Number-Average and Viscosity-Average Molecular Weights of Popular Drag Reducing Polymers

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The number-average and viscosity-average molecular weights of poly(ethylene oxide) (PEO) and poly(acrylamide) (PAM) polymers have been tabulated together with the polymer drag reduction efficiencies. Neutron-irradiated poly(ethylene oxide) polymers have a different drag reduction dependence on molecular weight than the nonirradiated polymers. Commercial PEO samples have much higher polydisperity indices than commercial PAM samples. The interplay of molecular structure and molecular weight distribution on the observed drag reduction are clearly indicated in the data.

A large number of natural and synthetic polymers have been shown to have drag reducing properties (3) and of this rather large group the poly(ethylene oxide) (PEO) and poly(acrylamide) (PAM) polymers have been the most widely investigated. While much drag reduction data has been collected on these two families, information on their molecular properties has not been given in the majority of cases. In this report a collection of vis-cosity-average (M_v) and number-average (M_n) molecular weights of commercial samples of these two families is offered as an aid to recognizing the importance of these molecular parameters—particularly in the correlation of drag reduction data with polymer characteristics.

Table I reports a variety of data obtained with selected members of these two families. The intrinsic viscosities of the PEO family were determined at 25 °C and a shear rate of 15 s^{-1} in water while those for PAM were taken at 30 °C and 20 s^{-1} in 0.5 M MgSO$_4$; in both cases a Cannon multiple bulb viscometer was used. The viscosity-average molecular weight of PEO was calculated from the relation of Bailey et al. in water (2) while that for PAM was estimated from the equation developed by Suen et al. in 1 M NaNO$_3$ (7). The osmotic data, taken at 25 °C, were obtained with a Hewlett-Packard membrane osmometer connected to a digital voltmeter and printer; data for PEO were obtained in distilled water while those for PAM were collected in 0.1 M NaCl solutions. The reduced osmotic pressure, $(\pi/c)_0$, was determined by extrapolation to zero concentration. The values

of the second virial coefficient, A_2, for the PEO samples were widely scattered but those for the PAM samples followed the relation $A_2 = 1.5 \times 10^{-2}M_n^{-0.21}$. The polydispersity of the samples is reported as M_v/M_n. The apparatus employed for drag reduction measurements has been previously described in some detail (9). Essentially, it was an automated version of a type previously used by Hoyt (3). The flow pipe, however, was a Pyrex capillary tube with the first tap 200 diameters from the entrance, and the second tap 100 diameters from the first and 54 diameters from the tube exit. The tube diameter was 0.1575 cm. The pressure transducer output and the dc generator output (which monitored the flow rate) were converted to logarithmic signals and fed to an x–y recorder. In the last column the drag reduction index (9), DR$_M$/[c], in water for each polymer is listed.

Several interesting features arise out of Table I. First of all, for the PEO series the WSRN polymers which have been neutron-irradiated in the manufacturing process have lower values of the polydispersity index, M_v/M_n, than do the WSR series. The WSR samples have polydispersities covering the astonishing range of 12 to 72 while those for the WSRN series vary from 4.6 to 11. With respect to the PEO polymers the PAM polymers are far less polydisperse and their indices range from 2 to 5 from the samples studied here. A plot of the drag reduction index, DR$_M$/[c], vs. M_v for the Polyox data is shown in Figure 1. The graph indicates that the neutron-irradiated materials behave differently from untreated polymers although nominally they are of the same chemical family. In the case of the commercial polyacrylamides, however, no clear family relationship (see Figure 1) can be expected because of the varying degree of hydrolysis and its effect on polymer coil expansion (4). While the solid circles (PAM data) indicate a general increase of the drag reduction index with molecular weight the scatter of points and the nonlinearity of the data suggest the interplay of molecular weight and hydrolysis effects which cannot be separately accounted for by the limited data presented here. In addition, plots of the drag reduction index vs. intrinsic viscosity for these four samples also show no precise linear relation (6). On the other hand, laboratory-synthesized nonionic PAM samples (nonhydrolyzed) have demonstrated an excellent linear correlation between their drag reduction indices and their intrinsic viscosities

Table I. Number-Average and Viscosity-Average Molecular Weights of Selected Commercial Poly(ethylene oxide) and Poly(acrylamide) Polymers

| Compound	Manufacturer	Family	$[\eta]$	M_v	$(\pi/c)_0$	M_n	M_v/M_n	DR$_M$/[c]
WSRN-80	Union Carbide	PEO	2.8	4.8×10^5	0.591	4.2×10^4	11	0.063
WSRN-750	Union Carbide	PEO	3.7	6.9×10^5	0.300	8.4×10^4	8.2	1.97
WSRN-3000	Union Carbide	PEO	4.0	7.6×10^5	0.160	1.6×10^5	4.8	4.72
WSR-205	Union Carbide	PEO	3.9	7.4×10^5	0.407	6.2×10^5	12	4.00
WSR-1105	Union Carbide	PEO	4.3	8.4×10^5	0.582	4.3×10^4	19	5.00
Coagulant	Union Carbide	PEO	12.5	3.3×10^6	0.172	1.5×10^5	22	33.3
WSR-301	Union Carbide	PEO	18.0	5.3×10^6	0.344	7.3×10^4	72	52.6
MAGNIFLOC	American Cyanamide	PAM	4.5^a	1.8×10^6	0.0412^b	6.1×10^5	3.0	3.4
WP-20	Dow Chemical	PAM	8.4^a	4.5×10^6	0.115^b	2.2×10^6	2.0	18.9
P-250	American Cyanamide	PAM	10.0^a	6.0×10^6	0.215^b	1.2×10^6	5.0	17.2
MAGNIFLOC 905N	American Cyanamide	PAM	13.4^a	9.4×10^6	$(\sim0.007)^b$	(3×10^6)	3.0	27.3

^{a} In 0.5 M MgSO$_4$. ^{b} In 0.1 M NaCl.
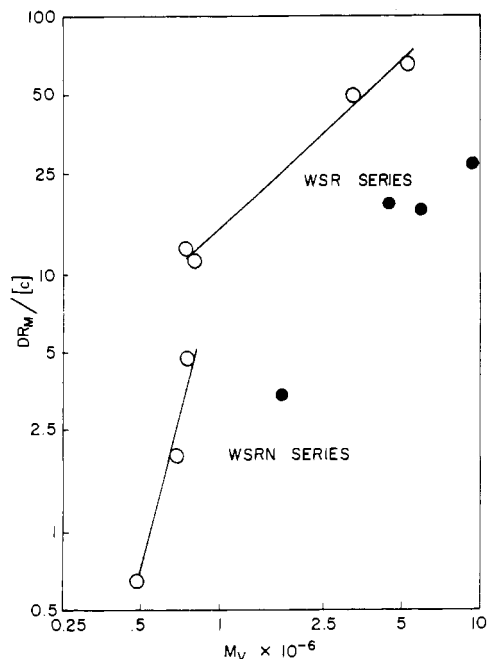
Figure 1. Drag reduction index vs. viscosity-average molecular weight for commercial Polyox (open circles) and polyacrylamide compounds.

(5). Thus, the effect of changes in molecular structure and molecular weight distribution on the observed drag reduction are clearly indicated here.

For purposes of comparison the ratio of the weight-average to the number-average molecular weight M_w/M_n was determined by Abdel-Alim and Hamielec (1) for a commercial PAM sample (Polyball 402, Stein-Hall, Ltd.) and found to be 2.43 again indicating the narrower molecular weight distribution of commercial PEO samples. Unfortunately, the equation of Collison et al., i.e., $[\eta] = 6.8 \times 10^{-4} M_n^{0.66}$ was used in the molecular weight computations by these authors. The Mark Houwink exponent of 0.66 appears rather low and is thought to be the result of the original experiments by Collison et al. having been made in solutions approximately 0.1 M in perchloric acid and 0.05 M in ferric

and/or ferrous ion. Such high ionic concentrations can easily reduce the value of the exponent. For example, Suen et al. (7) obtained the relation $[\eta] = 3.37 \times 10^{-4} M_w^{0.66}$ for PAM polymers in 1 M NaNO$_3$. Sholton (8), on the other hand developed the relation $[\eta] = 6.31 \times 10^{-5} M_w^{0.80}$ for PAM polymers in pure water.

While the literature contains an abundance of drag reduction measurements for a large variety of materials in a decade and a half of active research by many groups the characterization of the individual materials used has been neglected. A minimum characterization of drag reducing agents in terms of their molecular weight averages would ensure the quality of future reports published in this area and also promote the possibility of reproducing the experimental results.

Glossary

M_v	viscosity-average molecular weight
M_n	number-average molecular weight
$[\eta]$	intrinsic viscosity
π	osmotic pressure
c	concentration
$(\pi/c)_0$	reduced osmotic pressure extrapolated to zero concentration
A_2	second virial coefficient in equation $\pi/c = RT(1/M_n) + A_2 C)$
DR$_M$	maximum drag reduction in equation DR/DRM = $c/(c + [c])$
$[c]$	intrinsic concentration
DR$_M$/$[c]$	drag reduction index

Literature Cited

(1) Abdel-Alim, A. H., Hamielec, A. E., J. Appl. Polym. Sci., 18, 297 (1974).
(2) Bailey, F. E., Kucera, J. L., Imhof, L. G., J. Polym. Sci., 32, 517 (1958).
(3) Hoyt, J. W., Polym. Lett., 9, 851 (1971).
(4) Kim, O. K., Ting, R. Y., Little, R. C., AIChE Symp. Ser., 69, No. 130, 39 (1973).
(5) Kim, O. K., Little, R. C., Ting, R. Y., J. Colloid Interface Sci., 47, 530 (1974).
(6) Patterson, R. L., Hunston, D. L., Ting, R. Y., Little, R. C., J. Chem. Eng. Data, 20, 381 (1975).
(7) Suen, T. J., Jen, Y., Lockwood, J. V., J. Polym. Sci., 31, 481 (1958).
(8) Sholtan, W., Makromol. Chem., 14, 169 (1954).
(9) Ting, R. Y., Little, R. C., J. Appl. Polym. Sci., 17, 3345 (1973).

Thermodynamic Properties of Liquid Sulfur Hexafluoride from 0 to 50 °C to 200 Bars

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The density of SF$_6$ was measured from 0 to 50 °C at 5 °C intervals with pressures ranging from saturation to 170 bars. Rational functions representing the experimental isotherms and isobars were developed from which entropy, enthalpy, and isothermal compressibility were calculated.

The purpose of this paper is the presentation of the thermodynamic properties (density, isothermal compressibility, entropy, and enthalpy) of SF$_6$ in the compressed liquid region. Although some data on the density of liquid SF$_6$ are available in the liter-

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ature (3), the amount of the available data does not allow the accurate calculation of the derived properties. In the present work, the density of liquid SF$_6$ was measured along isotherms from 0 to 50 °C at 5 °C intervals; the pressure ranged from saturation to 170 bars.

Experimental Section

A detailed discussion of the method used for the measurement of the density is given in ref 1 and 2. The method employed a device which operates on the principle of buoyancy. The device which is supported by a pivot is housed in a pressure vessel and is completely immersed by the fluid under study. The angular orientation of the device is uniquely related to the density of the