Thermochimica Acta, 57 (1982) 5–11
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

FREE ENERGY OF INTERCHANGE BETWEEN COO AND CH_3 OR CH_2 GROUPS

G. GIOIA LOBBIA, G. VITALI and G. BERCHIESI

Istituto Chimico della Università di Camerino, 62032 Camerino (Italy)

(Received 26 January 1982)

ABSTRACT

The liquid–solid equilibrium temperatures in the binary systems between *n*-octacosane and methyl or ethyl octadecanoate 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 an 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 et al. [5,6]. Following the Thermodynamics of Organic Mixtures (TOM) project [6], Kehiaian proposes the determination of interchange parameters from experimental measurement of equilibrium properties of very simple systems.

In the present paper we begin a systematic study of liquid–solid equilibrium temperatures in the binary systems alkane + ester, where only two types of surface are present. The systems *n*-octacosane + methyl or ethyl octadecanoate (stearate) are reported here.

THEORY

The thermodynamic condition of liquid–solid equilibrium is expressed by [13]

$$d\mu_s = d\mu_L \tag{1}$$

which changes to

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

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

$$\ln x_j + \bar{g}_{\mathrm{E}_j} + \bar{g}_j^0 = 0 \qquad (3)$$

where $\bar{g} = g/RT$, $\bar{g}_j^0$ is the Gibbs function of fusion, and $\bar{g}_{\mathrm{E}_j}$ is the Gibbs partial molar excess energy of compound j. $\bar{g}_{\mathrm{E}_j}$ depends on the temperature and composition. $\bar{g}_j^0$ is dependent only on the temperature.

Kehiaian et al. [8] express the thermal capacity as a function of the reduced temperature $\tau = T^0/T$

$$\bar{c}_p = A_3 + A_4(\tau^{-1} - 1) \qquad (4)$$

Integration of eqn. (4) gives the enthalpy

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

Integration of eqn. (5) gives the Gibbs free energy

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

Equation (6) may be written as

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

For the fusion quantity $\bar{g}_j^0$ of eqn. (3), eqn. (7) may be obtained from thermodynamic data of fusion considering that

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

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

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

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

For the Gibbs excess partial molar free energy of 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, i.e.

$$\bar{g}_{\mathrm{E}_j} = G_{xj,1} + G_{xj,2}(\tau - 1) + G_{xj,3}\ln\tau + G_{xj,4}(\tau^{-1} - 1) \qquad (8)$$

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

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

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

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

Equations (3), (7), (8), (9) and (10) give the following basic equations

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

TABLE 1

Liquid–solid equilibrium temperatures in the binary systems $C_{28}H_{58} + C_{20}H_{40}O_2$ and $C_{28}H_{58} + C_{19}H_{28}O_2$

$C_{28}H_{58} + C_{20}H_{40}O_2$		$C_{28}H_{58} + C_{19}H_{38}O_2$	
x_2	T(K)	x_2	T(K)
0.0000	334.6_5	0.0000	334.6_5
0.0178	334.4_0	0.0076	334.5_5
0.0279	334.2_5	0.0141	334.4_5
0.0490	333.9_5	0.0309	334.2_1
0.0790	333.3_5	0.0513	333.8_9
0.1379	332.8_0	0.0716	333.6_0
0.2108	331.1	0.1093	333.2
0.2903	330.1	0.1409	332.5
0.3828	328.6	0.2080	331.1
0.4708	327.6	0.3204	329.4
0.5150	326.7	0.4268	328.1
0.5436	326.3	0.5047	327.0
0.5940	325.3	0.5433	326.4
0.6668	323.8	0.5923	325.6
0.7136	322.6	0.6632	324.1
0.7720	320.8	0.7186	322.8
0.8389	318.8	0.7672	321.4
0.8982	314.9	0.8117	320.4
0.9363	310.8	0.8478	318.5
0.9627	305.5	0.8784	316.6
0.9817	303.9_8	0.9200	312.7
0.9935	304.1_5	0.9434	310.2
1.0000	304.2_5	0.9490	308.8
		0.9732	309.7_3
		0.9765	309.8_5
		0.9876	310.1_3
		0.9911	310.2_3
		0.9960	310.3_5
		1.0000	310.4_5

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

Details of the equipment used are as reported previously [11,14]. The chemicals employed were Ega products of high purity 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 by x_1 and x_2, respectively. In Broadhurst's [15] analysis, octacosane is reported to melt at 334.4 K and to undergo a solid–solid transition at 331.2 K; also, the enthalpy of fusion is reported as 14.45 kcal mole^{-1}. These data give a cryoscopic constant of 5.68 K molality^{-1}. The first data of Table 1 may be employed in order to give the experimental cryoscopic constant of octacosane that results in 5.5 ± 0.1 and 5.3 ± 0.2 with methyl octadecanoate and ethyl octadecanoate, respectively. The agreement between the thermodynamic and experimental cryoscopic constants is good; therefore the presence of solid solutions in the crystallization region of the alkane is excluded. A similar conclusion cannot be made on the crystallization region of the ester due to the lack of fusion data. The melting point of octacosane given here is 334.7 K, in satisfactory agreement with the value reported in the literature [15].

ESTIMATION OF THE PARAMETERS OF THE STATISTICAL EQUATIONS

In order to apply eqn. (11), the values of fusion $A_{fj,m}$ 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 lower 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 calculation of $A_{fj,m}$, the value of T^0 given in the literature is employed. The interaction parameters, estimated on the experimental curve, were also recommended by Kehiaian [17]: $G_{ab,1} = 4.0$, $G_{ab,2} = 6.78$. The parameters $G_{ab,3}$ and $G_{ab,4}$ do not seem to be important in these calculations.

Previously [11] the g_{ab} value was approximately determined as 4400 J

TABLE 2

Parameters of fusion concerning *n*-octacosane

T(K)	334.7
T(K) [15]	334.4
$A_{fj,2}$	23.252
$A_{fj,3}$	13.085
$A_{fj,4}$	-122.013

TABLE 3

Geometric values of the compounds used in the calculations

	$C_{28}H_{58}$	$C_{20}H_{40}O_2$	$C_{19}H_{38}O_2$
q	13.5655	10 1331	9 6690
r	17.1332	12.6432	12 0572
α_{CH_3,CH_2}	1.0000	0.9253	0.9215
α_{COO}	0.0000	0.0747	0 0785

mole^{-1} in the system ethyl octadecanoate + nonanedioic acid [11] in a temperature range near 373 K [18], i.e., $g_{ab} = 1.4$; 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 Bondi's method [19], are given in Table 3.

CONCLUSIONS

The curve calculated following eqn. (11) and the experimental values of T are shown in Fig. 1. In the concentration range $0.8 < x_1 < 1$, eqn. (11), using the parameters reported here, satisfactorily represents 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 the octacosane suggests that the parameters given in Table 2 are not so far correct, but in the literature only ΔH_{tr} values are reported, while c_p values for solid phases are not found. 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, i.e., the coordination number $z = \infty$, also the combinatorial part of the excess function is given by the Flory Huggins expression.

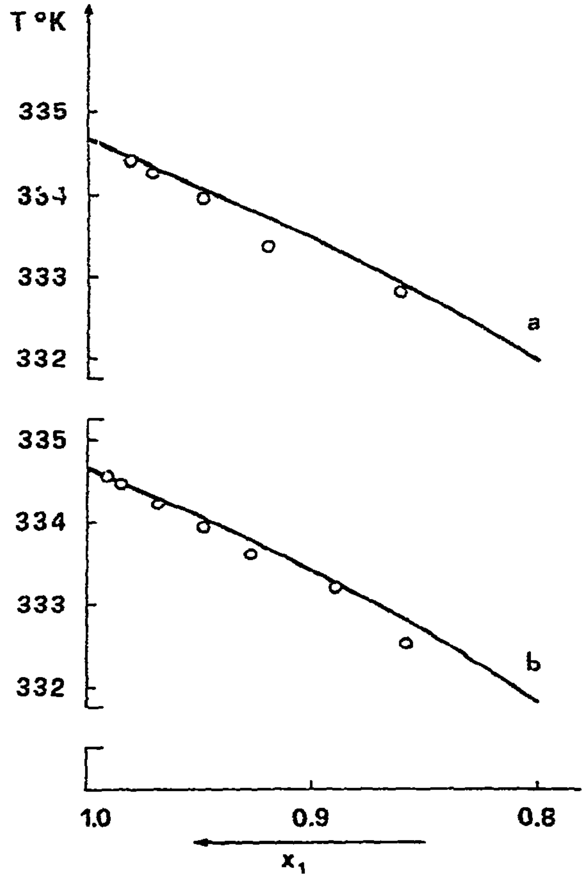

Fig. 1. Calculated curve and experimental points concerning the liquid–solid equilibrium temperature in the binary systems: (a) *n*-octacosane + ethyl octadecanoate; (b) *n*-octacosane + methyl octadecanoate.

NOTATION

μ_s, μ_L	Chemical potential of the solid and liquid, respectively
T	Temperature
T^0	Reference temperature (in the present work this refers to the melting temperature of the pure compound)
x_j	Mole fraction of compound j
γ_j	Activity coefficient of species j
$\bar{g}_{Ej}$	$= g_{Ej}/RT$
g_{Ej}	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 compound j
h_{fj}	Enthalpy of fusion of compound j
c_{plj}, c_{psj}	Thermal capacity at constant pressure of, respectively, liquid and solid compound j
g_{ab}	Gibbs free energy of interchange between 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 molecule i (unit = area of CH_4)
α_{ai}	$= q_{ai} / q_i$
q_{ai}	Area of the surface of type a in molecule i

ACKNOWLEDGEMENTS

The authors are grateful to C.N.R. (Rome) for financial support, and Dr. H.V. Kehiaian for helpful discussions.

REFERENCES

1 O. Redlich, E.J. Derr and G.J. Pierotti, J. Am. 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. Orwoll and P.J. Flory, J. Am. Chem. Soc., 89 (1967) 1383.
11 G. Berchiesi, G. GioiaLobbia, G. Vitali and M.A. Berchiesi, Can. J. Chem., 59 (1981) 1375.
12 G. GioiaLobbia, G. Vitali, M.A. Berchiesi and G. Berchiesi, Ber. Bunsenges. Phys. Chem., 85 (1981) 628.
13 G. Petit, La Cryométrie à Haute Temperature et Ses Applications, Masson, Paris, 1965, pp. 10 ff.
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) 3, 241.
16 J.F. Messerly, G.B. Guthrie, G.S. Todd and H.L. Finke, J. Chem. Eng. Data, 12 (1967) 338.
17 H.V. Kehiaian, private communication, 1981.
18 G. Gioia Lobbia, G. Berchiesi and M.A. Berchiesi, Gazz. Chim., 107 (1977) 43.
19 A. Bondi, J. Phys. Chem., 68 (1964) 441.