Density and Viscosity of Low-Molecular Weight Triglycerides and Their Mixtures

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The viscosities of tributyrin (C4:0) and binary mixtures of this triglyceride with a diesel fuel, tricaproin (C6:0), and tricaprylin (C8:0) were determined for the temperature range −5 to 85°C and for shear rates of 1.62–64.7 s^{-1}. The resulting dynamic viscosities were fit to a power law model to obtain values for the consistency coefficient and the flow behavior index. These results indicated slightly pseudoplastic flow behavior (indices ranged from 0.94 to 0.99) for tributyrin and its mixtures. The calculated consistency coefficients for tributyrin and those previously obtained for tricaproin, tricaprylin and tricaprin were fit by a least-squares method to the three-parameter Vogel model to account for the effect of temperature. An ideal solution relationship and the Kendall-Monroe model were used to predict the density and consistency coefficients, respectively, for binary and quaternary mixtures of these low-molecular weight triglycerides.

KEY WORDS: Consistency coefficient, dynamic viscosity, flow behavior index, shear rate, tributyrin, tricaprin, tricaproin, tricaprylin.

Vegetable oils have potential use as alternate fuel sources or fuel extenders (1). Unfortunately, most vegetable oils have viscosities sufficiently higher than diesel fuel, making it impractical to use them without chemical modification. Oils that contain significant fractions of low-molecular weight triglycerides may be suitable for direct use as fuel extenders. In fact, a few oilseed crops, such as *Cuphea* species (2), contain oils predominantly composed of these triglycerides (particularly tricaprylin and tricaprin). Recombinant DNA transfer techniques might make it possible to transfer genes that control the synthesis of low-molecular weight triglycerides from species such as *Cuphea* into more well established oilseed crops. An understanding of the physical properties of these triglycerides will be necessary to support the development of fuel or fuel extenders and diesel engines for these plant oils. Previous investigations of physical properties of pure low-molecular weight triglycerides include vapor pressure (3) and density (4) measurements over wide ranges of temperature. This work continues a previous study (5) that examined the density and the rheological properties of four low-molecular weight triglycerides (tributyrin, tricaproin, tricaprylin and tricaprin) and diesel fuel, as well as their mixtures. Tributyrin (C4:0), tricaproin (C6:0), tricaprylin (C8:0) and tricaprin (C10:0) are an analogous series of saturated triglycerides from straight-chain fatty acids with molecular weights of 302.3, 386.5, 470.7 and 554.9 g/mol, respectively.

The density (ϱ) of a fluid is its mass per unit volume. The density of an ideal mixture at a given temperature is related to the summation of each pure component (i) density and mole fraction (x) by:

$$\varrho_{MIX} = \sum x_i \varrho_i \qquad [1]$$

The apparent dynamic viscosity (η) of a fluid is equal to the ratio of the shear stress to the applied shear rate, $\dot{\gamma}$. This ratio is a constant for Newtonian fluids, and therefore the viscosity does not depend on the shear rate for these fluids. Non-Newtonian fluids exhibit viscosity behavior that is a function of the applied shear rate. One common method used to characterize the general relationship between shear rate and the viscosity of fluids is a simple power law equation that contains a proportionality constant, called a consistency coefficient (K):

$$\eta = K \dot{\gamma}^{N-1} \qquad [2]$$

This equation simplifies greatly for Newtonian fluids, which have a flow behavior index (N) of unity. For such fluids, Equation 2 reduces to $\eta = K$, and thus the apparent viscosity remains constant. A flow behavior index less than unity indicates pseudoplastic behavior, whereas an index greater than unity corresponds to dilatant behavior. The consistency coefficient (K) is proportional to the viscosity of the fluid. Because viscosity is a strong function of temperature, the values of the two parameters, N and K, may change with temperature. No general law exists for predicting the effect of temperature on the flow behavior index. If one assumes that the value of this index does not change significantly with temperature, then the consistency coefficient of pure compounds may be related to temperature by one of several empirical models, such as that suggested by Vogel (6):

$$\ln K = A + \frac{B}{C + T} \qquad [3]$$

The units of temperature (T) in Equation 3 are degrees Celsius (°C), and A, B and C are fitted parameters.

Another common requirement in engineering calculations is a method to determine the viscosity of a mixture solely from more readily available viscosities of each pure component. Although several empirical and theoretical models exist for the prediction of mixture viscosities (7), a convenient model is based on the studies of Kendall and Monroe (8,9). The general equation is:

$$\eta_{MIX}^{1/3} = \sum x_i \eta_i^{1/3} \qquad [4]$$

If the flow behavior index for the mixture is identical to the indices for each pure triglyceride (i) at a given temperature, then Equation 4 may be rewritten in terms of the consistency coefficients:

$$K_{MIX}^{1/3} = \sum x_i K_i^{1/3} \qquad [5]$$

Newtonian behavior is not required for Equation 5 to be valid.

Equations 3 and 5 are useful for predicting mixture consistency coefficients and, hence, viscosities at any temperature. The procedure is to measure the viscosity of a pure component over a range of temperature, determine the component's consistency coefficients by Equation 2 and then calculate the three parameters in Equation 3. With these three parameters for each pure triglyceride, Equation 5 may be used to predict the consistency coefficient at any temperature for any mixture made up of these components.

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Formally, this procedure relies on the triglycerides having identical flow behavior indices and on the flow behavior indices not varying significantly with temperature. These assumptions may be made for mixtures of the molecularly similar triglycerides being considered, but must nevertheless be validated by experimental evidence.

MATERIALS AND METHODS

Oil and fuel samples. Samples of 99+% tributyrin, tricaproin, tricaprylin and tricaprin were purchased from Sigma Chemical Company (St. Louis, MO). A low-sulfur (0.05%) diesel fuel with an average molecular weight of 204 g/mol and a density at 25.0°C of 0.8399 g/mL (5) was obtained from the Phillips 66 Company (Borger, TX). Several mixtures were prepared by combining measured masses of pairs of these oils.

Density measurements. Liquid density at 25.0°C and atmospheric (room) pressure was calculated by measuring sample mass once in a 10-mL pycnometer. Results obtained with other test samples of known densities suggested an accuracy of approximately ± 0.0003 g/mL.

Viscosity measurements. Viscosity was measured for each liquid sample at least in triplicate with a Brookfield Synchro-metric LV viscometer and a UL adapter (Stoughton, MA). This immersion-type concentric cylinder viscometer generated eight discrete shear rates between 0.32 and 64.7 s^{-1}. The accuracy and reproducibility of this instrument were 1 and 0.2% of full-scale, respectively. Observations that fell below 5% of full-scale at a given shear rate were considered not to be within the instrument's range and were not recorded. A circulating temperature bath containing ethylene glycol/water provided up to seven constant temperatures for experimentation: −5, 10.0, 25.0, 40.0, 55, 70 and 85°C. During a series of viscosity measurements, the three temperatures of 10.0, 25.0 and 40.0°C were maintained to an accuracy of ±0.1°C by calibration with an ASTM 63C standard thermometer. The other temperatures were maintained to an accuracy of ±0.5°C.

RESULTS AND DISCUSSION

Pure liquids. The density of pure tributyrin at 25.0°C was measured to be 1.0279 g/mL. This liquid density is slightly higher than that of pure C6:0 (0.9742 g/mL) and pure C8:0 (0.9507 g/mL) (5). Pure C10:0 is a solid at 25.0°C.

Figure 1 shows the apparent viscosities of pure C4:0 as a function of shear rate for temperatures of −5–85°C. The solid curves on these figures result from least-squares regressions of each data set to Equation 2 (the correlation coefficient ranged from 0.84 to 0.95). Figure 1 shows that the apparent viscosity of tributyrin decreased with increasing shear rate, indicating pseudoplastic behavior. In the temperature range studied, the viscosity descreased by about 40% for each 15°C temperature increase. As expected, the viscosity of C4:0 at a given temperature and shear rate was lower than the viscosity for C6:0, C8:0 or C10:0, as measured previously (5).

Figure 2 presents the actual fitted values for the consistency coefficient and the flow behavior index of pure C4:0 viscosities at each temperature. Because the viscosity is proportional to the consistency coefficient, these data in Figure 2 illustrate the effect of temperature on viscosity. The solid curve in this figure is the resulting least-squares regression of the data to the Vogel model, Equation 3. Because only two or three viscosity measurements fell within the instrument's range at the three highest temperatures, the values determined for the consistency coefficient and the flow behavior index are less accurate at these temperatures than at lower temperatures. The calculated Vogel parameters are shown in Table 1 in addition to those for the three larger triglycerides (5). The flow behavior index data illustrate that C4:0, like the other three pure triglycerides (5), is slightly pseudoplastic.

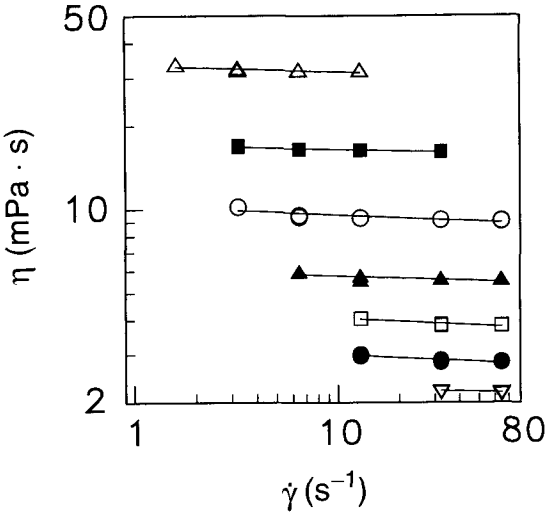

FIG. 1. Apparent dynamic viscosity (η) of tributyrin (C4:0) vs. shear rate: −5.0°C, △; 10.0°C, ■; 25.0°C, ○; 40.0°C, ▲; 55°C, □; 70°C, ●; and 85°C, ▽. Solid curves are results of least-squares regression of data to Equation 2.

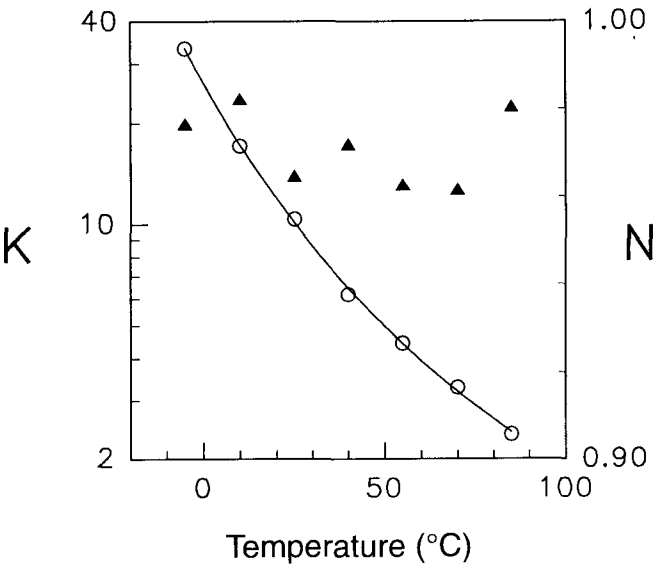

FIG. 2. Consistency coefficient (K, ○) and flow behavior index (N, ▲) for pure tributyrin (C4:0) vs. temperature. Solid curve indicates result of least-squares regression of consistency coefficient to the Vogel model (Equation 3).

TABLE 1

Calculated Parameters in the Vogel Model, Equation 3, Relating the Consistency Coefficient to Temperature for Pure Triglycerides[a]

Triglyceride	A	B	C	n	R
C4:0	−3.047	882.0	139.6	7	1.000
C6:0	−0.744	336.6	76.6	6	1.000
C8:0	−2.911	996.7	138.7	6	1.000
C10:0	−1.332	559.2	89.7	4	0.998

[a]n is the number of data points in the regressed model; R is the correlation coefficient.

Binary mixtures. Three binary mixtures containing tributyrin were studied—C4:0/C6:0, C4:0/C8:0 and C4:0/diesel. Figure 3 shows the liquid densities for these mixtures as functions of C4:0 mole fraction. The density for each of the three mixtures was close to linear with respect to composition, with C4:0/C6:0 showing a slight (less than 1%) negative departure from ideal solution behavior, and C4:0/C8:0 showing a 1–2% negative departure from ideal solution behavior. Using Equation 1 to predict the densities of the two triglyceride mixtures would result in as great as a 2% overprediction of the true density. Although a multicomponent mixture, C4:0/diesel showed a 1% positive departure from "ideal" solution behavior.

The viscosity of each of these binary mixtures was measured as a function of shear rate and temperature. For each mixture studied, such measurements yielded apparent viscosity data analogous to those shown in Figure 1. For each temperature and composition, these data were fit to Equation 2 to yield values for the consistency coefficient and flow behavior index (correlations of the lower temperatures ranged from 0.85 to 0.98).

Figure 4 shows the consistency coefficient for the C4:0/C6:0 mixture as a function of C4:0 mole fraction for the seven temperatures studied. As expected, the larger the fraction of C6:0 in the fluid, the greater the consistency coefficient (and therefore the greater the apparent viscosity). The solid curves on this figure are predictions from Equations 3 and 5. As Equation 5 predicts, the consistency coefficients were roughly linear with mole fraction. In other words, a 50:50 (mole percent) mixture of C4:0 and C6:0 resulted in a fluid with a consistency coefficient and viscosity midway between those of pure C4:0 and C6:0 on the log scale.

Figure 5 shows the consistency coefficient for the C4:0/C8:0 mixture as a function of C4:0 composition. As expected, the larger the fraction of C8:0, the greater the

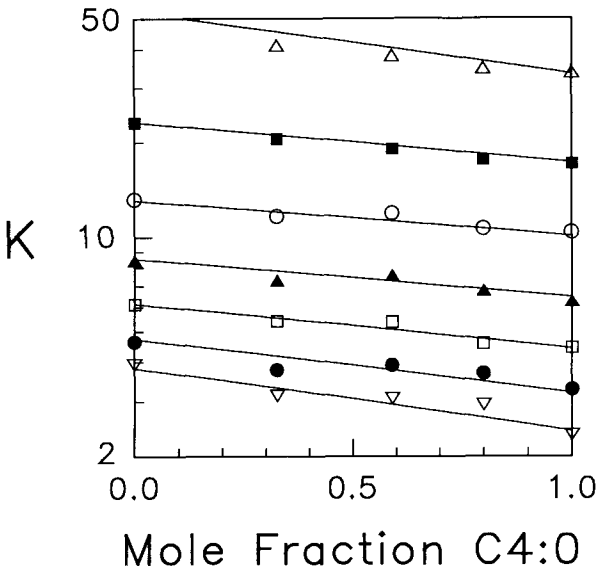

FIG. 4. Consistency coefficient (K) for binary mixtures of tributyrin (C4:0) and tricaproin (C6:0): −5.0°C, △; 10.0°C, ■; 25.0°C, ○; 40.0°C, ▲; 55°C, □; 70°C, ●; and 85°C, ▽.

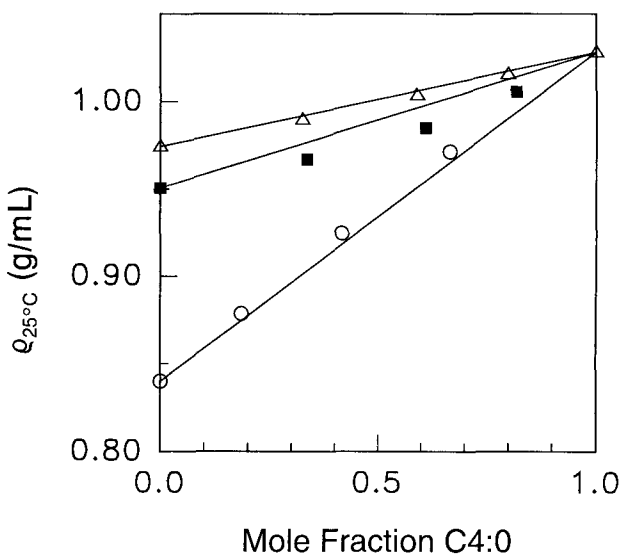

FIG. 3. Densities (ϱ) at 25.0°C of binary mixtures containing tributyrin and diesel (○), tricaproin (C6:0, △) and tricaprylin (C8:0, ■). Solid lines are theoretical predictions given by Equation 1.

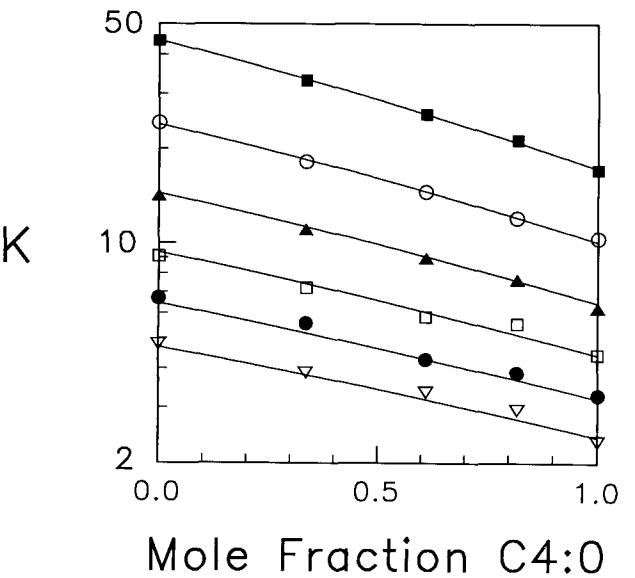

FIG. 5. Consistency coefficient (K) for binary mixtures of tributyrin (C4:0) and tricaprylin (C8:0): 10.0°C, ■; 25.0°C, ○; 40.0°C, ▲; 55°C, □; 70°C, ●; and 85°C, ▽.

viscosity of the mixture. The data in Figures 4 and 5 at higher temperatures become more scattered because, as noted before, only two or three measurements were within the instrument's range.

The flow behavior index (not shown) for each of these two mixtures decreased slightly with temperature (−5 to 85°C) from approximately 0.97 to 0.93. For temperatures less than 55°C, where more measurements could be made, the flow behavior index for each mixture studied remained between 0.960 and 0.975.

Figure 6 shows the consistency coefficient at seven temperatures for the binary mixture of C4:0/diesel. Although Equation 5 was not used for the prediction of these consistency coefficients (because diesel is heterogeneous), the mixtures at the three lowest temperatures do follow this ideal empirical model. That is, a 50:50 mixture would have a viscosity midway on the logarithmic scale between the viscosities of pure C4:0 and diesel. At −5°C, tributyrin was about 350% more viscous than diesel, whereas at 85°C this difference was reduced to 40%.

Quaternary mixtures. Equations 1 and 5 provide means to estimate the density and consistency coefficient, respectively, for multicomponent mixtures, provided they behave as ideal mixtures.

Table 2 shows the composition of six different quaternary mixtures of the four low-molecular weight triglycerides selected for study. This table also compares the observation with the densities predicted by Equation 1 for these mixtures. In general, the predicted densities are greater than the observed values by about one percent. These results are further evidence that mixtures of triglycerides show slight negative departure from ideal solution behavior at 25°C.

Figures 7, 8 and 9 show the observed and predicted consistency coefficients for the six quaternary mixtures studied. Except for mixture C (Fig. 8), the prediction by Equations 3 and 5 is excellent. For mixture C, which has the highest fraction of C6:0 of all the mixtures, the model overpredicts the observation by less than 2% at low temperature, but by about 20% at the highest temperature. There is no explanation for the difference between the observed and predicted consistency coefficients for this composition. The measured flow behavior indices for all these mixtures were between 0.94 and 0.99.

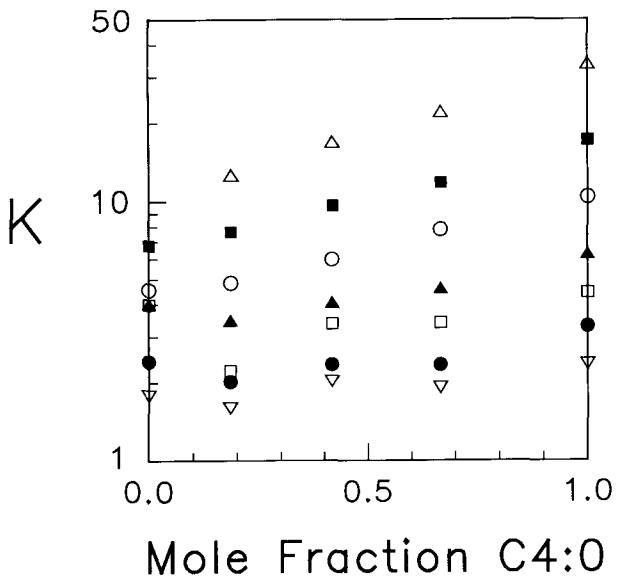

FIG. 6. Consistency coefficient (K) for mixtures of tributyrin (C4:0) and diesel: −5.0°C, △; 10.0°C, ■; 25.0°C, ○; 40.0°C, ▲; 55°C, □; 70°C, ●; and 85°C, ▽.

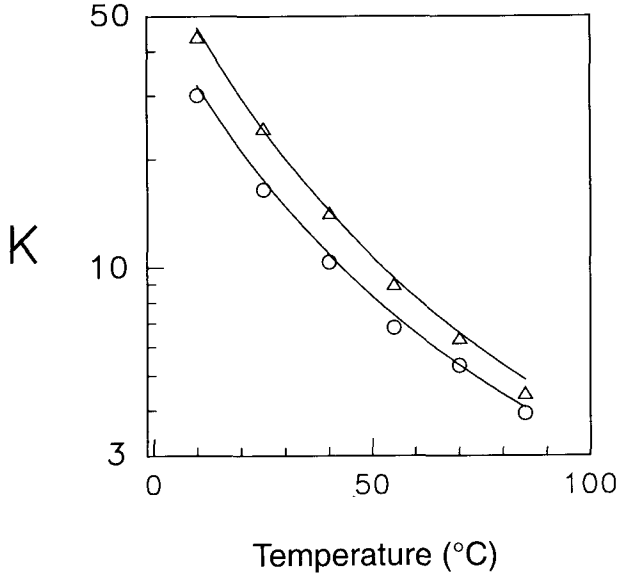

FIG. 7. Consistency coefficient (K) vs. temperature for quaternary mixtures of triglycerides (see Table 2 for compositions): mixture A, ○; mixture B, △. Solid curves are theoretical predictions given by Equation 5.

TABLE 2

Compositions and Predicted (PRED) and Observed (OBS) Densities at 25.0°C for Quaternary Mixtures of Triglycerides Selected for Study

Mixture	x_{C4}	x_{C6}	x_{C8}	x_{C10}[a]	ϱ_{OBS}	ϱ_{PRED}	% Error
A	0.1368	0.4151	0.3632	0.0849	0.9635	0.9693	−0.60
B	0.1159	0.0988	0.4067	0.3786	0.9479	0.9543	−0.67
C	0.1105	0.5948	0.1975	0.0972	0.9639	0.9712	−0.75
D	0.1568	0.1457	0.5977	0.0999	0.9563	0.9642	−0.82
E	0.3091	0.2516	0.2370	0.2023	0.9658	0.9764	−1.09
F	0.6047	0.1844	0.1078	0.1031	0.9878	0.9996	−1.18

[a]Liquid density of pure tricaprin estimated at 25.0°C to be 0.9304 g/mL from extrapolation of data from Phillips and Mattamal (4).

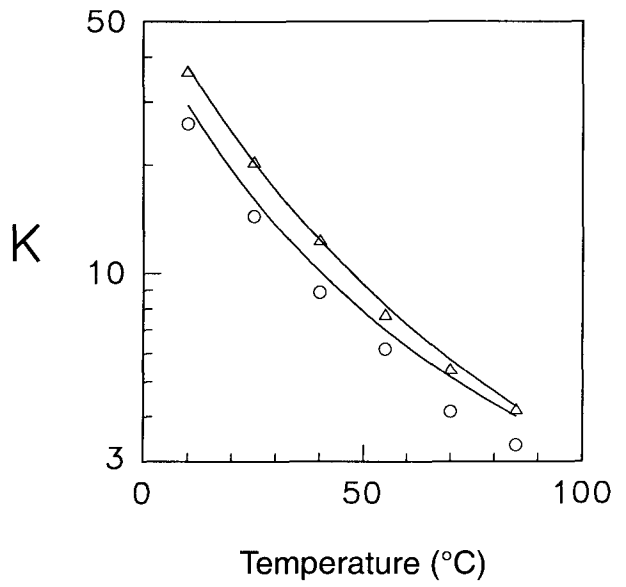

FIG. 8. Consistency coefficient (K) vs. temperature for quaternary mixtures of triglycerides (see Table 2 for compositions): mixture C, ○; mixture D, △. Solid curves are theoretical predictions given by Equation 5.

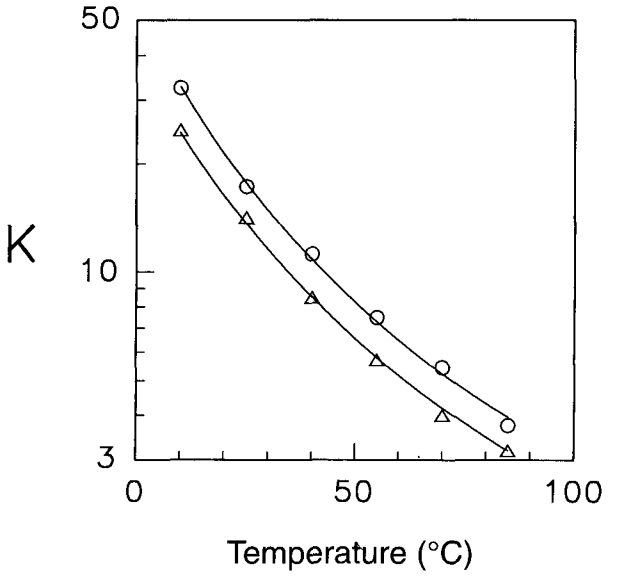

FIG. 9. Consistency coefficient (K) vs. temperature for quaternary mixtures of triglycerides (see Table 2 for compositions): mixture E, ○; mixture F, △. Solid curves are theoretical predictions given by Equation 5.

The power law equation provided a successful model of the rheological behavior of tributyrin and the three binary mixtures with this triglyceride. The behavior of all liquids studied was slightly pseudoplastic, with flow behavior indices being slightly less than one. As expected, the viscosity at any temperature and shear rate studied increased for triglycerides and mixtures of progressively larger molecular weight. While progressively lower-molecular weight triglycerides approached the viscosity of diesel, they departed from the low density of diesel fuel. The three-parameter Vogel model was excellent for correlating the consistency coefficients of the pure triglycerides for the temperature range of −5 to 85°C. Mixtures of triglycerides showed slight negative departure from ideal solution behavior for the calculation of density. For the prediction of the viscosity of mixtures, the Kendall-Monroe empirical model provided generally excellent correlation of the observed consistency coefficients of binary and quaternary mixtures.

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