Viscosity Index. II. Correlation with Rheological Theories of Data for Blends Containing n-Octadecyl Acrylate

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Synopsis

The viscosities obtained for the copolymer blends of the previous paper were correlated with several relations derived to describe more fundamental behavior of polymer–diluent mixtures at both infinite dilution and finite concentrations. Only the most efficient blends showed any appreciable expansion of hydrodynamic volume as temperature increased from 25° to 98.9°C. However, in spite of restricted coil expansion, all of the copolymers were effective viscosity index improvers. The mechanism of viscosity index improvement in multigrade oils was shown to be largely regulated by the translational friction generated by the polymer coils. This greatly increased the apparent negative entropy change of the blends; the enthalpy change characteristic of the base oil was retained. Efficiency resulted from coil contraction at low temperatures, but enthalpy decrease below that of the base oil was small. In contrast, viscosity index improvement using higher molecular weight solvents was accompanied by large enthalpy increases. Thus, undesirably high viscosities resulted at low temperatures. The structure of these blends was uncomplicated by polymer chain entanglements; unit values of the Fox-Flory exponent were obtained for the relation between viscosity and weight-average carbon backbone length. The lack of evidence for coil compression in the thermodynamically miscible blends above a critical reduced concentration was anomalous. Intermingling of side chains and their interaction may have overcome normal excluded volume effects.

INTRODUCTION

In the previous paper of this series,[1] selected copolymers, all containing n-octadecyl acrylate as a common comonomer, were evaluated as viscosity index improvers in a common base oil under low shear conditions only. In this paper, rheological data of the previous work are correlated with relationships having origins in fundamental theories of viscosity behavior. Basic studies of the liquid state for simple solvents including those used in lubrication[2,3a,b] and for polymers in bulk and in diluents[4,5] have revealed complexities that cannot be expressed by simple, single-parameter expressions like the viscosity index relation[6] and ASTM slope[7,8] considered so far. To a first approximation,[5] the viscosity of polymers in bulk and in diluents over very large temperature ranges can be expressed simply as the product of a structurally sensitive factor F dependent on molecular weight and chain entanglements, and a frictional factor ζ dependent on temperature and density. However, on closer scrutiny, even the three-parameter Vogel equation[9] (modified by incorporation of expressions reflecting the molecular weight of polymer and the effect of concentration on entanglements,[4,5,10] variable free volume[11–14] in the T_g-to-$(T_g + 100°)$ temperature region,[15] and the predominance of activation processes at higher temperatures[16,17]) fails to completely describe viscosity at all temperatures.

Fortunately, the concerns of this work are more limited in scope. It was recognized that the classical description of polymer coils at infinite dilution[18a,b] would be unrealistic for the present systems, where temperature effects on viscosity were modified only because concentration was finite. However, both the concentrations and temperatures employed covered relatively narrow ranges. Crystalline phase separation, which discontinuously increases viscosity, occurred in the temperature range of interest. This is considered in the next paper.[19] Above the melting points, activation parameters[16,17] for flow should be adequate to describe the frictional effects. Structural contributions of the polymer coils to viscosity magnitude should be restricted to essentially hydrodynamic effect without complications of entanglement coupling because of the relatively small polymer concentrations employed. However, the concentrations were high enough that coil compression[20,21] might limit to some extent the hydrodynamic volume, as reflected in the observed intrinsic viscosities.[22–24] This work tests some of these concepts.

More specifically, in this work, the influence of temperature on the intrinsic viscosities of the copolymers in base oil S105 will be correlated with their structural contributions to efficiency, as defined and treated in the previous paper. Differences in mechanisms for the viscosity–temperature effect exhibited by oils and their multigrade blends will be discussed. Finally, exponents of the Fox-Flory equation[25,26] will be used to monitor the extent of chain entanglement coupling, and the relations of Simha et al.[20,22] will test other effects of finite concentration on coil interactions.

EXPERIMENTAL

Weight-Average Molecular Weights

These were described in the previous paper.[1]

Density and Intrinsic Viscosity Determinations

Density of the base oil S105 was determined at three temperatures, 30°, 60°, and 80°C, using a 25-ml pycnometer; density at any temperature was computed from the linear constants. Density of the copolymers was estimated using the group additivity method of Van Krevelen.[27] By assuming additivity of volume, densities of the mixtures were used to convert the experimental weight fraction of copolymers in the blends[1] to concentration in g/dl. These concentrations were used in estimating intrinsic viscosities and in the Simha relationship. The densities were also used to obtain absolute viscosities in correlating viscosity with the weight-average chain length $\bar{Z}_w$. The latter quantity was taken as two times the weight-average degree of polymerization.[4,5] Average values of the copolymer units[1] were used to obtain the degree of polymerization. Most of the calculations and all of the curve fittings were done using an IBM 1130 computer.

In spite of the relatively large polymer concentrations employed in S105 (See Table I of the previous paper[1]), plots of η_{sp}/c versus c were significantly linear by computer fit. Results in benzene, when plotted using the concentrations of this work and smaller concentrations more appropriate for use of the Huggins equation,[18c] fell on the same line. Consequently, the need for the log form of

the Huggins equation (the Martin equation) was avoided. Further aspects of these observations are discussed in the last section of this paper. Corrections for rate of shear were not required.[18c]

In this paper, as in the previous one, subscript 2 designates copolymer and subscript 1, solvent in the mixture; w_i and m_i are weight and mole fraction, respectively. Subscript b designates n-octadecyl acrylate in the copolymer; subscript a designates the other comonomer. Kinematic viscosities at specific temperatures (98.9°C, for instance) are described as $\eta_{98.9°C}$ in centistokes and absolute viscosities as η_{cp} in centipoises.

RESULTS AND DISCUSSION

Intrinsic viscosities at the four experimental temperatures (25°, 37.8°, 54.5°, and 98.9°C) are listed in Table I for the same experiments whose viscosity–temperature indices were presented, in the same order, in the previous paper of this series.[1] Weight-average molecular weights, estimated by gel permeation chromatography,[1] are listed for the systems for which they were available. As can readily be seen, there was very little change in the intrinsic viscosities as temperature changed for most of the copolymers. In fact, only those samples exhibiting maximum efficiencies at standard SAE viscosities in Table II and V of the previous paper,[1] namely, experiments 3 and 4 and the acryloids, experiments 22–24, exhibited any appreciable increase in $[\eta]$ with increase in temperature. Some (experiments 6–11) even showed a small decrease. These observations are discussed at greater length in the sections below. In column 10 are listed ratios of specific viscosities at a constant weight fraction of polymer in the blend, w_2, of 0.025. Ratios of specific viscosities have been used by others[28,29] to denote efficiency, following a suggestion by Bondi.[2] In the last column, concentration was eliminated by using ratios of intrinsic viscosity. Efficiencies in both columns show essentially the same results. However, intrinsic viscosity ratios would appear to be more accurate because variable, concentration-dependent interactions affecting the magnitude of the Huggins constant k' for different systems[18c] have been eliminated. Again, it can be seen that efficiencies are greatest with experiments 3, 4, and 22–24 although some poly(n-octadecyl acrylate) homopolymers are satisfactory. The same basic trends are noted in the previous paper, where viscosity index values at fixed SAE viscosities are compared.[1] Clearly, hydrodynamic expansion of the polymeric additive with temperature governs efficiency.[2,3,18a,b,28–32]

Temperature Effect on Intrinsic Viscosity

In Figure 1, intrinsic viscosities for all of the copolymers investigated in base oil S105 are plotted as a function of temperature. Intrinsic viscosities selected from the extensive data of Berry[33] for reasonably monodisperse polystyrene fractions in a theta solvent (decalin) are also presented in the figure. Data for the fractions having weight-average molecular weights similar (see legend) to those of the copolymers of this work were selected. The intrinsic viscosities of even the most efficient copolymers of this work (inserts A and D) rose significantly less than those of their polystyrene counterparts (closer to curve b in both inserts). In insert B, there was an apparent small contraction of the copolymer

TABLE I
Intrinsic Viscosities, Weight-Average Molecular Weights, and Efficiency Ratios for Various Copolymers in S105

Experiment no.[a]	Experiment description	w_b[b]	GPC $\overline{M}_w$	$\overline{DP}_w$	Intrinsic viscosity [η], dl/g 25°C	37.8°C	54.5°C	98.9°C	$\eta_{sp98.9°C}/\eta_{sp37.8°C}$[c]	$[\eta]_{98.9°C}/[\eta]_{37.8°C}$
1	Base oil									
2	OA + MMA	0.636			0.168	0.174	0.206	0.226	1.25	1.30
3	OA + MMA	0.798	479,200	2143	0.345	0.422	0.470	0.530	1.16	1.26
4	OA + MMA	0.883	800,000	3110	0.641	0.702	0.751	0.768	1.03	1.09
5	OA + MMA	0.948	1,138,000	3912	0.946	0.942	0.957	0.995	0.957	1.06
6	OA + EHA	0.085	271,000	1417	0.419	0.393	0.374	0.390	0.874	0.992
7	OA + EHA	0.164			0.448	0.426	0.404	0.417	0.891	0.979
8	OA + EHA	0.237			0.482	0.469	0.452	0.444	0.860	0.947
9	OA + EHA	0.306	337,000	1587	0.486	0.460	0.453	0.438	0.853	0.952
10	OA + EHA	0.430			0.554	0.535	0.535	0.534	0.909	0.998
11	OA + EHA	0.540	397,000	1652	0.638	0.619	0.608	0.614	0.889	0.992
12	OA + DA	0.253			0.973	1.042	1.014	1.037	0.941	0.995
13	OA + DA	0.367			1.115	1.121	1.099	1.106	0.924	0.987
14	POA	1.00	1,622,000	4998		1.028	1.047	1.037	0.884	1.01
15	POA	1.00				0.597	0.588	0.593	0.930	0.993
16	POA	1.00				0.340	0.337	0.347	0.956	1.02
17	POA	1.00				0.222	0.221	0.215	0.953	0.968
18	POA	1.00				0.156	0.154	0.147	0.933	0.942
19	POA	1.00				0.084	0.081	0.083	0.965	0.988
20	POA	1.00				0.057	0.057	0.052	0.946	0.912
21	POA	1.00				0.042	0.040	0.039	0.901	0.929
22	Acryloids[d]	0.425			0.347	0.367	0.373	0.416	1.062	1.13
23	Acryloids[d]	0.425	372,500	1880	0.396	0.406	0.422	0.465	1.044	1.15
24	Acryloids[d]	0.425			0.448	0.445	0.469	0.502	1.051	1.13

[a] Experiment numbers and description correspond to those of Table I of the previous paper.[1]

[b] Weight fraction of n-octadecyl acrylate in the copolymer, except for experiments 22–24, where w_b is thought to be n-dodecyl methacrylate (see previous paper[1]).

[c] Viscosities at a concentration of w_2 = 0.025 were used.

[d] Acryloid (Rohm and Haas) designations were: experiment 22, 732; 23, 710; 24, 772.
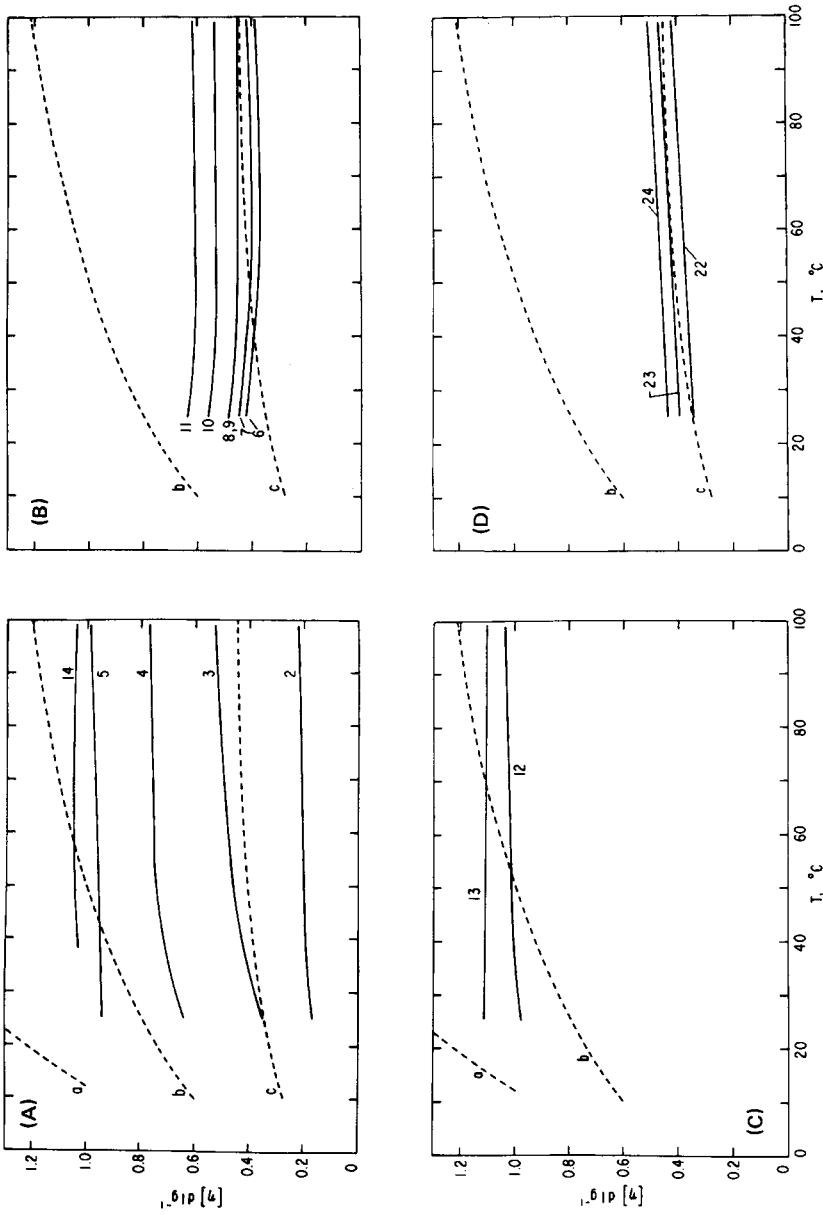
Fig. 1. Intrinsic viscosity vs. temperature for copolymers in base oil S105 (solid lines) and for polystyrene in decalin, a theta solvent (dashed lines). The latter is from the extensive data of Berry.[33] For the polystyrene fractions, weight-average molecular weights were: (a) 15.6×10^5; (b) 6.20×10^5; (c) 1.25×10^5. Numbers refer to the experiments of Table I. Weight-average molecular weight (Table I) are within the range of curves (a), (b), (c).

coils with increase in temperature. Comparison of the polystyrene data and that of this work is, of course, justifiable only in a qualitative sense.[18a,b] The purpose here is to permit the experimental data to be contrasted with a system showing a typical hydrodynamic expansion in the neighborhood of the theta temperature (limit of the dashed curves at the left). It may be concluded that the efficiency displayed by even the best copolymers of this work (experiments 3, 4, 22–24) made use of only a small fraction of the expansion possible if the base oil had behaved as a true theta solvent. That is, for all of these copolymers (Table I), even the most efficient, T_θ, was displaced considerably below the experimental range (25°–98.9°C, Table I), yet all of the copolymers of this paper were effective viscosity index improvers.[1] It may be helpful, therefore, to examine these data in terms of infinite dilution theory[18a,b] to see what factors are important in tailoring copolymer structures to be effective viscosity index improvers.

The classical[18a,b] relation between intrinsic viscosity and molecular weight for a polymer dissolved in a good solvent is, at infinite dilution,

$$[\eta] = KM^{1/2}\alpha^3 \tag{1}$$

where $K = \Phi(\bar{r}_0^2/M)^{3/2}$; Φ is the Flory universal constant; $\bar{r}_0$ is the unperturbed end-to-end distance; M is the molecular weight; and α is the expansion coefficient of the Flory-Krigbaum treatment. In poor solvents at T_θ, eq. (1) simplifies to

$$[\eta]_\theta = KM^{1/2} \tag{2}$$

In the design of viscosity index improvers for maximum low-temperature efficiency,[28,29,34,35] the empirical approach usually taken is to select a polymer-solvent system in which the solvent is a relatively poor one for the polymer[36] in the temperature range of 37.8°–98.9°C (100°–210°F). Consequently, for maximum efficiency, T_θ should lie only slightly below 37.8°C. Only then will the expansion factor, α in eq. (1), achieve its maximum rate of increase, as is apparent from the relation

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - T_\theta/T)M^{1/2} \tag{3}$$

where ψ_1 is the proportionality constant relating the contribution to partial entropy of dilution due to nearest-neighbor polymer–solvent interactions, ΔS_M, to the square of the volume fraction v_2 of polymer in the solvent,

$$\Delta S_M = R\psi_1 v_2^2 \tag{4}$$

and where C_M in eq. (3) is a constant combining theoretical constants for the intramolecular excluded volume effect of the polymer–solvent system. The magnitude of the coefficient of M in eq. (3), namely, $\psi(1 - T_\theta/T)$, is determined finally by the enthalpic partial molar coefficient κ_1 for low concentrations, defined by

$$\Delta H_1 = RT\kappa_1 v_2^2 \tag{5}$$

because

$$\psi_1 - \kappa_1 = \psi_1(1 - T_\theta/T) \tag{6}$$

In an athermal solvent, where κ_1 and T_θ are zero, the temperature coefficient of $[\eta]$ should be zero; in a very good solvent, where κ_1 and thus T_θ are negative, the coefficient should be negative. Systems like these should exhibit no viscosity

index improvement. For all systems where VI improvement is possible, the solvent is considered to be poor for the polymer. However, eq. (3) shows that the rate of change of $[\eta]$ with T is large only close to T_θ. Consequently, the copolymers used in this work all behave as though the base oil were a poor solvent, in consideration of the system of classification introduced above. That all probably fit this classification is implied from plots of $\ln [\eta]$ versus $\ln \overline{M}_w$ in Figure 2. All of the available data, regardless of structure, fit the Mark-Houwink relation, $6.47 \times 10^{-5} \overline{M}_w{}^{0.681}$, at 37.8°C, in Arco S105. The rather severe scatter exhibited by some of the points is random. This probably reflects the extremes of experimental error to be expected for plots that include several different copolymer types.

Similar plots and constants of similar magnitude were found at the other temperatures. It is unlikely that intrinsic viscosities for individual systems, where the base oil is acting either as a good or athermal solvent, would fall near this line.[18b] The proximity of experiments 3 and 23 to the line of Figure 2, coupled with the behavior shown in insert A of Figure 1, demonstrates that for even the most efficient experiments, $d[\eta]/dT$ is smaller than it would be in the vicinity of T_θ. Only careful adjustment of composition between that of experiment 3 and experiment 2 (where precipitation occurs) should enable T_θ to approach the temperature range of interest (25°–98.9°C) and be most efficient in the application. It may be concluded that optimization of viscosity index improvers requires that κ_1 in eq. (6) be made strongly positive thus raising T_θ to the initial temperature (~37.8°C) of the useful range. This can, in principle, be accomplished in paraffinic oils by making the copolymers more polar[37] so that the factor $\psi_1(1 - T_\theta/T)$ in eq. (3) achieves its maximum value. Then α^3 in eq. (1) can expand to the maximum permissible value over the temperature range. However, to avoid polymer precipitation,[18a,b] T_θ should be below the minimum temperature encountered in service (below −18°C). Clearly, a compromise is required in industrial practice. Fortunately, the accepted cold crank simulator
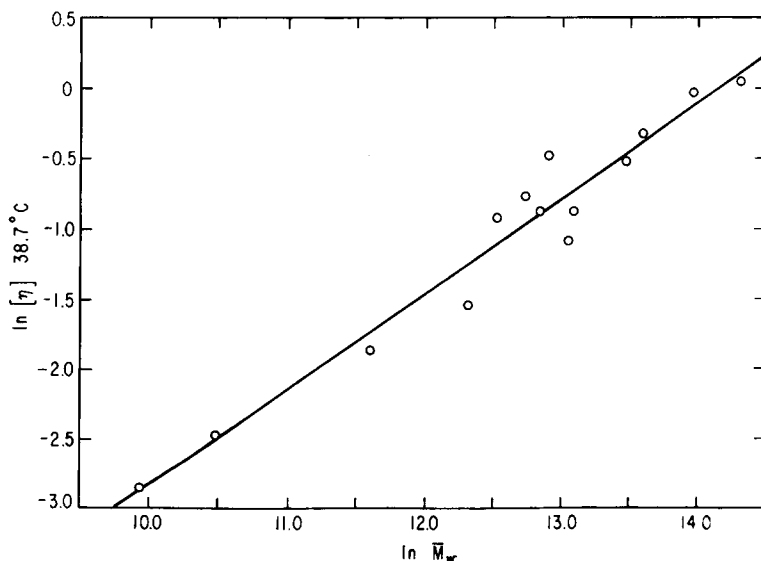

Fig. 2. The Mark-Houwink relation between $[\eta]$ and $\overline{M}_w$ for the combined experiments of Table I and in S105 at 37.8°C.

test[38] for grading oil blends at low temperatures avoids these complications, and these produced by the non-Newtonian nature of these systems at high rates of shearing,[39] by determining viscosities under simulated engine conditions.[40]

Thus far, viscosities at the limit of zero concentration exclusively have been considered; the balance of this paper is concerned with the more complex effects of finite concentration. These are, of course, important in that they govern the mechanism of practical viscosity index improvement.

Mechanism of Behavior of Polymer-Thickened Oils

As discussed in the introduction, the relation between viscosity and temperature, over a very wide span of temperature, is complex. Concentrating in this section on only the translational frictional aspect of the problem and treating data only at temperatures high enough to be far removed from $T_g + 100°C$, one can use simple activation parameters as an adequate description of flow viscosity. Thus, the theoretical relation of Eyring[16,17] based on a free volume model[10-15] can be used as a description of the relation between viscosity and temperature over narrow temperature intervals. This relation can be stated as

$$\eta = (hN/V)\, e^{-\Delta S_a/R} e^{\Delta H_a/RT} \qquad (7)$$

where h is Planck's constant, N is Avogadro's number, and V is the average molar volume; ΔS_a and ΔH_a are the entropy and enthalpy of activation for viscous flow. Unfortunately, except at very high temperatures ΔH_a is not constant with temperatures for either simple liquids[2,3] or polymer diluent mixtures[4,5] because of the complications alluded to in the introduction. Because $\ln \eta$ versus $1/T$ was not linear over the temperature range of this work, the relation $-R[d\eta/d(1/T)]$ was solved for $\Delta(1/T)$ using the experimental temperature spans $25°-37.8°C$, $37.8°-54.5°C$, and $54.5°-98.9°C$, respectively, and the upper and lower viscosity of each span. Data for selected systems are presented in Table II for three concentrations of polymer in base oil S105, together with an average value for the concentrations. The value of ΔH_a was taken to correspond to the midpoint of the respective temperature range.

In this simple model of the liquid state, the enthalpy of activation represents the energy barrier to segmental jumps on a lattice grid containing holes created by thermal agitation. These holes, in part, constitute the so-called free volume.[10-14] The entropy term governs the long-range effects in pure solvents and in polymer blends. Because whole solvent molecules are thought to make a lattice jump and since solvent dominates the total volume fraction of multigrade blends, the enthalpy term should largely reflect solvent.[2,4,16] In addition, polymer segments, being similar in size to the solvent molecules, have similar energies.[4,17] Translational motion of molecules of polymer and solvent contribute to the entropy term; because the frictional coefficient of polymer coils is large compared to that of molecules of simple liquids,[41a,b] the entropy term of eq. (9) should largely determine the viscosity and therefore the ASTM slope of multigrade blends.

In support of these principles, the quantities in Table II show that ΔH_a for most of the copolymers at all concentrations is close to that of the solvent (see also the last column, Table I). In contrast, ΔS_a (and, of course, $\ln A_0$) are highly sensitive to the molecular weight and concentration of the copolymer used as

TABLE II

Apparent Enthalpy and Entropy of Activation for Viscous Flow at 76.7°C for Selected Copolymers in S105 at Several Concentrations

Experiment no.	System	ΔH_a, cal/mole				ΔS_a, cal/mole deg.			ln A_0		
		0.025[a]	0.050	0.075	Ave.[b]	0.025[a]	0.050	0.075	0.025[a]	0.050	0.075
1	S105	6.27				-8.74			-7.13		
3	OA + MMA	5.97	5.97	5.88	6.00	-11.6	-12.7	-14.0	-5.66	-5.14	-4.46
4	OA + MMA	6.27	6.19	6.22	6.24	-11.3	-12.9	-14.0	-5.85	-5.01	-4.45
5	OA + MMA	6.46	6.53	6.50	6.44	-11.1	-12.6	-13.9	-5.91	-5.18	-4.50
8	OA + EHA	6.60	6.57	6.65	6.53	-9.06	-10.6	-11.1	-6.80	-5.99	-5.78
12	OA + EHA	6.40	6.56	6.63	6.48	-11.6	-12.8	-13.9	-5.70	-5.08	-4.52
14	POA	6.53	6.57	6.50	6.48	-11.5	-13.1	-14.5	-5.73	-4.95	-4.21
15	POA	6.47	6.51	6.58	6.46	-10.2	-11.5	-12.3	-6.38	-5.75	-5.31
17	POA	6.34	6.44	6.39	6.38	-9.39	-9.84	-10.8	-6.80	-6.57	-6.08
19	POA	6.28	6.36	6.39	6.33	-9.06	-9.17	-9.41	-6.99	-6.91	-6.77
21	POA	6.30	6.30	6.33	6.31	-8.75	-8.96	-9.04	-7.12	-7.01	-6.97
23	Acryloid	6.20	6.20	6.27	6.22	-10.6	-11.9	-12.7	-6.19	-5.52	-5.09

[a] Weight fraction of copolymer in S105.
[b] Average includes data for $w_2 = 0.005$.

thickener, ΔS_a having a larger negative value with increase in both. The decrease in the negative value of ln A_0 with increase in concentration also reflects this.

The difference in mechanism of polymer-thickened blends and untreated base oils can be seen from the data displayed in Figure 3. Here, the ΔH_a and ΔS_a quantities of Table II (but including data at w_2 of 0.005) were fitted by computer as a function of ASTM slope s. The solid line is the regression line for the enthalpy of activation data; the dashed line, for the entropy of activation. Limits of both relations are the terminus of both lines at the right and represent the base oil. It may be seen that as VI improvement increases (ASTM slope decreasing right to left in the figure), there is little change in the enthalpy of activation between blend and solvent. Even the spread between the most efficient systems and the least (limits of the vertical bars) is not great. In contrast, the rate of change of the negative entropy values with ASTM slope was large. Here, the bars represent statistical variation; no trends pertaining to efficiency effects were observed. The data clearly support the principles just discussed. The activation enthalpy of the solvent was essentially preserved, and the major VI improvement was produced by the decreased entropy of the blends. Efficiency resulted from coil contraction at low temperatures, which lowered enthalpy below that of the solvent, but the effect was relatively small.

Improvement in the ASTM slope of untreated oils[2] (decrease in s) followed the dotted line in Figure 3. In contrast to the blends, ΔH_a for the base oils increased as ASTM slope decreased. Entropy effects (experiments on line marked (X), base oil S105 and benzene, respectively) parallel the change in ΔH_a; their behavior was very different from that of the blends. Thus, as the molecular weight of the oils increased in going from right to left in the figure, ΔH_a also increased.[2,4,16] Consequently, in lube oils, increasing viscosity in an effort to raise VI by using higher molecular weight oils of similar structure will result in increased activation enthalpy because of reduced jump frequencies. The VI improvement will be unsatisfactory, and high viscosities at low temperatures will result. The principlex outlined above have been presented by others[2,42] but are here supported by considerable experimental evidence.
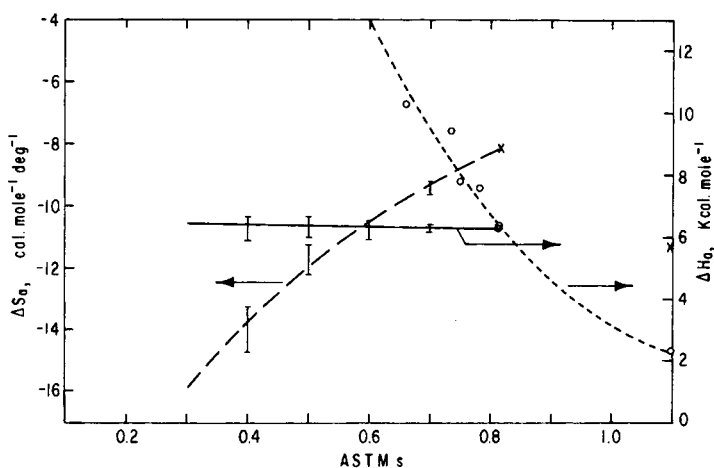

Fig. 3. Plot of entropy of flow ΔS_a (dashed line) and enthalpy of flow ΔH_a (solid line) vs. ASTM slope s for selected polymer-thickened oils. Dotted line is a plot of the enthalpy of flow ΔH_a vs. ASTM slope s for selected lube oils,[2] including S105 and benzene of this work. Symbols marked (X) denotes the computed entropy of flow for untreated S105 and pure benzene, respectively.

The Fox-Flory Relation at Finite Concentration

Thus far, the discussion has been concerned only with the frictional aspects of blend rheology. The structural factor F, sensitive to molecular weight at finite polymer concentration, has been neglected so far. To partially rectify this, some data collected in this investigation are presented below. It has long been recognized that the molecular weight contribution to the isothermal flow properties of bulk polymer or copolymers is governed by the relation of Fox and Flory.[4,5,25,26] Thus,

$$\eta_T = K_T Z^a \qquad (8)$$

where K_T is a constant for the polymer or copolymer, a has the value 3.4 for $Z \geq Z_c$, and $1.0 \leq a \leq 2.5$ for $Z < Z_c$. The parameter Z is the number of chain atoms (or groups), and Z_c is a critical quantity. The appropriate quantity to use for Z is the weight-average value[4] $\overline{Z}_w$ (see experimental section). Entanglement coupling is considered to occur in polymer systems as a passes discontinuously[4,5] from unity to 3.4 with increase in molecular weight. In the presence of a constant amount of diluent but varied $\overline{Z}_w$, Nakuyasu and Fox[43] and many others[4,5] showed that eq. (8) was obeyed but plots of log η_T versus $\phi_2 \overline{Z}_w$ shifted vertically[5,43] with volume fraction ϕ_2 of polymer. The exponent a in eq. (8) was near unity for small $\overline{Z}_w$ and 3.4 for $\overline{Z}_w \geq Z_c$. In somewhat analogous experiments, the viscosity data of this work[1] for the copolymers of Table I, for which weight-average molecular weights were available, were plotted as functions of $w_2 \overline{Z}_w$ in Figure 4, inserts A, B, and C, at the four experimental temperatures (25°, 37.8°, 54.5°, and 98.9°C). The plots are linear with slopes, a of eq. (8), close to unity (Table III). The vertical shift of the curves in this figure was produced by the effect of temperature on the viscosities. This follows from the often observed equivalence of temperature and diluent in producing free volume.[41a,b] Because a is near unity in these dilute systems (Table III), entanglement coupling must be considered absent. This supports well-known effects of diluent in reducing entanglements in blends containing high molecular weight polymers.[41b] These plots also demonstrated insensitivity to structural effects when S105 was the solvent; viscosities for all members of the same series (OA + MMA, OA + EHA + OA + DA, and POA) fell on a common line. In benzene (insert D), however, the plots of OA + MMA copolymers shifted horizontally as the copolymer composition changed. The similar values of molar volumes of polymer chain units and solvent in S105 blends might be responsible for the structural insensitivity. The smaller viscosities in benzene for similar polymer concentrations are also apparent in insert D.

The vertical shift with temperature of the plots in Figure 4, inserts A, B, and C, suggested that the intercept of eq. (8) may be modified by an Arrhenius-type function and might apply to the data fitted isothermally by eq. (8). When the natural log of the intercepts in the least-squares fit of eq. (8) were plotted as functions of reciprocal temperature and average values of a for isothermal data at the four temperatures were used, the relation obtained was

$$\ln \eta_{cp} = [\ln \eta_{cp0} + k'(1/T)] + a \ln(w_2 \overline{Z}_w) \qquad (9)$$

Constants for the three copolymer systems investigated are displayed in Table III. Errors in using this equation to predict viscosities were less than 5% and generally were 1%–2% over the temperature span of 25°–98.9°C. However, it
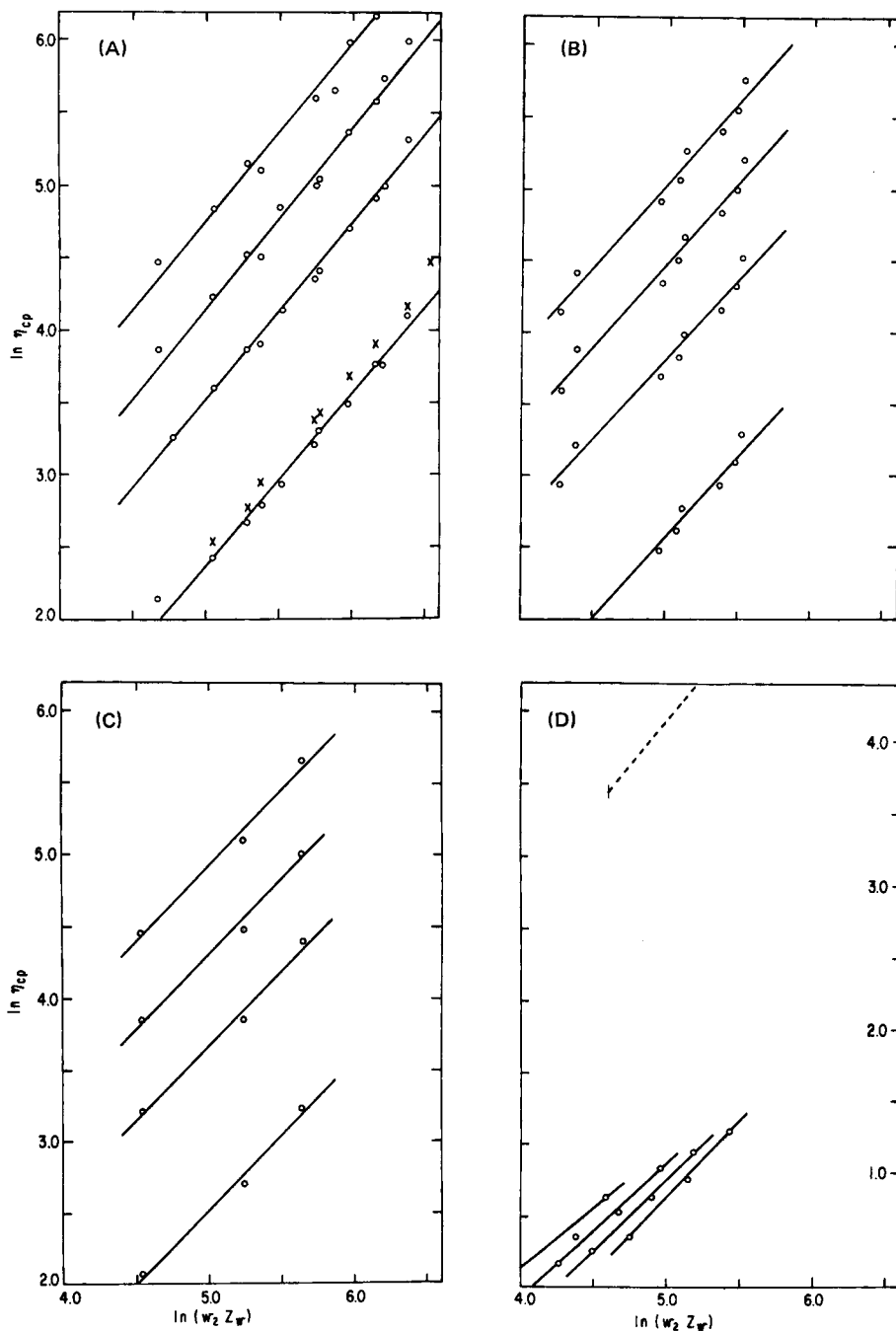
Fig. 4. Plot of log viscosity (centipose units) vs log $w_2\overline{Z}_w$: (A) copolymers of n-octadecyl acrylate and methyl methacrylate (experiments 2–5, Table I); (B) copolymers of n-octadecyl acrylate and di-2-ethylhexyl acrylate (experiments 6–11, Table I); (C) commercial acryloids, experiments 22–24; (D) copolymers of n-octadecyl acrylate and methyl methacrylate (experiments 2–5, Table I) in benzene at 30°C. In inserts (A) through (C), temperatures are (reading from bottom to top in the individual inserts): 98.9°, 54.5°, 37.8°, 25.0°C. Symbols marked (×) were calculated using eq. (9); the rest of the data using this equation fell on the fitted isothermal lines. Dashed line in insert (D) is for OA + MMA copolymers at 37.8°C in S105.

Constants for the General Fox-Flory Equation, Eq. (9), for Several Copolymer Systems in S105 and Benzene

Polymer system	Experiment no.[a]	$\ln \eta_{cp0}$	k'	a
OA + MMA	2–5	−12.20	3168.0	1.232
OA + EHA	6–11	−12.17	3399.0	1.140
Acryloids	22–24	−12.28	3525.0	1.058

[a] As in Table I.

can be seen that Rk' is of the same magnitude as ΔH_a in Table II. Because ΔH_a was already shown to vary with temperature, k' will not be constant over wide temperature ranges. In support of this, the displacement from the fitted isothermal line of the points computed using eq. (9) and marked (×) in Figure 4, insert A, demonstrates the inconstancy of ΔH_a, and hence of k', of eq. (9).

Corresponding-State Treatment of Viscosity at Finite Concentration

Since the concentration range used in this work on polymer-thickened lubrication oils was far in excess of that ensuring isolated hydrodynamic effect, conclusions concerning performance based on infinite dilution extrapolation might be in error. Simha and co-workers[20-24] developed a corresponding-state treatment especially applicable to polymer–diluent systems in the concentration range of this work.[5] To accomplish this, concentration and molecular weight were reduced by a reduction factor c/c_0, where c is polymer concentration and c_0 is the concentration of incipient coil overlap.

Weissberg, Simha, and Rothman,[20] starting from a reduced form of the Baker equation,[44] relating viscosity to concentration,

$$\eta_{sp}/S = 1/S[1 + (S/n)]^n - 1 \tag{10}$$

where $S = c[\eta]$ and n depends on the polymer-solvent system, derived a reduced expression,

$$\eta_{sp/c[\eta]} = 1 + K_b(c/c_0) + K_b'(c/c_0)^2 + \cdots \tag{11}$$

where c_0 is the concentration of incipient coil overlap. The value of c_0 was subsequently[21] shown to follow $c_0 = 1.08/[\eta]$ and thus be generally useable for many polymer–diluent mixtures. Plots of $\eta_{sp}/c[\eta]$ versus c/c_0, similar to those in reference 22, are shown in Figure 5 for selections of the various systems studied in this work. Data for poly(n-octadecyl acrylate), POA (experiments 14–21, Table I), in S105 are shown in insert A and in benzene in insert B.

Simha has shown[22] that as polymer molecular weight decreased in good solvents beyond a critical amount, the slopes should rise rapidly. While this was found for the benzene data (insert B), the effect was reversed in S105. The reason for this is not understood. Because the relation for polystyrene ($\overline{M}_n$ 165,000), taken from reference 22 and shown in both inserts, is similar to that in experiment 14 ($\overline{M}_n$ 162,000[1]), the effect of a multicomponent solvent does not seem contributory. In addition, the data in both inserts can be correlated reasonably with a reference curve from the Baker equation,[20,22] eq. (10), with $n = 2$. Plots for selected copolymers of this work (OA + MMA, insert C, and the acryloids, insert D) at two temperatures also seem reasonable. Temperature
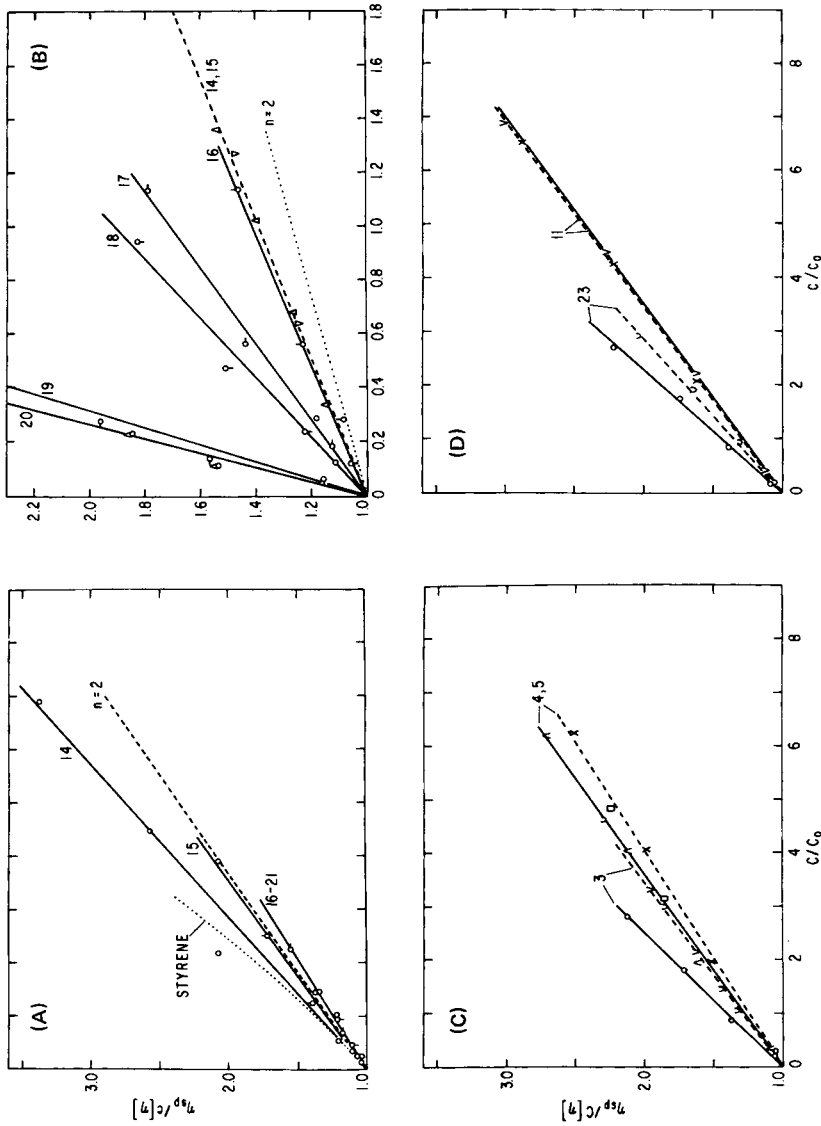
Fig. 5. Experimental reduced viscosity–concentration curves for the following systems: (A) poly(n-octadecyl acrylate) of varied $\overline{M}_n$, in S105 at 37.8°C; (B) the same in benzene at 30°C; (C) n-octadecyl acrylate–methyl methacrylate copolymers in S105 at 37.8°C, solid lines, and 98.9°C, dashed lines; (D) acryloid 710, experiment 23 and experiment 11 (Table I) in S105 at 37.8°C, solid line, and 98.9°C, dashed lines. In insert (A), the dotted curve is literature data for polystyrene[22] ($\overline{M}_n$ 165,000) in toluene at 30°C.   Dashed line in inserts (A) and (B) represents the Baker equation, eq. (22), with $n = 2$.

effects were small in both inserts. The more efficient copolymers had steeper slopes (experiment 3, insert C, and 23, insert D), which is in the expected direction. However, the most noteworthy feature of all of the data using S105 as solvent is the failure of any of the illustrated slopes to exhibit a rapid increase beyond a c/c_0 value of unity,[22] which is the critical ratio for coil overlap. Since it has already been established that T_θ is low enough in this solvent for the oil to be a good solvent for all of the copolymers at the temperatures of interest, significant coil compression leading to a rapid rise in slope[20-22] should have been found. Its absence is not understood. The effect may have been caused by the marked tendency for ciliary side chains to order the structure of their solutions[45] through interactions independent of their main chain units. This could overcome the usual excluded-volume tendencies.

It may be concluded that the apparent hydrodynamic interactions characteristic of infinite dilution appear to persist even into the concentration region where effect of coil overlap and polymer aggregation should become important. This rheological simplification may be contributing in part to the ordered passage from first to second Newtonian transitions at increasing shear rates found for methacrylate copolymers in a lube oil,[46] compared to the more complex interactions found for other polymer–diluent mixtures.[47]

SUMMARY AND CONCLUSIONS

The viscosity data of the previous paper were analyzed with respect to several theories developed to describe the properties of polymers in solvents at both infinite dilution and finite concentration. Effects of the theoretical parameters pertinent to the frictional and structural nature of the blend were considered. However, the temperature range was restricted to the practical range employed with multigrade oils, thus simplifying the problem. At infinite dilution, the temperature coefficient of intrinsic viscosity was close to zero for most of the copolymers; only the most efficient displayed any significant hydrodynamic expansion at high temperatures. Yet all of the copolymers were effective in producing lower viscosity–temperature slopes than the base oils. This was shown to result from the retention of flow-activation enthalpy of the solvent, whereas increased negative entropy, produced by sluggish translational motion of the polymer coils, was responsible for viscosity increase with decreasing temperature and corresponding viscosity index improvement. In contrast, increasing the molecular weights of lube oils to increase their viscosity produced a correspondingly disadvantageous increase in their activation enthalpy. At finite concentration, the unit value of the exponent for the relation between viscosity and weight-average chain length of the copolymer, reduced by solvent dilution, was evidence that chain entanglement did not contribute to the structure of the blends. A seemingly anomalous absence of evidence for coil compression in the thermodynamically good base oil solutions at the finite polymer concentrations employed in this work may have been produced by side chain interaction, which could reduce excluded volume coil repulsions.

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