maximum height-area method following well-established procedures [6]. As is customary for synthetic boundary cells [7], the diffusion coefficient refers to the mean concentration, $\bar{C} = (C_1 + C_2)/2$, of two solutions of the initial concentrations C_1 and C_2 .

A polystyrene sample was obtained from Pressure Chemical Co., Pittsburgh, Pennsylvania, and was characterized by $\bar{M}_w = 111,000$ as received. The solvent toluene was of reagent grade and was further purified by fractionating through a 5-ft column. Polymer solutions were made in special weighing stoppered bottles and agitated for at least 2 h before use.

RESULTS AND DISCUSSION

Table 1 and Fig. 1 contain the results of our measurements of D for polystyrene in toluene. Over a broad range of concentrations there is almost a perfect linear dependency of D with concentration C . The concentration dependence of D is frequently expressed by [8]

$$D = D_0(1 + K_D C + \dots) \quad (1)$$

where D_0 is the diffusion coefficient at infinite dilution, and K_D is the hydrodynamic interaction parameter. From a least-squares analysis of the data, the values of D_0 and K_D were obtained and are presented in Table 1.

Very recently, Roots and Nystrom [9] measured D for the same system employing photon correlation spectroscopy. These measurements were done at varying pressures and the concentration range covered was up to 0.02 g/cm^3 . As suggested by Roots and Nystrom, assuming that the pressure on the boundary in a centrifuge experiment may amount to about 50 atm, our values of D are in reasonable agreement with those of Roots and Nystrom [9] at 1 atm.

According to thermodynamics of irreversible processes [8], K_D can be written as

$$K_D = 2A_2M - K_f - \bar{v} \quad (2)$$

TABLE 1. Diffusion Data for Polystyrene in Toluene at 25°C

| \bar{C} (g/cm ³) | $D \times 10^7$ (cm ² /s) |
|-----------------------------------|---|
| 0.0025 | 4.201 |
| 0.005 | 4.452 |
| 0.010 | 4.975 |
| 0.015 | 5.500 |
| 0.020 | 6.022 |
| 0.025 | 6.550 |
| 0.0275 | 6.700 |

$$D_0 \times 10^7 \text{ (cm}^2\text{/s)} = 3.954 \pm 0.002^a$$

$$K_D \text{ (cm}^3\text{/g)} = 25.8 \pm 0.003^a$$

^aStandard error at 95% confidence level.

where M is the molecular weight, A_2 is the second virial coefficient, K_f is the first-order frictional coefficient term, and \bar{v} is the partial specific volume of the polymer. For a coiled linear chain in a good solvent, K_f can be expressed as [8]

$$K_f = 1.2A_2M + N_A V_H/M \quad (3)$$

where N_A is Avogadro's number and V_H is the chain hydrodynamic volume given by

$$V_H = (4/3)\pi R_H^3 \quad (4)$$

where R_H is the hydrodynamic radius which can be estimated from the D extrapolated to zero concentration using the Stokes-Einstein equation

$$R_H = kT/6\pi\eta D_0 \quad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent. From Eqs. (2)-(4) it follows that

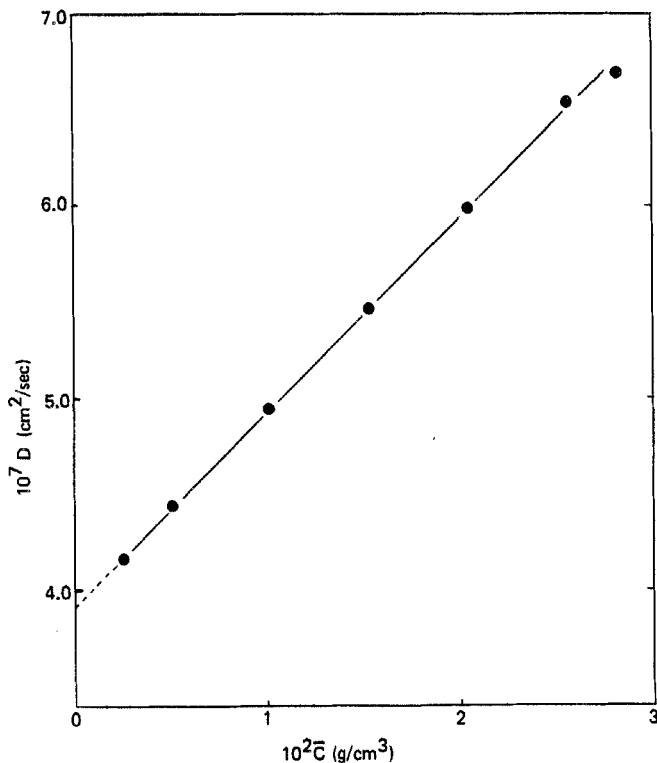


FIG. 1. Translational diffusion coefficient D versus the average concentration \bar{C} of polystyrene in toluene at 25°C . The dotted line indicates the extrapolation to zero concentration.

$$K_D = 0.8A_2M - (4/3)\pi(N_A/M)R_H^3 - \bar{v} \quad (6)$$

It should be noted that additional support for the observed values of K_D as obtained from Eq. (1) also comes from Eq. (6) by using literature values [10-12]; the observed K_D , however, was in reasonable agreement with that of theoretical Eq. (6), thus strengthening the accuracy of the present results.

CONCLUSIONS

A linear dependency of D with concentration was observed for the polystyrene-toluene system from moving boundary experiments

performed in a centrifuge. The observed values of K_D confirmed the theoretical predictions for this system.

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