Thermochimica Acta, 67 (1983) 111–119
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

CRYOSCOPIC BEHAVIOUR OF MIXTURES. ETHYLENETETRACARBONTETRAETHYL ESTER + ALKANE

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(Received 1 March 1983)

As part of a wider research on the energy interaction parameters between alkylic and ester groups [1–4], in this note the liquid–solid and liquid–liquid equilibrium temperatures are reported for mixtures of $(COOC_2H_5)_2$–C=C–$(COOC_2H_5)_2$ with *n*-alkanes: $C_{16}H_{34}$, $C_{18}H_{38}$, $C_{19}H_{40}$, $C_{24}H_{50}$.

The fusion enthalpy of the ester is also measured in order to ascertain the cryoscopic behaviour in the region of low alkane concentration.

EXPERIMENTAL

The visual method adopted for the cryoscopic measurements has been described in previous papers [4,5]. The calorimetric measurements were performed with a DSC-2C calorimeter equipped with a computer for analysis of the signals obtained. The compounds employed were: ethylenetetracarbontetraethyl ester (Ega-Chemie) and *n*-hexadecane, *n*-octadecane, *n*-nonadecane and *n*-tetracosane of high purity (J.T. Baker) which were used without further purification. These compounds were stored in a desiccator under dynamic vacuum

RESULTS AND DISCUSSION

Values of temperature, enthalpy, entropy of fusion and thermodynamic cryoscopic constant, $RT_0^2M/1000 \times \Delta H_f$, are given in Table 1. The experimental values of equilibrium temperatures at different compositions of the binary systems investigated are listed in Table 2. Figures 1–4 show the experimental trend T_{sl} and T_{ll} vs. ester mole fraction.

The thermodynamic cryoscopic constant is generally higher than the experimental one. $\Delta T/m$ values extrapolated to $m = 0$ are: 4.9 (solute, $C_{16}H_{34}$), 4.9 (solute, $C_{19}H_{40}$) and 5.0 (solute, $C_{18}H_{38}$). In the case of $C_{24}H_{50}$ solute, the range between pure ester and the beginning of liquid–liquid equilibrium is very narrow and only one measurement of T_{sl}

0040-6031/83/$03.00

TABLE 1

Thermodynamic data of fusion of ethylenetetracarbontetraethyl ester

$T_{fus.}$	$\Delta H_{fus.}$ (cal mole^{-1})	$\Delta S_{fus.}$ (cal mole^{-1})	$K_{cryosc.}$ (K molality^{-1})
327.7	9840	30.0	6.8_6

TABLE 2

Liquid–solid (T_{sl}) and liquid–liquid equilibrium temperatures in the binary systems

X_{Ester}	T_{sl} (K)	T_{ll} (K)
n-*Hexadecane + ethylenetetracarbontetraethyl ester*		
0.0000	290.8	
0.0049	302.4	
0.0176	319.3	
0.0289	326.5	332.0
0.0434	326.4	346.0
0.0520	326.3	352.1
0.0689	326.5	364.5
0.0974	326.6	377.9
0.1327		390.2
0.1842		401.3
0.2321		408.2
0.3115		412.7
0.3592		415.0
0.4252	326.6	416.3
0.5342		417.8
0.6213		416.6
0.7169	326.6	411.1
0.7907		401.0
0.8555	326.6	382.1
0.9013	326.6	355.7
0.9481	326.5	333.6
0.9618	326.9_4	
0.9751	327.2_5	
0.9903	327.5_4	
1.0000	327.7_0	
n-*Octadecane + ethylenetetracarbontetraethyl ester*		
0.0000	301.2	
0.0090	311.8	
0.0194	322.8	
0.0299	327.6	334.0
0.0369	327.7	343.9
0.0515	327.5	352.0
0.0823	327.4	371.5
0.1395	327.2	393.7
0.2132	327.0	412.1
0.2801		419.2

TABLE 2 (continued)

X_{Ester}	T_{sl} (K)	T_{ll} (K)
0.3188		421.9
0.3945		425.3
0.4912		428.2
0.5745		429.6
0.6259		427.8
0.6672		425.9
0.7212	327.3	422.9
0.7800		417.2
0.8242	327.2	410.5
0.8904	327.1	392.7
0.9331	327.2	369.0
0.9625	327.4	334.3
0.9828	327.3_6	
0.9901	327.5_4	
1.0000	327.7	
n-*Nonadecane + ethylenetetracarbontetraethyl ester*		
0.0000	304.8_5	
0.0117	317.6	
0.0280	327.2	334.2
0.0413	327.3	348.8
0.0562	327.4	360.0
0.0804	327.5	377.0
0.1214		394.3
0.1875		413.4
0.2469		422.3
0.3558		432.2
0.4113		434.3
0.4889		434.4
0.5696		431.9
0.6271		430.0
0.6950	326.7	425.1
0.7542	326.6	421.2
0.8378		410.7
0.9052		389.3
0.9456	327.1	369.5
0.9550	326.9	357.7
0.9685	327.1	338.2
0.9810	327.3_8	
0.9925	327.5_8	
1.0000	327.7	
n-*Tetracosane + Ethylenetetracarbontetraethyl ester*		
0.0000	323.7_5	
0.0042	323.7_3	
0.0114	325.7	
0.0372	326.4	348.0
0.0631	326.6	368.6
0.0899	326.3	388.4

TABLE 2 (continued)

X_{Ester}	T_{sl} (K)	T_{ll} (K)
0.1363	326.2	407.5
0.1903	326.4	420.3
0.3026	326.5	435.2
0.3670	326.4	444.8
0.4151		448.8
0.5051		454.7
0.6393		457.5
0.7249		457.3
0.7897		454.5
0.8495	327.2	448.3
0.8993	326.9	435.2
0.9370	327.0	417.2
0.9603	327.1	383.2
0.9838	327.2	345.9
0.9939	327.5_5	
1.0000	327.7	

was performed; the corresponding $\Delta T/m$ value is 7.7 K molality^{-1}.

From these data, formation of mixed crystals is expected with lower alkanes. For this reason it is not possible to interpret the T_{sl} data in terms of the theory of groups interaction [6–9].

The values of the upper critical consolute temperature (obtained by the Cailletet and Mathias rule) are given in Table 3 with the corresponding composition values. The upper consolute temperature, T_{max}, increases with the chain length of the alkane; the composition (expressed as mole fraction of ester) corresponding to this temperature is around 0.5 for lower alkanes but is 0.67 for tetracosane. The linear relation between T_{max} and n_c which fits these systems is $T_{max} = 338.0 + 5.0_2\ n_c$ (reliability coefficient = 0.9993). The presence of an extended phenomenon of immiscibility in these system is,

TABLE 3

Upper critical consolute temperature and corresponding ester mole fraction

System	T_{max} (K)	X_{Ester}
Ethylenetetracarbon-tetraethyl ester +		
n-hexadecane	417.7	0.504
n-octadecane	428.7	0.530
n-nonadecane	434.2	0.485
n-tetracosane	458.2	0.670

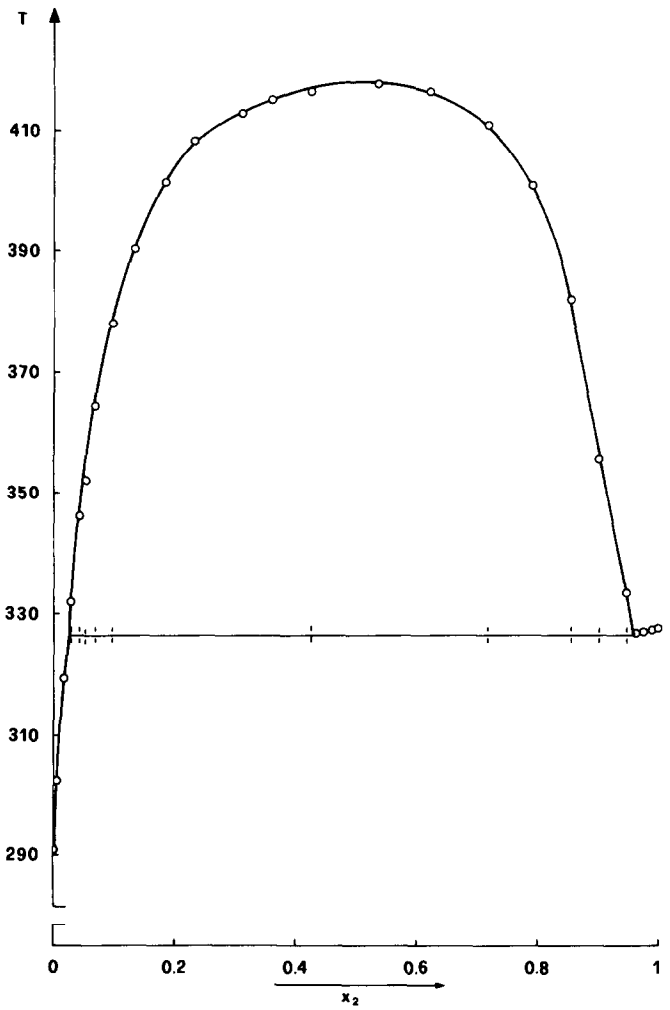

Fig. 1. Liquid–liquid and liquid–solid temperatures (K) of the binary mixture *n*-hexadecane–ethylenetetracarbontetraethyl ester.

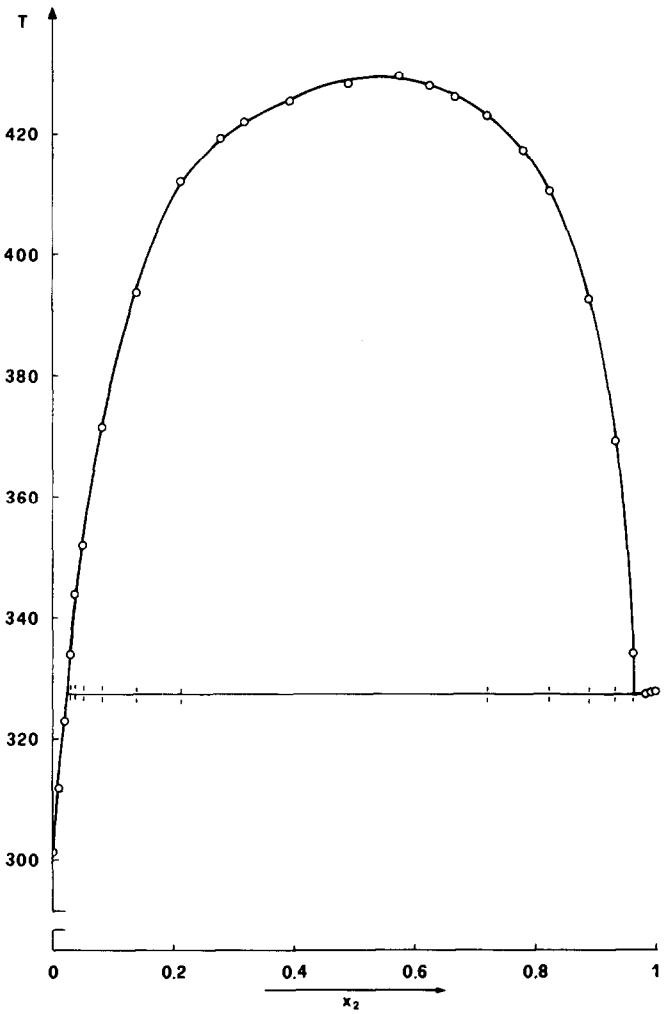

Fig. 2. Liquid–liquid and liquid–solid temperatures (K) of the binary mixture *n*-octadecane–ethylenetetracarbontetraethyl ester.

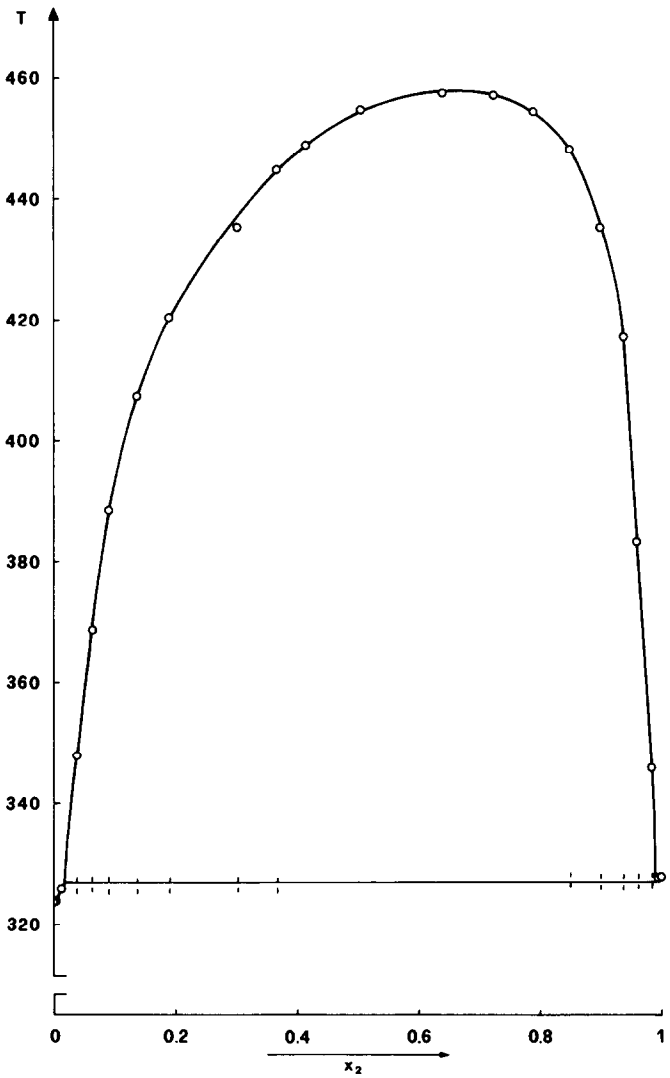

Fig. 4. Liquid–liquid and liquid–solid temperatures (K) of the binary mixture *n*-tetracosane–ethylenetetracarbontetraethyl ester.

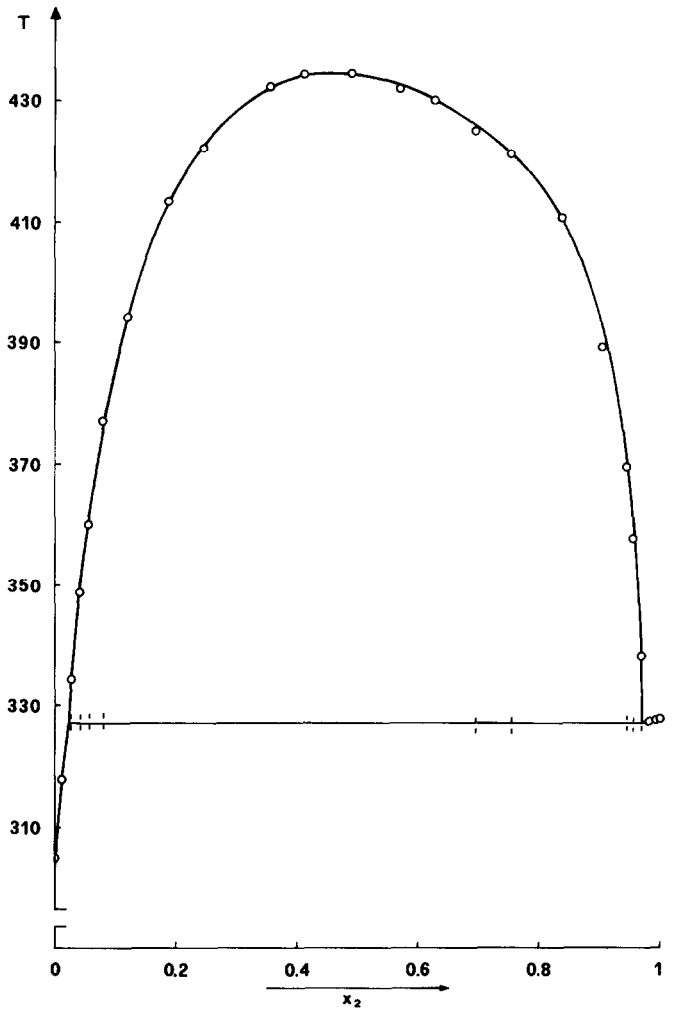

Fig. 3. Liquid–liquid and liquid–solid temperatures (K) of the binary mixture *n*-nonadecane–ethylenetetracarbontetraethyl ester.

from a thermodynamic point of view, a consequence of a rise of free energy in the corresponding range of concentration: the experimental trend T_{max}/n_c may be explained by considering that the increase of alkylic surface of one component may cause a rise of ΔG_{mix}, owing to the contacts $COO-CH_3$.

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