

Effect of sorbitan-based surfactants on glass transition temperature of cellulose esters

Jorge Amim Jr. · Leandro S. Blachechen ·
Denise F. S. Petri

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Abstract Thermal behavior of mixtures composed of cellulose acetate butyrate (CAB), carboxymethylcellulose acetate butyrate (CMCAB), or cellulose acetate phthalate (CAPH), and sorbitan-based surfactants was investigated as a function of mixture composition by means of differential scanning calorimetry (DSC). Surfactants with three different alkyl chain lengths, namely, polyoxyethylenesorbitan monolaurate (Tween 20), polyoxyethylenesorbitan monopalmitate (Tween 40), and polyoxyethylene sorbitan monostearate (Tween 60) were chosen. DSC measurements revealed that Tween 20, 40, and 60 act as plasticizers for CAB, CMCAB, and CAPH (except for Tween 60), leading to a dramatic reduction of glass transition temperature (T_g). The dependence of experimental T_g values on the mixture composition was compared with theoretical predictions using the Fox equation. Plasticization was strongly dependent on mixture composition, surfactant hydrophobic chain length, and type of cellulose ester functional group.

Keywords Cellulose ester · DSC · Sorbitan-based surfactants · Fox equation · Plasticization

Introduction

Cellulose esters have been attractive materials in different area of science and technology, for example, cellulose

acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), and carboxymethylcellulose acetate butyrate (CMCAB) are extensively used in the coating industry because they reduce dry time, improve flow and leveling, control viscosity and gloss, are stable carriers for metallic pigments, improve UV stability, and reduce plasticizer migration, and recently, in pharmaceutical formulations, among many other benefits [1, 2]. Cellulose acetate phthalate (CAPH) has been largely used as a pharmaceutical excipient for enteric film coating of capsules and tablets, because it can form films resistant to hydrolysis and enzymatic action of gastric fluids, but it disintegrates rapidly once it reaches the large intestine at pH 6.2–6.8 [1, 3]. Thin films of CA, CAP, CAB, and CMCAB also proved to be efficient supports for selective adsorption of proteins [4, 5] and for the successful immobilization of lipases [6].

Plasticizers are added to polymers to make them flexible, resilient, and easier to handle and to process. Triethyl acetate, dibutyl sebacate, triethyl citrate, sorbitol, PEG, and glycerin are the class of compounds mostly used to prepare these formulations [7–12]. However, some of these plasticizers have been linked to a high toxicity, moderate water solubility, and low boiling points [13]. Therefore, due to these characteristics, sugar-based surfactants and ionic liquids are compounds that were studied as possible plasticizers for polymer samples [13–16]. In a previous study [17], sorbitan monopalmitate (Span 40) and polyoxyethylenesorbitan monopalmitate (Tween 40) were added to carboxymethyl cellulose acetate butyrate (CMCAB), which acted as a plasticizer for CMCAB, leading to dramatic reduction of glass transition temperature of CMCAB, namely, $\Delta T_g = -158$ and -179 °C, respectively. The aim of this study is to assess the properties of three kinds of sorbitan-based surfactants as plasticizers for cellulose esters by means of differential

J. Amim Jr. (✉)
Universidade Federal do Rio de Janeiro, Campus Macaé,
Av. Aluizio Gomes da Silva 50, Macaé 27930-560, Brazil
e-mail: amim@iq.ufrj.br

L. S. Blachechen · D. F. S. Petri
Instituto de Química, Universidade de São Paulo,
Av. Prof. Lineu Prestes 748, São Paulo 05508-900, Brazil

scanning calorimetry (DSC). Particularly, the effect of surfactant chain length and cellulose ester substituent on the plasticization was investigated.

Experimental

Materials

Cellulose ester powders free of plasticizers were kindly supplied by Eastman Chemical Co., Brazil. The characteristics of cellulose esters are provided in Table 1. The surfactants, such as, polyoxyethylenesorbitan monolaurate (Tween 20), polyoxyethylenesorbitan monopalmitate (Tween 40), and polyoxyethylenesorbitan monostearate (Tween 60) were purchased from Sigma-Aldrich. Polymers and surfactants were used as received. Analytical grade ethyl acetate and isopropanol (Synth, Brazil) were used to prepare cellulose ester/surfactants mixtures. The chemical structures of cellulose esters and surfactants are schematically represented in Fig. 1.

Methods

Sample preparation

Mixtures of CAB and CMCAB with Tween 20, 40, and 60 were prepared by casting from ethyl acetate solutions at 80 °C. For CAPH, the mixture of ethyl acetate and isopropanol (1:1 in volume) was used as a solvent. The samples were dried until constant mass. The content of surfactants (as weight fraction *W*) in the dried mixture with CAB, CMCAB, or CAPH ranged from 0.05 to 0.70.

Differential scanning calorimetry (DSC) curves were obtained in a TA-DSC Q10V9.0 equipment. Closed Al crucibles with ~3 mg of each sample under a dynamic N₂ atmosphere (50 mL/min) were heated and cooled down at rates of 10 °C/min, in the temperature range from -80 to 200 °C. Empty pans were used as reference. The second heating was considered for the determination of the glass transition temperature (*T_g*), melting temperature (*T_m*), and ΔH_{fus} of the samples. The DSC cell was calibrated with In (*T_m* = 157 °C; ΔH_{fus} = 28.54 J g⁻¹) and Zn (*T_m* = 420 °C).

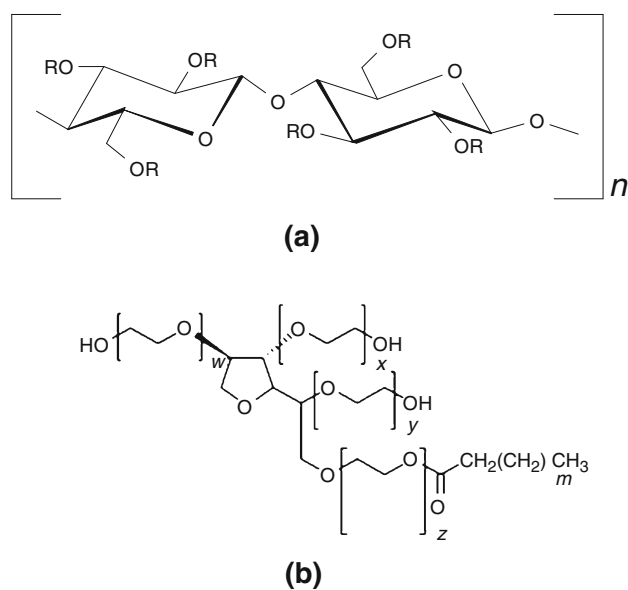


Fig. 1 Schematic representation of chemical structures of **a** cellulose esters: CAB where R refers to H, COCH₃, and/or COC₃H₇, CMCAB where R refers to H, COCH₃, COC₃H₇, and/or CH₂COOH, and CAPH where R refers to H, COCH₃, and/or COC₆H₅COOH and **b** surfactants: Tween 20, Tween 40, and Tween 60. These surfactants possess 12, 16, and 18 carbons in alkyl chain, respectively. Where $x + y + z + w = 20$

One should notice that, typically, the standard deviation determined for triplicates was 1 °C.

Results and discussion

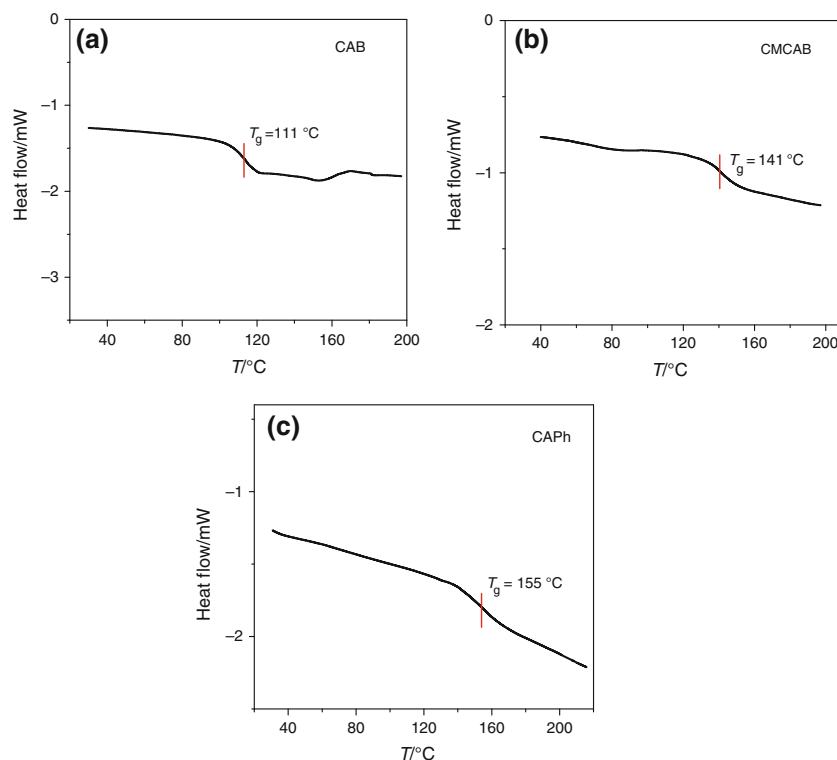
In order to gain insight about miscibility between cellulose esters and sorbitan-based surfactants, DSC measurements were performed for pure components and mixtures. DSC curves recorded for pure cellulose esters are shown in Fig. 2. The *T_g* values for CAB, CMCAB, and CAPH were determined as 111, 141 and 155 °C, respectively. The highest *T_g* value was found for CAPH. It can be explained by the strong intra and intermolecular interaction among CAPH chains that causes lower chain flexibility. Phthalate groups are bulky and CAPH chains are more tightly bound to each other [18]. With regard to the *T_g* values determined for CAB and CMCAB, one notices that the presence of

Table 1 Cellulose esters characteristics: weight-average molar mass (\bar{M}_w), degree of substitution for acetate (DS_{Ac}), propionate (DS_{Pr}), butyrate (DS_{Bu}), and hydroxyl (OH)

| Cellulose ester | Code | \bar{M}_w /g/mol | DS _{Ac} | DS _{Bu} | DS _{CM} | DS _{Ph} | OH |
|-----------------------------------------|---------------|--------------------|------------------|------------------|------------------|------------------|------|
| Carboxymethylcellulose acetate butyrate | CMCAB 641-0.2 | 20,000 | 0.44 | 1.64 | 0.33 | – | 0.59 |
| Cellulose acetate butyrate | CAB 551 | 20,000 | 0.2 | 2.5 | – | – | 0.3 |
| Cellulose acetate phthalate | CAPH | 40,000 | 2.1 | – | – | 0.9 | – |

The degree of esterification is the ratio of ester groups to glucose residues. Data provided by the producer

Fig. 2 DSC curves obtained for **a** CAB, **b** CMCAB, and **c** CAPH



carboxymethyl group in the polymer structure increased 30 °C in the T_g value. This is an interesting finding, because it shows that even in the case of low degree of substitution ($DS_{CM} = 0.33$), the insertion of polar groups like carboxylic acids along the chain, decreases the molecular mobility due to intermolecular H bonding and, therefore, increases the T_g values. The T_g values determined for CAB, CMCAB, and CAPH could be correlated to their surface energy values, which amount to 46.6 ± 0.3 , 51.9 ± 0.3 , and 64.1 ± 0.6 mJ/m², respectively [18]. Strong intermolecular interactions yield high surface energy and T_g values, leading to the following sequence: CAB < CMCAB < CAPH. Events related to crystallization or fusion could not be observed for these cellulose esters.

DSC curves obtained for Tween 20, Tween 40, and Tween 60 (Fig. 3) evidenced that all the three samples presented T_g at -61 °C. The branched structure of Tween polar head increases the free volume and, therefore, decreases T_g to such a low value. This also explains the liquid nature of surfactants under room conditions. However, Tween 20, Tween 40, and Tween 60 melted at different T_m values: Tween 20 at -15 °C (peak) and $\Delta H_m = 33.2$ J/g, Tween 40 at 18 °C (peak), and $\Delta H_m = 22.7$ J/g and Tween 60 at 22.6 °C (peak) $\Delta H_m = 50.26$ J/g. This discrepancy of the T_m values might be due to the presence of crystals of different sizes and/or orientations. Moreover, thermal properties can be influenced by alkyl chain length, as observed by Terrero et al. [19]. In this study, authors demonstrated that solidification enthalpy

values of *n*-alkylammonium chlorides were a function of the alkyl chain length. No decomposition peak could be observed within the temperature range used.

All mixtures of CAB, CMCAB, and CAPH with Tweens 20, 40, or 60 presented only one T_g in the DSC curves (not shown) except for mixtures prepared with CAPH and Tween 60, which presented two T_g values corresponding to the pure components.

Experimental values of T_g determined for mixtures of CAB or CMCAB, and surfactants are presented in Fig. 4 along with the corresponding T_g values predicted by Fox equation (Eq. 1). Similarly, Fig. 5 shows the experimental and calculated T_g values for mixtures of CAPH and surfactants. Fox equation is often applied for estimating the effect of mixtures' composition involving a polymer and a plasticizer or a second polymer on the T_g values:

$$\frac{1}{T_g} \equiv \frac{W_a}{T_{g(a)}} + \frac{W_b}{T_{g(b)}} \quad (1)$$

where $T_{g(a)}$ and $T_{g(b)}$ denotes glass transition temperature of the plasticizer (surfactant, in this case) and polymer, respectively. W_a and W_b corresponds to mass fraction of the plasticizer and polymer in the mixture. Such behavior is expected when the mixture presents ideal behavior and $\Delta H_{mix} \sim 0$.

Comparing the T_g values of pure cellulose esters with those determined for the mixtures, one can notice that T_g values decreased dramatically upon increasing surfactant

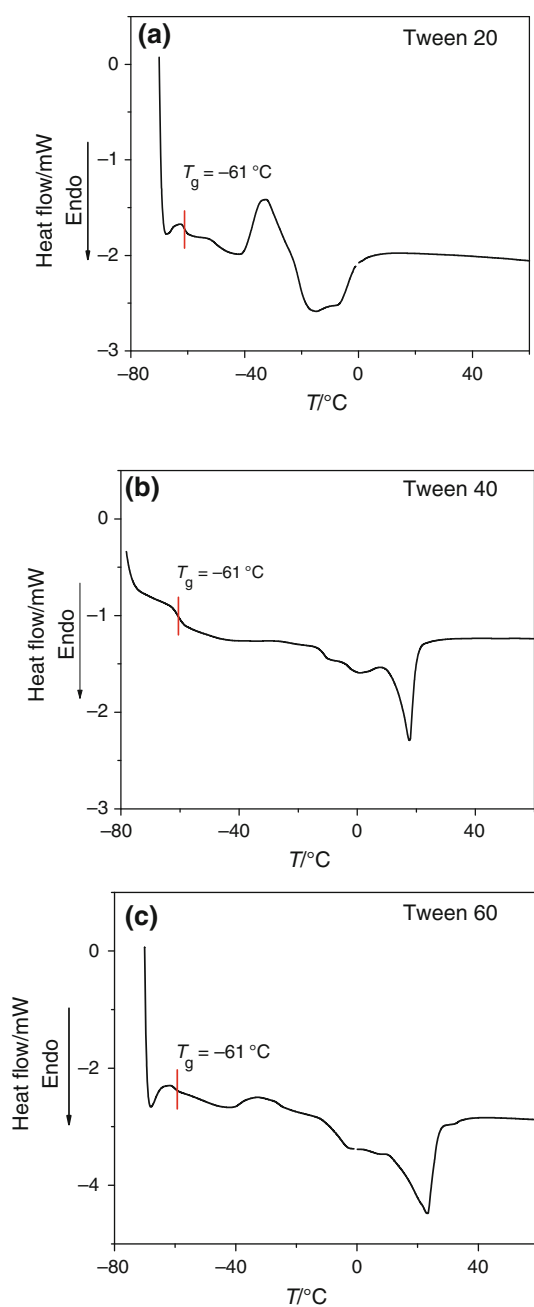


Fig. 3 DSC curves obtained for **a** Tween 20, **b** Tween 40, and **c** Tween 60

(Tweens 20, 40, or 60) content in the mixtures (Figs. 4 and 5). This effect might be due to an increase in the polymer chain mobility and flexibility, when the surfactants were incorporated in the free volume of polymer. A similar behavior was observed for mixtures of Tween 80 and hydrophilic polymers, commonly used as active pharmaceutical ingredients [13, 20]. In this case, the authors attributed the reduction of T_g to the similarity between Hansen solubility parameters of Tween 80 and hydrophilic polymers [13].

Fox equation described well the T_g variation for the mixtures CAB and Tween 20, or Tween 40 up to $W \sim 0.30$ of plasticizer, as shown in Fig. 4a, b, respectively. For $W > 0.30$ negative deviations are observed. However, in case of the mixtures CAB and Tween 60, Fox equation fitted the experimental data only up to $W \sim 0.10$ of plasticizer (Fig. 4c), and for larger W values experimental T_g data were smaller than the theoretical data. It seems that there is a critical content of plasticizer in the mixture, which depends on its size and on the interactions between polymer and plasticizer molecules. Up to this critical content, the decrease in the T_g results mainly from increase of flexibility since, free volume was occupied by the plasticizer and $\Delta H_{\text{mix}} \sim 0$. Therefore, the smaller the plasticizer, the larger is the critical W value, because more plasticizer molecules can be arranged in the polymer-free volume. For that reason, in the case of mixtures of CAB with Tween 20, Tween 40, or Tween 60, the smaller critical W value was observed for the largest molecule (Tween 60). The negative deviations observed for W values larger than the critical one are due to specific favorable interaction ($\Delta H_{\text{mix}} < 0$) between surfactants and cellulose esters. The ethylene oxide residues in the Tween polar head might build H bonding with carbonyl and hydroxyl groups of cellulose ester. Feldstein and co-workers observed similar behavior for poly(*N*-vinyl pyrrolidone) and plasticizers rich in hydroxyl groups [21]. In that case, H bonding was also responsible for the negative deviations between the experimental T_g value from that predicted with Fox equation.

In the case of CMCAB and Tween 20, Tween 40, or Tween 60 mixtures, and Fig. 4d, e, f, respectively, the critical W values amounted to ~ 0.15 Tween 20, ~ 0.15 Tween 40, and ~ 0.10 Tween 60. The mixtures of CMCAB with Tween 20 and Tween 40 obtained critical W values which were smaller than those in the mixtures with CAB. One possible explanation for this is the reduction of polymer-free volume due to the presence of carboxylic acid groups in the CMCAB. For $W > 0.30$, all mixtures containing CMCAB presented negative deviations due to H bonding between the components. In general, the trend observed for CMCAB mixtures was similar to that found for CAB mixtures.

The variation in T_g values determined for CAPH and surfactant mixtures as a function of Tween 20 (Fig. 5a) or Tween 40 (Fig. 5b) content could not be fitted with Fox equation. In both the cases, the T_g values found for mixtures with W ranging from 0 to ~ 0.15 were practically the same as that determined for pure CAPH. However, at $W \sim 0.3$ Tween 20 and $W \sim 0.2$ Tween 40, T_g values decreased abruptly to ~ -43 and ~ -33 °C, respectively. These values are slightly above the T_g value of pure surfactants (-61 °C). Considering that, within the whole

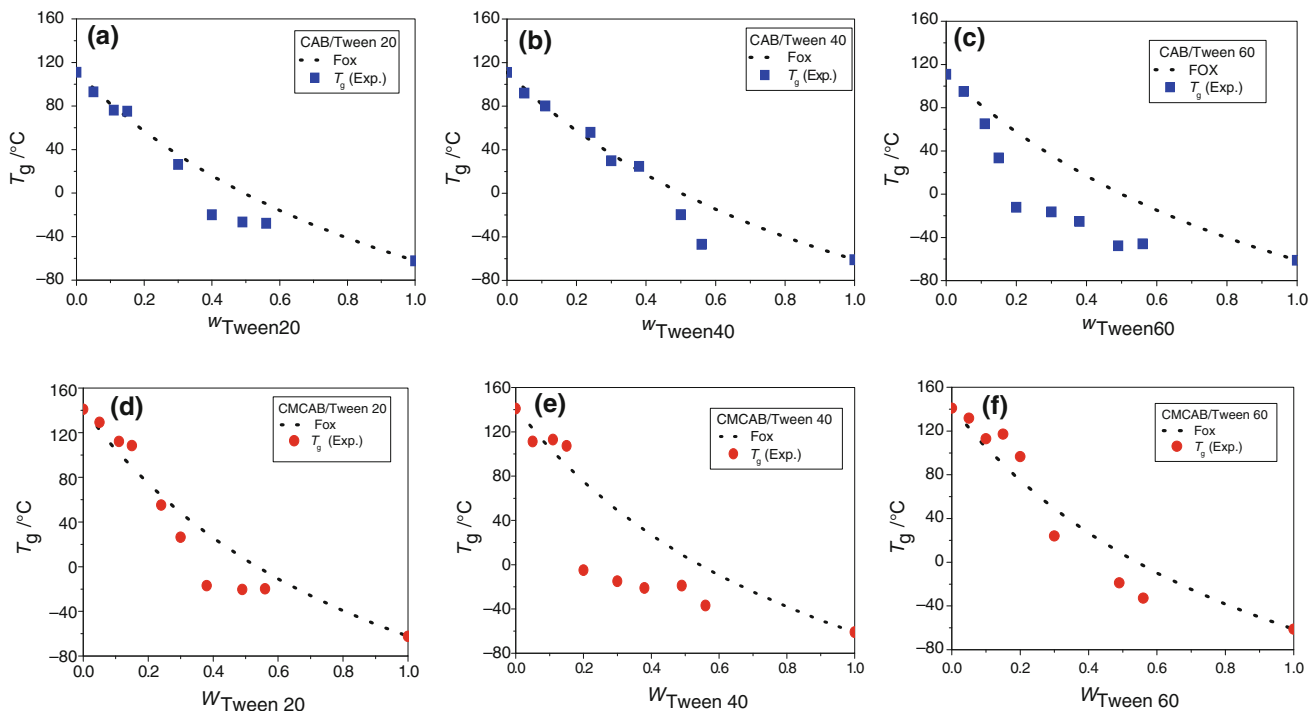


Fig. 4 Glass transition temperatures (T_g) of CAB and CMCAB determined by Fox equation (dotted lines) and DSC experiments (exp.) as function of weight fraction of surfactants in polymer/surfactant mixtures. Where: **a** CAB/Tween 20, **b** CAB/Tween 40, **c** CAB/Tween 60, **d** CMCAB/Tween 20, **e** CMCAB/Tween 40, and **f** CMCAB/Tween 60

Fig. 5 Glass transition temperatures (T_g) of CAPH determined by (dotted lines) Fox equation and DSC experiments (exp.) as function of weight fraction of surfactants in polymer/surfactant mixtures. Where: **a** CAPH/Tween 20 and **b** CAPH/Tween 40

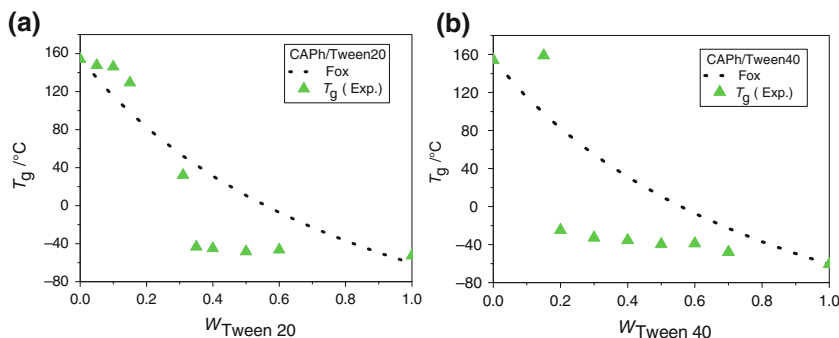
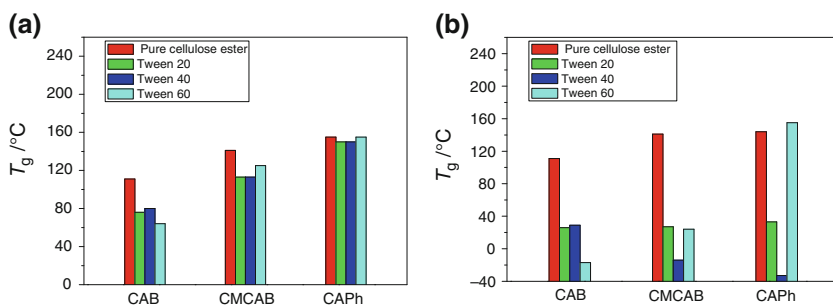


Fig. 6 Effect of the size of the hydrophobic chain of surfactant on T_g of cellulose esters in polymer/surfactant mixtures. Graphically corresponds to the glass transition temperature (T_g) of CAB, CMCAB, and CAPH obtained with $W_{\text{surfactant}} =$ **a** 0.10 and **b** 0.30



composition range only one T_g was observed, indicating miscibility between CAPH and Tween 20 or Tween 40, the most plausible explanation for this behavior is the stiffness of CAPH chains. The presence of phthalate group along the chain surely increases the persistence length and, therefore,

at $W < 0.15$ plasticizer effect in chain mobility (decrease in T_g) is achieved only at a marginal level. The abrupt decrease in T_g values might result from the large free volume of CAPH caused by the bulky phthalate groups. Once, the chains become more flexible, the Tween 20 or

Tween 40 molecules occupy the large free volume, and act as molecular lubricants reducing substantially the intermolecular friction.

The amount of plasticizer added to polymers, depends to a large extent upon the empirical results and final applications [22]. In order to understand the effect of surfactants and alkyl chain length on the T_g values, two compositions were chosen, namely, $W = 0.10$ and 0.30 , Fig. 6a, b, respectively. In the former, the experimental T_g values fitted Fox equation ($\Delta H_{\text{mix}} \sim 0$), whereas in the latter negative deviations were observed ($\Delta H_{\text{mix}} < 0$). The number of carbon atoms in the alkyl chains was 12, 16 and 18, for Tween 20, Tween 40, and Tween 60, respectively [23]. In Fig. 6a, one notices that the surfactants alkyl chain length has practically no effect on the T_g values, and in comparison with the T_g of pure cellulose esters, the decrease in the T_g values was small due to the small content of surfactant in the mixture, as predicted by Fox equation. Nevertheless, in the case of mixtures with negative deviations (Fig. 6b), no general trend could be drawn, instead each system presented a particular tendency. For mixtures composed of CAB and surfactants, T_g values tend to decrease with increasing surfactant alkyl chain length (Fig. 6b). The same tendency was observed for mixtures of CMCAB or CAPH and Tween 20 or Tween 40, and corroborate with the literature report [24]. However, in the presence of Tween 60, the longest alkyl chain of all the three surfactants, the mixtures with CMCAB presented T_g values similar to that in the presence of Tween 20, and with CAPH was completely immiscible. Such anomalous behavior might be due to the different structures of surfactants in the mixtures (see discussion about Fig. 3).

Conclusions

Sorbitan-based surfactants caused plasticization of CAB, CMCAB, and CAPH. The level of plasticization varied with the weight fraction (W) of surfactant in the mixture. In general, for $0 < W < 0.10$ the mixtures presented “ideal” behavior, and experimental T_g values agreed with those predicted with Fox equation and for larger W values the experimental T_g values presented negative deviations, due to H bonding between surfactant polar head and cellulose ester polar groups (carboxylic acid and carbonyl groups). The experimental T_g values decreased with increasing surfactant alkyl chain length in mixtures composed of cellulose ester and Tween 20 or Tween 40. These findings show the application of biocompatible sorbitan-based surfactants to plasticize cellulose esters in a controlled way, so that the plasticizer molecular characteristics and its content in the mixture can be chosen according to the final application.

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