phase does not affect solubilities of triglycerides in the supercritical phase.

In order to model the CO_2 solubilities of triglyceride mixtures, it is necessary to take into account intermolecular interactions between unlike triglycerides in both the supercritical and liquid (or solid) phases. Research is underway to use a multicomponent version of the lattice EOS to correlate solubility data of mixtures by using pure component parameters and binary interactions parameters δ_{ij}, from independent measurements, along with a fitted interaction parameter that would take into account interactions between unlike solute species.

Glossary

K	partition coefficient
P	pressure
q	effective chain length of a chain molecule
R	gas constant
r	number of segments per molecule
T	absolute temperature
v	specific volume
v_H	lattice unit cell volume
x	mole fraction, in particular in the heavy phase
y	mole fraction in the light phase
z	lattice cell coordination number

Greek Letters

δ_{ij}	binary interaction parameter in EOS
ϵ_{ij}	interaction energy between molecule segments
Γ	nonrandomness correction
μ	chemical potential
ϑ	molecular surface area fraction

Superscripts

•	reducing quantity
~	reduced quantity
L	liquid phase
V	vapor phase

Subscripts

i	species i
j	species j
M	mixture property

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Registry No. LLL, 538-24-9; MMM, 555-45-3; PPP, 555-44-2; CO_2, 124-38-9; lauric acid, 143-07-7; myristic acid, 544-63-8; palmitic acid, 57-10-3.

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Enthalpies of Mixing of Diethyl Sulfide + Carbon Tetrachloride and Diethyl Sulfide + Chloroform at 25 °C

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Enthalpies of mixing of mixtures of diethyl sulfide with carbon tetrachloride and with chloroform at 298.15 K are reported. The diethyl sulfide mixtures are more exothermic than the corresponding dimethyl sulfide mixtures measured earlier by Gray and Williamson by about 300 J mol^{-1}.

Introduction

The measurements reported here are part of a continuing study of solutions of ether and thioether mixtures with chlorinated hydrocarbons being carried out in this laboratory in which both weak and strong specific interactions are observed.

Experimental Section

The calorimeter used in this work is of the type originally developed by McGlashan and his colleagues (*2*) and has been fully described elsewhere (*3*). The measurements from this calorimeter are expected to be accurate to ±1-2% for exothermic systems.

Materials

Carbon tetrachloride and chloroform were purified as described by Beath and Williamson (*3*). The alkyl sulfides were

Table I. Enthalpies of Mixing of CCl_4 and Diethyl Sulfide at 298.15 K

x_{CCl_4}	H^E/J mol^{-1}	H^E_{calcd}/J mol^{-1}
0.1132	-252.0	-242.7
0.1429	-300.5	-303.7
0.1930	-383.4	-400.3
0.2846	-541.0	-548.8
0.3406	-617.0	-616.7
0.4427	-705.1	-687.4
0.4954	-697.4	-695.3
0.5582	-696.7	-678.7
0.6982	-534.7	-547.3
0.7730	-429.1	-432.3
0.9312	-149.4	-132.2

Table II. Enthalpies of Mixing of $CHCl_3$ and Diethyl Sulfide at 298.15 K

x_{CHCl_3}	H^E/J mol^{-1}	H^E_{calcd}/J mol^{-1}
0.1111	-524.0	-545.6
0.1780	-806.4	-830.1
0.3103	-1253.9	-1277.1
0.4343	-1569.4	-1533.8
0.4925	-1595.6	-1592.7
0.5170	-1648.7	-1604.8
0.6279	-1564.1	-1559.1
0.7278	-1343.4	-1366.0
0.8176	-992.3	-1058.0
0.9337	-510.5	-455.2

Table III. Parameters in Eq 1

system	B_1	B_2	B_3	σ
$(C_2H_5)_2S + CCl_4$	-2780	-146	794	11
$(C_2H_5)_2S + CHCl_3$	-6389	1111		37

purified as described by Gray and Williamson (*1*). All components were examined by gas-liquid chromatography on a 2-m column of 5% SE30 and showed only one peak.

Results

Tables I and II show the experimental results. Table III lists the parameters in the equation (*4*)

$$H^E/(\text{J mol}^{-1}) = x(1-x)\sum_{n=1}^{m} B_n(1-2x)^{n-1} \qquad (1)$$

where x is the mole fraction of halocarbon. Also shown are the values of

$$\sigma = [\sum_i \delta_i^2/(N-m)]^{1/2}$$

where δ_i is the difference between the experimental and calculated values of H^E. N is the number of experimental points and m is the number of parameters in eq 1. The parameters listed are those for which σ is a minimum.

Figure 1 compares the enthalpies of mixing for the two systems with the data for the corresponding dimethyl sulfide mixtures.

Discussion

The exothermic mixing suggests a strong interaction between the sulfide group and the chlorine similar to that inferred for the oxygen-chlorine interactions in ether + halocarbon mixtures (*5*). The very exothermic mixing in the chloroform mixtures is consistent with the hydrogen bond involving the sulfide and the chloroform hydrogen. Such hydrogen bonding has been confirmed in alkyl sulfide + chloroform mixtures by the NMR studies of Jolley et al. (*6*).

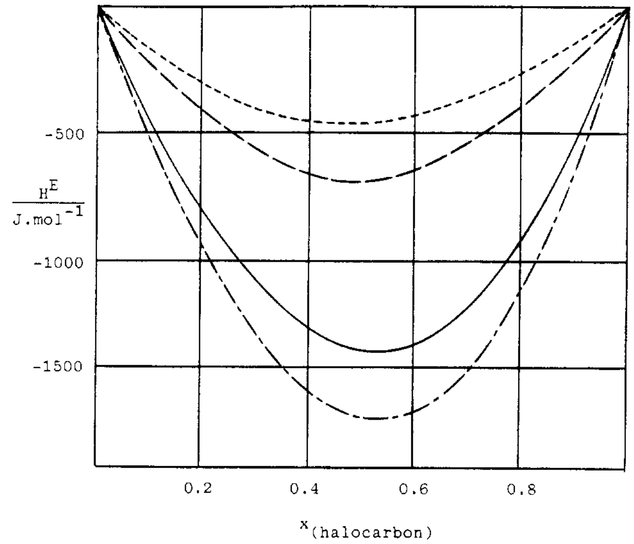

Figure 1. Enthalpies of mixing at 298.15 K: (- - -) $(CH_3)_2S + CCl_4$; (— — —) $(C_2H_5)_2S + CCl_4$; (—) $(CH_3)_2S + CHCl_3$; (— — — —) $(C_2H_5)_2S + CHCl_3$.

These workers measured the equilibrium constants for hydrogen-bond formation in mixtures of chloroform with diethyl sulfide and dimethyl sulfide over a range of temperatures and hence deduced enthalpies of formation of the hydrogen bonds. These were then used to calculate the expected enthalpies of mixing of -1550 and -1050 J mol^{-1} for equimolar mixtures of chloroform with diethyl sulfide and dimethyl sulfide, respectively. They comment that their predicted value is in good agreement with the measured H^E for diethyl sulfide (-1597 J mol^{-1}) but in poor agreement with that for dimethyl sulfide (1) (-1338 J mol^{-1}).

However, the values of $H^E(CHCl_3 + R_2S) - {}^3/_4H^E(CCl_4 + R_2S)$ which we expect to be a reasonable estimate of the contribution of the hydrogen bond to the enthalpy of mixing at $x = 0.5$ are -1076 and -990 J mol^{-1} for R = C_2H_5 and R = CH_3, respectively. This interpretation implies a good agreement between the NMR and calorimetric results for the dimethyl sulfide + chloroform mixtures and poor agreement for diethyl sulfide + chloroform mixtures, reversing the conclusions of Jolley et al.

Registry No. $(C_2H_5)_2S$, 352-93-2; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; $(CH_3)_2S$, 75-18-3.

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