Viscosity Index. I. Evaluation of Selected Copolymers Incorporating *n*-Octadecyl Acrylate as Viscosity Index Improvers

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Synopsis

Compositionally and structurally varied copolymers all containing *n*-octadecyl acrylate were prepared and evaluated as viscosity index improvers in a common base oil under conditions of low shear. Systems evaluated over a range of copolymer and blend composition were: copolymers of *n*-octadecyl acrylate with, respectively, methyl methacrylate, 2-ethylhexyl acrylate, and *n*-dodecyl acrylate; and homopolymers of poly(*n*-octadecyl acrylate), prepared with a wide range of molecular weights. Properties were compared with those of blends of commercial methacrylate copolymers (acryloids) which had been freed of their entraining liquid. Mixtures of base oil with copolymers of *n*-octadecyl acrylate and methyl methacrylate, compared at fixed SAE viscosities, were the most efficient of all blends studied. They had the smallest rate of change of viscosity with temperature (as measured by their ASTM slopes), particularly in the composition region of incipient polymer precipitation at room temperature. Efficiency of certain of these compositions was somewhat greater than that of the acryloids. A parameter that related concentration and weight-average molecular weight was used to correlate all of the data for ASTM slope and viscosity. Empirical relations developed by using this parameter enabled rheological data to be estimated that agreed within 6% of experimental values for the case of thermodynamically good base oil solvents. These data demonstrated the relatively small contributions of copolymer structure to viscosity index improvement.

INTRODUCTION

Over the last 35 years, the major industrial uses found for homopolymers and copolymers containing long linear side chains have been as viscosity index-improving and pour point-depressing additives in lubricating oils.[1-4] In these applications, to produce multigrade lubricating oils, small amounts (1–5 wt-%) of the polymeric additive are added to light paraffinic or naphthalenic lubricating oils to increase their viscosity and regulate the blend crystallinity. Viscosity index (VI) improvers decrease the temperature coefficient of viscosity of the blends to such an extent that the viscosity of the dewaxed base oil at low temperatures (usually 0°F) is approached. Thus, the cold-starting facility of the light base oil is substantially retained.[2] The blends provide proper engine lubrication at service temperatures near 210°F (98.9°C) by maintaining higher viscosities than the base oil alone at such temperatures. Pour point depressants act by adsorption and cocrystallization mechanisms to prevent the low-temperature deposition of wax in network structures,[1-4] which gives rise to adverse Bingham rheological behavior in cold starting.[5] The same polymer usually serves both to maintain viscosity and to depress pour point.

Viscosity index improvers and pour point depressants must be soluble in the

usual nonpolar paraffinic and aromatic lubricating oils, at least in the temperature range of interest ($-30°$–$100°C$). Consequently, polymer chains containing segments having a multiplicity of methylene groups, either in the main chain or in side chains, are usually required, especially in paraffinic oils. Thus, homopolymer and copolymer systems having long linear side chains have been extensively studied in these applications. In the older patent literature,[1,4,6] these have included selections from the homologous series of the atactic polymeric methacrylates,[7–9] acrylates,[10–12] vinyl esters,[13,14] maleate esters,[15,16] allyl esters,[17,18] n-alkyl styrenes,[19] and isobutenes,[20] and the syndiotactic poly(n-alkyl methacrylates).[21] Modifications of the above systems continue to be studied, and industrial scientists have recently investigated many new structures, including polybutadiene copolymers, ethylene copolymers, polyesters, and block copolymers of ethylene–propylene rubber.[22,23] Many polymer formulations today incorporate relatively small amounts[1] of some polar comonomer units, such as diethylaminoethyl methacrylate, vinylpyridine,[24] or vinylpyrrolidone,[25] which serve as ashless nonaqueous polymeric detergents in preventing and removing sludge deposits. Thus, the combined function of viscosity index improvement, pour point depression, and detergency are included in a single additive polymer.[1] In spite of the intensity and diversity of industrial investigation of these lubricant modifiers, only two distinct types, namely, polyisobutylene[26] and polymethacrylate copolymers,[27] appear to be in substantial use today. These have been in continuous use for over 35 years. However, the poly(n-alkyl acrylates), the alkyl fumarate copolymers, and the alkylated styrenes may also be used in small amounts.[1]

Copolymers are utilized more than homopolymers, both as viscosity index improvers and as pour point-reducing agents.[1] For greatest efficiency as viscosity index improvers, the average side chain length is maintained at about 8 carbon atoms; for pour point reduction, the alkyl length is increased to 12–14 carbon atoms.[1]

Although considerable progress has been made in ascertaining the most favorable copolymer structures required to increase viscosity index values of blends prepared at a fixed viscosity, little attention has been given to use of fundamental thermodynamic parameters in describing blend behavior[28] and in studying the rheological mechanisms involved. Instead, reliance has been placed on single parameter substitutes for exact viscosity–temperature relations. These include the viscosity index[29] and ASTM slope methods,[30] both of which are discussed frequently in this paper and in the two that follow.[31,32]

The viscosity index (VI) of an oil or blend was originally obtained by determining its viscosity at $100°F$ ($37.8°C$) and $210°F$ ($98.9°C$), together with the viscosity at $100°F$ for those fractions of two standards that had the same viscosity at $210°F$ as the unknown oil. The standards were assigned VI values of 0 and 100, respectively. The equation $VI = (S_1 - V)/(S_1 - S_2) \times 100$ was then solved, where S_1 is the viscosity of the lower standard and V is that of the unknown, all at $100°F$. The standards were selected from oils having the greatest and smallest viscosity–temperature coefficient known at the time (1929). Viscosity index values of today's blends and refined oils far exceed those of the original standards. Viscosity indexes are now read from published charts using viscosities of unknowns obtained at $100°F$ and $210°F$.[33] As a consequence of the rating system, the higher the viscosity index, the lower the viscosity–temperature coefficient.

Because of its empirical nature[2,3] and the complexities of rheological behavior of dilute polymer solutions,[34,35] the method is certainly not quantitative and is especially unreliable in the high VI range.

The ASTM slope method is based on the empirical equation of Walther,[36] which requires that viscosity η in centistokes be plotted as $\log^2 (\eta + a)$ versus log T, where a is 0.8. In the standard method, experimental viscosities for unknown blends are plotted on standard charts made for this purpose, usually at the same temperatures used for viscosity index. Lower slopes (designated ASTM slopes) reflect smaller viscosity–temperature coefficients, of course. However, the double log function masks the actual rate of change of apparent activation enthalpy for viscous flow[5] with temperature which is normally observed even over the limited temperature range of interest[5,34,35] ($\sim$120°C). Consequently, plots on the charts are usually linear. This method, based more on fundamental principles than on viscosity index, is clearly empirical and its use can lead to erroneous predictions when used over too wide a temperature span.

Both of these methods depend on the viscosity of the base oil; the lower its viscosity, the larger both the change in ASTM slope and VI with blending.[1–3] Consequently, blends must be made up to fixed viscosities at some temperature to provide a meaningful comparison of different systems. In addition, blend viscosities must be of the right magnitude at high temperatures ($\sim$210°F) to provide proper engine lubrication, yet possess enough fluidity at low temperatures ($\sim$0°F) to move under the low shear stresses generated by engine-starting motors. To meet all these requirements, the SAE (Society of Automative Engineers) system of classification of multigrade oils was created. Sufficient polymer is added to a light (low viscosity) base oil to provide fixed viscosity ranges (SAE 20, 30, 40, etc.) at 210°F (98.9°C), the viscosity increasing with SAE number and added polymer. From the viscosity obtained at 0°F, the blend is again classified. The 0°F viscosity is obtained either by extrapolation on the ASTM plot by a line drawn through experimental viscosities determined at 100°F (37.8°C) or is obtained experimentally using the cold crank simulator.[40] The viscosities found at 0°F for specific blends determine the winter (W) classification number. The lower the viscosities found at this temperature (i.e., those closer to that of the untreated base oil, in the range of SAE 5 or 10), the better the starting performance.

Thus, a polymer blend rated 10W-30 has a lower ASTM slope (higher VI) than one rated 20W-30, and the polymer used is considered more efficient in this application. In this paper, this meaning of efficiency is retained throughout. The most effective commercial blends (SAE 10W-40, for example) must be sparingly soluble at low temperatures (polymer chain tightly coiled) in order to tolerate the greater amount of polymer present. In addition, molecular weights must be low enough that permanent shear losses are kept to a minimum.[1–4,41–43] Consequently, such blends are the most expensive and are given the MS classification.[38]

In this work and the following two papers, we apply these practical and fundamental considerations to three selected copolymer blends all containing n-octadecyl acrylate as a major component on a single light base oil. Acrylate esters have received relatively little attention in the literature so far[10–12,43–45] compared to methacrylates.[1–4,7–9,27,38,39,44,45] Viscosities (in centistokes), viscosity index values, and ASTM slopes are collected in this first paper for 24 homopolymers

and copolymers at four concentrations and four temperatures. Copolymers studied with the common comonomer n-octadecyl acrylate were methyl methacrylate, 2-ethylhexyl acrylate and n-dodecyl acrylate. Thus, effects of the extremes of side chain length and effects of shorter side chains of intermediate length could be contrasted. Benzene and another paraffinic oil were also employed as solvents of varied molecular weight. All data are compared with those obtained for several commercially available methacrylate copolymers (acryloids) which were freed of their entraining oils. For all systems, a parameter based on the relation between concentration and molecular weight was used to correlate both viscosity and ASTM Slope.

EXPERIMENTAL

Monomers

Commercial monomers of the same quality were treated to remove inhibitor as in reference 46. n-Octadecyl acrylate was prepared as in reference 47.

Polymerization Procedure

All polymerizations were carried out in benzene (4 Moles/Mole of monomer) under nitrogen in sealed bottles at 60°C for 48 hr, using 0.2 mole-% azo*bis*isobutyronitride (AIBN) as initiator, except for the n-octadecyl acrylate–methyl methacrylate copolymers, with which 0.5 mole-% AIBN was used. Copolymers were precipitated by pouring the reaction mixture into methanol (5 ml/g mixture) and were freed of monomer by extraction with refluxing methanol (5 ml/g polymer) until an aliquot was clear on precipitation in excess water. The copolymers were dried in thin films under vacuum at 50°C. Conversions were 92%–98% for all copolymers.

Acryloids

Acryloids, obtained through the courtesy of Rohm and Haas, were general purpose viscosity index improvers, numbers 732, 710, and 772, and varied only in molecular weight. They were freed of their entraining oil as follows: Each polymer was extracted (10 ml/g mixture) 15 times with a 50/50 mixture of acetone and methanol. Elemental analysis on the first six extractions showed no copolymer, as evidenced by the absence of elemental oxygen. Therefore, the polymer did not appear to be fractionated by the solvent treatment. Extractions were continued till the polymers were free of oil as shown by the aqueous precipitation method indicated above. They were also dried by the above method. Polymer concentrations in the oil were (sample number, concentration): 732, 43%; 710, 37%; 772, 36%.

From elemental analysis and empirical relationships between their glass transition temperatures T_g, the components of all three samples of copolymers and their respective mole fractions were estimated to be as follows: n-hexyl methacrylate, 0.669; n-dodecyl methacrylate, 0.331. Elemental analysis, calculated for the above compositions and compared with found values, were: C calcd. 72.2%, found, 74.2%; H calcd. 11.06%, found 11.33%. Assuming a linear

relation between T_g of each homopolymer and the copolymer weight fraction,[48] the T_g values were: calcd. 242°K, found 242°K. Glass transitions by the Fox equation were: calcd. 239.2°K, found 242°K. No side chain crystallinity was present in any sample as determined by differential scanning calorimetry.[46-47] Consequently, methacrylate copolymers higher than n-dodecyl were probably not present in analogy with findings for the poly(N-n-alkylacrylamides) which also have stiff backbone chains. In those homopolymers, crystallinity was substantially present only when side chain lengths were 14 carbon atoms or longer. It was vanishingly small for C_{12}.[47] In copolymers, crystallinity was always further suppressed.[46] This analysis of the copolymer composition may well be incorrect; a similar analysis would apply approximately to poly(n-octyl methacrylate). However, for the purpose of these papers, it can be considered accurate enough to permit valid structural comparison with the experimental copolymers.

Calculations and Molecular Weight Determinations

Number-average molecular weights were determined using a membrane osmometer as described in reference 49. All equations were fitted, and most of the calculations were made on an IBM 1130 computer. Vapor pressure osmometry was used for the base oils.

Weight-average molecular weights were estimated from gel permeation chromatography (GPC) determinations carried out by Waters Associates, Framingham, Massachusetts. Five Styrogel columns were used in series for all of the copolymers. All columns had polystyrene contour length exclusion limits of 1×10^6, 1×10^5, 1×10^4, 1×10^3, and 500 Å, respectively. The solvent, tetrahydrofuran, was maintained at a flow rate of 2 ml/min at 22°C. Elution volumes for the unknowns were correlated with a calibration curve for the elution volumes and average molecular weights of essentially monodisperse polystyrene fractions. Because values of number-average molecular weight $\overline{M}_n$ by osmometry and GPC were similar, the computed values of weight-average molecular weight $\overline{M}_w$ were considered to be accurate enough for the purposes of this paper.[50] The comparison of $\overline{M}_n$ values were (experiment number in Table I, $\overline{M}_n$ osmometry, $\overline{M}_n$ GPC): 3, 93,900, 102,000; 4, 119,400, 119,000; 5, 144,300, 143,000; 6, 72,800, 66,900; 9, 74,800, 77,600; 11, 93,200, 95,900; 14, 162,000, 132,000; 23, 108,000, 99,200. The polydispersity index ($\overline{M}_w$ GPC/$\overline{M}_n$ osmometry) ranged from 4 to 8, except for experiment 23, for which it was 3.4.

Intrinsic viscosities in benzene at 30°C were obtained on the poly(n-octadecyl acrylate) (POA) homopolymers. From a correlation of weight-average molecular weight values on a limited number of polymers, together with use of their respective polydispersity index values for a correlation with values of $\overline{M}_n$ for all of the POA polymers, the relation $[\eta] = 4.11 \times 10^{-5} \overline{M}_w^{0.704}$ was determined. It was used to calculate $\overline{M}_w$ for the POA samples.

Base Oil

A light, solvent-refined, paraffinic base oil, Arco Topaz Oil S105, having a viscosity meeting specification as a borderline SAE 5W and 10W oil, was selected as a convenient compromise between the two standard levels. Elemental analysis

showed C 84.97%, H 12.35%, and the pour point was −18°C. The number-average molecular weight by vapor pressure osmometry was 345.

In addition to this oil, another highly refined, pure paraffin oil (Fisher 0119) of higher molecular weight ($\overline{M}_n$ 441) was used for certain correlations.

Other Copolymers Evaluated

Selected methacrylate copolymers, not described below, were also used in limited correlations with the above base oils. These were copolymers of n-octadecyl methacrylate and methyl methacrylate containing mole fractions of n-octadecyl ester of 0.35, 0.55, 0.70, 0.85, and 1.0, respectively. Also studied were copolymers of n-octadecyl methacrylate and isodecyl methacrylate containing mole fractions of the C_{18} ester of 0.15, 0.35, 0.45, 0.55, 0.70, and 0.85, respectively. Each of the above copolymers was used with the base oil 0119 at the concentration of 0.025 weight fraction. The n-octadecyl and isodecyl methacrylate monomers were purchased from Rohm and Haas.

Viscosity Determinations

Viscosities were determined by ASTM Method D445-72. Viscosity indexes were obtained by the procedure of reference 33; ASTM slope measurements followed reference 30. Four temperatures were employed to ensure statistical accuracy in estimating linearity over the temperature range and to aid in accurate extrapolations to low temperature. Viscosities at specific temperatures are designated η, indicating centistoke viscosity at the indicated centigrade temperature.

RESULTS AND DISCUSSION

General Considerations

Viscosity index values and ASTM slopes are listed in Table I for all copolymers studied in this work. Compolymer compositions m_i, molecular weights $\overline{M}_n$ and $\overline{M}_w$, and average side chain length n_c are also listed. The data followed expected patterns.[1-3,27] Viscosity index increased and ASTM slope declined as the copolymer concentration was increased in all experiments. The ASTM slopes of all the blends markedly decreased below that of the base oil. Progressive reduction in molecular weight to the oligomer range (experiments 14–21) for poly(n-octadecyl acrylate) (POA) produced a steady decline in VI and increase in ASTM slope at each concentration, as expected.[27,45,51] The molecular weight influence of the remaining copolymers is obscured by the variety of molecular weights for the tabulated experiments. Thus, it becomes difficult to separate effects of structure, molecular weight, and concentration in evaluating individual copolymers from data in the table. However, it is worth noting that these copolymers behave similarly to the standard acryloids (experiments 22–24).

The most important trends of Table I may be conveniently seen for selected data in Figure 1. Here, relative efficiency (inserts B and C) and effects of temperature (insert A) and molecular weight (insert D) on ASTM slope s of POA blends are graphically illustrated. Increasing temperature (insert A) shifts

TABLE I
Copolymer Compositions, Molecular Weights, and ASTM Slopes for their Solutions in Base Oil S105

Experiment no.	Experiment description[a]	Copolymer[b] composition m_b	Molecular weight		n_c[c]	ASTM slope s[d]			
			$\overline{M}_n$	$\overline{M}_w$		0.005[e]	0.025	0.050	0.075
1	Base oil		345	345		0.814			
2	OA + MMA	0.350	73,000		6.95	0.774	0.733	0.548	0.525
3	OA + MMA	0.550	93,850	479,200	10.4	0.738	0.759	0.480	0.430
4	OA + MMA	0.700	119,350	800,000	12.9	0.724	0.557	0.458	0.407
5	OA + MMA	0.850	144,300	1,138,000	15.5	0.715	0.534	0.439	0.394
6	OA + EHA	0.050	72,800	271,000	8.50	0.777	0.682	0.578	0.530
7	OA + EHA	0.100	75,000		9.00	0.772	0.620	0.579	0.511
8	OA + EHA	0.150	76,300		9.50	0.777	0.652	0.565	0.516
9	OA + EHA	0.200	74,800	337,000	10.0	0.777	0.655	0.562	0.510
10	OA + EHA	0.300	85,800		11.0	0.764	0.628	0.552	0.497
11	OA + EHA	0.400	93,200	397,000	12.0	0.759	0.627	0.550	0.490
12	OA + DA	0.200	171,200		13.0	0.712	0.523	0.432	0.387
13	OA + DA	0.300	147,000		13.8	0.712	0.518	0.423	0.369
14	POA	1.00	162,300	1,622,000	18.0	0.715	0.511	0.416	0.371
15	POA	1.00	101,000	711,500[f]	18.0	0.748	0.599	0.505	0.450

TABLE I (Continued from previous page.)

Experiment no.	Experiment description[a]	Copolymer composition[b] m_b	Molecular weight		n_c^c	ASTM slope s^d			
			$\bar{M}_n$	$\bar{M}_w$		0.005[e]	0.025	0.050	0.075
16	POA	1.00	83,000	461,200[f]	18.0	0.775	0.667	0.581	0.527
17	POA	1.00	64,500	224,800[f]	18.0	0.748[g]	0.707	0.644	0.581
18	POA	1.00	42,400	107,700[f]	18.0	0.761[g]	0.739	0.671	0.631
19	POA	1.00	22,400	35,751[f]	18.0	0.779[g]	0.766	0.725	0.694
20	POA	1.00	12,300	20,836[f]	18.0	0.793[f]	0.779	0.761	0.734
21	POA	1.00	7,700	7,199[f]	18.0	0.793[g]	0.789	0.770	0.752
22	Acryloid	0.331	95,200		8.0	0.762[g]	0.622	0.536	0.482
23	Acryloid	0.331	108,200	372,500	8.0	0.760	0.611	0.516	0.452
24	Acryloid	0.331	123,000		8.0	0.680	0.599	0.514	0.455

[a] The base oil was Arco S105. Other designations are as follows: OA, n-octadecyl acrylate; MMA, methyl methacrylate; EHA, 2-ethylhexl acrylate; DA, n-dodecyl acrylate; POA, poly(n-octadecyl acrylate); Acryloids are methacrylate copolymers from Rohm and Haas. Rohm and Haas designations are as follows: experiment 22, 732; experiment 23, 710; experiment 24, 772. Copolymers were separated from their containing oils and characterized.

[b] Mole fraction m. The letter b denotes the comonomer having the longer side chain, usually C_{18}; the letter a, that having the shorter side chain.

[c] Average side chain length.

[d] ASTM D341. Corresponding viscosity index (ASTM D 2270-64) values at weight fractions of 0.025 and 0.050, respectively, are: 1—552; 2—117, 208; 3—188, 221; 4—189, 227; 5—191, 224; 6—126, 173; 7—155, 175; 8—143, 178; 9—142, 178; 10—156, 183; 11—159, 186; 12—192, 226; 13—193, 231; 14—192, 234; 15—165, 199; 16—143, 171; 17—125, 153; 18—111, 139; 19—97, 116; 20—83, 99; 21—74, 91; 22—166, 194; 23—170, 204; 24—174, 201.

[e] Copolymer concentration, wt. fraction.

[f] Computed from intrinsic viscosities in benzene at 30°C using $[\eta] = 4.11 \times 10^{-5} \bar{M}_w^{0.704}$.
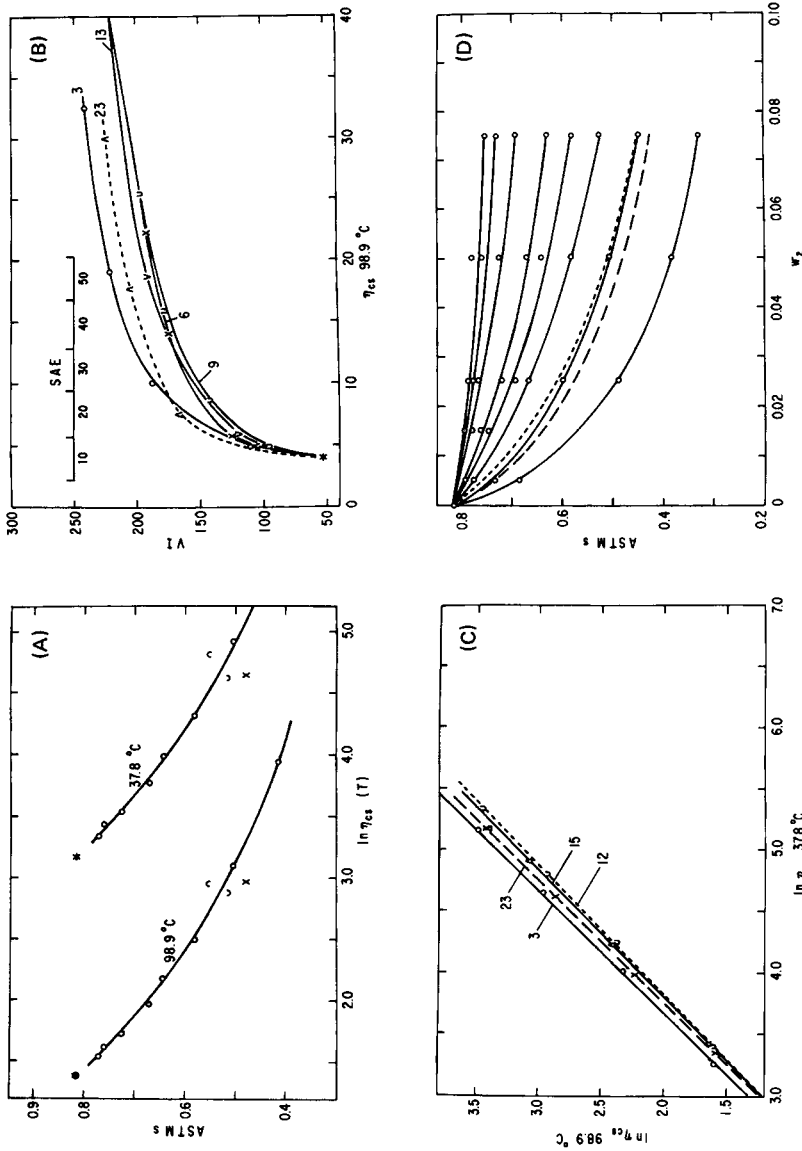
[g] Weight fraction of homopolymer was 0.015.

Fig. 1. (A) Plot of the ASTM slope s vs natural log of centistoke viscosity η_{cs} at two temperatures in base oil S105. Solid line represents data for poly(n-octadecyl acrylate) over a wide range of polymer molecular weights (experiments 14–21): (X) experiment 3; (∪) experiment 23; (∩) experiment 11. (B) Viscosity index (VI) vs η_{cs} 98.9°C for selected experiments. (C) Plot of ln η_{cs} 98.9°C versus ln η_{cs} 37.8°C for selected experiments. (D) Effect of molecular weight and concentration on ASTM slope s. Solid lines represent poly(n-octadecyl acrylate) experiments 14–21; dashed line represents experiment 3; dotted line, acryloid 710, experiment 23.

viscosity of both blends (solid lines) and base oil (starred point) to lower values, but the curves are not superimposable through any reduction factor. Individual points for other systems falling below the line indicate greater efficiency than POA (solid line); those above indicate less efficiency.[2] Effect of structure on relative efficiency is best seen in inserts B and C. The copolymers of experiment 3 (Table I) and the acryloids (experiment 23) are more efficient than the copolymers of experiments 9, 6, and 13 in insert B in raising VI at similar values of $\eta_{98.9°C}$ or in reducing $\eta_{37.8°C}$ at fixed $\eta_{98.9°C}$[45,51] (insert C) compared with those of experiments 12 and 15. Increasing the weight fraction of polar functionality[52] (experiment 3) and main chain stiffness (experiment 23) were responsible for this improvement in efficiency. The steady increase in ASTM slope with decreasing molecular weight at fixed concentrations is apparent from the data in insert D. Thus, the frictional contributions to the work of laminar flow[5] produced by the cooperative action of chain units is apparent from the data in the insert.[27]

Much of the data of this paper is evaluated and discussed in terms of the ASTM slope[30,36] instead of the more generally used Dean and Davis[29] viscosity index method.[1-5,33] A comparison of the two methods was obtained (Fig. 2) by correlating all of the data collected in Table I. Except for the highest ASTM slopes (where $\overline{M}_n$ values or concentration are very low), the data fall between the indicated confidence limits. Thus, the interchange values for the two index methods may be estimated from the figure.

The relative efficiencies of many of the compositions tested in this work are displayed at three 98.9°C SAE viscosities in Table II. Because constant viscosity then prevails at 98.9°C for all of the systems, relative efficiency as measured by the viscosity index will have real significance. Experiments are numbered and labeled as in Table I. The data were obtained by the following procedure: For the remainder of this paper, subscript 1 designates base oil, subscript 2, the polymeric additive, and w_i, the weight fraction. The weight fraction of copolymer, w_2, corresponding to each of the three SAE levels at 98.9°C was read from plots of $\eta_{98.9°}$ versus the experimental value of w_2. Each value of $\eta_{37.8°}$ corresponding to the SAE w_2 at 98.9°C was, in turn, read from plots of $\eta_{37.8°}$
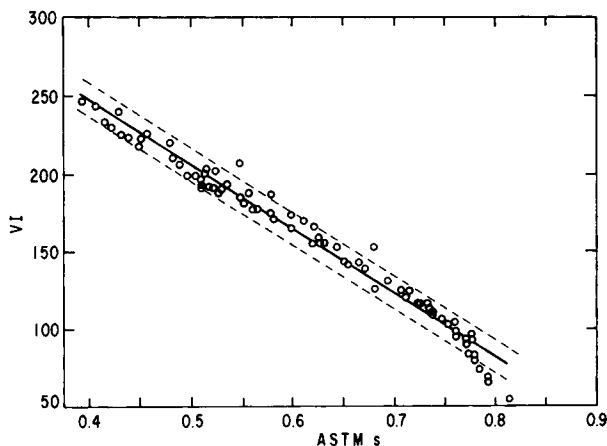

Fig. 2. Viscosity index (VI) vs ASTM slope s for data collected in this work. Solid line is the regression line; dashed lines are the predictive 95% confidence limits.

TABLE II
Viscosity Index Values of Selected Copolymers and Their Extrapolated 0°F Viscosities at Three 98.9°C SAE Viscosities

Experiment no.	System	SAE 20				SAE 30				SAE 40			
		Polymer %	η_{cs} 37.8°C	VI	0°F[a]	Polymer %	η_{cs} 37.8°C	VI	0°F[a]	Polymer %	η_{cs} 37.8°C	VI	0°F[a]
1	S105	0	23.7	55.2	1100	0	23.7			0	23.7		
3	S105	1.73	41.8	170	1000	2.85	59.8	196	1200	3.90	81.0	205	1600
4	S105	1.27	45.3	152	1400	2.00	63.0	185	1500	2.70	83.4	199	1750
5	S105	0.95	43.0	163	1200	1.60	66.0	175	1800	2.20	89.0	187	2200
6	OA + EHA	2.47	48.5	138	1900	3.90	73.0	156	2450	5.23	95.7	173	2850
9	OA + EHA	2.15	48.5	138	1970	3.40	70.3	163	2200	4.58	94.0	176	2750
11	OA + EHA	1.58	48.0	140	1900	2.74	70.5	162	2100	3.84	95.0	174.5	2800
12	OA + DA	1.00	52.0	125	3200	1.60	75.0	151	2900	2.08	95.0	174	2900
14	POA	0.85	50.0	132	2300	1.35	71.0	161	2300	1.85	94.0	176.5	2750
15	POA	1.54	45.0	153	1430	2.55	68.0	169	1970	3.48	92.5	179	2500
16	POA	2.68	46.8	145	1650	4.50	68.0	169	2000	6.17	92.0	180	2400
17	POA	4.20	48.0	140	1800	6.75	67.3	171	1830	8.75	85.5	194	2000
23	Acryloids	1.94	44.5	155	1400	3.17	62.5	186	1400	4.25	85.5	194	2000

[a] Extrapolated from plots on ASTM D341, chart C. Grade upper limits at 0°F are: 5W, 1303 cs; 10W, 2600 cs; 20W, 10,426 cs. Corresponding cold crank simulator (CCS) limits (tentative ASTM method D2602-67T) are, respectively: SAE 20, 1314 cs; SAE 30, 2628 cs; and SAE 40, 10,510 cs.

versus experimental w_2. This procedure was considered to be justified because all the data lay on smooth curves.

For confirmation of this, a number of points were checked experimentally. Viscosity index values were estimated[31] and viscosities at 0°F were obtained by ASTM chart extrapolation.[30] On the basis of the ASTM extrapolations and the estimated VI values of the table, many experimental compositions (experiments 3–5, 23) met the SAE 5W-20 specifications (columns 3–6). Most passed the SAE 10W-30 classification (columns 7–10). Because of the more stringent requirements,[38,39] a smaller number (experiments 3–5, 15–17, 23) met the specifications for SAE 10W-40 blends in spite of the low viscosity of the borderline base oil S105. It is also clear that if the cold crank simulator had been used to determine the low-temperature viscosity of these blends, the number meeting specifications would probably have been somewhat reduced.[37,38] The percentage of polymer required for the various blends (columns 3, 7, 11) varied widely because of differences in molecular weight of the polymeric additive (Table I). Data for experiments 18–21 of Table I could not be obtained because the SAE viscosities were not obtainable even at the highest experimental concentrations.

These data illustrate that all the copolymers were capable of producing multigrade oils. Efficiency, however, depended on structure. Those acrylate copolymers having the greatest difference between the side chain lengths of the components studied (OA + MMA, experiments 3–5) were more effective than the others. They appeared to be better even than the acryloids (experiments 22–24). It is noteworthy that the effective side chain length η_c (Table I) was not a determinant of efficiency. Compare experiments 3 and 4 with experiments 9 and 11 at both SAE levels in Table II. However, in the methacrylate copolymers (experiments 22–24) (Table I) while η_c could be a factor, chain stiffness, producing higher cohesive energy densities, probably played the greatest role. It is well known that the behavior of comb-type polymers and copolymers in solution is strongly affected by the relative stiffness of their main chains.[53]

As discussed in the introduction, knowledge of a relationship between molecular weight and concentration would be valuable in avoiding the interpretation confusion existing in Table I, only partly resolved in Figure 1 and Table II. Viscosity index improvement (Fig. 1, inserts B, C, and D) was strongly affected by both concentration and molecular weight, while reduced thermodynamic interactions, produced by structural contributions, largely determined efficiency. Consequently, in the sections below we discuss relationships between concentration and molecular weight that will enable predictions of both ASTM slope and viscosity to be made for systems in thermodynamically good solvents. A good solvent in this paper is defined as one in which the theta temperature for the blend is considerably lower than the application range, namely, −18°–210°C; a somewhat different definition will be introduced in the next paper.[31] With this as background, the extent of additional reduction in the temperature coefficient of viscosity contributed by decreased solvent interaction with specific polymer structures may be ascertained.

Correlation of the Concentration–Molecular Weight Parameter

It is usually assumed that both whole solvent molecules and segments of polymer chains contribute additively to the jump frequencies that largely de-

termine the viscous flow at high temperaturs of polymer–dilute mixtures.[5,34,35,54,55] Restraints on the polymer segments by the attached chain are responsible for the decreased entropy that results in sharply increased viscosities for the mixtures over those of pure solvents. Consequently, a parameter $\overline{S}_w$ that might reflect these restraints, at least empirically, can be taken as the weight-average molecular weight of the polymer–diluent mixture. If it is assumed that the molar volumes of solvent molecule and polymer chain units are similar, then to a first approximation[56]

$$\overline{S}_w = w_1 M W_1 + w_2 \overline{M}_w \tag{1}$$

where MW_1 is the average molecular weight of the solvent considered to be a monodisperse liquid. The relation between ASTM slope s and $\overline{S}_w$ follows

$$s = s_0 + \alpha \overline{S}_w + \beta \overline{S}_w{}^2 \tag{2}$$

where s_0, α, and β are constants. This is shown in Figure 3. While all curves for individual series from Table I show a monotonic decline with increase in $\overline{S}_w$, they are widely distributed around a composite relation incorporating all of the available data. These deviations occur because $\overline{S}_w$ is a function of $\overline{M}_w$. Data to the left of the composite curve at any fixed value of s have lower average molecular weights than those to the right and are generally distributed proportionately. Even so, the greater efficiencies of experiments 2 and 23 in lowering ASTM s values are revealed as perturbations. It follows from eq. (1) that the weight fraction required for any prescribed value of ASTM slope s may be obtained from

$$w_2 = (\overline{S}_w - MW_1)/\overline{M}_w \tag{3}$$

The effect of solvent molecular weight on the rate of change of ASTM s with $\overline{S}_w$ is shown in Figure 4. Copolymers OA + MMA (experiments 2–5 of Table I) were used in benzene; the methacrylate copolymers described in the experimental section were used in Fisher Oil 0119. Unmodified oils (dashed line) were
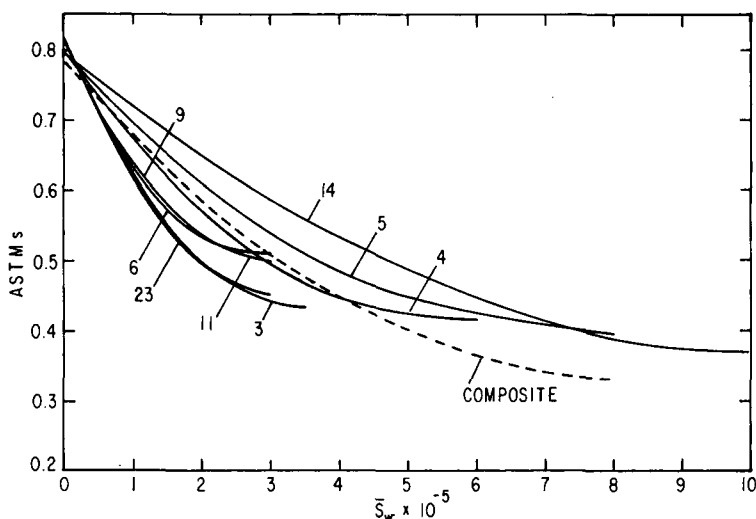

Fig. 3. Plot of ASTM slope s vs blend molecular weight parameter $\overline{S}_w$, using eq. (2). Dashed line is the fitted line for the combined data.
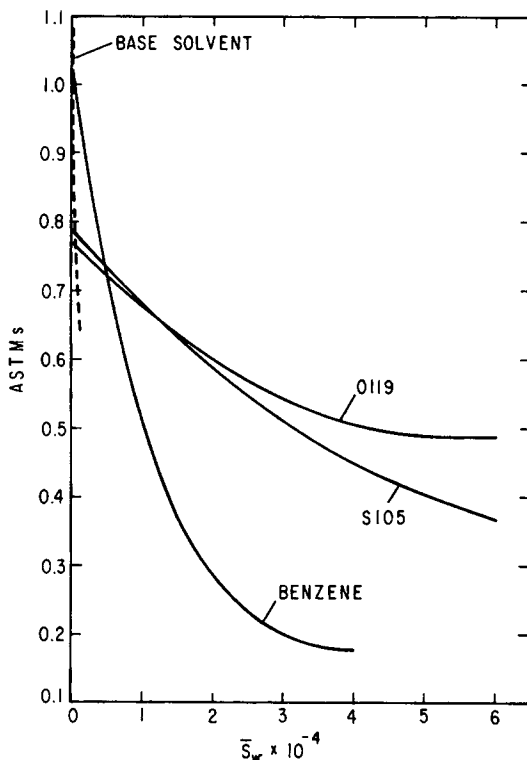
Fig. 4. Effect of base solvent on the relation between ASTM slope s and average blend molecular parameter $\overline{S}_w$.

compared with the copolymers by an empirical relation fitted to the solvent used in this work, $s = 1.94 \pm 0.004 - 0.192 \pm 0.001 \ln MW$. A similar relation, $s = 2.15 \pm 0.047 - 0.251 \pm 0.008 \ln MW_1$, was found for ASTM s with molecular weights for a variety of pure solvents taken from the work of Sanderson[57] and Murphy and Zisman.[58]   The differences between the proportionality constants (0.192 and 0.251) may be the result, in a manner not understood, of the polycomponent nature of the oils used in this work.   The rest of the curves in Figure 4 (solid lines) support the well-known observation[1,3,5] that the rate of change of ASTM s decreases as the molecular weight of the lube oil increases.   However, the effect on the molecular weight ranges characteristic of light oils (300–500) is apparently relatively small compared to that for volatile solvents.

Equations for Calculating Viscosities and ASTM Slopes

In view of the dependence of $\overline{S}_w$ on molecular weight (Fig. 3) at fixed s, a relation was sought between these parameters that would enable calculations of ASTM s $\eta_{98.9^\circ C}$ and $\eta_{37.8^\circ C}$ with a minimum of constants.   The relation should apply to any polymer soluble in a variety of lubricating oils.   It was recognized that such calculated values would be only approximate and would not be capable of predicting the beneficial effect of limited solubility contributed by a polymer in a thermodynamically poor solvent.   Nevertheless, such a calculation would have some practical value.   Knowledge of only the weight-average molecular

weight of oil and polymer would be the only variables required to calculate blending conditions. Because oils lie in a relatively narrow molecular weight range, these equations should apply to many blend combinations and thus be an improvement over certain existing predictive relations.[45,51]

For the data of this paper, the relation between $\overline{S}_w$ and $\overline{M}_w$ for ASTM s equal to 0.500 is

$$\overline{S}_w = \overline{S}_{w0} + C\overline{M}_w \tag{4}$$

where $\overline{S}_{w0} = 10{,}004$ and $C = 0.02333$. Because an ASTM s of 0.5 was the approximate midpoint of the ordinate in Figure 3 and it was selected for correlation in eq. (4), the data showed the greatest sensitivity in this range. The composite curve (dashed line) of Figure 3 followed eq. (2), with $S_{c0} = 0.7809$, $\alpha_c = 0.111 \times 10^{-4}$, and $B_c = 0.6903 \times 10^{-10}$, subscript c denoting composite. With the use of these constants, a general equation, applicable to much of the data in Table I, is

$$s_c = s_{c0} - \alpha_c(f\overline{S}_{wc}) + \beta_c(f\overline{S}_{wc})^2 \tag{5}$$

where f is defined as

$$f = (w_2/w_{2c})_{s=0.50} = \{[(\overline{S}_{w0} + C\overline{M}_w) - MW_1]/\overline{M}_w\}/[(\overline{S}_{wc} - MW_1)/\overline{M}_{wc}] \tag{6}$$

where $\overline{S}_{wc} = 31{,}000$ and $\overline{M}_{wc} = 899{,}960$. Thus, estimates of w_2 should follow $(1/f\overline{S}_{wc} - MW_1)/\overline{M}_w$ for selected values of s.

In analogous fashion, the relation between viscosity and the parameter $\overline{S}_w$ was found to follow a simple relation:

$$\ln \eta(t) = \ln \eta_0 + \alpha' \ln \overline{S}_w + \beta'(\ln \overline{S}_w)^2 \tag{7}$$

where α', β', and $\ln \eta_0$ are constants, the last sensitive to temperature. Data for specific experiments in the series on Table I are compared with composite data (dashed line) in Figure 5. Again the dependence of $\overline{S}_w$ or $\overline{M}_w$ is apparent. The correlating parameter f, eq. (6), could be substituted in eq. (7) to compute values of $\eta_{37.8°C}$ and $\eta_{98.9°C}$, with the constants appropriate to the composite curve (dashed line) in inserts A and B, respectively, of the figure. A correction factor of 0.83 had to be introduced for data other than the composite to correct the unidirectional drift of the uncorrected viscosities. This drift was apparently a result of the log functions in eq. (7) in contrast to those of eq. (5). The revised equation is

$$\eta(T) = 0.83 \exp[\ln \eta_{c0} - \alpha' \ln (f\overline{S}_{wc}) + \beta'(f\overline{S}_{wc})^2] \tag{8}$$

For a temperature of 37.8°C, $\ln \eta_{c0} = 7.965$, $\alpha' = 1.514$, and $\beta'_c = 0.1184$; for a temperature of 98.9°C, $\ln \eta_{c0} = 6.133$, $\alpha'_c = 1.494$, and $\beta'_c = 0.1168$.

Typical data calculated with eqs. (5) and (8) for fixed values of $\overline{S}_w$ are compared (Table III) with smoothed data (labeled experimental) obtained by computer fit of each listed experiment. Agreement was found to be fairly good for all of the data collected, with difference between experimental and calculated values averaging about 6% (extremes 0 to 15%) for the viscosity data at both temperatures and 3.7% for the ASTM s values (extremes 0 and 12%). This close agreement permitted estimates of viscosities at 37.8°C to be made for blends at three 98.9°C SAE viscosities, as in the procedure used for the quantities in Table II. This was accomplished by solving eq. (8) graphically for the three fixed SAE
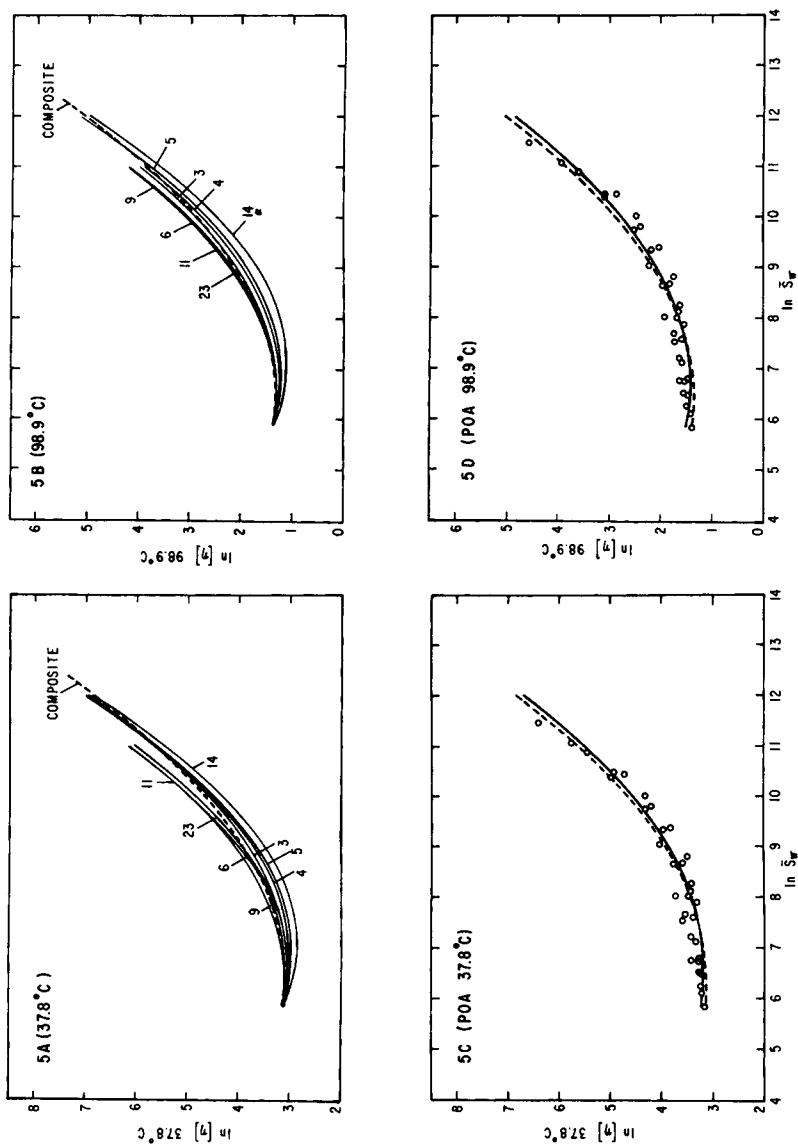
Fig. 5. Plot of ln $\eta(T)$ vs blend molecular weight parameter $\overline{S}_w$. (A) and (B) represent curve fits, eq. (7), for the indicated experimental data from Table I. (C) and (D) represent similar data for poly(n-octadecyl acrylate) using a wide range of weight-average molecular weights estimated from intrinsic viscosities. Dashed line in all inserts is the composite curve fit for the combined data of inserts (A) and (B).

viscosities, 20, 30, and 40, respectively, at 98.9°C and substituting the appropriate values of $\overline{S}_w$ into eq. (8), with the constants for 37.8°C. Data comparable to those in Table II are displayed in Table IV. In general, the calculated values of $\eta_{37.8°C}$ and viscosity index are close to experimental values taken from Table II; experimental values of $\eta_{37.8°C}$ for experiments 3 and 23 are somewhat lower. Thus, these would yield lower values of ASTM s if plotted on ASTM charts. These experimental values reflect the limited solubility already discussed for these experiments. Consequently, these copolymer blends are the most efficient VI improvers (higher VI, Table IV) of the series in Table I. In contrast, the common

TABLE III
Experimental and Calculated Values of ASTM Slopes and Centistoke Viscosities

Experiment no.	ASTM s				$\eta_{37.8°C}$			
	$\overline{S}_w = 10{,}000$		$\overline{S}_w = 20{,}000$		$\overline{S}_w = 10{,}000$		$\overline{S}_w = 20{,}000$	
	Exptl.	Calcd.[a]	Exptl.	Calcd.[a]	Exptl.	Calcd.[b]	Exptl.	Calcd.[b]
3	0.623	0.651	0.501	0.543	51.3	55.2	89.5	99.9
4	0.674	0.673	0.573	0.580	47.9	49.5	84.2	83.7
5	0.697	0.683	0.612	0.598	44.3	46.1	77.6	76.5
9	0.641	0.628	0.537	0.507	66.0	65.0	123.5	118.1
14	0.720	0.691	0.651	0.611	38.4	43.6	65.6	71.4
23	0.616	0.635	0.496	0.518	60.5	62.8	112.6	112.4

[a] Calculated using eq. (5).
[b] Calculated using eq. (8).

TABLE IV
Experimental and Calculated Viscosity Index Values of Selected Copolymer Blends at Two
98.9°C SAE Viscosities

Experiment no.	SAE[a] no.	$\eta_{37.8°C}$		ASTM s	VI		$\eta_{0°F}$
		Exptl.[b]	Calcd.[c]	Calcd.	Exptl.[b]	Calcd.	Calcd.
3	20	41.8	46.0	0.600	170	148	1100
	40	81.0	90.1	0.550	205	184	2600
4	20	45.3	46.3	0.603	152	147	1150
	40	83.4	89.3	0.550	199	186	2400
5	20	43.0	46.1	0.595	163	148	1080
	40	89.0	90.0	0.550	187	184	2600
9	20	48.5	46.1	0.599	138	148	1100
	40	94.0	89.3	0.550	176	186	2400
14	20	50.0	46.3	0.603	132	147	1150
	40	94.0	88.6	0.550	177	187	2500
23	20	44.5	46.2	0.599	155	148	1100
	40	85.5	89.4	0.550	194	186	2400
Composite	20		46.1	0.599		148	1100
	40		88.3	0.550		186	2400

[a] Viscosities at 98.9°C same as in Table II.
[b] Table II.
[c] Calculated using eq. (8) for appropriate values of $\overline{S}_w$ for indicated SAE viscosities at 98.9°C.

values calculated (column 4) for $\eta_{37.8°C}$ and that for the composite reflect values of viscosities expected for blends with thermodynamically good solvents. The differences in $\eta_{37.8°C}$ are small between the best and average systems.

Viscosities obtained for poly(n-octadecyl acrylate) (POA) are shown as a function of $\overline{S}_w$ in Figure 5, inserts C and D. The solid line is the plotted curve. This lies close to the dashed line, which is the composite line discussed for the data above. The constants of this curve form the basis of eq. (8). Agreement between the curves is good, suggesting the utility of the parameter relating concentration to weight-average molecular weight even in the range of low molecular weight. However, the scatter in the individual points along the curve is not statistical but does indicate trends. The initial slope α' of eq. (7) increases for each series as $\overline{M}_w$ decreases; this would follow from the dependence of $\overline{S}_w$ or $\overline{M}_w$ as previously discussed. The effect may be seen better in Figure 6. Solid lines are curve-fitted data; dashed lines were computed by eq. (8). Agreement between fitted and calculated is good at high molecular weight (experiment 15)
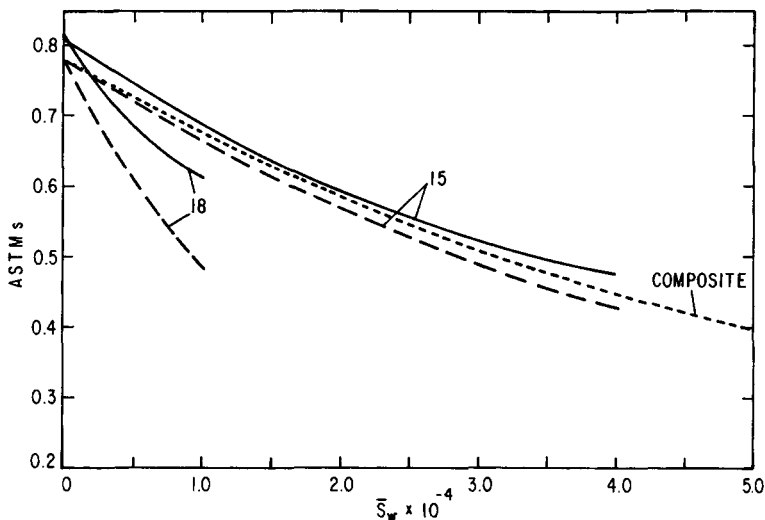
Fig. 6. Effect of weight-average molecular weight of poly(n-octadecyl acrylate) on the rate of change of ASTM s vs $\overline{S}_w$ curves for curve-fitted data (solid lines) and data calculated using eq. (8) (dashed lines). Dotted line represents base composite curve of eq. (5).

but rather poor (15% difference at ASTM s of 0.65) for experiment 18. Experiment 15 lies close to the composite line (dotted line) while α' is greater for experiment 18. These trends probably reflect the increased importance of the molecular weight of the oil in blends with lower molecular weight polymers, see eq. (3). However, polymers of such low molecular weight require too much sample to be practical.

The foregoing discussion suggests that the use of concentration and weight-average molecular weight as a single parameter offers some simplification both in the interpretation of data and in guiding blending operations over certain procedures.[28,45,51] Further refinements could lead to relations having even greater utility.

SUMMARY AND CONCLUSIONS

Three types of essentially n-alkyl acrylate copolymers, all containing n-octadecyl acrylate, were prepared and tested as viscosity index improvers under conditions of low shear viscosity only. The first type (OA + MMA) possessed units having extremes of side chain lengths of one and 18 methylene groups, including methyl, respectively. In the second type, (OA + EHA) and (OA + DA), the modifying counit was of intermediate length (eight and 12 methylene groups, respectively). A third type, poly(n-octadecyl acrylate), was prepared over the entire molecular weight range. Data for all three types were compared with well-known commercially available methacrylate copolymers (acryloids). The efficiency of (OA + MMA) copolymers was greater than those of (OA + EHA) and (OA + DA) copolymers, although the average side chain length of the first type was often somewhat greater. In fact, these copolymers compared favorably with the acryloids in efficiency, even though their effective side chain length was again considerably greater. A relationship was established between the weight-average molecular weight of base oil and polymer and their respective

concentrations, which yielded the weight-average molecular weight of the blend. Correlation of this parameter with ASTM slope and viscosity at two temperatures (37.8°C and 98.9°C) produced relations that predicted values for the rheological parameter in close (~6%) agreement with experimental values.

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