

Representation of hydrodynamic data as a function of molecular weight for semi-rigid and rigid-chain polymers*

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Analytical expressions for the molecular-weight dependences of intrinsic viscosity $[\eta]$, sedimentation constant s_0 and diffusion coefficient D are suggested:

$$\begin{aligned}[\eta] &= M^2(K_1 + K_2M^{1/2})^{-3} \\ s_0 &= K_3 + K_4M^{1/2} \\ D &= M^{-1}(K_5 + K_6M^{1/2})\end{aligned}$$

As employed for semi-rigid and rigid-chain polymers, the coefficients K_i in these equations are non-sensitive to molecular-weight variation over a wider M range than the numerical coefficients in the well known empirical Mark-Kuhn-Houwink equations: $[\eta] = K_\eta M^a$, $s_0 = K_s M^{1-b}$ and $D = K_D M^{-b}$.

(Keywords: intrinsic viscosity; sedimentation; diffusion; molecular weight; analytical representation)

INTRODUCTION

The intrinsic viscosity $[\eta]$, sedimentation constant s_0 and diffusion coefficient D as functions of molecular weight M are usually represented by well known and widely used Mark-Kuhn-Houwink (MKH) empirical equations:

$$[\eta] = K_\eta M^a \quad (1)$$

$$s_0 = K_s M^{1-b} \quad (2)$$

$$D = K_D M^{-b} \quad (3)$$

The numerical values of coefficients a , b and K_i in equations (1)–(3) have been collected in numerous tables¹.

According to equations (1)–(3), in double-logarithmic scales the dependence of $[\eta]$, D and s_0 on M must be linear. The experimental data obtained over a wide range of M , however, do not always satisfy this requirement.

DISCUSSION

Flexible-chain polymers

For flexible-chain polymers the excluded-volume effects increase the slope of the plots of $\log[\eta]$ and $\log D$ versus $\log M$, i.e. they increase the scaling exponents a and b with increasing M . For polymer-solvent systems with non-linear dependence of $\log[\eta]$ on $\log M$, a few attempts have been made to compose more universal expressions than equation (1) to describe adequately the dependence of $[\eta]$ on M . For this purpose Palit² has proposed the relation:

$$100\rho_0[\eta] + \ln M = K'M^{2/3} + K'' \quad (4)$$

where ρ_0 is the polymer density at solute concentration $c \rightarrow 0$, and K' and K'' are numerical coefficients.

A more convenient analytical expression has been suggested by Dondos and Benoit³:

$$1/[\eta] = -A_2 + A_1M^{-1/2} \quad (5)$$

The linearity of $1/[\eta]$ plotted against $M^{-1/2}$ confirmed by experimental data^{4,5} over a wide M range allows the dependence of $[\eta]$ on M for a flexible-chain polymer to be described by relation (5) with two numerical coefficients A_1 and A_2 .

Rigid-chain polymers

For semi-rigid and rigid-chain polymers over a wide M interval, the experimental dependences of $\log[\eta]$ (Figure 1) and, to a lesser degree, $\log D$ and $\log s_0$ on $\log M$ are more non-linear functions. The data in Figure 1 are consistent with the hydrodynamic theory for worm-like chains^{11,12}. In particular, Kolomiets and Tsvetkov have shown¹³ that the scaling exponent a in equation (1) is a function of the length L and diameter d of the macromolecule and its equilibrium rigidity, which may be characterized by the Kuhn segment length A of the equivalent chain (Figure 2). In good agreement with this conclusion are the experimental double-logarithmic plots of $[\eta]$ versus M for the most rigid-chain polymers represented by S-shaped curves, which may be approximated by a straight line only in a narrow M range.

A similar conclusion is also valid for the diffusion-sedimentation data. We have used the theory for translational friction of worm-like spherocylinders developed by Yamakawa^{11,15} and Fujita *et al.*¹⁶, which yields expressions (6) and (7) for high and low M values. For $L/A \geq 2.278$:

$$D = (kT/3\pi\eta_0L) \left(B_1(L/A)^{1/2} + B_2 + \sum_{i=3}^{\infty} B_i(A/L)^{(i-2)/2} \right) \quad (6)$$

* Dedicated to Professor V. N. Tsvetkov's 80th birthday

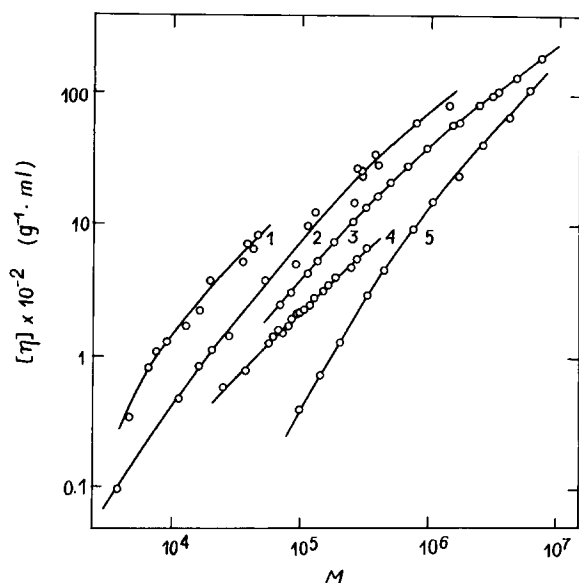


Figure 1 Log-log plots of intrinsic viscosity $[\eta]$ vs. molecular weight M for some semi-rigid and rigid-chain polymers: (1) poly(1,4-phenylene terephthalamide) in 96% H_2SO_4 (ref. 6), (2) poly(*n*-butyl isocyanate) in CCl_4 (ref. 7), (3) poly(*n*-hexyl isocyanate) in *n*-hexane (ref. 8), (4) cellulose cyanoethyl in acetone (ref. 9), (5) schizophyllan in water (ref. 10)

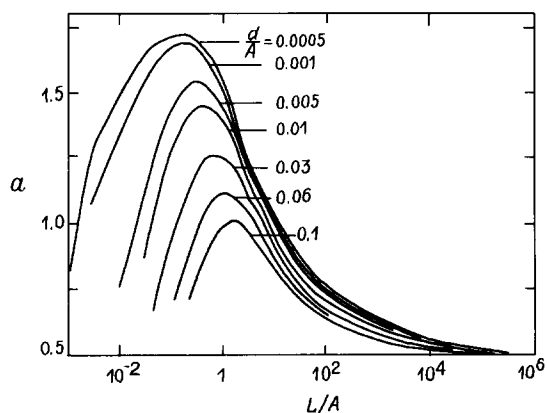


Figure 2 Variation of the MKH exponent a in equation (1) with reduced chain length L/A according to theory^{12,14} for worm-like sphero-cylinders with reduced diameter d/A from 0.0005 to 0.1 as calculated by Kolomiets and Tsvetkov¹³

and for $L/A < 2.278$:

$$D = (kT/3\pi\eta_0L) \left(C_1 \ln(L/d) + C_2 + \sum_{i=3}^{\infty} C_i (L/A)^{i-2} \right) \quad (7)$$

where k is the Boltzmann constant, T is the absolute temperature and η_0 is the solvent viscosity. The relations for coefficients B_i and C_i given in refs. 11 and 16 have been applied to build the dependence of D on M according to equations (6) and (7).

The scaling exponent b in equation (2) was calculated by $b = -(L/D) dD/dL$. The values of b are listed in Table 1. A comparison of Figures 2 and 3 shows that the dependence of the exponent b on the reduced chain length is similar to that of the exponent a .

Consequently, equations (1)–(3) with constant numerical coefficients are applicable to polymers only in a narrow molecular-weight range, where the plots of

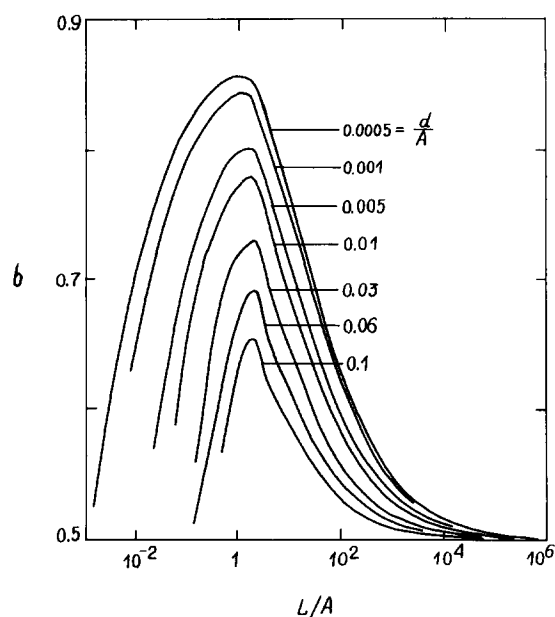


Figure 3 Variation of the exponent b in equations (2) and (3) with reduced chain length L/A for worm-like sphero-cylinders with indicated values of reduced diameter d/A according to the theory^{11,16}

Table 1 Theoretical values of the scaling exponent b in equations (2) and (3) for worm-like sphero-cylinders as a function of reduced chain length L/A and diameter d/A according to theory^{11,16}

L/A	d/A						
	0.0005	0.001	0.005	0.01	0.03	0.06	0.1
0.001	0.511	—	—	—	—	—	—
0.01	0.717	0.661	0.510	—	—	—	—
0.05	0.800	0.770	0.660	0.590	0.503	—	—
0.1	0.822	0.799	0.714	0.658	0.544	0.500	—
0.5	0.853	0.838	0.788	0.757	0.686	0.624	0.568
1.0	0.857	0.844	0.801	0.775	0.719	0.669	0.623
2.0	0.851	0.840	0.802	0.779	0.732	0.691	0.653
2.275	0.850	0.838	0.800	0.778	0.731	0.692	0.655
5.0	0.803	0.790	0.749	0.727	0.681	0.644	0.611
7.0	0.785	0.771	0.730	0.708	0.665	0.630	0.599
10	0.764	0.750	0.710	0.688	0.647	0.615	0.587
20	0.722	0.708	0.670	0.651	0.615	0.588	0.566
50	0.668	0.655	0.623	0.607	0.580	0.560	0.544
70	0.649	0.638	0.608	0.594	0.569	0.551	0.538
100	0.631	0.621	0.594	0.581	0.559	0.544	0.532
10 ³	0.552	0.546	0.534	0.529	0.520	0.515	0.510
10 ⁴	0.517	0.515	0.511	0.509	0.507	0.505	0.503
10 ⁵	0.506	0.505	0.504	0.503	0.502	0.502	0.501
10 ⁶	0.502	0.502	0.501	0.501	0.501	0.500	0.500

$\log[\eta]$, $\log D$ and $\log s_0$ versus $\log M$ may be approximated by straight lines. For this reason, some investigators of rigid-chain polymers do not use the MKH equations to describe the hydrodynamic characteristics of the polymers in solution as a function of M . This is especially true for viscometric data. At the same time practical needs stimulate the search for simple analytical relations to describe the dependences of $[\eta]$, D and s_0 on M . Among them, linear equations are of the greatest interest and preference.

Relations (4) and (5) are inapplicable for this purpose, as the character of the $[\eta]$ variation with increasing M for the above polymers is quite different from that for flexible-chain polymers. Yamakawa¹⁷ has found the properties of polymers that can be better modelled by worm-like chains to show a more complicated molecular-weight dependence, which is perhaps better described by the equation:

$$g = KM^f + K'$$

An attempt to use this equation to describe the viscous properties of rigid-chain polymers was made by Skazka¹⁸, who showed the parameter K' in the relation

$$[\eta] + K' = KM^a \quad (8)$$

to be sensitive to the molecular diameter. However, relation (8), containing one more numerical parameter than equation (1), has not found wide practical application.

Now we present another way of solving the problem in the form of an expression with two parameters.

Numerous experimental data¹⁹ show that for rigid-chain polymers (for $L/A > 2$) the dependence of s_0 (or DM) on $M^{1/2}$ is linear over a wide M range, which agrees with the Hearst-Stockmayer theory²⁰ for hydrodynamic properties of worm-like chains. The invariance (non-sensitivity to M variation) of the expression $D(M[\eta])^{1/3}$ leads to the conclusion that the plot* of $(M^2/[\eta])^{1/3}$ versus $M^{1/2}$ should also be linear²³.

In fact, the experimental data in Figure 4 may be adequately approximated by straight lines to confirm the theoretical prediction and suggest the expressions (9)–(11)

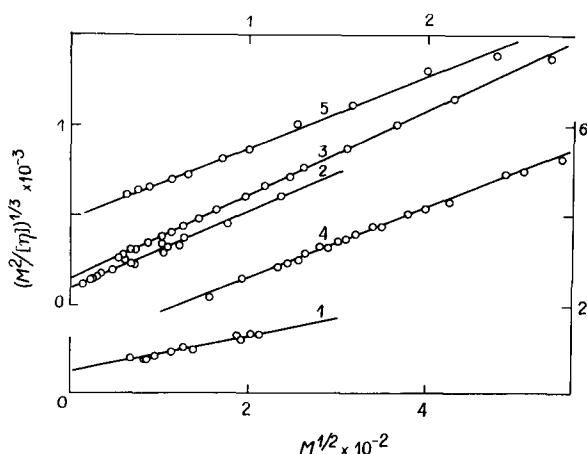


Figure 4 $(M^2/[\eta])^{1/3}$ plotted against $M^{1/2}$ for the same polymers as in Figure 1: (1) poly(1,4-phenylene terephthalamide) in 96% H_2SO_4 (ref. 6), (2) poly(n-butyl isocyanate) in CCl_4 (ref. 7), (3) poly(n-hexyl isocyanate) in n-hexane (ref. 8), (4) cellulose cyanoethyl in acetone (ref. 9), (5) schizophyllan in water (ref. 10) with $[\eta]$ expressed in $ml\ g^{-1}$

* The linear character of the dependence of $(M^2/[\eta])^{1/3}$ on $M^{1/2}$ for rigid-chain polymers was first established by Bushin *et al.*²¹. Later, this result was analysed in ref. 22

for the description of molecular-weight dependences of $[\eta]$, s_0 and D :

$$[\eta] = M^2(K_1 + K_2M^{1/2})^{-3} \quad (9)$$

$$s_0 = K_3 + K_4M^{1/2} \quad (10)$$

$$D = M^{-1}(K_5 + K_6M^{1/2}) \quad (11)$$

where the numerical coefficients K_3 – K_6 may be related by the expressions:

$$K_5 = K_3RT/1 - \bar{v}\rho \quad K_6 = K_4RT/1 - \bar{v}\rho \quad (12)$$

with R as the gas constant, \bar{v} the partial specific volume of the polymer and ρ the solvent density.

The numerical coefficients K_i may also be related to the conformational parameters of the macromolecule A , d and the mass per unit length M_L along the chain contour²³:

$$K_1 = M_L^{1/2}\phi_\infty^{-1/3}A^{-1/2} \quad (13)$$

$$K_2 = kM_L(3\pi A_0)^{-1}[\ln(A/d) - \gamma] \quad (14)$$

$$K_3 = M_L(1 - \bar{v}\rho)(3\pi\eta_0 N_A)^{-1}[\ln(A/d) - \gamma] \quad (15)$$

$$K_4 = M_L^{1/2}(1 - \bar{v}\rho)(\eta_0 P_\infty N_A)^{-1}A^{-1/2} \quad (16)$$

with $\phi_\infty = \lim_{L/A \rightarrow \infty} \phi = 2.870 \times 10^{23} \text{ mol}^{-1}$ (ref. 12); $P_\infty = 5.11$ (ref. 11), $\gamma = 1.056$ (ref. 11), N_A is the Avogadro number and A_0 the hydrodynamic invariant²³. The coefficients K_5 and K_6 can be calculated like in (12).

The coefficients K_i determined by the least-mean-square method for some semi-rigid and rigid-chain polymers are listed in Tables 2 and 3. One may note that, for a flexible-chain polymer under θ -conditions (poly(α -methylstyrene) in cyclohexane at θ -temperature²⁸), an analytical description of hydrodynamic properties as a function of M , using equations (9)–(11), is also consistent with the experimental data.

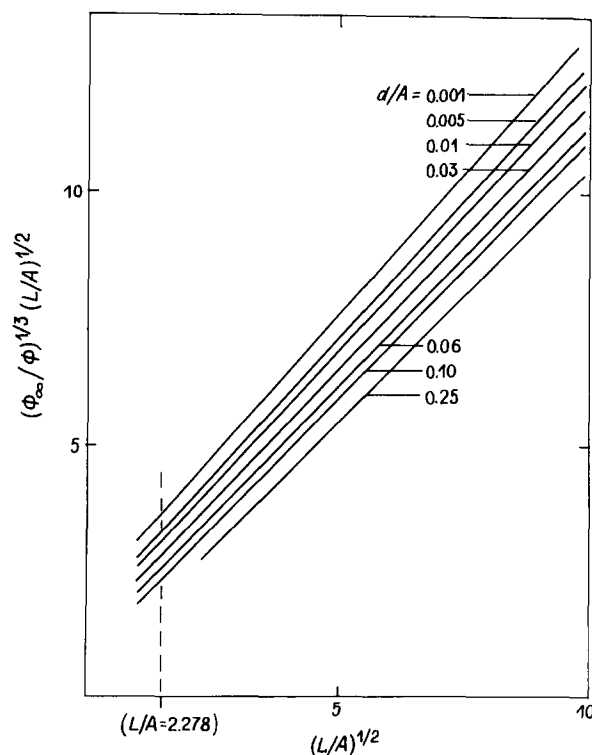


Figure 5 Theoretical dependence of $(\phi_\infty/\phi)^{1/3}(L/A)^{1/2}$ on $(L/A)^{1/2}$ for worm-like chains¹² taken from the table of Bushin²¹. The numbers attached to the curves indicate the values of d/A

Table 2 Experimental values of coefficients K_1 and K_2 in equation (9), coefficient of linear correlation r and least-squares deflection $(\overline{\Delta^2})^{1/2}$ for the points of dependence of $(M^2/[\eta])^{1/3}$ on $M^{1/2}$, with $[\eta]$ expressed in ml g^{-1}

Polymer, solvent	$M \times 10^{-3}$	L/A	K_1	K_2	r	$(\overline{\Delta^2})^{1/2}$
Poly(n-butyl isocyanate) (PBIC) in CCl_4 (ref. 7)	3.8–1380	0.07–27	95 ± 7	0.43 ± 0.01	0.9920	17
Poly(n-hexyl isocyanate) (PHIC) in n-hexane (ref. 8)	68–7240	1.1–121	153 ± 3	0.463 ± 0.003	0.9997	8
Poly(chlorohexyl isocyanate) (PCIHIC) in CCl_4 (ref. 24)	12–306	0.4–9.5	156 ± 6	0.56 ± 0.02	0.9911	11
Poly(1,4-phenylene terephthalamide) (PPPT) in 96% H_2SO_4 (ref. 6)	4.5–45	0.5–5	48 ± 5	0.42 ± 0.03	0.9754	5
Poly(naphthoylene imidobenzimidazole) (PNIB) in 96% H_2SO_4 (ref. 25)	6.7–190	1.6–45	46 ± 8	0.62 ± 0.03	0.9771	13
Cellulose cyanoethyl (CCE) in acetone (ref. 9)	24.5–317	1.2–16	111 ± 5	0.76 ± 0.01	0.9975	6
Polysaccharide native schizophyllan in water (ref. 10)	96–5700	0.1–6.6	490 ± 10	0.39 ± 0.01	0.9976	20
Polysaccharide xanthan in 0.1 M aqueous NaCl (ref. 26)	74–7400	0.3–32	430 ± 10	0.51 ± 0.01	0.9984	23
Poly(γ -benzyl-L-glutamate) (PBLG) in <i>N,N</i> -dimethylformamide (DMF) (ref. 27)	40–660	0.1–1.8	300 ± 10	0.50 ± 0.03	0.9805	21
Poly(α -methylstyrene) (PMS) in cyclohexane (ref. 28)	120–2900	125–3023	0 ± 20	2.44 ± 0.02	0.9997	29

Table 3 Experimental values of coefficients K_3 – K_6 in equations (10) and (11), coefficient of linear correlation r and least-squares deflection $(\overline{\Delta^2})_s^{1/2}$ for the points of dependence of s_0 (or DM) on $M^{1/2}$, with s_0 and D expressed in s and $\text{cm}^2 \text{s}^{-1}$

Polymer, solvent ^a	$M^b \times 10^{-3}$	L/A	$K_3 \times 10^{13}$	$K_4 \times 10^{16}$	$K_5 \times 10^4$	$K_6 \times 10^6$	r	$(\overline{\Delta^2})_s^{1/2} \times 10^{13}$
PBIC in CCl_4 (ref. 7)	15–1380	0.3–27	-1.6 ± 0.1	-3.3 ± 0.2	90	19	0.9800	0.2
PHIC in n-hexane (ref. 8)	68–7240	1.1–121	3.8 ± 0.2	12.2 ± 0.2	250 ^c	80 ^c	0.9980	0.6
PCIHIC in CCl_4 (ref. 24)	12–306	0.4–9.5	-0.88 ± 0.05	-4.1 ± 0.2	81	38	0.9895	0.09
PPPT in 96% H_2SO_4 (ref. 6)	4.5–45	0.5–5	–	–	1.3 ± 0.1	1.09 ± 0.08	0.9773	0.1 ^d
PNIB in 96% H_2SO_4 (ref. 25)	6.7–190	1.6–45	–	–	1.4 ± 0.3	1.9 ± 0.1	0.9772	0.4 ^d
CCE in acetone (ref. 9)	24.5–317	1.2–16	3.0 ± 0.1	18.0 ± 0.4	180	105	0.9967	0.2
Schizophyllan in water (ref. 10)	250–5700	0.3–6.6	5.2 ± 0.2	4.0 ± 0.1	340 ^c	26 ^c	0.9972	0.2
Xanthan in 0.1 M NaCl (ref. 26)	500–7400	2.1–32	5.3 ± 0.2	4.0 ± 0.1	330	24.7	0.9989	0.1
PBLG in DMF (ref. 27)	150–660	0.4–1.8	2.2 ± 0.2	3.1 ± 0.3	214	30.2	0.9642	0.1
PMS in cyclohexane (ref. 28)	120–2900	125–3023	-0.6 ± 0.1	17.8 ± 0.1	48	142	0.9998	0.2

^a The same abbreviations as introduced in Table 2

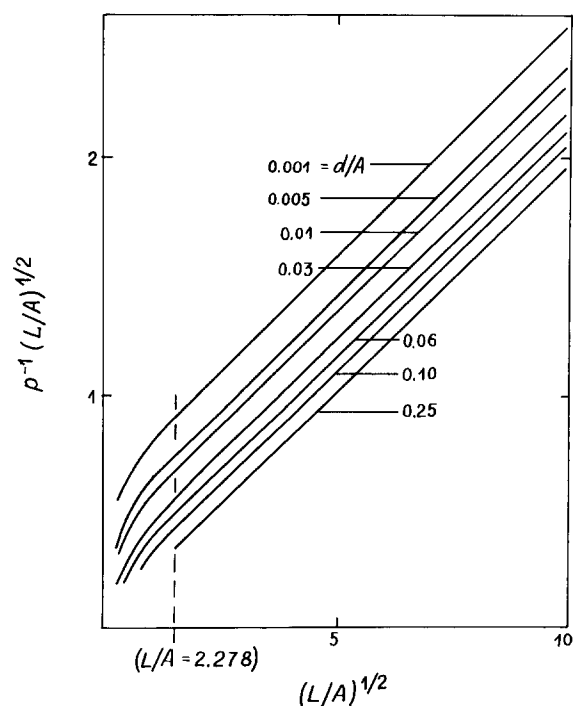
^b Range of M where the dependence of s_0 or DM on $M^{1/2}$ may be approximated by a linear function

^c Values calculated from equation (12)

^d Values of $(\overline{\Delta^2})_s^{1/2} \times 10^4$

Figure 4 shows plots of $(M^2/[\eta])^{1/3}$ versus $M^{1/2}$ to be linear over the whole M range with $L/A > 2.3$. Moreover, for schizophyllan, for instance, the experimental points satisfy the straight-line approximation (curve 5 in Figure 4) over all the M range, including the range with $L/A < 2.3$. For the other polymers, too, the range for reliable linear approximation of the viscosity data by (9) is wider than that for the sedimentation–diffusion data, as one can see from comparison of Tables 2 and 3.

This experimental fact agrees with the theoretical results shown in Figures 5 and 6 using a spherocylindrical model. According to these theories, the plot of $(\phi_\infty/\phi)^{1/3}(L/A)^{1/2}$ versus $(L/A)^{1/2}$ (Figure 5), equivalent to the dependence of $(M^2/[\eta])^{1/3}$ on $M^{1/2}$, is linear over a wider L range than the plot of $P^{-1}(L/A)^{1/2}$ versus $(L/A)^{1/2}$ (Figure 6), equivalent to the dependence of s_0 (or DM) on $M^{1/2}$.


Figure 6 Theoretical dependence of $P^{-1}(L/A)^{1/2}$ on $(L/A)^{1/2}$ for worm-like chains¹¹ with indicated values of d/A

CONCLUSIONS

Thus, from the foregoing presentation one can see the wider non-sensitivity of coefficients in equations (9)–(11) to M variation than in the MKH equations, and as a result their wider applicability for adequate analytical description of hydrodynamic characteristics as a function of molecular weight.

Moreover, the numerical coefficients in equations (9)–(11) are related to the conformational parameters of the macromolecule via expressions (13)–(16). This means that one can compare the properties of different polymers from the numerical values of the coefficients K_1 – K_6 (taking into account the different M_L values). This circumstance makes equations (9)–(11) advantageous over the empirical MKH equations. Finally, equations (9)–(11) allow one to predict the hydrodynamic properties of rigid-chain polymers with known values of M_L , A and d in solution.

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