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CRYSTALLIZATION CURVE OF HEXADECANE IN MIXTURES WITH METHYL NONADECANOATE, METHYL OCTADECANOATE, ETHYL OCTADECANOATE, AND METHYL HEXADECANOATE. A COMPARISON OF THE EXPERIMENTAL AND CALCULATED CURVES

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ABSTRACT

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

INTRODUCTION

The group interaction theories have the task of predicting some thermodynamic properties of the liquid systems, on the basis of a quasi-lattice model of the mixtures. In previous papers * [3,4] we applied the theory of Kehiaian et al. [1,5], and as a continuation of this research, in the present work we report the liquid–solid equilibrium temperatures in the binary systems between hexadecane and methyl nonadecanoate, methyl or ethyl octadecanoate, and methyl hexadecanoate.

EXPERIMENTAL

Details of the equipment employed are as reported previously [6]. Ega products of high purity were used without further purification. The experimental temperatures and corresponding compositions (in mole fraction) are

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* In ref. 3 the following corrections must be performed because of printing errors: p. 630, second column A–D (39th line), E, F (40th line), A–D (41st line), E, F (42nd line), B–D (44th line), A, E, F (45th line) must be changed to A–C; E, D; A–C; E, D; B–C; A, E, D, respectively.

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TABLE 1

Liquid–solid equilibrium temperatures in the hexadecane + ester systems

X_2	T(K)	X_2	T(K)
Hexadecane – methyl hexadecanoate		*Hexadecane – methyl nonadecanoate*	
0.0000	291.3_3	0.0000	291.3_3
0.0082	291.2_2	0.0121	291.1_6
0.0155	291.1_2	0.0257	290.9_8
0.0252	290.9_8	0.0437	290.7_3
0.0448	290.6_5	0.0671	290.3_3
0.0620	290.3_6	0.0833	289.8_8
0.0780	290.1	0.1235	289.3
0.1194	289.0	0.1793	291.9
0.1738	289.6	0.2458	294.7
0.2443	290.2	0.2930	296.5
0.3038	290.7	0.3123	296.9
0.3769	292.8	0.3635	298.6
0.5098	293.4	0.4340	300.8
0.5768	294.2	0.5276	303.4
0.6444	294.9	0.6134	304.6
0.7392	296.2	0.6571	305.8
0.8196	297.9	0.7270	307.2
0.8781	299.5	0.7866	308.3
0.9337	301.3	0.8522	309.8
0.9554	301.7_8	0.8893	310.5
0.9773	302.2_4	0.9292	311.1_8
0.9880	302.4_5	0.9693	311.8_5
1.0000	302.7	0.9821	312.0_8
		1.0000	312.4
Hexadecane – methyl octadecanoate		*Hexadecane – ethyl octadecanoate*	
0.0000	291.3_3	0.0000	291.3_3
0.0052	291.2_6	0.0040	291.2_7
0.0196	291.0_6	0.0130	291.1_5
0.0408	290.7_7	0.0324	290.8_9
0.0567	290.5_8	0.0573	290.4_8
0.0756	290.1_8	0.0792	290.1
0.0902	289.7	0.0881	289.9
0.1198	289.3	0.1288	288.8
0.1643	289.9	0.1769	289.0
0.2121	291.1	0.2420	290.4
0.2812	293.3	0.3037	292.0
0.3430	295.9	0.3416	291.6
0.4070	297.0	0.4064	294.0
0.4570	299.1	0.5167	296.4
0.5011	299.9	0.5965	298.1
0.6087	302.5	0.6905	299.7
0.6986	304.4	0.7865	301.7
0.7848	306.9	0.8390	302.7
0.8570	308.6	0.8848	303.9
0.9210	309.4	0.9306	305.0
0.9534	310.1	0.9519	305.3_5
0.9744	310.5_8	0.9702	305.7
0.9845	310.8_2	0.9837	305.9_5
1.0000	311.2	1.0000	306.2_5

given in Table 1. The mole fraction of the alkane is indicated by X_1. The melting temperature of hexadecane given by Broadhurst [7] is in excellent agreement with the experimental value given in this work.

RESULTS AND DISCUSSION

The thermodynamic data of fusion concerning hexadecane [7] allow the thermodynamic cryoscopic constant to be calculated and a comparison to be made with the experimental values. $\Delta T/m$, at infinite dilution (in the crystallization curve of the alkane), is 3.0 (methyl octadecanoate, solute), 3.0 (methyl hexadecanoate, solute), 3.1 (methyl octadecanoate), and 3.1 (ethyl octadecanoate). The thermodynamic value $RT_0^2M_1/1000\ \Delta H_f$ is 2.99 which is in good agreement with the experimental $(\Delta T/m)_0$ values. This fact allows the assumption that in these mixtures the liquid is in equilibrium with the pure solid. The values of $(\Delta T/m)_0$ in the crystallization region of the esters (ester: solvent, hexadecane: solute) are 5.6 (methyl nonadecanoate), 5.6 (methyl hexadecanoate), 7.5 (methyl octadecanoate), and 5.7 (ethyl octadecanoate).

Thermodynamically the liquid–solid equilibrium temperature depends on the fusion parameters (ΔH, $\Delta C_p\ldots$) of the compound and the excess free energy. Kehiaian expresses this dependence as

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

where the $G_{bj,m}$ parameters may be obtained as indicated by Kehiaian et al. [5] from the fusion data [7], while the $G_{xj,m}$ parameters are obtained from the group interaction theory [1], depending on surfaces and volumes of the groups (a,b) and some interaction parameters, $G_{ab,m}$, giving the temperature dependence of the interchange free energy, g_{ab}.

These calculations are carried out only in the crystallization curve of the alkane because of the lack of fusion data for the esters. Table 2 gives the surface and volume values employed. In a previous work [4] the interaction parameters $G_{ab,1}$ and $G_{ab,2}$ were checked on the liquid–solid curve of *n*-octacosane in mixture with some esters. Values of $G_{ab,1} = 4.0$ and $G_{ab,2} = 6.78$ gave satisfactory agreement between the calculated and experimental curves. In the present case, these values are not so correct, owing to the change in temperature. In fact the melting temperatures of the pure compounds (which are also the reference temperature T^0 [5]) are 334.4 and 291.3 K for octacosane and hexadecane, respectively.

In Fig. 1 the experimental curve of hexadecane is compared with the curves calculated by means of $G_{ab,1} = 4.0$ and $G_{ab,1} = 2.0$ It is evident that a lowering of the interaction parameter allows better agreement between the

TABLE 2

(a) Geometrical properties of the molecules

	q(area)	r(volume)	q(alif.)	q(–COO)
Hexadecane	7.9793	9.9626	7.9793	
Methyl nonadecanoate	10.1345	12.6548	9.3759	0.7586
Methyl hexadecanoate	8.7379	10.8622	7.9793	0.7586
Methyl octadecanoate	9.6690	12.0572	8.9103	0.7586
Ethyl octadecanoate	10.1345	12.6548	9.3759	0.7586

(b) Thermodynamic properties of the pure compound deduced from Broadhurst [7]

	A_1	$A_2 = \Delta H_f/RT_0$	$A_3 = \Delta C_p/R$	$A_4 = T_0/R\,(\mathrm{d}\Delta C_p/\mathrm{d}t)_{T=T_0}$
Hexadecane	0	22.0308	8.8475	−49.6075

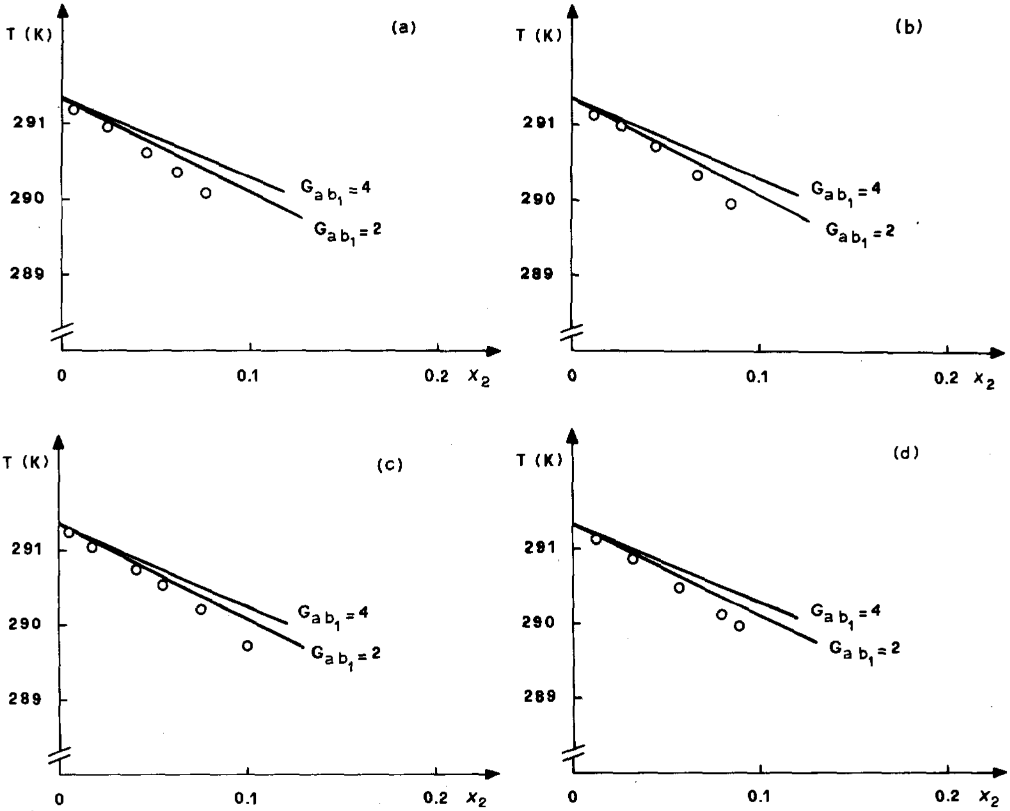

Fig. 1. A comparison of the calculated curve ($G_{ab,1} = 4.0$, $G_{ab,1} = 2.0$) and experimental measurements of liquid–solid equilibrium temperatures in the binary systems: (a) hexadecane–methyl hexadecanoate; (b) hexadecane–methyl nonadecanoate; (c) hexadecane–methyl octadecanoate; (d) hexadecane–ethyl octadecanoate.

experimental and calculated curves. A change in the $G_{ab,2}$ parameter does not appreciably affect the calculated curve in the concentration range of the experiment. The parameters $G_{ab,3}$ and $G_{ab,4}$, as in previous papers, are ignored [4]. The group interaction theory in this note is employed in the zero approximation with the Flory–Huggins expression for the combinatorial part of the excess chemical potential.

The fact that these experimental curves are fitted by a value of $G_{ab,1}$ lower than in preceding systems must be considered as a possible consequence of a number of factors other than a difference in temperature, i.e. the cancellation of $G_{ab,3}$ and $G_{ab,4}$, the small mole fraction range in which the alkane crystallizes (this causes a loss in sensitivity of the curve from $G_{ab,1}$), or the fact that in previous systems [4,8,9] alkanes with chains approximately double that of hexadecane were employed.

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