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Effect of Pressure on Diffusion in Polymer Solutions*

A. H. EMERY, JR., L. H. TUNG, AND H. G. DRICKAMER

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois

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Diffusion measurements have been made using two molecular weights of polysulfide polymer at 25°C and 59°C in toluene solution. One isotherm for the low molecular weight was obtained in chloroform solution.

The results indicate that there are two mechanisms of motion in solution. At low pressure the dominant mode involves the expulsion of a solvent molecule from the coiled polymer. At high pressure the motion is segmental.

PREVIOUS work in this laboratory¹⁻⁵ on diffusion in liquids under pressure has indicated that high pressure is a very useful tool in the study of the structure of the liquid state and the nature of molecular motion. In particular the concept of the activation volume has proven useful for the elucidation of the mechanism of diffusion.

This paper presents some measurements of diffusion of high polymer in solution. The polymer used was polysulfide of the forms $[S-(CH_2)_6-S]_n$. Two molecular weight fractions were made (5500 and 42 000). Four isotherms were obtained using the low molecular weight polymer [1 percent (by weight) solution in toluene at 25°C and 50 percent C, 5 percent solution in toluene at 59°C, and 2 percent solution in chloroform at 25 percent C]. The upper limit of the pressure range, 100-6000 atmospheres, was determined by the point at which the viscosity of the solution interfered with the operation of the cell.

EXPERIMENTAL PROCEDURE

A. Synthesis of the Polymer

The synthesis of the polymer was made in three steps. The methods used were those described in the literature.

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¹ R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.* **21**, 267 (1953).

² R. C. Koeller, and H. G. Drickamer, *J. Chem. Phys.* **21**, 575 (1953).

³ R. C. Koeller, Cuddeback, and Drickamer, *J. Chem. Phys.* **21**, 589 (1953).

⁴ R. B. Cuddeback and H. G. Drickamer, *J. Chem. Phys.* **21**, 1359 (1953).

⁵ E. P. Doane and H. G. Drickamer, *J. Chem. Phys.* **21**, 1359 (1953).

ture⁶⁻⁹ modified slightly to insure maximum yield on sulfur. The radioactive sulfur was obtained as BaS from Oak Ridge National Laboratory. H₂S was generated and bubbled through an aqueous cyanamide solution to form thiourea. This was reacted with hexamethylene dibromide to form the dimercaptan. This was polymerized in an emulsion with KOH and lauric acid. The length of time determined the average molecular weight. Larger batches of nonradioactive polymer were prepared by exactly the same procedure. These were carefully fractionated and molecular weights were determined by light scattering.† The results from light scattering were correlated against intrinsic viscosity measurements on the same fractions. The molecular weights of the fractions used in diffusion measurements were obtained from these correlations.

B. Measurement of Diffusion

The apparatus and method of operation was substantially identical with that used in previous diffusion measurements.¹⁻⁵ Because of the slow diffusion it was necessary to shorten the cell length substantially. The upper part consisted of a slice of medium porosity fritted glass 0.088 cm thick. The lower layer consisted of two pieces of Whitman No. 1 filter paper. The effective path length was established by runs with 0.1-N

⁶ L. F. Audrieth, *Inorganic Syntheses* (McGraw-Hill Book Company, Inc., New York 1950), Vol. III.

⁷ R. L. Frank and P. V. Smith, *J. Am. Chem. Soc.* **68**, 2103 (1946).

⁸ R. R. Renshaw, and D. E. Searle, *J. Am. Chem. Soc.* **59**, 2056 (1937).

⁹ L. E. Olson, Ph.D. thesis, University of Illinois, 1953.

† We are indebted to F. T. Wall and H. Terayama for the use of the light scattering apparatus.

Na_2SO_4 solution. It was found possible to duplicate almost exactly the curve previously obtained at 25° to 5000 atmospheres.³ Although the two parts of cell were no longer the same length, one of the methods of calculation used previously^{1,10} still applied. Very numerous preliminary runs indicated a reproducibility at least within 10 percent.

In each case the lower part of the cell (filter paper) was filled with a solution of nonradioactive polymer, and the upper sleeve was filled with radioactive polymer solution of the same concentration and molecular weight.

RESULTS

The results are listed in Tables I-III and are plotted in Figs. 1-4. Figures 5-7 show the calculated quantities

TABLE I. Low molecular weight polymer.

Temperature °C	1% in toluene Pressure atmos	Diffusion coefficient D $\text{cm}^2/\text{sec} \times 10^6$
25	80	1.59
25	200	2.36
25	360	2.18
25	360	2.99
25	640	3.24
25	970	2.63
25	1180	2.55
25	1600	1.83
25	1970	1.37
25	2000	1.24
25	3500	0.64
25	3500	0.83
25	3850	0.91
25	6000	0.68
25	6400	0.47
50	250	2.15
50	600	4.0
50	1050	6.8
50	1470	5.9
50	1870	3.29
50	3600	1.57
50	4550	1.20

TABLE II. High molecular weight polymer.

Temperature °C	1% in toluene Pressure atmos	Diffusion coefficient D $\text{cm}^2/\text{sec} \times 10^6$
25	200	0.276
25	370	0.75
25	610	1.74
25	1220	1.50
25	1970	0.88
25	3650	0.45
50	200	0.73
50	350	1.24
50	600	1.19
50	1200	0.73
50	2000	0.71
50	2000	0.82
50	3500	1.12
50	3600	1.20
50	4500	1.21
50	4500	1.43
50	5650	0.45

¹⁰ K. D. Timmerhaus and H. G. Drickamer, J. Chem. Phys. 19, 1242 (1951).

TABLE III. Low molecular weight polymer.

Temperature °C	5% in toluene Pressure atmos	Diffusion coefficient $\text{cm}^2/\text{sec} \times 10^6$
25	220	1.22
25	400	2.71
25	630	2.34
25	1280	2.16
25	1980	1.23
25	2850	0.80

Low molecular weight polymer 2% in chloroform

25	190	1.94
25	220	1.39
25	600	2.20
25	1200	2.22
25	2020	1.79
25	3000	1.84
25	3600	1.65

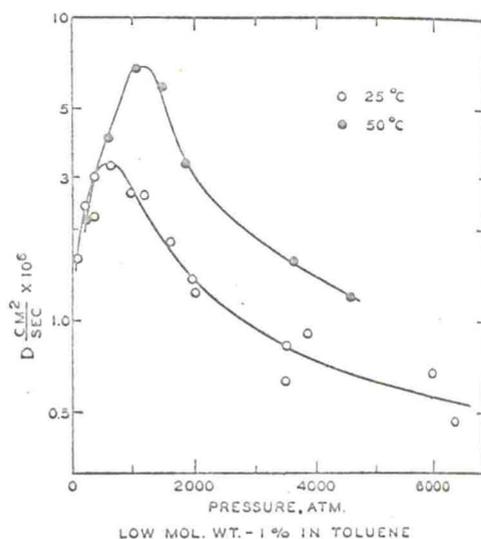


FIG. 1. Diffusion coefficient versus pressure low molecular weight 1 percent in toluene 25° and 50° isotherms.

(activation volumes, enthalpies, entropies, and free energies) for 1 percent toluene solutions of both molecular weights. Figure 7 shows activation volumes for the 5 percent toluene solution and 2 percent chloroform solution (both low molecular weight).

All the diffusion curves versus pressure (except the 50° isotherm for high molecular weight) show qualitatively the same features. In each case there is a rapid rise in D with pressure to 500 or 1000 atmospheres, followed by a slower decrease with increasing pressure. The low pressure part of the curve corresponds to a large negative activation volume in the low pressure region, and above 1000 atmospheres a positive activation volume decreasing with further increase in pressure.

Figure 3 indicates that there is only a minor effect of increasing the concentration from 1 percent to 5 percent by weight. The chloroform isotherm (Fig. 4) is qualitatively similar in shape to the corresponding toluene

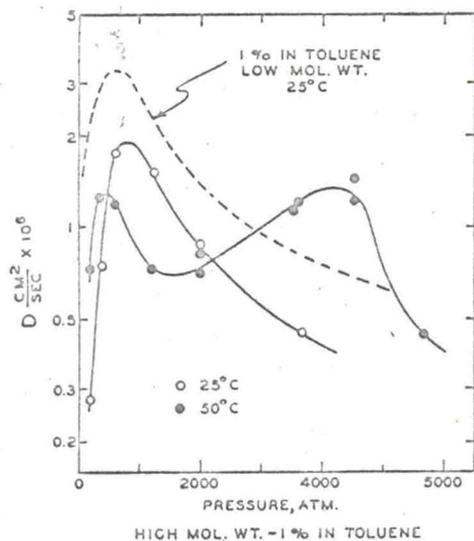


Fig. 2. Diffusion coefficient versus pressure high molecular weight 1 percent in toluene 25° and 50° isotherms.

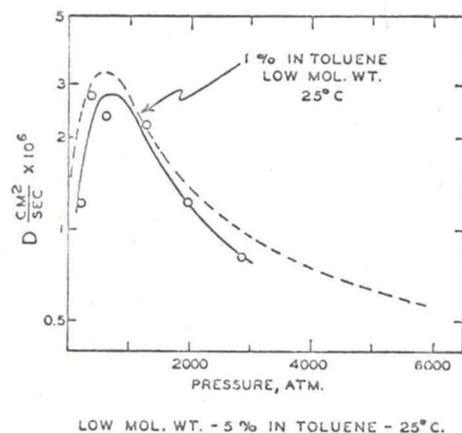


Fig. 3. Diffusion coefficient versus pressure low molecular weight 5 percent in toluene 25° isotherms.

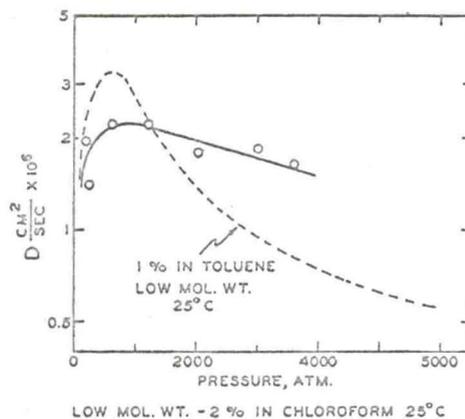


Fig. 4. Diffusion coefficient versus pressure low molecular weight 2 percent in chloroform.

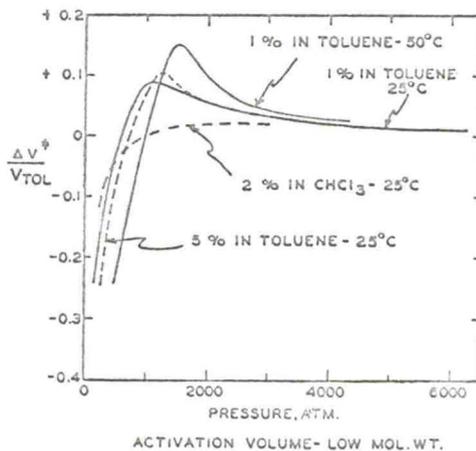


Fig. 5. $\Delta V^\ddagger/V_s$ versus pressure—low molecular weight polymer.

of a polymer molecule as loosely coiled in solution with large numbers of solvent molecules trapped in the coils. If a solvent molecule were expelled from one part of the coil, with or without trapping another solvent molecule in a different part of the coil, this would constitute molecular motion which might easily be characterized by a negative activation volume. Further, this mode of motion would become more difficult with increasing pressure, as the solvent molecules become squeezed out and the solvent structure more rigid. It is reasonable to believe that the segmental motion is controlling at the higher pressure.

The high molecular weight isotherm at 50°C is more difficult to explain. If the other curves are the result of two competing modes of motion it would seem that there are at least three competing modes in this case. The indicated reproducibility of the results shows that the shape of the curve is definitely radically different from the others. If the portions of the curve below 400 atmospheres and above 4500 atmospheres are extended to meet, the resulting curve is qualitatively similar to the other curves obtained. It is then the premature drop, at 500 atmospheres, which makes diffusion at

curve although chloroform is a considerably better solvent for this polymer. The chloroform solutions proved to be very difficult to handle, which made further work along these lines impractical.

Evidently there are two mechanisms of molecular motion, one controlling at low pressure, and the second at high pressure.

The two mechanisms described below are consistent with our results and with other evidence of structure of polymers in solution, although they are certainly not the only possible descriptions of our results.

One possible mode of motion is segmental. This would result in a positive activation volume, and would therefore describe the controlling mechanism of motion in the high pressure region. The decrease in activation volume (per molal volume of solvent) and of activation enthalpy with pressure in this region would indicate a decrease in the size of the moving segment with pressure.

The second mode of motion depends on the picture

polymer.

Diffusion coefficient D
cm²/sec $\times 10^4$

1.22
2.71
2.34
2.16
1.23
0.80

form

1.94
1.39
2.20
2.22
1.79
1.84
1.65



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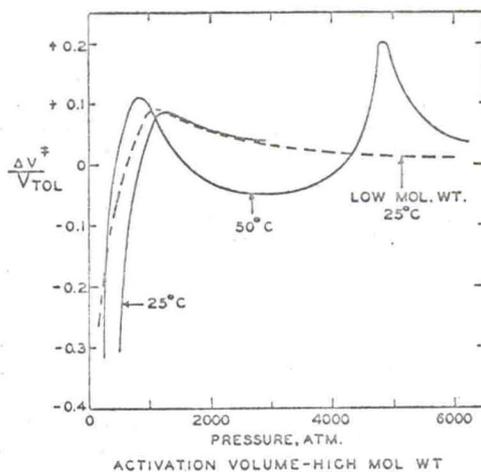


FIG. 6. $\Delta V^\ddagger/V_T$ versus pressure—high molecular weight versus pressure.

50°C slower than at 25°C in the region (500–2000 atmospheres) which is to be explained, rather than the rise beginning at 1500 atmospheres.

It is possible that the molecular weight distribution of the high molecular weight polymer is bimodal, and that the "average" rate of diffusion is controlled by different molecular weights at different pressures. Unfortunately, because of the microsynthesis methods used, not enough of a cut was made to determine molecular weight distribution, but the fractionation was not sharp. Various other possible explanations can be put forward, but they are not particularly convincing. The high molecular weight polymer may be coiled in such manner at high temperature and low pressure that expulsion of solvent is not a particularly easy mode of

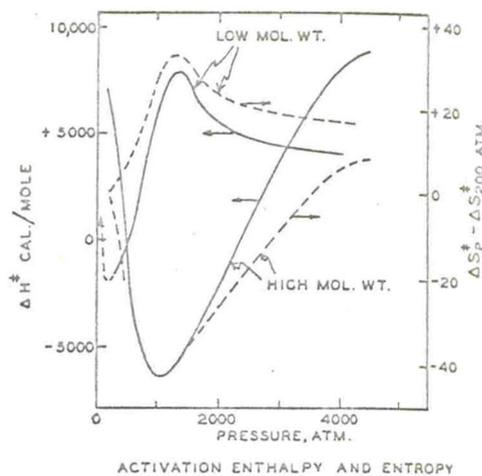


FIG. 7. Enthalpy and entropy of activation.

motion. The increase of pressure may increase coiling and increase the likelihood of this mechanism.

Light scattering experiments over this range of pressure are planned for the near future. It is hoped these will throw some light on the structure of polymer molecules in these solutions.

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