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A STATISTICAL ANALYSIS OF THE LIQUID–SOLID EQUILIBRIUM TEMPERATURES IN BINARY DOTRIACONTANE + ESTER SYSTEMS

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ABSTRACT

The liquid–solid equilibrium temperature in the binary systems between *n*-dotriacontane and methyl or ethyl octadecanoate and methyl nonadecanoate are determined in order to obtain the interchange parameters between CH_3 or CH_2 and COO groups, by means of the statistics of group interaction.

INTRODUCTION

The idea of group interaction developed by several authors [1–10] points out the important fact that the thermodynamic properties of mixtures of complex compounds may be predicted with appreciable accuracy on the basis of a small number of interaction parameters between the functional groups of the molecules. Recently, on this basis a large number of binary systems of acids and esters have been interpreted [11,12] with some approximations, following the statistics of group interaction proposed by Kehiaian [5,6].

Following the TOM (thermodynamics of organic mixtures) project [6], Kehiaian proposes the determination of interchange parameters from experimental measurements of equilibrium properties of very simple systems. In a previous paper [13] the results concerning liquid–solid equilibria in binary systems between *n*-octacosane and esters were given. In this paper we report the results of the liquid–solid equilibria in the binary *n*-dotriacontane + ester systems. For the symbols employed in this paper, see ref. 13.

EXPERIMENTAL

Experimental details of the equipment employed have been reported elsewhere [11,14]. The chemicals employed are Ega products of high purity

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and were used without further purification. The liquid–solid equilibrium temperatures are given in Table 1. The mole fraction of the alkane and that of the ester are indicated by x_1 and x_2, respectively. In the analysis of

TABLE 1

Liquid–solid equilibrium temperatures in the dotriacontane + ester systems

x_2	T (K)	x_2	T/K
Dotriacontane + methyl octadecanoate		0.6762	331.9
		0.7218	330.8
0.0000	342.2_5	0.7673	329.6
0.0130	341.0_9	0.7988	328.6
0.0248	341.9_2	0.8428	327.4
0.0426	341.7_2	0.8621	326.6
0.0694	341.3_5	0.9147	322.9
0.1114	340.7_5	0.9501	318.9
0.1728	339.9_0	0.9741	313.7
0.2268	339.1	0.9867	309.3
0.2652	338.5	0.9966	304.2_0
0.3267	337.4	1.0000	304.2_5
0.4165	336.4		
0.5175	335.1	*Dotriacontane + methyl nonadecanoate*	
05859	333.8		
0.6553	332.4	0.0000	342.2_5
0.7299	331.2	0.0154	342.0_5
0.7327	331.1	0.0318	341.8_5
0.8102	329.2	0.0481	341.5_5
0.8730	325.9	0.0877	341.1_5
0.9182	322.8	0.1260	340.6_5
0.9556	318.2	0.1790	339.8_0
0.9768	313.9	0.2551	338.6
0.9977	310.4_0	0.3423	337.2
1.0000	310.4_5	0.4336	336.2
		0.5219	334.9
Dotriacontane + ethyl octadeconoate		0.6070	333.6
		0.6662	332.3
0.0000	342.2_5	0.7102	331.2
0.0193	342.0_1	0.7466	330.1
0.0354	341.8_1	0.7794	329.2
0.0628	341.4_5	0.8007	328.4
0.0926	340.9_5	0.8619	326.1
0.1659	339.9_7	0.9051	323.3
0.2610	338.3	0.9407	320.0
0.3629	336.9	0.9772	313.0
0.4166	335.7	0.9910	312.1_0
0.5182	334.4	1.0000	312.3_5
0.5856	333.5		
0.5989	333.4		
0.6353	332.9		

Broadhurst [15], *n*-dotriacontane is reported to melt at 342.5 K and to perform a solid–solid transition at 338.7 K; the enthalpy of fusion is reported as 18.30 kcal mole^{-1}. These data give a thermodynamic cryoscopic constant of 5.74 K molality^{-1}. The data of Table 1 may be employed in order to obtain the experimental cryoscopic constants of *n*-dotriacontane, viz. 5.5 ± 0.04, 5.4 ± 0.1, and 5.6 ± 0.2 with methyl octadecanoate, ethyl octadecanoate and methyl nonadecanoate, respectively. The agreement between the thermodynamic and experimental cryoscopic constants is good; for this reason we exclude the presence of solid solutions in the crystallization region of the alkane. A similar conclusion cannot be made regarding the crystallization region of the ester, owing to the lack of fusion data. The melting point of *n*-dotriacontane given here is 342.3, in satisfactory agreement with the literature value [15].

ESTIMATION OF THE PARAMETERS OF THE STATISTICAL EQUATIONS

In order to apply the equation [8,13]

$$\ln x_j + G_{xj,1} + (G_{xj,2} + G_{fj,2})(\tau - 1) + (G_{xj,3} + G_{fj,3})\ln\tau + (G_{xj,4} + G_{fj,4})(\tau^{-1} - 1) = 0 \qquad (1)$$

the values of fusion $A_{fj,m}$ [8] must be known; $A_{fj,2}$ may be deduced from the literature [15], $A_{fj,3}$ and $A_{fj,4}$ may be obtained by extrapolation of the corresponding values of the lower even alkanes, for which Messerly et al. [16] have published data of c_p in the solid and liquid states. The values are given in Table 2; in the calculations of A_{fj}, T° given in the literature is employed. The interaction parameters $G_{ab,m}$ have been estimated on the experimental curve and are: $G_{ab,1} = 4.0$, and $G_{ab,2} = 6.78$. The parameters $G_{ab,3}$ and $G_{ab,4}$ do not seem to be important in the concentration range of the calculations carried out here. Previously [11] the g_{ab} value was determined (applying the statistics in an approximate manner) as 4400 J mole^{-1} in the system ethyl octadecanoate + nonanedioic acid in a temperature range near 373 K [17],

TABLE 2

Fusion parameters of dotriacontane

T^0 (K)	342.3
T^0 (K) [15]	342.5
$A_{fj,2}$	26.8901
$A_{fj,3}$	14.4439
$A_{fj,4}$	−144.7911

TABLE 3

Area and volume of the molecules

	q	r	α_{CH_3,CH_2}	α_{COO}
Dotriacontane	15.4276	19.5234	1.0000	0.0000
Methyl nonadecanoate	10.1331	12.6432	0.9253	0.0747
Ethyl octadecanoate	10.1331	12.6432	0.9253	0.0747
Methyl octadecanoate	9.6690	12.0572	0.9215	0.0785

that is $\bar{g}_{ab} = 1.4$; this value is a little lower than the value reported here, considering the influence of the difference in temperature following the equation

$$\bar{g}_{ab}(\tau) = G_{ab,1} + G_{ab,2}(\tau - 1) + G_{ab,3} \ln \tau + G_{ab,4}(\tau^{-1} - 1) \tag{2}$$

This difference may be ascribed to (1) the approximations used in the previous calculations, as already discussed [11], and (2) the uncertainty in the $A_{fj,3}$ and $A_{fj,4}$ values employed here. The molecular area and volume, calculated according to Bondi's method [18], are given in Table 3.

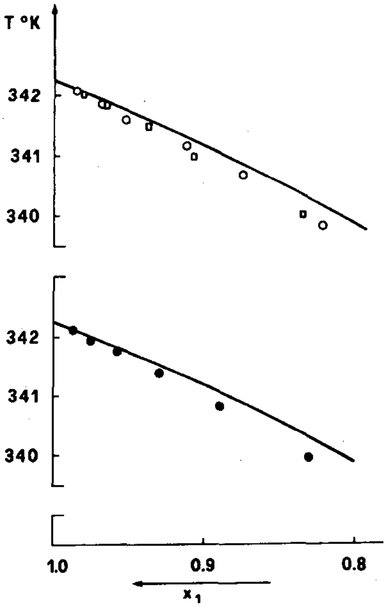

Fig. 1. Comparison between the calculated curve and the experimental measurements of liquid–solid equilibrium temperatures in the binary systems of *n*-dotriacontane with methyl nonadecanoate (○), ethyl octadecanoate (□); and methyl octadecanoate (●).

CONCLUSIONS

The curve calculated following eqn. (1) and the experimental values of T are shown in Fig. 1. In the concentration range $0.8 < x_1 < 1$, eqn. (1) with the parameters reported here represents satisfactorily the experimental trend of the two systems, showing that the interaction parameters $G_{ab,1}$ and $G_{ab,2}$, used here, are reasonably reliable. For $x_1 < 0.8$ the solid–solid transition occurring in dotriacontane suggests that the parameters given in Table 2 are not so far correct; but in the literature only T_{tr} is given, while c_p values for solid phases or ΔH_{tr} are not reported. Owing to this lack of data the statistics cannot be employed properly in the concentration range lower than $x_1 = 0.8$.

As previously reported [11,12], the systems with alkanes exhibit behaviour typical of mixtures in the zero approximation, that is, the coordinations number $z = \infty$, also the combinatorial part of the excess function is given by the Flory Huggins expression.

NOTATION

T^0	reference temperature (in this paper melting temperature of the pure compound)
x_j	mole fraction of compound j
c_p	thermal capacity at constant pressure
τ	reduced temperature
$\bar{g}_{ab}$	Gibbs free energy of interchange between groups a and b, divided by RT
r_i	volume of molecule i (unit = volume of CH_4)
ξ_i	$q_i x_i / \Sigma_j q_j x_j$
q_i	surface area of molecule i (unit = area of CH_4)
α_{ai}	q_{ai}/q_i
T	temperature

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REFERENCES

1 O. Redlich, E.J. Derr and G.J. Pierotti, J. Chem. Soc., 81 (1959) 2283.
2 J.A. Barker and F. Smith, J. Chem. Phys., 22 (1954) 375.
3 J.A. Barker, J. Chem. Phys., 20 (1952) 1536.
4 K.C. Chao, R.L. Robinson, Jr. M.L. Smith and C.M. Kuo, Chem. Eng. Prog. Symp. Ser., 63, 81 (1967) 121.
5 H.V. Kehiaian, Ber. Bunsenges. Phys. Chem., 81 (1977) 908.

6 H.V. Kehiaian, J.P.E. Grolier and G.C. Benson, J. Chim. Phys., 75 (1978) 1031.
7 H.V. Kehiaian, J.P.E. Grolier, M.R. Kechavarz and G.C. Benson, Fluid Phase Equilibria, 5 (1980/1981) 159.
8 H.V. Kehiaian, R. Guieu, A. Faraadjzadeh and L. Carbonnel, Ber. Bunsenges. Phys. Chem., 85 (1981) 132.
9 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1383.
10 R.A. Orwell and P.J. Flory, J. Am. Chem. Soc., 89 (1967) 1383.
11 G. Berchiesi, G. Gioia Lobbia, G. Vitali and M.A. Berchiesi, Can. J. Chem., 59 (1981) 1375.
12 G. Gioia Lobbia, G. Vitali, M.A. Berchiesi and G. Berchiesi, Ber. Bunsenges. Phys. Chem., 85 (1981) 628.
13 G. Gioia Lobbia, G. Vitali and G. Berchiesi, Thermochim. Acta, 57 (1982) 5.
14 M. Braghetti, D. Leonesi and P. Franzosini, Ric. Sci., 38 (1968) 116.
15 M.G. Broadhurst, J. Res. Natl. Bur. Stand., Sect. A, 66 (1962) 241.
16 J.F. Messerly, G.B. Guthrie, G.S. Todd and H.L. Finke, J. Chem. Eng. Data, 12 (1967) 338.
17 G. Gioia Lobbia, G. Berchiesi and M.A. Berchiesi, Gazz. Chim., 107 (1977) 43.
18 A. Bondi, J. Phys. Chem., 68 (1964) 441.