teraction leading to a partial neutralization of the cationic charge.

Registry No. Calcium nitrate tetrahydrate, 10022-68-1; urea, 57-13-6.

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Crystallization Curves for Binary Mixtures of Alkanes, Acids, and Alcohols

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The liquid–solid temperatures for the binary mixtures *n*-octacosane + hexadecanoic and dodecanoic acids, diphenyl + *n*-octacosane or *n*-tetracosane, cyclododecanol or cyclododecane + *n*-octacosane or *n*-tetracosane are measured by using a method previously described. The experimental cryoscopic lowering and thermodynamic values are discussed by comparison with literature data.

Introduction

In our laboratory we are at present studying (*1*, *2*) the use of group interaction theory in organic mixtures (*3*, *5*) and also parameters affecting the liquid–liquid equilibria (*6–8*). The statistical treatment of the systems previously studied (*1*) showed that, when there is high incidence of liquid–liquid equilibrium phenomena, a low coordination number is obtained (example, bicarboxylic acids + monocarboxylic acids, bicarboxylic acids + esters).

We plan to study extensively other binary systems which exhibit these features: a high coordination number (as was the case, in previous work (*1*), for mixtures with alkanes) and also differences in the polar character of the compounds. With this aim we report liquid–solid equilibrium temperatures for the following binary systems: *n*-octacosane + hexadecanoic and dodecanoic acids, diphenyl + *n*-octacosane or *n*-tetracosane, cyclododecanol or cyclododecane + *n*-octacosane or *n*-tetracosane.

Experimental Section

The experimental method employed has been widely described in previous papers (*10*, *11*). The initial crystallization temperature of the molten mixtures was determined with a chromel–alumel thermocouple (standarized with an NBS-certified Pt resistance thermometer) connected to a Leeds and Northrup type K-5 potentiometer. Pyrex tubes containing molten mixtures were put into a furnace where the temperature was controlled with a second thermocouple, connected to a Leeds and Northrup CAT control unit. If measurements had to be repeated, an auxiliary heater was used to ensure quick remelting.

A reliability of better than 0.3 K was expected, while a repeatability of within 0.06 K was obtained with a slow cooling rate (0.3 K/min).

The chemicals used were Fluka or Ega products of high purity and were not purified further before use. They were dried under dynamic vacuum.

Results and Discussion

Experimental values of the crystallization temperature are reported in Table I as a function of mole fraction and are shown in Figures 1–4. In Table II $\Delta T/m$ values extrapolated to $m = 0$ are reported. In Table III the coordinates of the eutectic point are given. When the enthalpy of fusion was available from the literature, a comparison between the experimental and thermodynamic cryoscopic constant was possible.

In *n*-tetracosane the solutes behaved regularly as shown by the agreement between K_T and $(\Delta T/m)_0$. In *n*-octacosane, monocarboxylic acids as solutes show $(\Delta T/m)_0$ values much lower than K_T. This behavior may be ascribed to dimer association as previously observed (*1*, *14*). Degrees of association of 0.74 and 0.60 may be calculated for dodecanoic and hexadecanoic acids, respectively, at low concentrations. The behavior of diphenyl–alkanes systems is more complicated. In fact, when diphenyl is the solvent, $(\Delta T/m)_0 \ll K_T$, contrary to when alkanes are solvents $(\Delta T/m)_0 \simeq K_T$. It is probable that formation of solid solutions occurs in the crystallization zone of diphenyl, while in the crystallization region of the alkane equilibrium occurs between liquid and pure solid alkane. For the alkane in hexadecanoic acid the cryoscopic behavior is regular. $(\Delta T/m)_0$ values for cyclododecane and cyclododecanol could not be used for critical analysis owing to the lack of thermodynamic fusion data. The $(\Delta T/m)_0$ value, concerning the systems with cyclododecane, predicts with reasonable accuracy

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Table I. Liquid-Solid Equilibrium Temperatures in the Binary Systems

X_2	T, K	X_2	T, K	X_2	T, K
		Dodecanoic Acid + *n*-Octacosane			
0.0000	317.2	0.2970	326.4	0.7849	333.0
0.0031	316.2_0	0.3348	327.1	0.8667	333.6
0.0142	315.6_0	0.3933	328.0	0.9314	334.1
0.0435	318.8_0	0.4558	328.6	0.9608	334.3_5
0.0892	320.9	0.5377	330.5	0.9722	334.4_5
0.1562	323.3	0.6172	331.6	0.9830	334.5_5
0.2301	325.3	0.6958	332.7	1.0000	334.7_0
		Hexadecanoic Acid + *n*-Octacosane			
0.0000	335.7_0	0.3349	327.7	0.8833	333.9
0.0124	335.4_5	0.4248	328.5	0.9294	334.0_3
0.0295	335.1_1	0.4776	329.5	0.9449	334.1_5
0.0467	334.8_0	0.5318	330.7	0.9758	334.4_6
0.0928	333.8	0.5825	331.5	0.9911	334.6_1
0.1701	332.5	0.6389	332.7	1.0000	334.7_0
0.2521	330.3	0.7110	333.2		
		Diphenyl + *n*-Octacosane			
0.0000	342.2_5	0.2500	333.4	0.7668	331.0
0.0035	342.1_3	0.3056	331.1	0.8530	332.3
0.0114	341.8_5	0.3994	326.2	0.9220	333.5
0.0229	341.4	0.4602	326.2	0.9523	334.0_4
0.0333	341.2	0.5045	327.3	0.9710	334.2_6
0.0725	339.9	0.5848	329.0	0.9855	334.4_9
0.1277	337.5	0.6701	329.5	1.0000	334.7_0
0.1872	335.7				
		Diphenyl + *n*-Tetracosane			
0.0000	342.2_5	0.2529	333.9	0.5857	318.0
0.0072	342.0_0	0.3388	330.5	0.6228	318.7
0.0117	341.8_5	0.3831	328.8	0.6411	319.1
0.0222	341.5_0	0.3946	327.8	0.7178	319.8
0.0436	340.8	0.4359	326.0	0.8043	320.6
0.0445	340.3	0.4771	323.9	0.8820	321.8
0.0677	339.5	0.5122	321.6	0.9424	322.7_5
0.0872	338.7	0.5340	320.8	0.9715	323.2_5
0.1200	337.6	0.5444	319.7	0.9802	323.4_0
0.1324	337.4	0.5676	318.6	1.0000	323.7_5
0.1833	336.1				
		Cyclododecanol + *n*-Octacosane			
0.0000	351.3_5	0.2377	340.5	0.6982	331.2
0.0049	351.0_7	0.2667	339.7	0.7917	332.2
0.0160	350.4_4	0.3056	337.9	0.8737	333.0
0.0258	349.9_8	0.3731	335.4	0.9407	333.8_9
0.0364	349.3_7	0.4453	333.1	0.9621	334.2_0
0.0794	347.3_5	0.5153	330.5	0.9796	334.4_2
0.1278	345.2	0.5730	330.2	0.9904	334.5_6
0.1819	342.6	0.6173	330.8	1.0000	334.7_0
		Cyclododecanol + *n*-Tetracosane			
0.0000	351.3_5	0.2150	339.9	0.7796	321.3
0.0082	350.8_8	0.2926	337.4	0.8198	320.7
0.0207	350.1_5	0.3456	335.4	0.8587	321.7
0.0295	349.6_5	0.4080	333.0	0.9075	322.2_3
0.0368	349.2_0	0.4853	330.4	0.9508	322.9_5
0.0608	347.8	0.5512	328.3	0.9692	323.2_5
0.0938	345.7	0.6029	326.9	0.9863	323.5_3
0.1329	343.6	0.6502	325.3	1.0000	323.7_5
0.1900	341.2	0.7203	322.7		
		Cyclododecane + *n*-Octacosane			
0.0000	334.2_0	0.2538	318.1	0.7076	330.2
0.0057	333.8_8	0.2884	320.1	0.7777	331.7
0.0135	333.4_4	0.3325	321.7	0.8484	332.4
0.0230	332.5_0	0.3964	324.0	0.9077	333.2
0.0534	330.5	0.4595	325.4	0.9682	334.2_4
0.0933	327.8	0.4995	326.1	0.9779	334.3_8
0.1347	324.6	0.5840	327.7	0.9876	334.5_2
0.1933	319.5	0.6426	329.2	1.0000	334.7_0
		Cyclododecane + *n*-Tetracosane			
0.0000	334.2_0	0.2061	319.6	0.7243	319.3
0.0070	333.8_0	0.2505	315.7	0.8076	320.1
0.0147	333.3_6	0.3041	310.8	0.8761	321.4_5
0.0300	332.4_5	0.3499	310.6	0.9043	322.1_5
0.0537	330.9	0.4009	312.3	0.9401	322.7_5
0.0829	329.2	0.4594	314.3	0.9689	323.2_3
0.1143	327.3	0.5355	315.7	0.9837	323.4_8
0.1567	323.5	0.6265	317.6	1.0000	323.7_5

Table II. Experimental and Thermodynamic Cryoscopic Constants

solvent	solute	$(\Delta T/m)_0$	K_T	ref
hexadecanoic acid	*n*-octacosane	5.2	5.2	*13*
cyclododecane	*n*-tetracosane	9.4		
	n-octacosane	9.4		
n-tetracosane	cyclododecane	5.5	5.4	*16*
	diphenyl	5.6		
	cyclododecanol	5.4		
n-octacosane	cyclododecane	5.6	5.7	*16*
	diphenyl	5.6		
	cyclododecanol	5.8		
	dodecanoic acid	3.6		
	hexadecanoic acid	4.0		
diphenyl	*n*-tetracosane	5.3	8.0	*12*
	n-octacosane	5.4		
cyclododecanol	*n*-tetracosane	10.7		
	n-octacosane	10.6		

Table III. Characteristic Points for Binary Systems

components	$X_{1\,(\mathrm{eut})}$	T, K
hexadecanoic acid (1)-*n*-octacosane (2)	0.6190	326.8
dodecanoic acid (1)-*n*-octacosane (2)	0.9882	315.2
diphenyl (1)-*n*-octacosane (2)	0.5815	325.3
diphenyl (1)-*n*-tetracosane (2)	0.4218	317.7
cyclododecane (1)-*n*-octacosane (2)	0.7740	316.4
cyclododecane (1)-*n*-tetracosane (2)	0.6800	309.0
cyclododecanol (1)-*n*-octacosane (2)	0.4620	329.4
cyclododecanol (1)-*n*-tetracosane (2)	0.1940	320.2

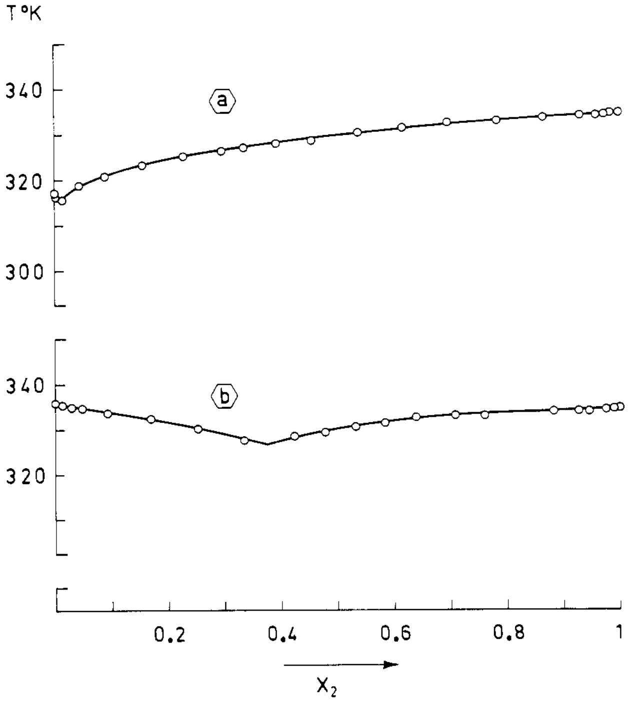

Figure 1. Liquid-liquid and liquid-solid equilibrium curves for the binary systems (a) dodecanoic acid + *n*-octacosane and (b) hexadecanoic acid + *n*-octacosane.

the cyclododecane liquidus curve.

The coordinates of the eutectic points given in Table III show, as expected, that the crystallization region for one component in a mixture is strongly affected by its melting temperature (*15*) in comparison to that of the other component. However, in two cases (cyclododecane + *n*-octacosane and

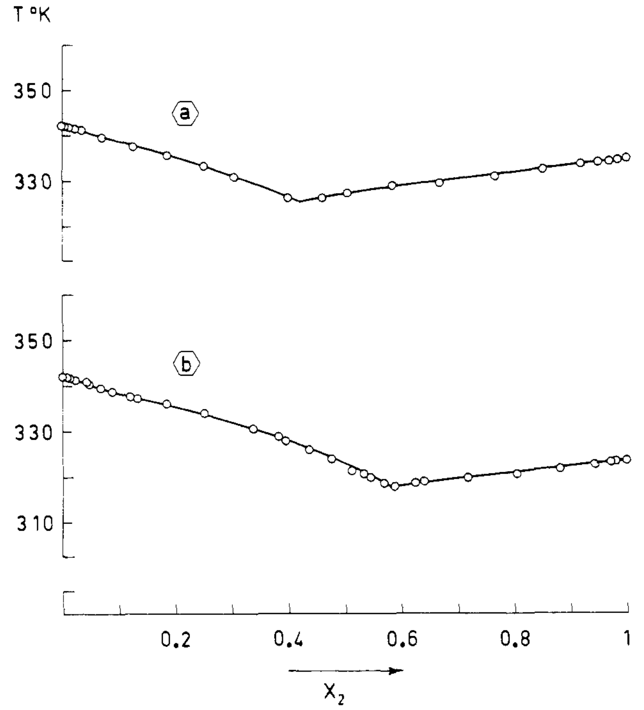

Figure 2. Liquid-liquid and liquid-solid equilibrium curves for the binary systems (a) diphenyl + *n*-octacosane and (b) diphenyl + *n*-tetracosane.

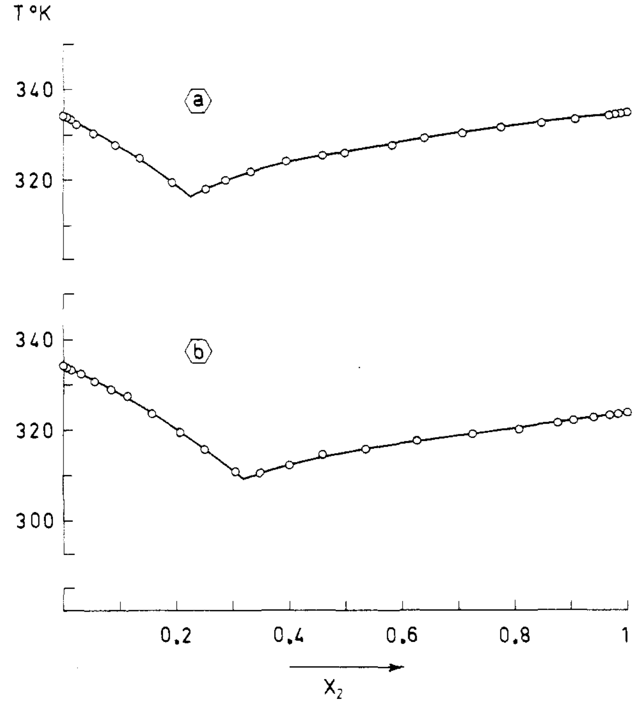

Figure 3. Liquid-liquid and liquid-solid equilibrium curves for the binary systems (a) cyclododecane + *n*-octacosane and (b) cyclododecane + *n*-tetracosane.

hexadecanoic acid + *n*-octacosane) where the two components of the binary system have almost the same fusion temperature, the following experimental behavior is observed: in a mixture of A and B, where component A exhibits a higher fusion entropy, the crystallization of A is obtained at higher concentrations of component B. This has been observed previously (*11*) in some ternary systems with ionic compounds. In fact, the sums of the melting and transition entropies (occurring in the temperature range investigated) of the compounds are as follows: hexadecanoic acid (*13*), 32.9 eu; *n*-octacosane (*16*), 71.8 eu; and cyclodecane (obtained from $\Delta T/m$) 11.9 eu; octacosane crystallizes over a wider composition range.

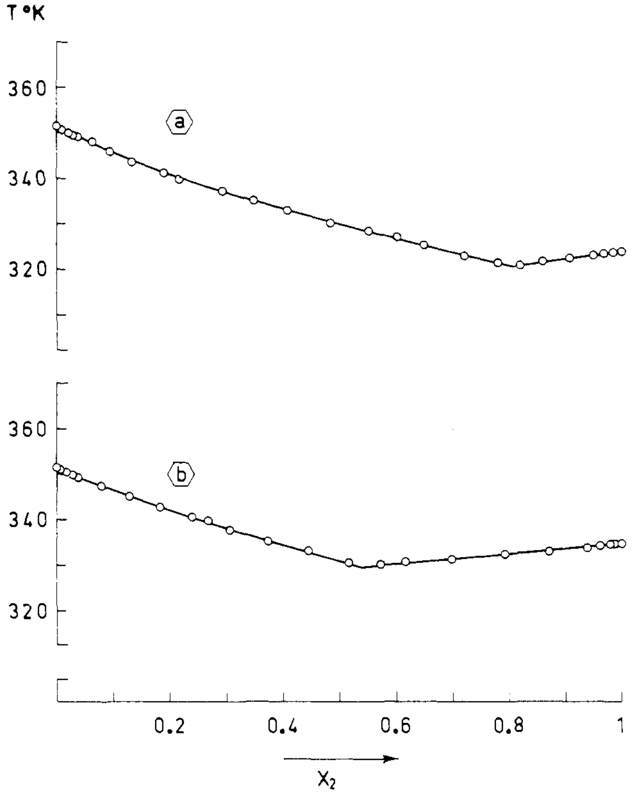

Figure 4. Liquid-liquid and liquid-solid equilibrium curves for the binary systems (a) cyclododecanol + *n*-tetracosane and (b) cyclododecanol + *n*-octacosane.

Registry No. Octacosane, 630-02-4; tetracosane, 646-31-1; hexadecanoic acid, 57-10-3; dodecanoic acid, 143-07-7; diphenyl, 92-52-4; cyclodecanol, 1724-39-6; cyclododecane, 294-62-2.

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