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Diffusivity and Solubility of Carbondioxide in Diluted Polymer Solutions

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Diffusion coefficients of CO_2 in aqueous Newtonian solutions of polyvinyl alcohol and polyethylene glycol with molecular weights varying from 1500 to 100,000 were obtained from absorption rate measurements in a wetted-wall column and the CO_2 solubilities determined independently. The exponent A of the diffusivity-viscosity relation is found to be a strong function of the molecular weight of the applied polymer. The data suggest the following correlation:

$$(D/D_o) = (\mu/\mu_o)^{-3.7\sqrt{M_o/M_P}}$$

which indicates that the exponent may vary from 0.04 to 0.4 for the solutions studied.

SCOPE

Correlations which permit estimation of diffusion coefficients are of considerable importance in all calculations concerning interphase mass transfer phenomena. Special attention deserve such correlations which relate D with easily available or measurable physico-chemical quantities as for instance the viscosity. Hayduk and Cheng (1971) critically reviewed the diffusivity-viscosity relation:

$$D\mu^A = K_1 \tag{1}$$

and concluded that the value of A depends on the diffusing substance only, but not on temperature, solvent molecular weight or molar volume. For large solute molecules diffusing in small solvent molecules the Stokes-Einstein relation with $A = 1$ results. For the other limiting case of small solute molecules in a solvent of large molecules Hiss and Cussler (1973) found an exponent of 2/3. However, experimental data show that A may vary from 0.5 to values above 1.

If a solute gas molecule diffuses in a diluted solution of a macro-molecule the situation is still more complicated. Experimental results (Astarita, 1965; Zandi and Turner, 1970; Wasan et al., 1972; Perez and Sandall, 1973; Mashelkar and Soylu, 1974) clearly indicate that diffusivities of small

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molecules in polymer solutions are not or only weakly dependent on viscosity. Some authors even observed a diffusivity increase, and qualitative models were developed which explain this unusual behavior (Metzner, 1965; Astarita, 1965; Li and Gainer, 1968; Mashelkar and Soylu, 1974).

A systematic study on the influence of the molecular weight of the solved polymer on the relation between the diffusivity of small molecules and the viscosity of the solution was not carried out hitherto. Such data are presented here for aqueous solutions of polyethylene glycol and polyvinyl alcohol which behave like Newtonian liquids. The molecular weight was varied from 1500 to 10^5. The measurements were carried out in a wetted-wall column at 25°C which leads to the product of solubility and the square root of diffusivity. For obtaining high absorption rates, and hence reliable diffusivities a gas of high solubility, i.e., carbondioxide, was absorbed in solutions having viscosities not larger than 12 mPa · s. The solubilities were determined by an independent method.

CONCLUSIONS AND SIGNIFICANCE

The diffusivities of CO_2 measured in each solution of a polymer with a certain molecular weight follow Eq. 1. The power of the viscosity (A) is however no longer limited to values larger than 0.5 or 2/3, respectively. For solutions of PEG 1500 the exponent A decreases already to a value of 0.39, and for the polymer with the highest molecular weight the value of A is dropped down to 0.043. Obviously, A does not depend only on the properties of the diffusing species as suspected by Hayduk and Cheng (1971) from their analysis of diffusivities in nonpolymeric solutions. In diluted polymer solutions A is mainly influenced by the molecular weight of the solved polymer. The power A is found to be inversely proportional to the square root of the molecular weight of the solved polymer: $A \propto 1/\sqrt{M_P}$. All data obtained suggest the following dimensionless correlation:

$$(D/D_o) = (\mu/\mu_o)^{-3.7\sqrt{M_o/M_P}}$$

The observed diffusivity-viscosity behavior can be understood qualitatively by theories provided by Metzner (1965) and Astarita and Mashelkar (1977). In agreement with the conclusions of Hiss and Cussler (1973) the findings show that the presence of polymers creates only long range entanglements which increase the macroscopic viscosity but do not effect as much diffusivity which is governed by short range interactions of the molecules.

All mass transfer theories predict the rate of interphase transport being mainly controlled by molecular diffusion. Therefore knowledge of diffusivities as well as empirical and theoretical equations which permit calculation of diffusivities are of considerable importance. It is particular the design engineer who needs reliable estimates of D as correlations for mass transfer coefficients usually involve D. Measurements of diffusivities are still cumbersome and time consuming. Special attention deserve therefore such correlations which relate D with easily available or measurable physico-chemical quantities as for instance the viscosity.

The diffusivity of solute gas molecules in a liquid medium is commonly governed by the molecular size of the solute gas, the viscosity of the solution, the molecular volume of the solvent, and the temperature. A typical example is the equation of Wilke and Chang (1954) which is based on the Stokes-Einstein relation and introduces an empirical association parameter which accounts for molecular attraction. Thaker and Othmer (1953), Scheibel (1954), Sitaraman et al. (1962), and Reddy and Doraiswamy (1967) have succeeded in substituting the empirical association parameter by expressions which involve only known properties of the diffusing solute gas and the solvent.

The absolute rate theory of Eyring and coworkers constitutes the basis of theoretical equations for D. For instance, Navari et al. (1971) presented a predictive theory for diffusion in polymer and protein solutions. It was found that the ratio of diffusivity in a polymeric solution to that in a pure solvent depends solely on solution and polymer properties and is completely independent of the diffusing solute. Akgerman and Gainer (1972) developed a theoretical equation for the diffusivity in low-viscosity liquids. The relation involves the energies of activation of diffusion and viscosity which can be calculated by means of equations given by Akgerman and Gainer (1972).

Hayduk and Cheng (1971) critically reviewed the relation between diffusivity and solvent viscosity. They concluded that, in general, diffusivity and viscosity were not inversely related

TABLE 1: DEPENDENCY OF D ON μ FROM VARIOUS EXPERIMENTAL STUDIES

Author	Studied Systems	Viscosity mPa · s	Exponent A of Eq. 1
Calderbank (1959)	CO_2/Glycol, Glycerol	1-20	0.74
Thomas and Adams (1964)	N_2O/Glycerol	1-2	0.94
Davies et al. (1967)	CO_2/Various Hydrocarbons	1.5-2.5	0.5
Hayduk et al. (1973)	Propane/Various n-Paraffins and Chlorobenzene	3-55	0.545
Hiss and Cussler (1973)	n-Hexane/Various n-Paraffins	0.5-5000	0.667
Sovova (1976)	CO_2, O_2/C_2-C_8 Alcohols, Cyclohexane, C_6-C_{16}-Paraffins	0.5-3	0.5
	CO_2, O_2/Aromates and Derivates, Acetone, Methanol	0.5-3	1.15
Hikita and Asai (1978)	O_2/Saccharose	2-31	0.667

but that the diffusivity depends on the solvent viscosity raised to some power:

$$D\mu^A = K_1 \tag{1}$$

As to Hayduk and Cheng (1971), the value of A depends on the diffusing substance only but not on temperature, solvent molecular weight or molar volume. Table 1 summarizes experimental data which follow Eq. 1. For the case of large solute molecules diffusing in relatively small solvent molecules the Stokes-Einstein relation with $A = 1$ results theoretically. For the other limiting case of small solute molecules in a solvent of relatively large molecules Hiss and Cussler (1973) found an exponent of 2/3 which can be rationalized on the basis of the Eyring rate theory. However the data compiled on table 1 indicate that A varies over a larger range.

The situation becomes still more complicated if dilute solutions of polymers are taken into account. Hiss and Cussler (1973) explicitly pointed out that Eq. 1 and, particularly, the exponent of 2/3 proposed by them does not apply to polymers. Experimental results (Clough et al., 1962; Quinn and Blair, 1967; Astarita, 1965; Zandi and Turner, 1970; Navari et al., 1971; Greif et al., 1972; Wasan et al., 1972; Perez and Sandall, 1973; Mashelkar and Soylu, 1974) show indeed that diffusivity of small molecules in diluted polymer solutions are not or only weakly dependent on viscosity. Some authors (Astarita, 1965; Zandi and Turner, 1970; Perez and Sandall, 1973; Mashelkar and Soylu, 1974) even reported a diffusivity increase in diluted solutions of polymers, and qualitative models have been presented to explain this unusual behavior (Metzner, 1965; Astarita, 1965; Li and Gainer, 1968; Osmers and Metzner, 1972; Mashelkar and Soylu, 1974).

PURPOSE

The purpose of this communication is to present new data on the diffusivity-viscosity dependency of solutions of polymers of different molecular weight. To our knowledge, the influence of the molecular weight of solved polymers on the relation between the diffusivity of small molecules and the viscosity of the solution was not studied systematically hitherto. A gas absorption technique was applied which yields the product of solubility and the square root of the diffusivity. The solubilities were therefore measured independently. Solutions of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) were used. The molecular weight of the added polymer was varied from 1500 to 100 000. These solutions behave like Newtonian liquids. In order to obtain high absorption rates and hence reliable diffusivities CO_2 was absorbed in solutions having viscosities not larger than 12 mPa · s, see Table 2.

TABLE 2. LOWEST AND HIGHEST CONCENTRATIONS AND CORRESPONDING VISCOSITIES OF POLYMER SOLUTIONS USED ($T = 25°C$)

Polymer	Concentration 10^{-3} mol/L	Concentration % wt.	Viscosity mPa · s
PEG 1 500	68.0	10.0	2.08
	218.0	31.0	9.41
PEG 3 000	27.0	8.0	2.12
	94.0	27.0	10.59
PEG 6 000	8.4	5.0	2.13
	34.5	20.0	12.15
PEG 10 000	5.0	5.0	2.47
	17.0	17.0	11.95
PEG 20 000	1.5	3.0	2.57
	5.1	17.0	11.72
PVA 49 000	0.82	4.0	7.11
	0.86	4.2	10.29
PVA 100 000	0.1	1.0	2.70
	0.23	2.3	10.34

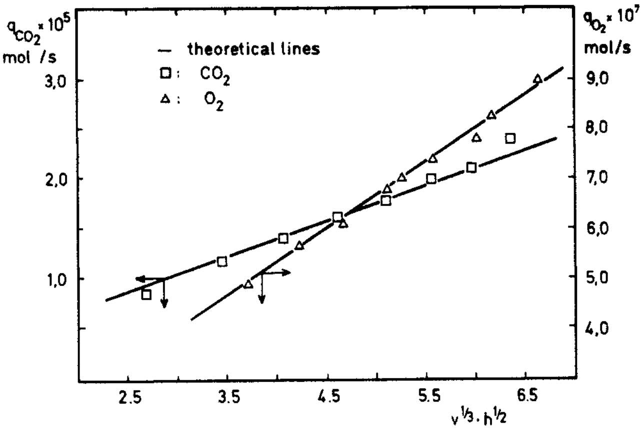

Figure 1. Check of efficacy of wetted-wall column.

EXPERIMENTAL

A wetted-wall column apparatus was used in the absorption measurements. Its design was similar to that of Roberts and Danckwerts (1962). The liquid was distributed via a teflon cap and the film was formed on the outside wall of 1.6 cm o.d. glass tubing. The solution was degased by spraying in vacuum. It was stored about 3 m above the absorption chamber. The liquid flow rate—due to hydrostatic head—was adjusted by means of a teflon valve and a calibrated rotameter.

The CO_2 was of 99.5% purity. It was saturated with the solvent by passing it through equilibrium cells maintained at a temperature of 25°C and stored in a balloon-reservoir. A soap film meter was used to measure the absorption rates. The liquid flow, the absorption chamber, and the soap film meter were adjusted to a constant temperature of 25°C which was the temperature where all measurements were carried out.

For the wetted-wall column operating at laminar flow conditions the exposure time of the fluid elements is given by:

$$t = \frac{2h}{3}\left(\frac{3\mu}{\rho g}\right)^{1/3}\left(\frac{\pi d}{\dot{V}_L}\right)^{2/3} \tag{2}$$

Higbie's penetration theory predicts then for the absorption rate (Danckwerts (1970)):

$$q = c^*\sqrt{(6hD)} \times d\left(\frac{\dot{V}_L}{d}\right)^{1/3}\left(\frac{\pi g \rho}{3\mu}\right)^{1/6} \tag{3}$$

which can be rearranged to give:

$$c^*\sqrt{D} = \frac{q}{\alpha h^{1/2} V_L^{1/3}} \tag{4}$$

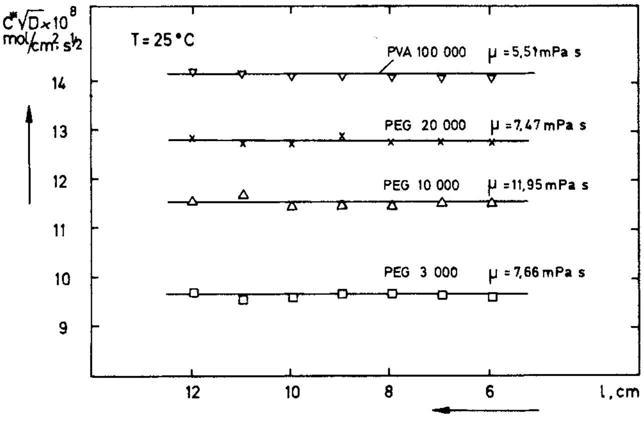

Figure 2. Measured values of $c^*\sqrt{D}$ at various film lengths.

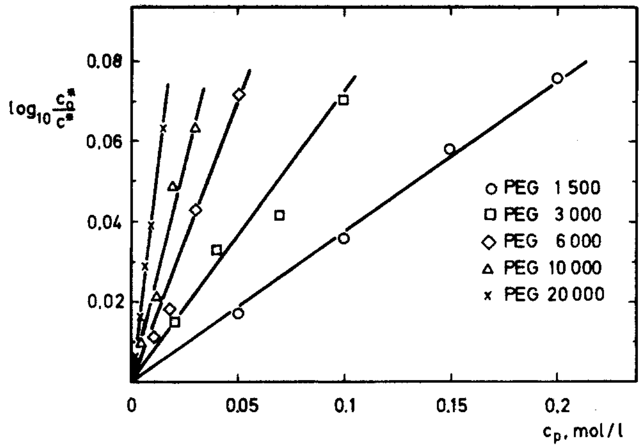

Figure 3. Plot of Eq. 5 to correlate solubility data.

TABLE 3. SOLUBILITY PARAMETER K OF EQ. 5 AND EXPONENT A OF EQ. 1 FOR VARIOUS POLYMER SOLUTIONS

Polymer	K, L/mol	A
PEG 1 500	0.379	0.392
PEG 3 000	0.683	0.310
PEG 6 000	1.375	0.210
PEG 10 000	2.139	0.138
PEG 20 000	3.807	0.114
PVA 49 000	23.17	0.060
PVA 100 000	49.82	0.043

where α comprehends all constants of the apparatus and the liquid.

In order to test the efficacy of the wetted-wall absorber, the absorption of CO_2 and O_2 was studied at various flow rates and column heights, in the absence and presence of a surface-active agent (i.e., Tween 80). It was found that addition of 30 mg/L Tween 80 suppresses all the ripples on a column less than 15 cm high. Figure 1 shows some typical results. The theoretical line for CO_2 was calculated by using $c^* = 3.39 \times 10^{-2}$ mol/cm^3 atm and $D = 1.92 \times 10^{-5}$ cm^2/s. From the O_2 absorption measurements, a diffusivity of 2.06×10^{-5} cm^2/s is obtained which is in good agreement with the results of other authors (Jordan, 1956; Chiang and Toor, 1959; Kolthoff and Izutsu, 1964; Duda and Vrentas, 1968; Tham et al., 1970; Wasan et al., 1972). For each polymer solution the absorption rates were measured at various lengths of the wetted-wall column. Figure 2 demonstrates that the $c^*\sqrt{D}$ calculated from Eq. 4 are constant.

The solubility of CO_2 in the polymer solutions was measured at 25°C by a manometric method. A given amount of degassed solution was brought into contact with a constant volume of CO_2. After equilibrium pressure was established the solubility was calculated from the measured pressure drop. The method is described in detail by Quicker (1980). Viscosities and densities of the solutions were determined by an Ubbelohde viscosimeter and pycnometry, respectively.

RESULTS

The measured CO_2 solubilities of the two polymers applied (i.e. polyethylene glycol (PEG) having mean molecular weights of 1500, 3000, 6000, 10,000, and 20,000, and polyvinyl alcohol (PVA) with mean molecular weights of 49,000 and 100,000) can be described by the following Eq. 5:

$$\log_{10}\frac{c_0^*}{c^*} = Kc_P \tag{5}$$

which is equivalent to the well-known Sechenov equation which describes the solubility decrease of gases caused by added electrolytes (salting out). In Eq. 5, c_0^* is the solubility of CO_2 in the solvent (water); c^*, the CO_2 solubility in the polymer solution, and c_p is the polymer concentration (in mol/L). Figure 3 shows that the solubility data in PEG solution follow Eq. 5 excellently. The constants K (in L/mol) characterizing the solubility decrease for the various solutions were calculated by means of a least square fit. They are given in Table 3. If c_p is given in g/L all the data of Figure 3 can be represented by one line only yielding a mean value of K equal to 2.23×10^{-4} L/g.

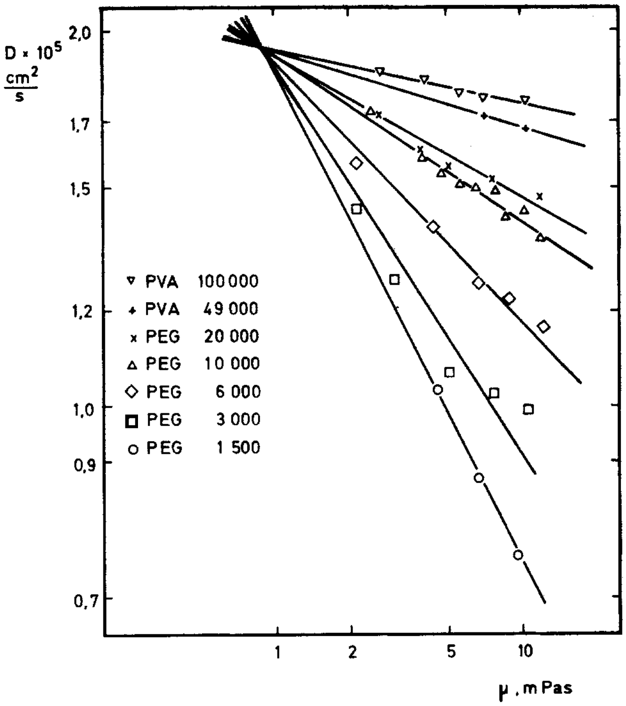

Figure 4. Measured diffusivities as function of viscosities.

Figure 4 presents a log-log-plot of the CO_2 diffusivities in the various polymer solutions as function of the viscosity. It can be clearly recognized therefrom that the dependency of D on μ is strongly influenced by the molecular weight of the polymer. The smaller the molecular weight of the polymer the stronger is the influence of μ on D. The data points for each polymer solution in Figure 4 can be approximated by straight lines and their slopes correspond to the exponent A in Eq. 1. The values of A are given in Table 3.

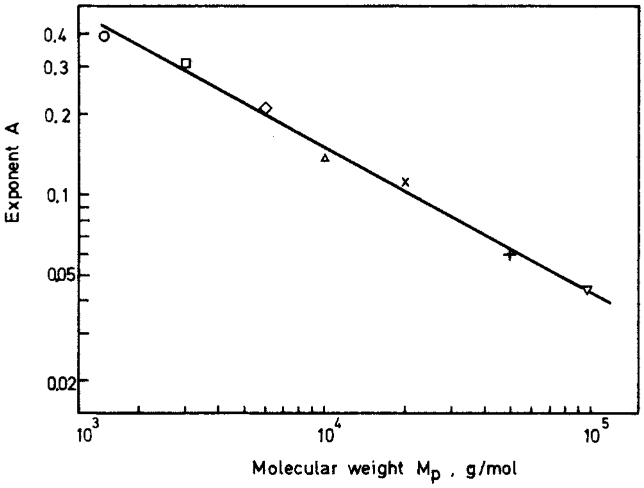

Figure 5. Dependency of exponent A of Eq. 1 on molecular weight of solved polymer.

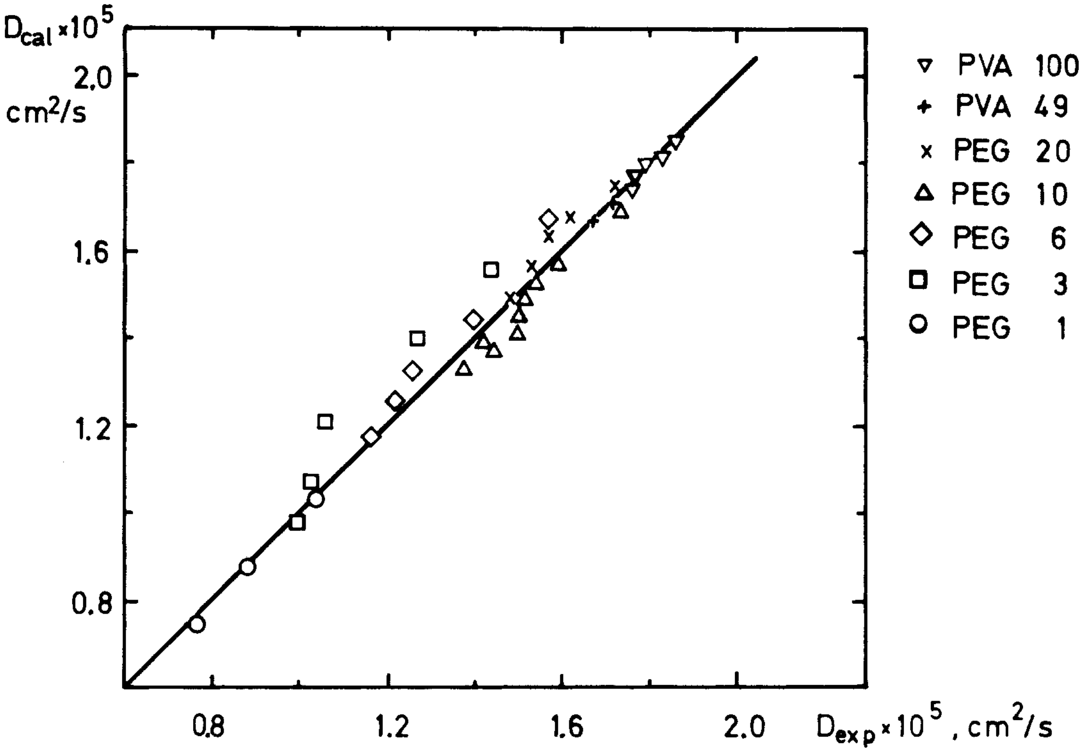

Figure 6. Comparison of experimental and computed diffusivities.

DISCUSSION

The results initially indicate that also for dilute solutions of polymers, Eq. 1 is capable to describe the diffusivity-viscosity dependency. However, the power of the viscosity is no more limited to values larger than 0.5 or 2/3 (Hiss and Cussler, 1973), respectively. It is remarkable that for the solutions of PEG 1500, the exponent of A drops already down to 0.39 while for solutions of saccharose (molecular weight 342) own measurements gave A = 0.7, a value being in good agreement with the results of Hikita and Asai (1978) for O_2 diffusivities (see Table 1).

In addition, one should point out that A does not only depend on the properties of the diffusing species as suspected by Hayduk and Cheng (1971) from their analysis of diffusivities in nonpolymeric solutions. In diluted polymer solutions, the value of the exponent A is mainly influenced by the molecular weight of the solved polymer. Obviously, A may become even negative as diffusivity enhancement was observed for some polymers in certain concentration ranges (Clough et al., 1962; Quinn and Blair, 1967; Astarita, 1965; Li and Gainer, 1968; Zandi and Turner, 1970; Navari et al., 1971; Greif et al., 1972; Wasan et al., 1972; Osmers and Metzner, 1972; Perez and Sandall, 1973; Mashelkar and Soylu, 1974).

The found diffusivity-viscosity behavior can be understood qualitatively (Metzner, 1965; Astarita and Mashelkar, 1977). The addition of the polymer to the water causes a structuring which yields a blocking of solvent molecules. The polymer-solvent interaction is expected to be considerable different from solvent-solvent interaction. Hence, the overall effect may be either an increase or decrease in diffusivity depending on the changes in the intermolecular forces. Hiss and Cussler (1973) emphasized that the presence of polymers creates long range entanglements which increase the macroscopic viscosity. However, diffusivity is not governed by any long range structuring effects but by short range interactions of the molecules.

In order to find a relationship between the exponent A of Eq. 1 and the molecular weight of the solved polymer a log-log-plot was prepared which is given in Figure 5. The log values follow a linear relation and a least square fit gives:

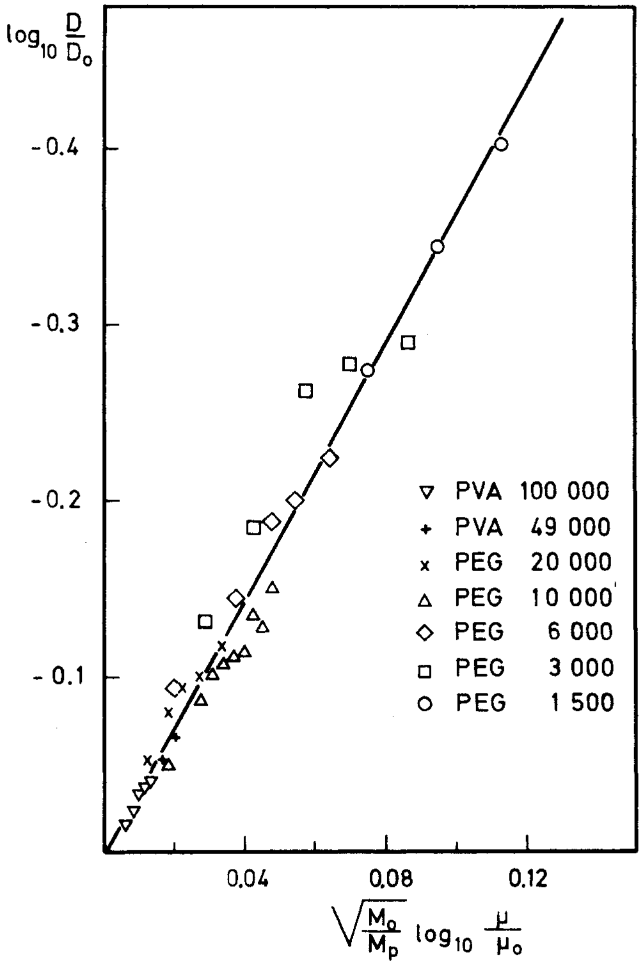

Figure 7. Measured diffusivities plotted as to Eq. 10.

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