

Thermodynamics of Glycerol Trioleate + n-Alkanes

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Excess volume measurements for glycerol trioleate + n-alkanes ($5 \leq n \leq 18$) at 30 °C are compared with predictions from a corresponding states theory of oligomeric mixtures. Quantitative discrepancies between theory and experiment suggest that glycerol trioleate does not behave like a long-chain hydrocarbon in its mixtures with n-alkanes.

Oils and fats are extracted from naturally occurring materials by dissolving them in low molecular weight hydrocarbons. A factor determining the efficiency of the extraction process is the thermodynamic mixing behaviour of the oil with the solvent. In this Note, we consider the excess volumes of mixing of glycerol trioleate (GT) with those normal alkanes that are liquid under ambient conditions. Glycerol trioleate, $(C_{17}H_{33}CO_2)_3C_3H_5$, is a major constituent of certain vegetable oils (e.g. olive oil) and we expect its thermodynamic mixing properties to be representative of many edible liquid fats.

In its thermodynamic mixing behaviour with the paraffins, to what extent can GT be regarded as being equivalent to a long-chain alkane? We attempt to answer this question by using the principle of corresponding states in the form adopted by Prigogine¹ and Patterson and Bardin² for oligomeric mixtures. Our justification for this approach lies in the fact that GT is found to be reasonably conformal with the n-alkanes, at least in terms of the molar volume and its first and second temperature derivatives.³ The answer to the question should give a clear indication as to the extent to which the double-bonds and ester linkages influence the solution properties of the liquid triglyceride.

According to the theory of corresponding states,¹ the thermodynamic configurational properties of an oligomeric liquid are related to dimensionless reduced quantities through reduction factors that depend only on chain length. For instance, the molar volume V_m at temperature T and pressure p is written in the form

$$V_m(T, p, n) = V^*(n) \tilde{V}(\tilde{T}, \tilde{p}). \quad (1)$$

The reduced volume \tilde{V} is a function of the reduced temperature $\tilde{T} = T/T^*$ and reduced pressure $\tilde{p} = p/p^*$. The quantities V^* , T^* and p^* are called volume, temperature and pressure reduction factors. In a mixture of conformal oligomers, eqn (1) becomes

$$V_m(T, p) = \langle V^* \rangle \tilde{V}(\langle \tilde{T} \rangle, \langle \tilde{p} \rangle) \quad (2)$$

where now $\langle \tilde{T} \rangle$ and $\langle \tilde{p} \rangle$ are the reduced temperature and pressure of the mixture. The average volume reduction factor $\langle V^* \rangle$ in a c -component mixture is given by

$$\langle V^* \rangle = \sum_{j=1}^c x_j V_j^* \quad (3)$$

where x_j is the mole fraction of component j .

The molar excess volume in a binary mixture can be expressed as a Taylor expansion in $\Delta\tilde{T} = \tilde{T}_1 - \tilde{T}_2$, the difference between the reduced temperatures of the components:^{2,4}

$$V_m^E = -\sum_i (i!)^{-1} \{x_1 X_2^i V_1^* + (-1)^i x_2 X_1^i V_2^*\} (d^i \tilde{V} / d\langle \tilde{T} \rangle^i) (\Delta\tilde{T})^i. \quad (4)$$

The reduced temperature $\langle \tilde{T} \rangle$ of the mixture is

$$\langle \tilde{T} \rangle = X_1 \tilde{T}_1 + X_2 \tilde{T}_2 \quad (5)$$

and X_1 is the segment fraction of component 1:

$$X_1 = x_1 p_1^* V_1^* / (x_1 p_1^* V_1^* + x_2 p_2^* V_2^*). \quad (6)$$

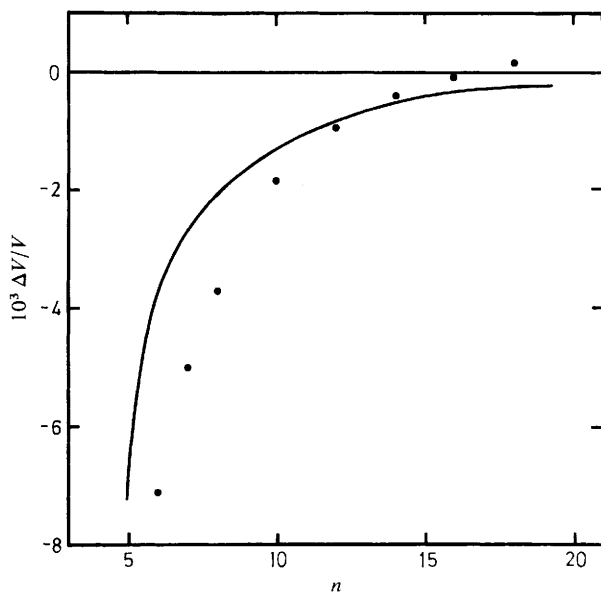


FIG. 1.—Change in volume on mixing glycerol trioleate (1) with n-alkanes (2) at 30 °C. The fractional volume change $\Delta V/V$ at $\phi_1 = 0.5$ is plotted against the alkane chain length n : ●, experiment; —, corresponding states theory with $p_1^* = p_2^*$. The experimental result for the n-pentane system ($\Delta V/V = -0.0170$) is not shown.

If the pressure reduction factors are the same, then X_1 is identical to the volume fraction $\phi_1 = x_1 V_1^* / \langle V^* \rangle$. The summation of eqn (4) can normally be curtailed at $i = 3$ with negligible error.

Fractional volume changes $\Delta V/V$ for GT (1) + n-alkanes (2) at 30 °C as predicted from corresponding states theory are shown in fig. 1 for mixtures with $\phi_1 = 0.5$. The reference substance was taken as n-decane and the derivatives $(d^i \tilde{V} / d\langle \tilde{T} \rangle^i)$ were calculated from thermal expansivity data fitted by Orwoll and Flory.⁵ Values of T^* and V^* were taken from Patterson and Bardin² and Dickinson *et al.*³ and p_1^* was set equal to p_2^* throughout. The assumption of a constant pressure reduction factor is valid for a mixture of two n-alkanes.² If the double-bonds and ester linkages have little effect on the mixing properties of GT, as compared with the equivalent hydrocarbon, the predicted curve should lie close to experimentally determined volume changes. The first term in the sum of eqn (4) disappears with $p_1^* = p_2^*$ and

the predicted volume change is negative for all n (as found experimentally with mixtures of homologues²). The absolute value of $\Delta V/V$ exceeds 0.6% for $n = 5$, but with increasing chain length it falls sharply in accordance with the reduction in $|\tilde{T}_1 - \tilde{T}_2|$. (The predicted $\Delta V/V$ is exactly zero for $n = 46$; it increases again for $n > 46$ where $\tilde{T}_1 > \tilde{T}_2$.) Two other predictions of the theory are that $\Delta V/V$ becomes more negative with increasing temperature (due to the positive sign of $d|\Delta T|/dT$) and that the maximum value of $\Delta V/V$ lies close to $\phi_1 = 0.5$.

To test the theory, we have measured $\Delta V/V$ at 30 °C and 1 bar for mixtures of GT with n-pentane, n-hexane, n-heptane, n-octane, n-decane, n-dodecane, n-tetradecane, n-hexadecane and n-octadecane. The alkanes (99 mol % pure) were obtained from Sigma Chemicals. The B.D.H. glycerol trioleate contained several per cent of unknown, but chemically similar, triglycerides. Depending on volatility, the liquids were de-aerated either by 'flash' boiling or evacuation in a desiccator.

The dilatometer was of the design described by Kumaran and McGlashan.⁶ The advantages of this type of dilution dilatometer have been set out in a recent review.⁷ The radii of the burette (6.002 ± 0.006 mm) and capillary tube (0.750 ± 0.002 mm) were measured by weighing mercury. The temperature (± 2 mK) was monitored by a Hewlett-Packard quartz thermometer (type 2804A). The high viscosity of GT necessitated vigorous stirring to ensure complete mixing. A compressibility correction was applied based on assumptions described previously.⁸ The performance of the dilatometer was established with a dummy run of the type cyclohexane + cyclohexane and a standard run of the type benzene + cyclohexane.⁷

The measured volume changes were symmetrical in volume fraction with the maximum occurring within ± 0.05 of $\phi_1 = 0.5$ for each of the mixtures studied. The experimental values of $\Delta V/V$ in fig. 1 are lower than the theoretical predictions for small n and higher than the predictions for large n . The experimental volume change is positive for $n = 18$; $\Delta V/V$ at $\phi_1 = 0.5$ for GT + n-octadecane falls from $(1.5 \pm 0.4) \times 10^{-4}$ at 30 °C to $(0.6 \pm 0.4) \times 10^{-4}$ at 44 °C. So we see that while the gross features of the experimental observations agree with the theory, there are significant numerical deviations.

We have not so far allowed for the possibility of the pressure reduction factors being different. A recent thermodynamic analysis³ gives $p^*(\text{GT})/p^*(36) = 0.80$ at $(\alpha_p T)^{-1} = 3.5$, where $p^*(36)$ refers to n-C₃₆H₇₄ and α_p is the thermal expansion coefficient. The ratio $p^*(\text{GT})/p^*(36)$ is sensitive to the reduced temperature at which it is calculated, which implies that, as far as p^* is concerned, GT does not follow the same principle of corresponding states as the n-alkanes. By setting $p_1^* < p_2^*$, the theory can be made to give a positive volume change for $n = 18$ to fit experiment, but the price to be paid is even poorer agreement at short chain lengths. Conversely, with $p_1^*/p_2^* > 1$, one can obtain improved agreement for small n only at the expense of poorer agreement for large n .

There is no way, then, to get quantitative agreement with experimental excess volumes of mixing for GT with the n-alkanes on the basis of a simple corresponding states treatment with a single set of reduction factors. We take this to infer that while the general features of the thermodynamic mixing behaviour are due to the extent of the difference in reduced temperature between the components, the triglyceride cannot simply be treated as if it were a large hydrocarbon. There are presumably additional 'energetic' effects which lead to deviations from conformality.

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