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Anomeric exchange and the structure of *n*-alkyl D-glucopyranosides. A study of binary phase behavior

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ABSTRACT

X-Ray diffraction and calorimetric data from the α and β anomers of *n*-alkyl D-glucopyranosides are analyzed to describe the molecular packing and co-solubility in the crystalline and liquid-crystalline phases. In the smectogenic chain-length series, the β-glucosides are co-soluble, with almost ideal mixing in the crystalline and meso-phases for chain-length differences of two carbon atoms. The smectic phases of octyl α- and β-glucosides are also co-soluble and a time sequence of phase diagrams (as well as lamellar X-ray data), as the solid obtained from the cooled melt is equilibrated, indicate that a metastable co-crystalline phase may exist until the respective hydrogen-bonding schemes are established. Lamellar spacings from a homologous series of the β anomers indicate that both the crystal structure and smectic-layer packings involve bilayer stacking of the molecules, a result that is difficult to reconcile with the respective surface-area requirements of the molecular acyl chain and sugar moieties.

INTRODUCTION

Of the detergent molecules commonly employed for the isolation and purification of integral membrane proteins, nonionic amphiphiles based on sugars have received considerable attention because of their ability to maintain proteins in their native form[1]. One class of detergents often considered is the alkyl D-glucosides, for which the anomeric disposition is a major determinant for the solubility of the two anomers in water. For example, octyl α-D-glucopyranoside can be crystallized from water, whereas the β anomer is highly soluble[2]. (This finding is consistent with the claim that α-D-glucose is crystallized under anhydrous conditions whereas β-D-glucose crystallizes when a concentrated aqueous solution is evaporated[3].) Because understanding the structural motifs of aqueous dispersions of octyl glucosides may be important for identification of "solvent" regions in X-ray crystal structures of membrane proteins stabilized by these detergents[4], numerous crystal-structure determinations have been carried out to provide model molecular-packing arrays for relevant liquid-crystalline phases[5].

It is somewhat frustrating that the crystal structure of *n*-octyl β-D-glucopyranoside has not been determined, even though the crystal packings of the α anomer in the anhydrous[6,7] or hydrated forms[8], are well described. Electron-diffraction studies have shown[9] that the presumed anhydrous structures are clearly different but, while the molecular packing of the α anomer is clearly consistent with the known X-ray crystal

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structures, the electron-diffraction data and/or powder X-ray data[10] from the β anomer do not correspond to any sugar amphiphile crystal structure reported to date. From rules formulated by Jeffrey and Mitra[11] in a survey of pyranose and pyranoside crystal structures, the crystal packings of anomers are expected to be quite different — a fact betrayed already for the glucopyranoses by the low water solubility of the α form[2], indicating that the hydrogen-bonding scheme is expected to be maximal for this anomer. The molecular geometry of the α-glucopyranosides evidently favors a more-efficient hydrogen-bonding network than that of the β anomers, and, and if this network is exceptionally strong, it may affect the solubility of the appropriate anomer[11]. Comparison of reported crystal structures for alkyl and aryl D-glucopyranoside seems to confirm this; the crystal structures of methyl[12], decyl[6] and phenyl[13] α-D-glucopyranosides show no water of hydration. Octyl α-D-glucopyranoside has an hemihydrate[9] and a hydrate[8] but also packs as an anhydrous[7] structure. On the other hand, methyl[14] and phenyl[15] β-D-glucopyranosides are both hydrated.

The structural similarities of the anomeric alkyl glucosides may be probed by the organic chemical crystallographic approach devised by A. I. Kitaigorodskii. According to his rules[16], continuous solid solutions will be formed between two structurally similar molecules only if they have similar molecular volumes and crystal structures with compatible symmetries. (The condition of similar molecular volumes may seem trivial here for two isomers of the same composition. What is actually implied here is *overlapping* volume, so that the two molecules are closely isomorphous.) This paper thus describes a calorimetric and low-angle X-ray study of binary alkyl glucoside combinations to ascertain the compatibility of such molecules in the solid and liquid-crystalline state.

EXPERIMENTAL

Materials. — *n*-Hexyl, *n*-nonyl, and *n*-decyl, β-D-glucopyranosides were purchased from Calbiochem-Behringer (La Jolla, CA) and the *n*-octyl β-D-glucopyranoside was obtained from Sigma (St. Louis, MO). A pure synthetic sample of *n*-octyl α-D-glucopyranoside was provided by Dr. M. Grabo.

X-Ray studies. — Powder X-ray diffraction experiments referred to earlier[10] had been performed on the anomeric octyl D-glucopyranosides, using a thermally regulated specimen holder for a GE XRD-5 diffractometer adapted to powder X-ray diffraction (CuKα radiation) with a home-made flat-film camera. Later X-ray experiments utilized a Rigaku rotating-anode generator with a CuKα X-ray source, and a specimen heater on a home-made camera. The detector used was a TEC 205 position-sensitive proportional counter.

Calorimetry. — For differential-scanning calorimetric (d.s.c.) measurements, small samples (3–5 mg) of binary detergent combinations were weighed into subsequently sealed aluminum pans for examination in a Mettler TA3300 instrument. After fusing the samples above the m.p. of the highest-melting component, the samples were scanned at 5.0° min at various times after the fusion — immediately thereafter, and then at 2, 6, or 21 days afterward. Melting temperatures were calibrated by fitting a polynominal of the heating curve to the melting temperatures of indium, lead, and zinc. The transition enthalpy was calibrated against the known value for indium. As the specimens slowly recrystallize to the thermodynamically stable form, the endpoint of the transformation was verified by comparing the transition enthalpies and temperatures of the pure detergents to values obtained for previously unheated samples that had been purified from solution.

COMPUTATIONS

Based on the ideal Raoult's Law behavior of a liquid solution, relations describing the freezing-point behaviors of a binary solid obtained from this liquid may be derived from the definition of chemical potential[17]. When a solid solution is formed from the liquid, relations of the type:

$$e^{-a} = \exp\left[-\frac{\Delta H_A}{R}\left(\frac{1}{T}-\frac{1}{T_A}\right)\right], e^{-b} = \exp\left[-\frac{\Delta H_B}{R}\left(\frac{1}{T}-\frac{1}{T_B}\right)\right]$$

may be defined for either component A or B where ΔH_A is the transition enthalpy or pure A and T_A its transition temperature. (This assumes that the calculation for mesogenic compounds can be carried out for each transition, e.g. at the crystal-smectic or smectic-melt transitions for these detergents.) As shown by Lee[17] and others, solidus and liquidus compositions, $x_B^{(S)}$ and $x_B^{(L)}$ may be defined:

$$x_B^{(S)} = \frac{e^{-a}-1}{e^{-a}-e^{b}} \qquad (1)$$

and

$$x_B^{(L)} = e^{-b} x_B^{(S)}$$

If the temperature T at the peak of the transition endotherm is measured by d.s.c. for a binary solid-solution or co-mesophase, this observation may be compared to the predicted mean mole-fraction of B:

$$\bar{x}_B = \tfrac{1}{2}(x_B^{(S)} + x_B^{(L)})$$

and a theoretical phase-diagram for solutions may be computed. When the cooled liquid solution fractionates, then the liquidus curve of the eutectic is defined by:

$$\ln x_A = \frac{-\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)$$

and (2)

$$\ln(1 - x_A) = \frac{-\Delta H_B}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right)$$

Both descriptions assume that the molecules have similar volumes and shapes, and that there is no enthalpy of mixing.

Deviations from ideal behavior have been treated in several ways. Thus the Flory–Huggins[18] theory includes differences in molecular volume interactions for nonideal mixing. Simpler theories, such as the Bragg–Williams model[17], account for the nonzero enthalpy of mixing, for instance:

$$\rho_0 \frac{(1 - x_A)^2}{\Delta H_A} = \frac{T}{T^{\text{ideal}}} - 1 \qquad (3)$$

Here ρ_0 is a molecular-interaction term which is zero for ideal mixing, positive when molecules of the same type preferably associate with each other, and negative when molecular compounds from the dissimilar molecules are favored[19]. The T^{ideal} would be predicted from Eq. *1* and *2*. The correction may be applied to either solid solutions or eutectics, although the latter adjustment is more convenient.

RESULTS

Interaction of β anomers. — Although the crystal structures for the *n*-alkyl β-D-glucopyranosides have not been determined, the influence of molecular-volume changes on the co-solubility of homologous pairs in the solid state may be investigated. According to Kitaigorodskii's postulates[15], this may be used to probe the importance of slight chain-length differences on the crystal structure in relation to such other polymethylene chains as alkanes and phospholipids.

Experimental lamellar spacings from crystalline alkyl β-glucosides are compared with previously determined values in Table I. If a least-squares line is fitted to these values for chain lengths from 6 to 10 carbon atoms (Fig. 1), the increase in lamellar spacing per increment of chain carbon atom is 2.61 Å, or somewhat higher than the 2.55 Å increment expected for untilted chains in a bilayer[20]. (This value is based on the zig-zag repeat along the chain of an untilted *n*-alkane.) A more reasonable value, 2.34 Å, is found if only chain lengths from 7–10 carbon atoms, corresponding to the structures in this series which transform to a mesophase, are used. (The rejection of the hexyl structure from this series will be justified later.) If the molecular lengths of anhydrous octyl and decyl α-D-glucopyranosides are calculated from their crystal structures and these values compared to the lamellar spacings of the β anomers in Table I, then a ratio somewhat greater than 2.0 indicates the presence of a bilayer crystal-packing. The methylene repeat for smectic structures is somewhat less than that found for the crystalline state, namely 2.15 Å/carbon atom (Fig. 1).

TABLE I

X-Ray lamellar spacings (Å) from *n*-alkyl D-glucopyranosides

D-*Glucopyranoside*	*Crystal this study*	*Lit.*[29]	*Smectic this study*	*Lit.*[29]
Octyl α	19.7		23.3	
Hexyl β	22.9			
Octyl β	29.0	29.4, 29.0	25.4	26.1
Nonyl β	31.7	32.6	27.5	27.6
Decyl β	34.2	34.0	29.8	29.5

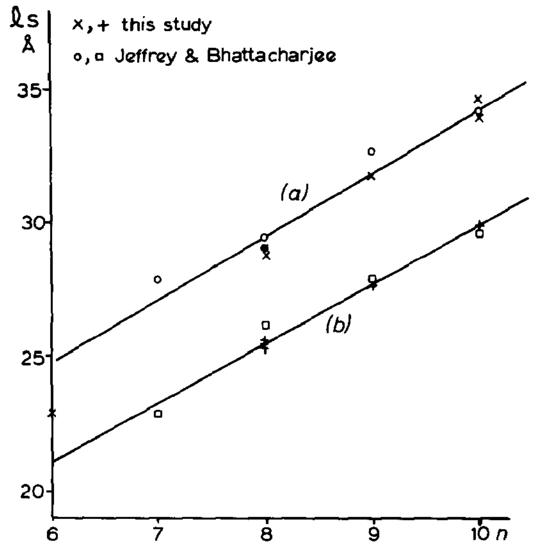

Fig. 1. Least-squares line through lamellar X-ray spacings (L) for crystalline and smectic phases of *n*-alkyl-β-D-glucopyranosides as a function of alkyl chain-length (n), using values obtained in this study and those reported by Jeffrey and Bhattacharjee[29]. (*a*) Crystalline phase, excluding $n = 6$, $L = (2.34n + 10.72)$ Å, (*b*) Smectic phase, $N > 6$, $L = (2.15n + 8.26)$ Å.

Phase diagrams constructed from d.s.c. scans of binary combinations of the alkyl β-glucosides that transform to a smectic phase show that there is nearly ideal solubility in the crystalline state as well as in the mesophase, even when the chain length differs by two carbon atoms (Fig. 2). Ideality of the phase transitions is determined by comparison of the experimental transition-boundaries, defined by the transition temperature plotted as a function of mole fraction, to theoretical curves calculated from Eq. *1*. Plots of lamellar spacings for the crystalline and smectic forms of these octyl β-glucoside/nonyl β-glucoside and octyl β-glucoside/decyl β-glucoside combinations (Fig. 3) also illustrate the continuous solubility of these concentration series. The lamellar spacings of intermediate concentrations lie very close to Vegard's law line connecting the spacings of the pure components. (Vegard's law states that molecular volume should increase linearly with increasing concentration of the larger component in a solid solution[21]. In the case of alkyl-chain derivatives, this is often expressed as a change of lamellar spacing, as the lateral packing distance is virtually unchanged with increasing chain-length).

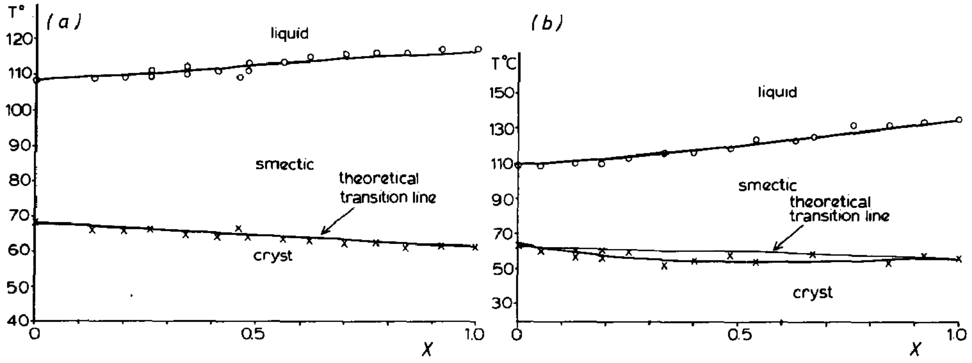

Fig. 2. Phase diagrams for binary combinations of mesogenic *n*-alkyl β-D-glucopyranosides: (*a*) octyl β-glucoside/nonyl β-glucoside (*b*) octyl β-glucoside/decyl β-glucoside. Both the crystal-to-smectic and smectic-to-melt transitions exhibits ideality by comparison to theoretical transition-curves calculated with Eq. 1.

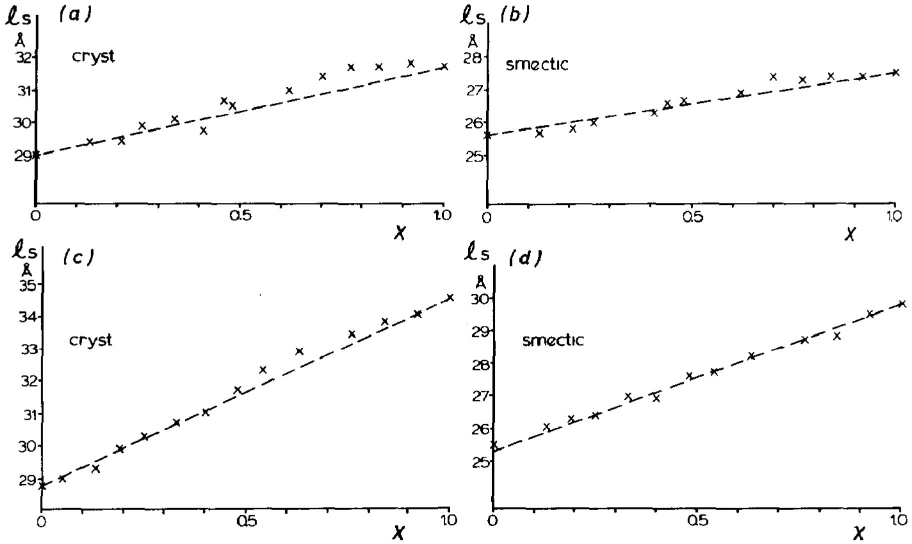

Fig. 3. Lamellar spacings for binary combinations of smectogenic *n*-alkyl β-D-glucopyranosides: octyl β-glucoside/nonyl β-glucoside; (*a*) crystalline phase, (*b*) smectic phase; octyl β-glucoside/decyl β-glucoside: (*c*) crystalline phase, (*d*) smectic phase. Lamellar spacings are smoothly continuous with concentration, corresponding to Vegard's law.

When one of the ingredients of the binary solid does not form a smectic mesophase, as with hexyl β-D-glucopyranoside, co-solubility with a mesogenic glucoside can still be demonstrated, although the melting behavior is nonideal (Fig. 4). Unlike the previous examples, the lamellar spacings of intermediate concentrations lie above Vegard's law line (Fig. 5) and the increase in lamellar spacing with concentration seems to be a step function, as with binary long-chain alcohol solids[22].

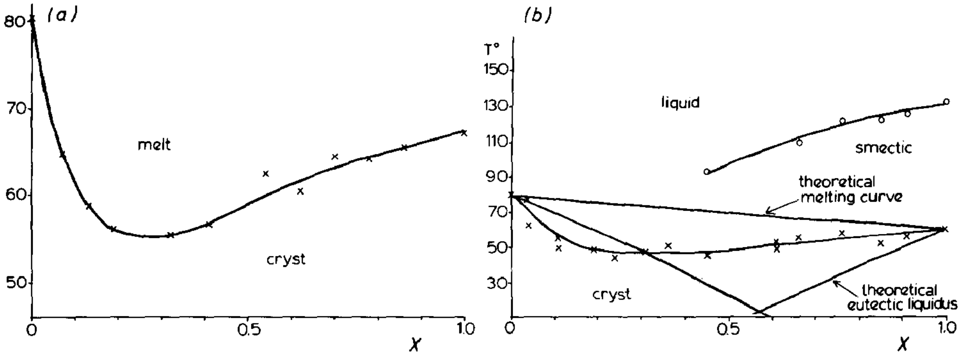

Fig. 4. Phase diagrams for binary combinations with the non-mesogenic *n*-hexyl glucoside: (*a*) hexyl β-glucoside/octyl β-glucoside (*b*) hexyl β-glucoside/decyl β-glucoside. The melting curves are nonideal.

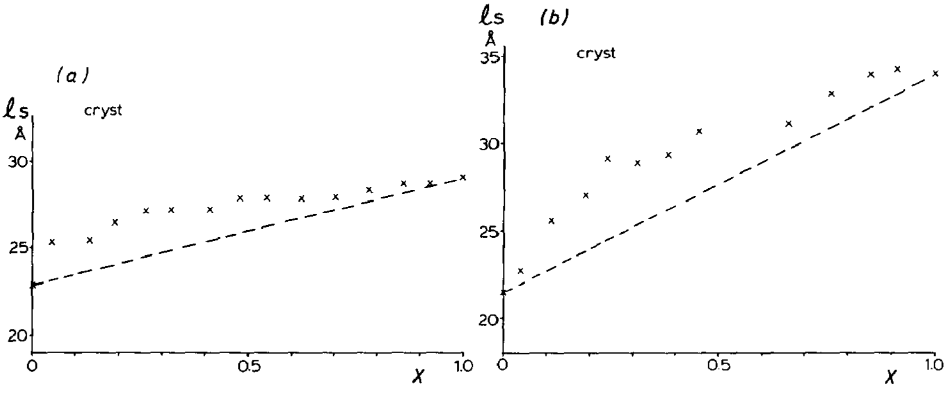

Fig. 5. Lamellar spacings of solid solutions with the non-mesogenic β-glucoside: (*a*) hexyl β-glucoside/octyl β-glucoside, (*b*) hexyl β-glucoside/decyl β-glucoside. The intermediate spacings lie on successive step-like plateaus at values above the ideal Vegard's law relationship for the pure components.

Interaction of anomers. — Thermotropic behavior of octyl α- and β-D-glucopyranosides are compared in terms of X-ray scattering in Fig. 6. The octyl α-glucoside diffracts at room temperature to produce a single intense lamellar order at 19.7 Å (characteristic of interdigitated bilayers) and relatively intense wide-angle reflections because of the methylene subcell packing. This pattern persists to just below the crystal-to-smectic transition, for example at 60° (Fig. 6a). Above this transition, as at

75° the lamellar reflection shifts to a spacing of 23.3 Å, with a single, intense wide-angle reflection at 4.9 Å, characteristic of liquid-like chain packing (Fig. 6b). When the sample is recrystallized from the smectic phase, a broad reflection at 43.8 Å can sometimes be observed in addition to the normal crystal lamellar spacing (Fig. 6c). When the sample is recrystallized from the melt, the pattern in Fig. 6a is reproduced.

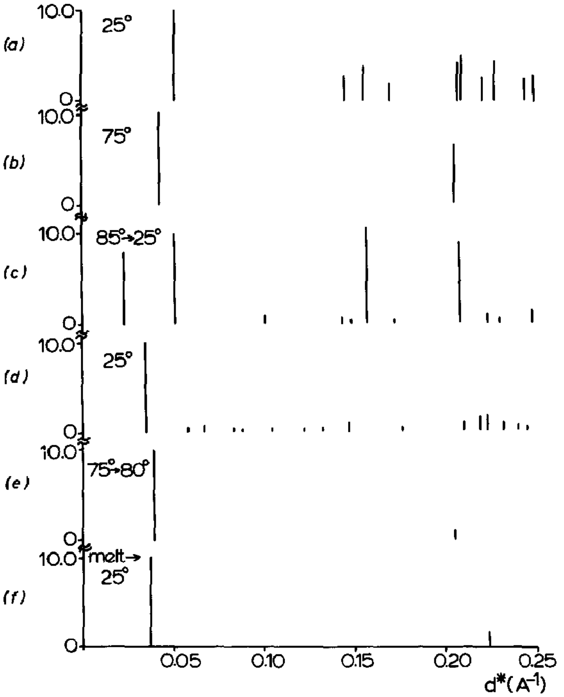

Fig. 6. X-Ray spacings for *n*-octyl D-glucopyranosides: For the α anomer: (*a*) room temperature up to first endothermic transition to smectic; (*b*) smectic phase (as at 75°); (*c*) Recrystallization from smectic phase — the new lowest-angle spacing is rather broad. For the β anomer: (*d*) crystalline phase; (*e*) smectic phase; (*f*) crystallization from the melt.

X-Ray patterns from the β anomer are somewhat different and are not readily explained by the electron-diffraction patterns obtained previously, despite an attempt to index these in terms of a three-dimensional reciprocal lattice[10]. One major difference between the two anomers is that the X-ray scattering from the crystalline octyl β-glucoside (Fig. 6d) has more reflections in the low-angle region and, while a single lamellar repeat is not seen, it is possible to index weak second- and third-order reflections of the lamellar spacing at 29.0 Å. The wide-angle intensities are relatively weak compared to the first-order lamellar reflection intensity. The pattern persists up to the crystal-to-smectic transition. Above this transition (as at 75°), a single lamellar spacing is seen at 25.4 Å with a single, broad, wide-angle reflection at 4.9 Å, again indicating that the alkyl chain packing is liquid-like (Fig. 6e). When the material is recrystallized from the smectic phase, the pattern in Fig. 6d is restored but, when it is recrystallized from the melt, a lamellar reflection is found at 27.2 Å with a wide-angle reflection at 4.5 Å (Fig. 6f). Crystalline order can be reestablished then by recrystallization of this solid from a solvent.

Although the octyl α- and β-glucosides have the same molecular volume, it is expected that they would form a eutectic at equilibrium because they must have quite different crystal structures[16]. Nevertheless, metastable co-solubility is indicated by calorimetric studies of binary combinations crystallized from the mesophase.

Lamellar spacings from binary solids equilibrated for 6 months (Fig. 7c) indicate that the respective pure components eventually crystallize as separate domains. Continuity of lamellar spacings is found in the mesophase, however (Fig. 7a); the smectic phases are therefore co-soluble. When the mesophase is allowed to equilibrate for a day (Fig. 7b) lamellar spacings attributable to the pure crystalline components can be found at high concentrations of either anomeric component. Other intermediate spacings, sometimes somewhat larger then the smectic spacing, are also found.

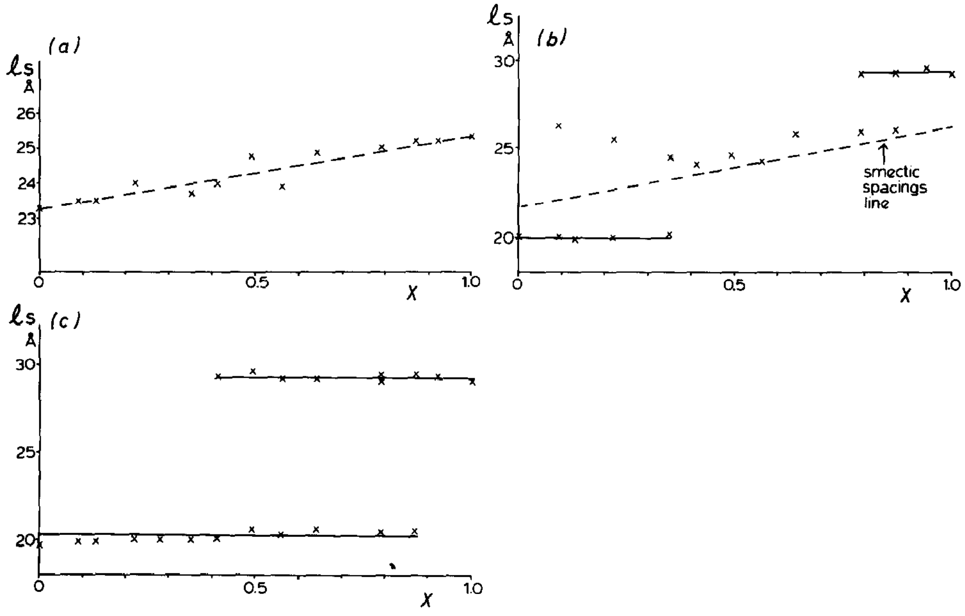

Fig. 7. Anomeric interaction between octyl α and β-D-glucopyranosides, X-ray lamellar spacings: (*a*) samples kept at 85° (within range of smectic), exhibiting total co-solubility. (*b*) Samples kept for 1 day at room temperature. High concentrations of either component recrystallize. At intermediate concentrations, the smectic and/or an incompletely separated co-crystalline solid exist as a metasable phase. (*c*) Samples equilibrated for 6 months at room temperature, showing total fractionation as separate crystalline components.

The recrystallization phenomenon may be understood from the sequence of phase diagrams. When samples are first crystallized from the melt (Fig. 8a), only the smectic-to-melt transition is found. Although the endotherms are often split for unknown reason, the mean transition-temperature lies close to the theoretical currve calculated by Eq. *1*. After 2 days, the crystal-to-smectic transition is observed (Fig. 8b). For the α anomer end of the concentration scale, the experimental transition-peaks lie close to the theoretical solid-solution melting line. At higher concentrations of the β anomer, these values deviate significantly from the theoretical curve. After 6 days of equilibration, a remnant of the solid-solution melting curve is observed at high concentration of α anomer (Fig. 8c) but a eutectic relationship between the two anomers becomes clear. Finally, after 3 weeks, the eutectic relationship becomes even more apparent, although some solid solution remains (Fig. 8d). In an attempt to calculate the liquidus curve with the Schröder equation (*2*), however, it is found that the true eutectic

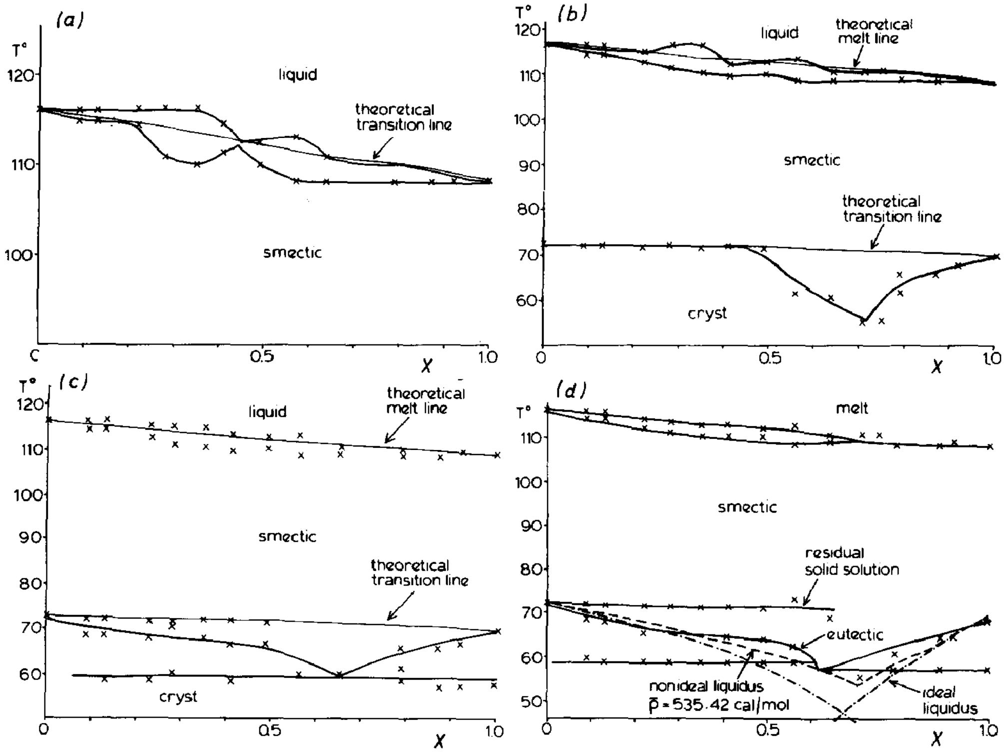

Fig. 8. Phase diagrams for binary combinations of the octyl α- and β-glucopyranosides recrystallized from the melt. (*a*) After direct recrystallization, showing only the smectic transition, corresponding roughly to the ideal transition calculated from Eq. *1*. (*b*) After 2 days, nearly ideal co-solubility being indicated for high concentrations of octyl α-glucoside. (*c*) After 6 days, fractionation being observed, although some co-soluble components are still observed. (*d*) For samples kept for 3 weeks, the fractionation being more clear. The observed liquidus curves do not correspond to freezing-point depression of an ideal liquid. Nonideal theory (Eq. *3*) produces a closer, but not perfect, match.

solidus near 59° is some 10° higher than the theoretical value. Use of Eq. *3* to calculate nonideal liquidus lines gives a slightly improved fit to the experimental curve when a mean value of the molecular interaction term ρ_o = 535.4 cal/mol is used.

DISCUSSION

To distinguish the crystal packings of alkyl α- and β-glucosides, it is useful to analyze the lamellar-spacing data from a homologous chain-length series of compounds having the same crystal structure. As discussed by Chapman[20], a line, $L = nc + k$, is obtained where L is the lamellar spacing, n the number of carbon atoms in the chain, c the increment in lamellar spacing per carbon atom, and k a constant related to the linear contribution from the polar group or end-plane packing. If c is <1.27 Å, an interdigitated structure may be indicated, but if it is larger than this value, a bilayer structure is expected and the chain tilt τ for the lamellar-surface plane may be estimated from the relationship:

$$\sin\tau = \frac{c}{c_S}$$

where c_s = 2.55 Å is a typical incremental value for an untilted zig-zag carbon chain.

Examples of this analysis can be given, for instance for an isostructural series of even-chain *N*(*n*-alkyl) gluconamides, which have the same crystal structure[23]. The lamellar increase per carbon, c = 1.85 Å, indicates that a bilayer is formed (as seen from the head-to-tail packing in the crystal structure) and that the chain tilt should be ~46°. The remaining distance, k = 17.4 Å, corresponds to two polar groups in the bilayer structure. Such an analysis for two homologous *n*-alkyl α-D-glucopyranosides[6,7] (anhydrous forms) reveals that c = 1.10 Å, indicating that an interdigitating bilayer may be found (as seen from the crystal structures) and k = 11.1 Å is the linear contribution from the two glucose residues. The calculated chain tilt $\tau = \sin^{-1}(1.10/1.27) = 60°$ is in reasonable agreement with the crystal structure. (For a interdigitated bilayer, the value $1/2\,(c_s) = 1.27$ Å is used).

A similar analysis for *n*-alkyl β-D-glucopyranosides, using the lamellar data in Table I or Fig. 1, leads to results that are somewhat puzzling. Excluding the value for the *n*-hexyl compound, which does not form a mesophase structure, a least-squares line $L = 2.34n + 10.7$ indicates that the contribution from the polar groups (k = 10.7 Å) is similar to the α anomer structures. The large c value of (2.34 Å) denotes a bilayer structure and τ = 66°, a less-tilted chain packing than found for the α anomers. The problem with this analysis is that, without exception, all crystal structures of closed-ring sugar-based amphiphiles[5] are interdigitated bilayers, for the very good reason that the polar headgroup cross-section at the lamellar surface must be compensated by the summed chain cross-sections. It is difficult to see how much a bilayer structure could be formed for the alkyl β-glucosides if the chains pack in an ordered parallel arrangement in a methylene subcell. That wide-angle intensities for octyl β-glucoside are relatively weak may indicate that the chains do not adopt an ordered subcell structure. Nevertheless, some minimization of the polar group cross-section must be achieved to allow an average single-carbon chain to be packed in a layer with the sugar moiety.

A more limited cross-section of this sugar ring may nevertheless be possible. For example Goodby and his co-workers[24,25] have found that two linear hydrogen-bonding smectogens are co-miscible with *n*-alkyl β-D-glucopyranosides, both of which crystallize with a head-to-tail bilayer packing. The alkyl α-D-glucopyranosides were also stated to be in the same smectic miscibility group. This correlation is shown directly by the phase diagram (Fig. 8a), where the smectic-to-melt transition for binary compositions of octyl α- and β-glucosides conforms to Raoult's law. This conclusion is also supported by the continuity of smectic lamellar spacings for the concentration series. The phase diagrams also indicate that a metastable co-crystalline phase should exist for the two anomers, such that a relatively slow polar-group rearrangement occurs to establish specific hydrogen-bonding patterns peculiar to each anomer. A preference for self-association at equilibrium is apparent from the deviation of the experimental liquidus curves from ideal freezing-point values. It is doubtful, however, that the smectic A phase characterized by Goodby *et al.*[26] is an interdigitated structure. A plot of lamellar spacings for this phase of the alkyl β-glucosides (Table I) leads to a least-squares line $L = 2.15n + 8.26$. As $c > 1.27$ Å, this must also be a bilayer structure. In addition, as the molecular length of *n*-octyl α-D-glucopyranoside is ~ 12.2 Å, the measured smectic lamellar spacing $L =$ 23.3 Å, indicates a bilayer packing for the α anomer.

Interestingly, the alkyl-chain length responsible for a change from normal melting behavior to mesogenic properties may also produce a change in crystal structure. As already stated, a least-squares line through all available lamellar spacings for the alkyl β-glucosides leads to an unreasonably large increase in lamellar thickness when one carbon atom is added to the chain. When the value for the *n*-hexyl compound is disregarded, the slope is reasonable. Thermal data also indicate a difference in these structures. For the smectogenic β-glucosides, a difference in two carbon atoms for the combined compounds in a binary solid causes virtually no deviation from ideal phase-transition behavior (Fig. 2). On the other hand, a similar chain-length difference involving the isotropically melting *n*-hexyl homolog with the mesogenic *n*-octyl β-D-glucopyranoside results in binary solids exhibiting nonideal melting behavior (Fig. 4) because of a nonrandom distribution of components in the solid.

To summarize these results, it is first of all apparent that volume changes due to chain-length differences are accommodated in binary solids composed of *n*-alkyl β-D-glucopyranosides much as they are in *n*-alkanes[27] or cholesteryl esters[28]. The transition line from the crystal to smectic phase is most affected by molecular-volume differences, in that it deviates from the behavior predicted by Raoult's law, whereas the true melting line is insensitive to this difference in chain length. For binary mixtures of the anomeric *n*-octyl D-glucopyranosides, the smectic phase is again co-soluble. Although there may be a metastable, crystalline solid-solution, the two anomers eventually separate into a eutectic solid. This behavior implies an effective difference in molecular shape for the anomers, leading to a significant non-overlapping volume which may be exaggerated by greatly different equilibrium hydrogen-bonding networks. That these different polar interactions are important for this phase separation is implied by the non-ideality of the liquidus transition for the eutectic solid, implying a favored self-association of the respective compounds.

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