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Lienhard et al.¹ report that the difference between the molar excess mixing entropies of supercooled 3- and 4-component liquids, ΔS̃_{mix}^̃, and glasses, ΔS̃_{mix}^g, might not be zero at the glass transition temperature, T_g. The authors (i) measure the T_g and heat capacity change ΔC_p of bulk and emulsified 2-, 3-, and 4-component solutions using differential scanning calorimetry (DSC) and (ii) calculate the T_g of 3- and 4-component solutions using two approaches from Refs. 8 and 28 cited in Ref. 1. The difference between the calculated and measured T_g's is accounted for by ∆S̃_{mix}^̃-∆S̃_{mix}^g ≠ 0.¹ However, although the authors promise “Experimental evidence…” they do not present thermograms from which their data are extracted. Neither do they give sufficient information about the materials and experimental procedure used. This complicates reproduction of their results and verification of the validity of the conclusion on entropy excess discontinuity, which essentially states that the glass transition is a first order transition, a notion which goes against the current view about the materials and experimental procedure used.

We measured bulk (∼5.5 mg) and emulsified (∼20-30 mg) CA/H₂O solutions of a concentration up to ∼63.5 wt.% CA between 278 and 133 K using Mettler Toledo DSC 822. We employed an emulsification procedure and a matrix of 77 wt.% mineral-oil⁴ + 23 wt.% lanolin (thereafter the ML-matrix) similar to that used in Ref. 1 in order to reproduce the results of Lienhard et al.. We also used a matrix of 80 wt.% halocarbon-oil + 20 wt.% lanolin, (HL-matrix),⁵,⁶ which produces a straight baseline between 278 and 133 K² and therefore does not perturb the T_g and ΔC_p of emulsified solutions. The droplet diameter in emulsions was ∼0.5–30 μm. More information about our measurement technique is given elsewhere.⁵,⁶ We employed a cooling/warming rate (3 K/min) lower than the 10 K/min used in Ref. 1. Earlier we showed⁵,⁶ that the T_g of a freeze-concentrated solution (FCS) observed at 3 K/min is similar to that observed at the atmospheric temperature change of ∼2 K. However, it is unclear whether this is the case for 10 K/min (600 K/h) used in Ref. 1. The fact that our ice melting temperatures, T_m's, are similar to those reported in Ref. 1 indicates that solution concentrations are similar in both studies. The origins of the inconsistencies between our and Lienhard et al.’s results are discussed below.

(i) ML-matrix or HL-matrix: Fig. 1(a) demonstrates that the ML-matrix vitrifies at T_g^ML ≈ 176.3 K. The T_g^ML is similar to the T_g ≈ 176.5 K of 55 wt.% CA droplets embedded into the ML- and HL-matrix, (Figs. 1(a) and 1(b)), and the T_g ≈ 176.6 K of 55 wt.% CA reported in Ref. 1. This similarity indicates that: (a) there is no effect of the ML-matrix on T_g for the case T_g ≈ T_g^ML, (b) the mineral oil used in this work and Ref. 1 is the same (see Ref. 4). However, the ML-matrix perturbs the ΔC_p of 55 wt.% CA droplets because it includes the ΔC_p^ML of the ML-matrix which is about twice as large as the ΔC_p of droplets. Further, the 60 wt.% CA thermogram demonstrates that the ML-matrix perturbs T_g's which are in the vicinity of the T_g^ML. The perturbed T_g ≈ 187 K is ∼7 K warmer than the unperturbed T_g ≈ 180 K of 60 wt.% CA droplets in the HL-matrix, Fig. 1(b). Our bulk 60 wt.% CA also produces T_g≈180 K (not displayed) which is ∼3 K colder than that of 60.1 wt.% CA in Ref. 1. Thus, the ML-matrix perturbs ΔC_p when T_g ≈ T_g^ML and T_g is in the vicinity of the T_g^ML.

(ii) Assignment of T_g': As diluted solutions are cooled, the maximum freeze concentration, C_g', and, consequently, the glass transition temperature of the maximally FCS, T_g', are constant and independent of the initial solution concentration¹,⁶ and can be reached at an infinitely slow cooling rate.⁸ In Ref. 1, the authors report only about the T_g = 214.3 K and T_g = 218.8 K of emulsified 20.4 and 50.1 wt.% CA.¹ However, the fact that these temperatures differ from each other by 4.5 K and the experimental accuracy is ±0.9 K¹ suggests that they are not true T_g'. This is confirmed by our thermograms displayed in Fig. 1(c) which show that only 20 wt.% CA droplets in the HL-matrix produce a subtle glass transition at ∼206 K. The thermogram of 20 wt.% droplets in the ML-matrix shows no indication of a glass transition. 50 wt.% droplets embedded in both ML- and HL-matrixes also do not produce a glass transition but instead a double exothermic event at ∼206 and 218 K which is not mentioned in Ref. 1. Thus, in contrast to what is
stated in Ref. 1, the value of $T'_g$ cannot be derived from emulsion experiments.

Yet, $T'_g$ is derived from bulk experiments which reveal two thermal events, $T_1 \approx 204$ K and $T_2 \approx 218$ K, Fig. 1(d). The $T_1$ is close to the intersection point of the extrapolated $T_m$- and $T_n$-curves which define the quasi-invariant point, $(C_{p}'T'_g)^{3,8}$. Our $T_m$-s are similar to those reported in Ref. 1 only for concentrations up to 55 wt. % CA but colder by $\sim 2$ and $5$ K for 60 and 63 wt. % CA (not shown). Also our $T_g$ of 63 wt. % CA is $\sim 3$ K colder than that in Ref. 1. Using our $T_m$- and $T_g$-values, the extrapolated $T_m$- and $T_g$-curves intersect between $\sim 203$ and $205$ K that is similar to $T'_g \approx 205$ K reported in Ref. 9.

(iii) Experimental procedure: The authors report the $T_g$s of bulk 70.2 and 75 wt. % CA and emulsified 70 and 75 wt. % MA (malonic acid). The solubility limit of CA is $\sim 62$ wt. % at 298 K$^{10}$ and that of MA is not known. The authors provide neither information on the temperature at which the concentrated solutions were prepared and then loaded into the calorimeter, nor on the temperature region of the measurements. Our experiments with such solutions prepared at $\sim 85^\circ$C show that MA crystallizes during emulsion preparation, (Fig. 1(e)), and CA crystallizes upon cooling both at 3 and 10 K/min (not shown). We therefore believe that the $T_g$s reported in Ref. 1 are perturbed by the crystallization of solute (not only CA). The MA-crystallization together with the ML-matrix (see above) can be responsible for the non-monotonous behavior of the $T_g$s of MA/H$_2$O in Ref. 1.

(iv) Uncertainty of $\Delta S_{mix} - \Delta S_{mix}^1$: The authors do not present its value. Their Eq. (12) shows that the values and uncertainty of $\Delta S_{mix}^1 - \Delta S_{mix}^1$ depend mainly on the $\Delta C_p^W = c_1^{11}$-$c_1^{8}$ of water and weakly depend on the scattering of experimental $T_g$s. From extrapolation in a dilution series in Fig. 3(c) in Ref. 1 they determine a $\Delta C_p^W$ of 34 J mol$^{-1}$ K$^{-1}$, which is much larger than the $\Delta C_p^W$ of $\sim 0.7$ J mol$^{-1}$ K$^{-1}$ measured directly on glassy water samples.$^{11}$ Also when using the approach of extrapolating to zero concentration, we arrive at a much lower value of the $\Delta C_p^W$ of 18 J mol$^{-1}$ K$^{-1}$ from the data in Fig. 3(c) in Ref. 1. Using this latter value instead of 34 J mol$^{-1}$ K$^{-1}$ we find a deviation of 7.4 J mol$^{-1}$ K$^{-1}$ from the $\Delta S_{mix}^1$-$\Delta S_{mix}^1 \approx 4 J$ mol$^{-1}$ K$^{-1}$ reported for 60.1 wt. % CA in Fig. 4 in Ref. 1 and an even a much larger deviation when using the directly measured $\Delta C_p^W$.

Based on this uncertainty in $\Delta C_p^W$ it cannot be decided whether the $\Delta S_{mix}^1$-$\Delta S_{mix}^1$ difference is zero or different from zero using the approach presented by Lienhard et al.

In conclusion, the material presented in this Comment shows that $T_g$ and $c_c$-$c_f$ data reported in Ref. 1 for the CA/H$_2$O are not persuasive, which casts doubt on the validity of their estimation of $\Delta S_{mix}^1$-$\Delta S_{mix}^1$. The thermograms presented here do not require evocation of a discontinuity in entropy at the glass transition, but are in agreement with the glass transition representing a continuous slow-down of dynamics and continuous change in entropy.

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4Lienhard et al.$^{1}$ did not report about the mineral-oil used. T. Koop, a co-author of Ref. 8 in Ref. 1, informed us that they used a mineral-oil with CAS number 8042-47-5 (Aldrich). Since D. Lienhard belongs to the same scientific group, we believe that he used the same mineral oil.