Heat Capacity of the Triglycerides: Tricaproin, Tricaprylin and Tricaprin

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Heat capacities of tricaproin, tricaprylin, tricaprin and their binary mixtures were determined between 325 and 423°K. In this temperature range, the heat capacity of tricaproin increased from 174 to 206 cal/mol-K, of tricaprylin from 221 to 281 cal/mol-K and of tricaprin from 276 to 309 cal/mol-K. Mixtures of tricaproin/tricaprin and tricaprylin/tricaprin behave as ideal solutions, while a mixture of tricaproin/tricaprylin did not behave as an ideal solution for this temperature range.

KEY WORDS: Excess heat capacity, tricaprin, tricaproin, tricaprylin.

Natural plant oils could be used as alternate fuels or as fuel extenders. Unfortunately, most natural oils have vastly different thermodynamic properties, and correspondingly different fuel properties, from the diesel fuels used in current engine designs and, therefore, cannot be used without chemical modification. As an alternative to chemical modification, oils with significant fractions of low-molecular weight triglycerides might be suitable for use as fuel extenders. For example, seeds of *Cuphea* species contain oils composed largely of relatively low-molecular weight triglycerides (particularly tricaprylin and tricaprin) (1). An understanding of the thermodynamic behavior of such low-molecular weight triglycerides is necessary to aid in the development of diesel engines that may use these oils.

This work examines the heat capacity of three low-molecular weight triglycerides, tricaproin, tricaprylin and tricaprin, and their mixtures.

Tricaproin (C6:0), tricaprylin (C8:0) and tricaprin (C10:0) are an analogous series of saturated linear triglycerides with molecular weights of 386.5, 470.7 and 554.9 g/mol, respectively. Previous studies of physical properties of these triglycerides include vapor pressure (2), density (3) and viscosity (4). The heat capacity of the pure triglycerides has also been investigated (5), although no previous work has studied mixtures of these triglycerides.

The measured heat capacity of an N-component mixture (C_P) is often related to the heat capacity of each pure component ($C^{\circ}_{P\,i}$) by an excess function (6):

$$C_P^{EX} = C_P - \sum_{i=1}^{N} x_i C^{\circ}_{P\,i} \qquad [1]$$

where x_i is the mole fraction of a particular component. The excess heat capacity (C_P^{EX}) is a measure of the nonideality of the mixture. Molecularly similar components, such as triglycerides, often behave as ideal solutions and, therefore, have essentially no C_P^{EX}. C_P^{EX} is often correlated with molar composition by truncating a Redlich-Kister polynomial. For example, for a binary mixture, the two-term polynomial is:

$$C_P^{EX} = A_0 x_1(1 - x_1) + A_1 x_1(1 - x_1)(2x_1 - 1) \qquad [2]$$

where x_1 is the mole fraction of component 1, and the coefficients A_0 and A_1 are functions of temperature only.

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EXPERIMENTAL PROCEDURES

Tricaproin, tricaprylin and tricaprin were purchased from Sigma Chemical Co. (St. Louis, MO). Several binary mixtures were prepared by combining measured masses of pairs of these oils. All samples were stored below their freezing temperature to avoid any degradation.

Heat capacity was measured for each liquid sample by thermal analysis in a differential scanning calorimeter (Model DSC-2C; Perkin-Elmer, Norwalk, CT) with sapphire as a standard. Aluminum sample holders were used for low-temperature measurements (i.e., below 373°K), and stainless-steel sample holders with O-rings were used for higher-temperature operation (i.e., above 373°K). The heat capacity for each sample was calculated in triplicate from thermograms obtained with the DSC. The accuracy of the instrument was set to 0.1 mcal/°K. A constant nitrogen purge was maintained around the sample cell to stabilize the sample environment. At low temperature, the standard error of the measurements was less than 1%, while at high temperature the standard error was approximately 8%.

RESULTS AND DISCUSSION

Figure 1 shows the observed heat capacities of the pure triglycerides. The observations for tricaprylin and tricaprin (C8 and C10) are slightly greater than the previous observations of Phillips and Mattamal (5), also shown on this figure. The heat capacities of these low-molecular weight triglycerides were also slightly higher than values reported for diesel fuel. At 373°K, diesel fuel was previously shown to have a (specific) heat capacity of 1.7 J/g-K (7), while tricaproin has now shown to have a heat capacity of 2.0 J/g-K, tricaprylin a value of 2.1 J/g-K and tricaprin 2.2 J/g-K.

Figures 2, 3 and 4 show the observed heat capacities for the tricaproin/tricaprylin (C6:C8) mixture, the tricaproin/tricaprin (C6:C10) mixture and the tricaprylin/tricaprin (C8:C10) mixture, respectively. As expected, for all

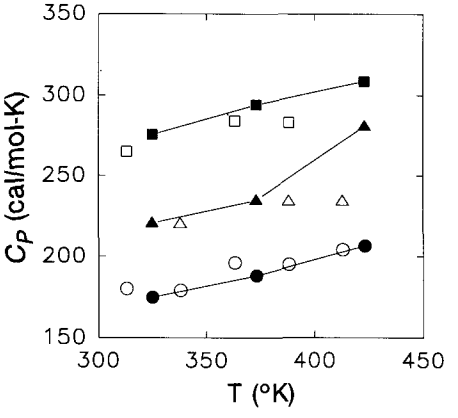

FIG. 1. Molar heat capacity of pure tricaproin (●), tricaprylin (▲) and tricaprin (■) vs. temperature. Data of Phillips and Mattamal (Ref. 5) are shown as open symbols. C_P = heat capacity.

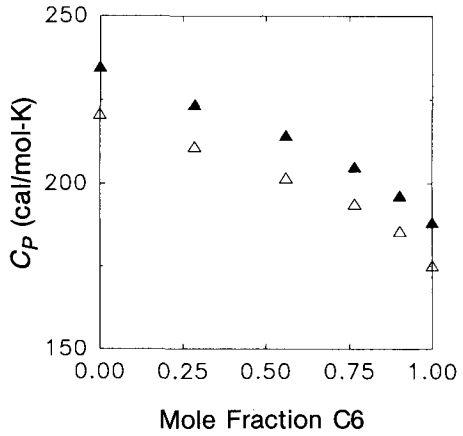

FIG. 2. Molar heat capacity of the binary mixture of tricaproin (C6) and tricaprylin (C8). Temperature: 325°K (△), 373°K (▲). See Figure for abbreviation.

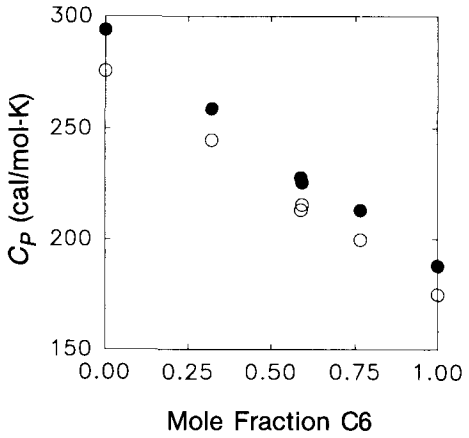

FIG. 3. Molar heat capacity of the binary mixture of tricaproin (C6) and tricaprin (C10). Temperature: 325°K (○), 373°K (●). See Figure 1 for abbreviation.

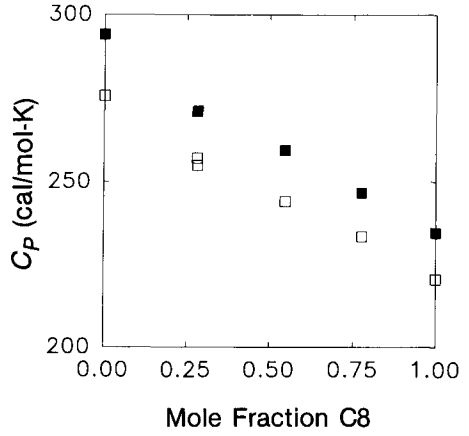

FIG. 4. Molar heat capacity of the binary mixture of tricaprylin (C8) and tricaprin (C10). Temperature: 325°K (□), 373°K (■). C_P = heat capacity.

mixtures the heat capacities at 373°K are greater than those observed at 325°K. Figures 3 and 4 show that the C6:C10 and C8:C10 mixtures behave as ideal solutions, with the calculated deviations from ideal behavior within

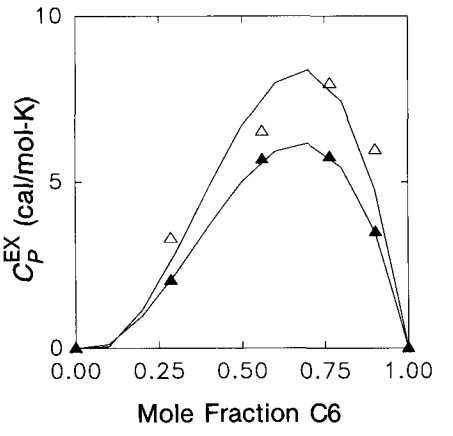

FIG. 5. Excess heat capacities for the binary mixture of tricaproin (C6) and tricaprylin (C8) at 325°K (△) and 373°K (▲). Curves indicate data fit to Equation 2. C_P^{EX} = excess heat capacity.

the experimental error. In both of these cases, the C_P^{EX}s calculated with Equation 1 were essentially zero. Therefore, one could predict heat capacities of these mixtures directly from heat capacities of the pure components.

In contrast, the C6:C8 mixture shown in Figure 2 exhibits significant departure from ideal solution behavior. (That is, the data are nonlinear with composition.) Equation 1 was used to calculate the C_P^{EX}. For each temperature studied, the C_P^{EX}s calculated were fit to Equation 2 by least-squares analysis. Figure 5 shows the resulting C_P^{EX}s for the C6:C8 mixture at 325 and 373°K. At 325°K, the coefficients in Equation 2 were calculated to be: A_0 = 26.8 cal/mol-K and A_1 = 32.8 cal/mol-K (correlation coefficient, R = 0.848), while at 373°K the values were A_0 = 20.0 cal/mol-K and A_1 = 23.3 cal/mol-K (R = 1.000). The lower value of both coefficients at the higher temperature indicates that the C6:C8 mixture behaves more closely to an ideal solution at 373°K than at 325°K. In this temperature range, even the C6:C8 mixture deviates from ideal solution behavior by less than 4%.

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