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INTERCHANGE FREE ENERGY BETWEEN COO AND CH_3 OR CH_2 GROUPS FROM LIQUID–SOLID EQUILIBRIUM TEMPERATURES IN BINARY SYSTEMS: ALKANE + ESTER

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ABSTRACT

The liquid–solid equilibrium temperatures in the *n*-tetracosane + methyl octadecanoate, methyl nonadecanoate or ethyl octadecanoate binary systems 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 statistics of group interaction developed by several authors [1–10] point out the fact that the thermodynamic properties of mixtures of complex compounds may be treated and 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 has been interpreted [11–14], applying the statistics 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 this note, we report the L–S equilibrium temperatures in the binary systems alkane + ester (*n*-tetracosane + methyl octadecanoate, methyl nonadecanoate or ethyl octadecanoate), where only two types of surface are present.

THEORY

The thermodynamic condition of liquid–solid equilibrium is expressed [15] by the equation

$$d\mu_s = d\mu_L \qquad (1)$$

that becomes

$$(\partial\mu_{sj}/\partial T)\,\mathrm{d}T = (\partial\mu_{Lj}/\partial T)\,\mathrm{d}T + (\partial\mu_{Lj}/\partial x_j\gamma_j)\,\mathrm{d}x_j\gamma_j \tag{2}$$

if the solid phase in equilibrium with the liquid mixture is a pure phase. Equation (2) may be easily changed to

$$\ln x_j + \bar{g}_{E,j} + \bar{g}_j^0 = 0 \tag{3}$$

where $\bar{g}_{E,j}$ depends on temperature and composition, and $\bar{g}_j^0$ only on temperature. Kehiaian [8] expresses the heat capacity as a function of the reduced temperature $\tau = T^0/T$

$$c_p = A_3 + A_4(\tau^{-1} - 1) \tag{4}$$

and by integration of eqn. (4) the enthalpy may be obtained

$$\bar{h} = A_2\tau + A_3\tau(\tau^{-1} - 1) + A_4/2\tau(\tau^{-1} - 1)^2 \tag{5}$$

This equation may be integrated in order to obtain the Gibbs free energy.

$$\bar{g} = A_1 + (A_2 - A_3 + A_4/2)(\tau - 1) + (A_3 - A_4)\ln\tau - A_4/2(\tau^{-1} - 1) \tag{6}$$

Equation (6) is written more fluently as

$$\bar{g} = G_1 + G_2(\tau - 1) + G_3\ln\tau + G_4(\tau^{-1} - 1) \tag{7}$$

This general relation between free energy and temperature may be applied to the fusion and, in this case, the parameters have the following meaning.

$$A_1 = A_{fj,1} = \bar{g}_{fj}(\tau = 1) = 0 \tag{7a}$$

$$A_2 = A_{fj,2} = \bar{h}_{fj}(\tau = 1) \tag{7b}$$

$$A_3 = A_{fj,3} = \left[c_{plj}(T^0) - c_{psj}(T^0)\right]/R \tag{7c}$$

$$A_4 = A_{fj,4} = T^0/R\left[\mathrm{d}(c_{plj} - c_{psj})/\mathrm{d}T\right] \tag{7d}$$

For the excess partial molar Gibbs free energy of the species j, function of τ and x_j, eqn. (7) must be considered as a sum of terms in which G_i are functions of the composition, that is

$$g_{E,j} = G_{xj,1} + G_{xj,2}(\tau - 1) + G_{xj,3}\ln\tau + G_{xj,4}(\tau^{-1} - 1) \tag{8}$$

The interchange free energy between the chemical groups a and b is expressed, according to eqn. (7)

$$\bar{g}_{ab}(\tau) = G_{ab,1} + G_{ab,2}(\tau - 1) + G_{ab,3}\ln\tau + G_{ab,4}(\tau^{-1} - 1) \tag{9}$$

Following the group interaction theory [5,6], $\bar{g}_{E,j}$ is the sum of two parts: the combinatorial and the interchange. In the systems studied previously [11,12] we concluded that the binary systems between a non-polar compound and a polar compound may be treated with the zero approximation [5,6] and for the combinatorial part with the Flory–Huggins expression, i.e.

$$g_{E,j} = \ln\varphi_j/x_j - \varphi_j/x_j + 1 - q_j\xi_j\xi_i(\alpha_{aj} - \alpha_{ai})(\alpha_{bj} - \alpha_{bi})\bar{g}_{ab} \tag{10}$$

Equations (3), (7)–(10) give the basic equations

$$\ln x_j + G_{xj,1} + (G_{xj,2} + G_{fj,2})(\tau - 1) + (G_{xj,3} + G_{fj,3}) \ln \tau + (G_{xj,4} + G_{fj,4})(\tau^{-1} - 1) = 0 \qquad (11)$$

where

$$G_{fj,2} = A_{fj,2} - A_{fj,3} + A_{fj,4}/2$$

$$G_{fj,3} = A_{fj,3} - A_{fj,4}$$

$$G_{fj,4} = -A_{fj,4}/2$$

$$G_{xj,1} = \ln \varphi_j/x_j - \varphi_j/x_j + 1 - q_j\xi_j\xi_i(\alpha_{aj} - \alpha_{ai})(\alpha_{bj} - \alpha_{bi})G_{ab,1}$$

$$G_{xj,m} = -q_j\xi_j\xi_i(\alpha_{bj} - \alpha_{bi})(\alpha_{aj} - \alpha_{ai})G_{ab,m} \qquad (m = 2, 3, 4)$$

EXPERIMENTAL

The experimental details of the equipment employed have been reported in previous papers [11,16] and for this reason are not given here. The measurements were repeated twice and the agreement generally was better than 0.1 K. The chemicals employed were Ega products of high purity (> 99%) and were used without further purification. The liquid–solid equilibrium temperatures are given in Table 1. In this paper, the mole fraction of the alkane and that of the ester are indicated x_1 and x_2, respectively. In the analysis of Broadhurst [17], tetracosane is reported to melt at 323.8 K and to undergo a solid–solid transition at 321.3 K; in addition, the enthalpy of fusion is reported as 13.12 kcal mole^{-1}. These data give a thermodynamic cryoscopic constant of 5.36 K molality^{-1}. The data of Table 1 may be used to obtain the experimental cryoscopic constants of tetracosane as 5.5 ± 0.1, 5.1 ± 0.1 and 4.9 ± 0.1 with methyl octadecanoate, ethyl octadecanoate and methyl nonadecanoate, respectively. The agreement between the thermodynamic and experimental cryoscopic constants is good for methyl and ethyl octadecanoate, and acceptable for the other compound; for this reason, we exclude the presence of solid solutions in the crystallization region of the alkane. A similar conclusion cannot be made for the crystallization region of the ester owing to the lack of fusion data. The melting point of tetracosane given in this note is 323.3 K, which is in satisfactory agreement with the value reported in the literature [17].

ESTIMATION OF THE PARAMETERS OF THE STATISTICAL EQUATIONS

In order to apply eqn. (11), the value of the fusion parameter $A_{fj,m}$ must be known; for $A_{fj,2}$, it may be deduced from the literature [17], while for $A_{fj,3}$

TABLE 1

Liquid–solid equilibrium temperatures in the binary systems *n*-tetracosane + ester

n-Tetracosane + Me octadecanoate		*n*-Tetracosane + Et octadecanoate		*n*-Tetracosane + Me nonadecanoate	
x_2	T (K)	x_2	T (K)	x_2	T (K)
0.0000	323.3_3	0.0000	323.3_3	0.0000	323.3_3
0.0082	323.2_1	0.0323	322.8_6	0.0168	323.0_9
0.0276	322.9_0	0.0593	322.4_9	0.0247	322.9_9
0.0492	322.6_0	0.0949	322.0_0	0.0468	322.7_5
0.0874	322.2_0	0.1100	321.8_7	0.0956	322.2_3
0.1393	321.5	0.2045	320.4_5	0.1316	321.9_5
0.2109	320.5	0.2513	320.1	0.2143	320.9
0.3106	319.3	0.2921	319.3	0.2731	320.2
0.4111	317.8	0.3481	318.5	0.3789	319.2
0.4670	317.2	0.3508	318.4	0.4690	318.0
0.5614	315.1	0.4197	317.1	0.5385	316.9
0.6399	313.3	0.4625	316.4	0.6123	316.2
0.7029	311.7	0.5575	314.7	0.6726	315.3
0.7535	310.3	0.6202	313.0	0.7074	314.7
0.8066	308.9	0.7104	310.7	0.7479	313.5
0.8336	308.2	0.7733	309.2	0.8041	313.2
0.8660	306.9	0.8544	306.5	0.8757	312.2
0.8873	307.0	0.9098	305.1	0.9220	311.9
0.9241	308.4	0.9571	304.3	0.9624	311.6_8
0.9446	309.1_0	0.9882	304.0_5	0.9704	311.8_2
0.9743	309.8_7	0.9952	304.1_7	0.9846	312.0_7
0.9925	310.3_5	1.0000	304.2_5	1.0000	312.3_5
1.0000	310.5_5				

and $A_{fj,4}$, it may be obtained by extrapolation of the corresponding values of the lower even alkanes, for which Messerly et al. [18] have published data of c_p in the solid and liquid states. The values are given in Table 2. In the calculation of A_{fj}, the value T^0 given in the literature [17] is employed. The

TABLE 2

Fusion parameters $A_{fj,m}$ for *n*-tetracosane

T^0 (K)	323.3
T^0 (K) [17]	323.8
$A_{fj,2}$	20.3920
$A_{fj,3}$	11.8269
$A_{fj,4}$	−99.4050

TABLE 3

Geometric parameters

	q	r	α_{CH_3,CH_2}	α_{COO}
n-Tetracosane	11.7035	14.7431	1.0000	0.0000
Methyl octadecanoate	9.6690	12.0572	0.9215	0.0785
Methyl nonadecanoate	10.1331	12.6432	0.9253	0.0747
Ethyl octadecanoate	10.1331	12.6432	0.9253	0.0747

interaction parameters $G_{ab,m}$ have been estimated from the experimental curve and were also recommended by Kehiaian [19] as $G_{ab,1} = 4.0$ and $G_{ab,2} = 6.78$. The parameters $G_{ab,3}$ and $G_{ab,4}$ seem to be unimportant in these systems in the concentration range over which the calculations are carried out, and, as an approximation, they were omitted.

Previously [11], the g_{ab} value was determined, in an approximate manner, as 4400 J mole^{-1} in the system ethyl octadecanoate + nonanedioic acid in a temperature range near 373 K [20], that is $\bar{g}_{ab} = 1.4$; eqn. (9) gives a value of 3.2 at 373 K. This difference may be ascribed to the approximations used in the previous calculations [11]. The molecular area and volume, calculated according to the Bondi's method (21), are given in Table 3.

CONCLUSIONS

In Fig. 1, the curves calculated from eqn. (11) and the experimental values of T are shown. In the concentration range $0.88 < x_1 < 1$, eqn. (11) with the parameters reported here represents satisfactorily the experimental trend of the three systems, showing that the interaction parameters $G_{ab,1}$ and $G_{ab,2}$ used here are reasonably reliable. For $x < 0.88$, the solid–solid transition occurring in tetracosane changes the parameters given in Table 2; but in the literature, only the ΔH_{tr} value is given, while c_p values for the solid phases are not reported. Owing to this lack of data, the statistics cannot be employed properly in the concentration range lower than $x_1 = 0.88$.

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

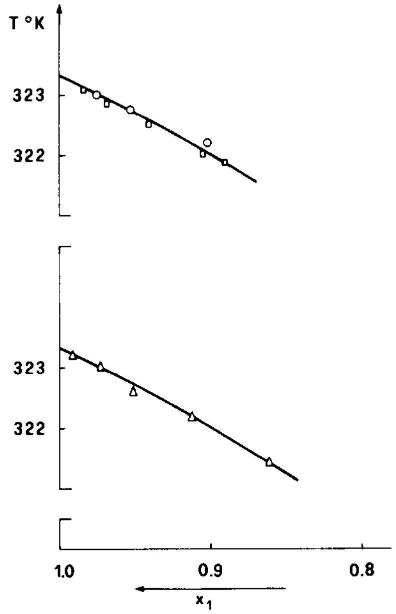

Fig. 1. Liquid–solid equilibrium temperature in the binary systems ○, *n*-tetracosane + methyl nonadecanoate; □, *n*-tetracosane + ethyl octadecanoate; △, *n*-tetracosane + methyl octadecanoate. ———, Theoretical curve.

NOMENCLATURE

μ_s, μ_L	Chemical potential of the solid and liquid, respectively
T	Temperature
T^0	Temperature of reference (in this note, the melting temperature of the pure compound)
x_j	mole fraction of the compound j
γ_j	activity coefficient of the species j
$\bar{g}_{E,j}$	$= g_{E,j}/RT$
$g_{E,j}$	excess chemical potential
$\bar{g}_j^0$	$= g_j^0/RT$
g_j^0	Gibbs free energy of fusion
$\bar{c}_p$	$= c_p/R$
c_p	thermal capacity at constant pressure
$\bar{h}$	$= h/RT$
h	enthalpy
τ	reduced temperature

g_{fj}^0	Gibbs free energy of fusion at $T = T^0$, concerning the compound j
h_{fj}	enthalpy of fusion of the compound j
c_{plj}, c_{psj}	thermal capacity at constant pressure of the liquid and solid compound j, respectively
$\bar{g}_{ab}$	Gibbs free energy of interchange between the groups a and b divided by RT
φ_i	$= r_i x_i / \Sigma_j r_j x_j$
r	volume of the molecule (unit = volume of CH_4)
ξ_i	$= q_i x_i / \Sigma_j q_j x_j$
q_i	area of the surface of the molecule i (unit = area of CH_4)
α_{ai}	$= q_{ai}/q_i$
q_{ai}	area of the surface of type a in the molecule i

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