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THE PHASE EQUILIBRIA IN SOME BINARY SYSTEMS CONTAINING STEARIC ALCOHOL

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The liquid - liquid and liquid - solid equilibrium temperatures are taken for the binary systems octadecanol + A (A = dicarboxylic acids, biphenyl or (K, Na) stearate). The results are discussed and a relation connecting the composition of the eutectics with the thermodynamic properties of fusion of the components is derived from the ideal equation and compared with the experimental one.

In previous papers the liquid–liquid and liquid–solid equilibria of binary systems stearic acid + dicarboxylic acids [1] and dicarboxylic acids + monocarboxylic acids (from C_{14} to C_{17}) [2] were discussed.

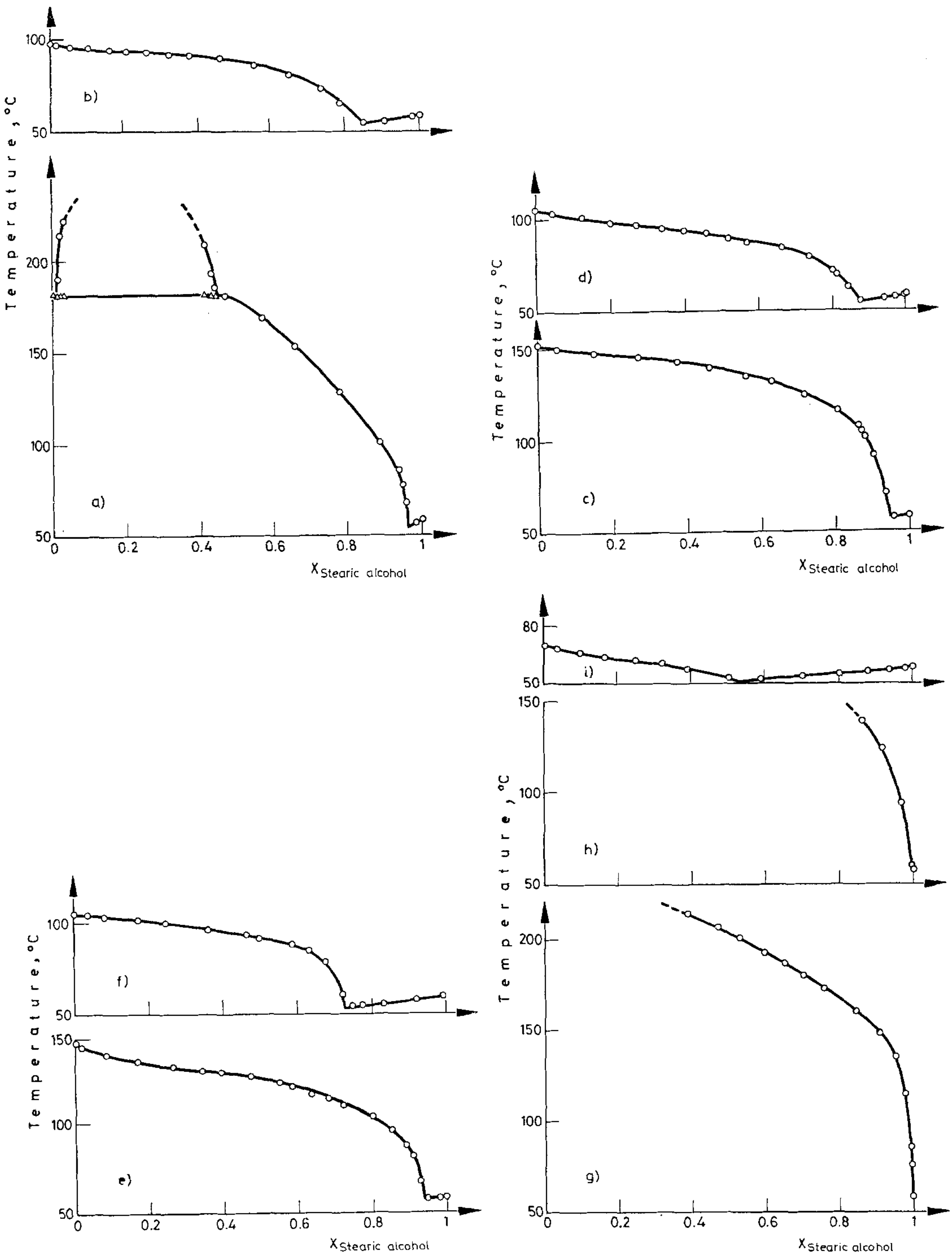
In order to understand the importance of the structure on the demixing phenomenon, the present note deals with the phase equilibria in the binary systems stearic alcohol + dicarboxylic acids.

Experimental

The visual and calorimetric methods adopted are described in detail in previous papers [3, 4]. Purissimum Fluka 1-octadecanol was employed without further purification. Dicarboxylic acids, (K, Na) stearates and biphenyl were as in the previous work [1, 2].

Results and discussion

The curve 1-octadecanol fusion exhibits a prefusion phenomenon, a transition peak arising on the tail of the move; the curve is 9° wide. The thermodynamic data of the fusion are given in Table 1. The liquid – solid and liquid – liquid equilibria curves are shown in Fig. 1 and the coordinates of the characteristic points in Table 2. In a previous paper we discussed the demixing regions in the systems monocarboxylic acids + dicarboxylic acids [2]. We pointed out that the miscibility gaps appear when the "polar character" of the dicarboxylic acid molecules exceeds that of the monocarboxylic acids by a certain amount. If the carboxylic



b)
a)
Temperature, °C
$X_{\text{Stearic alcohol}}$
d)
c)
Temperature, °C
$X_{\text{Stearic alcohol}}$
i)
h)
g)
Temperature, °C
$X_{\text{Stearic alcohol}}$
f)
e)
Temperature, °C
$X_{\text{Stearic alcohol}}$
0
0.2
0.4
0.6
0.8
1
50
80
100
150
200

group of stearic acid is substituted by an alcoholic group, the solubility in the liquid state increases and the miscibility gap appears only with succinic acid and probably with the lower member (malonic acid), that is thermally unstable. This effect is probably due to the more polar character of the alcohol than of the acid; in fact in the acid the hydrogen bonds are neutralized within the dimeric molecule. The instability of succinic acid prevents us from studying the miscibility gap completely. This is asymmetrically placed in the dicarboxylic acid richer region, as pointed out in the monocarboxylic acid systems; the reason is probably the same as given previously [2]. The soaps (K, Na stearates) do not give any demixing phenomenon in the investigated region, probably due to the high solvation power of the alcoholic group on the ions. In contrast, in the systems dicarboxylic acids + (K, Na) stearates some demixing phenomena are evident. Probably, as pointed out previously, the polar character is not the only parameter that account for the demixing; the difference of the rigidity of the liquid structure is also involved [2].

Table 1

Thermodynamic data for stearic alcohol fusion

$T_{fus,}$, K	$\Delta H_{fus,}$, Kcal/mole	$\Delta S_{fus,}$, eu
331.2	15.3	46.1

Table 2

Characteristic points of the binary systems stearic alcohol (1) + component 2

Component 2	$x_{1,eut}$	T_{eut}, °C	$x^{l}_{1,m}$	$x^{r}_{1,m}$	T_m, °C
Succinic acid	0.9630	54.3	0.0140	0.4480	181.5
Glutaric acid	0.8510	53.8			
Adipic acid	0.9500	56.7			
Pimelic acid	0.8780	54.0			
Suberic acid	0.9400	57.0			
Azelaic acid	0.7350	52.0			
K stearate	≃0.9950	57.7			
Na stearate	≃0.9960	57.5			
Biphenyl	0.5360	50.0			

$x_{1,eut}$ = molar fraction of stearic alcohol at the eutectic composition;

$x^{l}_{1,m}$, $x^{r}_{1,m}$ = molar fractions of stearic alcohol on the left and right hand sides of the miscibility gap at the monotectic temperature;

T_{eut}, T_m = temperatures of eutectic and monotectic points

←

Fig. 1. a) Stearic alcohol + succinic acid; b) stearic alcohol + glutaric acid; c) stearic alcohol + adipic acid; d) stearic alcohol + pimelic acid; e) stearic alcohol + suberic acid; f) stearic alcohol + azelaic acid; g) stearic alcohol + Na stearate; h) stearic alcohol + K stearate; i) stearic alcohol + biphenyl

As in the systems with the acids, biphenyl is completely soluble in the liquid state with stearic alcohol, demonstrating that the interaction alcohol chain ↔ biphenyl is a very important factor in the solvation of this system. The eutectic composition does not vary regularly in the different systems, an alternating behaviour being evident. If the ideal curve [5] is considered for the two components of the binary system:

$$T_i = \Delta H_{\mathrm{fus},\,i}/(\Delta S_{\mathrm{fus},\,i} - R \ln x_i) \tag{1}$$

and at the eutectic composition the condition $T_1 = T_2$ is imposed, one can readily obtain:

$$\lg \frac{(1 - x_1)^{\frac{\Delta H_{\mathrm{tot},1}}{\Delta H_{\mathrm{tot},2}}}}{x_1} = - \frac{0.434\, \Delta S_{\mathrm{tot},\,1}}{R} + \frac{0.434\, \Delta H_{\mathrm{tot},\,1}}{R} \cdot \frac{\Delta S_{\mathrm{tot},\,2}}{\Delta H_{\mathrm{tot},2}} \tag{2}$$

where x_i = molar fraction of the i-th component at the eutectic composition;

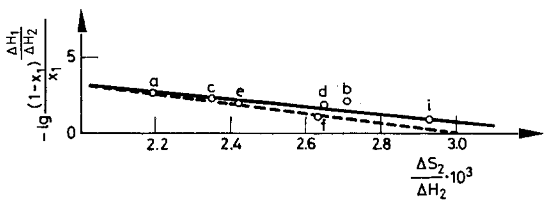


Fig. 2. Dependence of the eutectic composition on the thermodynamic properties of fusion and transition of component 2. ———— Experimental curve; — — — — — Theoretical curve. The difference between the experimental and theoretical curves is due to the partial functions of excess

$\Delta H_{\mathrm{tot},\,i}$ = sum of the fusion enthalpy and transition enthalpy (in the temperature range investigated of the i-th component); and

$\Delta S_{\mathrm{tot},\,i}$ = sum of the fusion entropy and transition entropy of the i-th component.

If no transition phenomenon occurs between the melting temperature and the eutectic temperature ΔH_{tot} and ΔS_{tot} are as in the Eq. (1) ΔH_{fus} and ΔS_{fus}.

If the non-ideal behaviour of the systems is considered, and the equation

$$T = (\Delta H_{\mathrm{fus},\,i} + \bar{H}_{\mathrm{mix},\,i})(\Delta S_{\mathrm{fus},\,i} + \bar{S}_{\mathrm{mix},\,i}) \tag{3}$$

is used [6], the thermodynamic functions in (2) can be replaced by the sum of the transition and fusion functions and of the excess functions.

The systems 1-octadecanol + dicarboxylic acids and with biphenyl roughly obey Eq. (2) as shown in Fig. 2, where the index 1 refers to the alcohol. ΔS_{tot} and ΔH_{tot} for component 2 are given in the literature [7, 8].

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Résumé — On a mesuré les températures des équilibres liquide-liquide et liquide-solide des systèmes binaires octadécanol + A (A = acides dicarboxyliques, diphényle ou stéarate de potassium, sodium). On discute les résultats et l'on établit une relation entre la composition des eutectiques et les propriétés thermodynamiques de fusion des constituants, dérivée de l'équation initiale et comparée avec la relation expérimentale.

Zusammenfassung — Die Flüssig-Flüssig- und Flüssig-Fest-Gleichgewichtstemperaturen der binären Systeme Octadecanol + A (A = Dicarboxylsäuren, Diphenyl oder (K, Na/ Stearat) wurden ermittelt. Die Ergebnisse werden diskutiert und ein Zusammenhang zwischen der Zusammensetzung der Eutektika und den Thermodynamischen Eigenschaften der Schmelze der Komponenten wird aus dem Vergleich der idealen und der auf dem Versuchswege erhaltenen Gleichungen abgeleitet.

Резюме — Установлены равновесные температуры жидкость-жидкость и жидкость-твердое тело для бинарных систем октадеканол + A (A = дикарбоновые кислоты, дифенил или (K, Na) стеарат). Полученные результаты обсуждены и выведены из идеального уравнения соотношение, связывающее состав эвтектики с термодинамическими свойствами плавления компонентов и которые сопоставлены с экспериментальными.