

Figure S1: Dependence of melting point on degree of unsaturation in amphiphiles with C18 hydrocarbon chains. Comparison of monoethanolamide amphiphiles to fatty acids, ureas, amides, alcohols and monoglycerides. The amides and ureas have the highest melting points, which tend to level out with increasing degree of unsaturation. The fatty acids and alcohols, have much lower melting points but also tend to level out with increasing degree of unsaturation. The monoethanolamides like the monoglycerides display an almost linear dependence on degree of unsaturation.<sup>20, 40-44</sup>

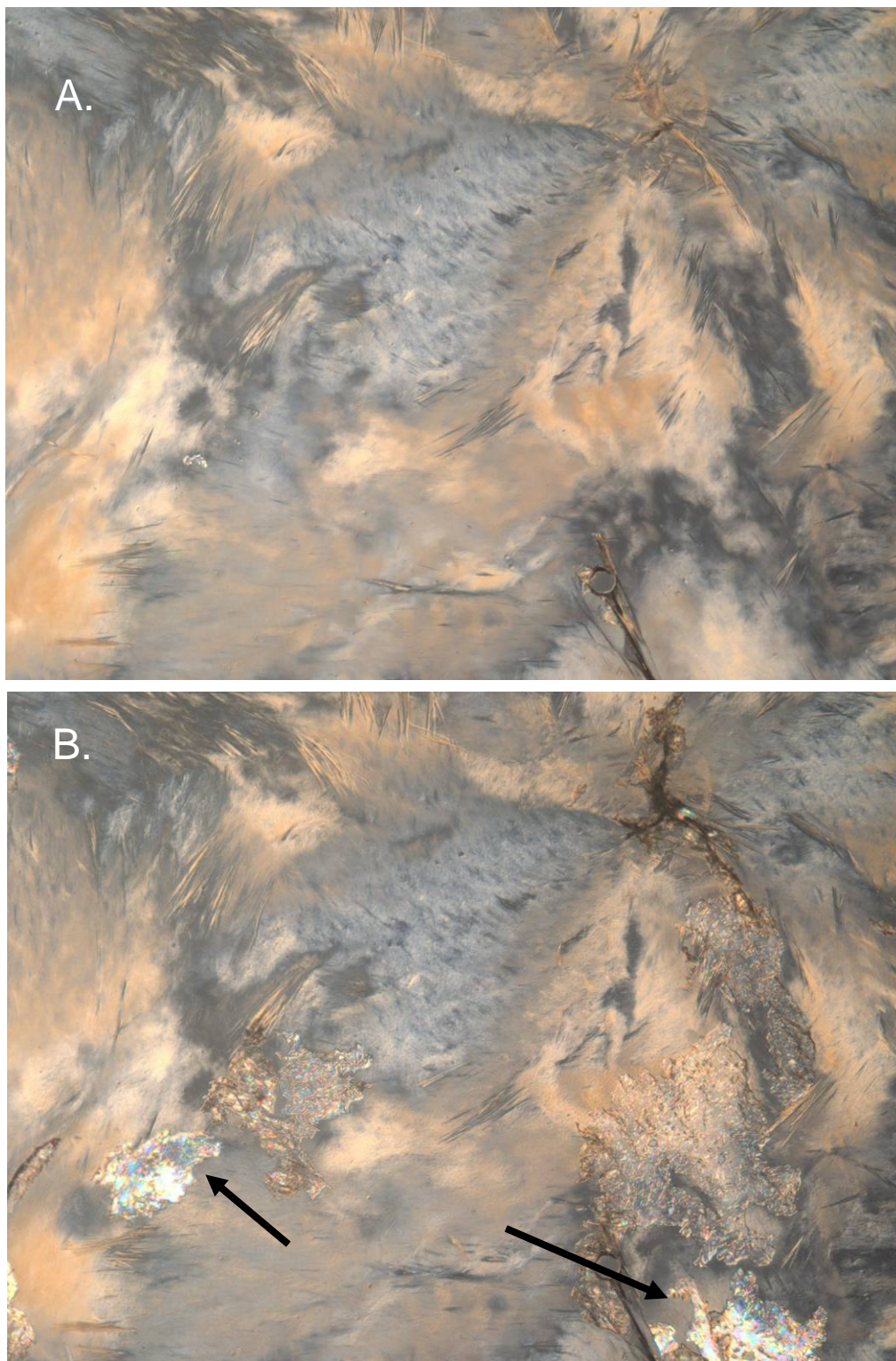


Figure S2: Optical microscopy of neat oleoyl ethanolamide. A. Image acquired at 25°C, B. Image acquired from same position at 36°C. A polymorphic transition visible in the crystal structure occurs in parts of the amphiphile (indicated by arrows). This transition occurs at a similar temperature to one of the pre-transitions indicated by DSC.

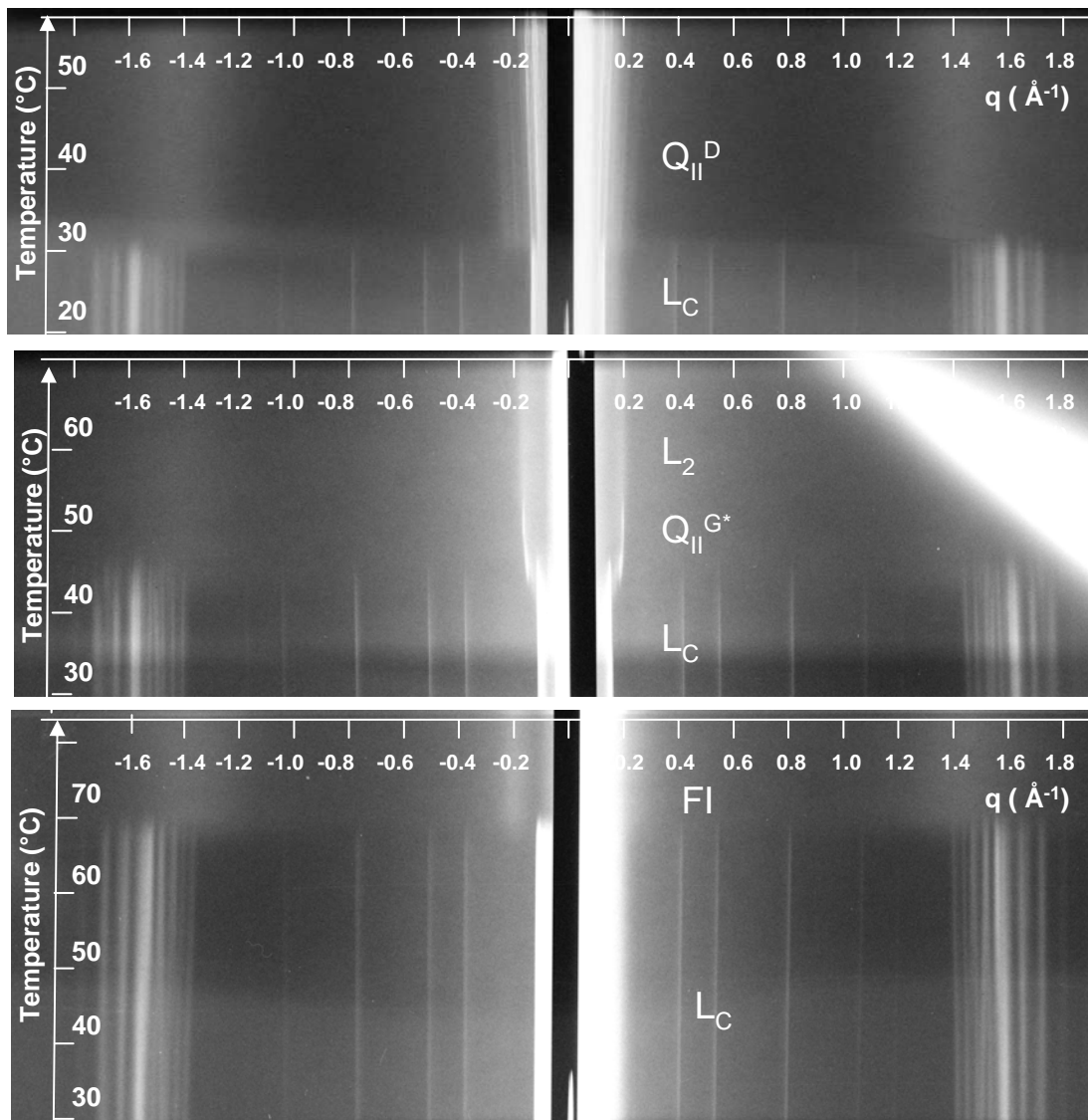


Figure S3: Representative temperature scans of diffraction data for the oleoyl ethanolamide – water system with:

(top) 35 wt% water. The temperature was scanned from 20 to 60°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c - Q_{II}^D$ .

(middle) 10wt% water. The temperature was scanned from 30 to 70°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c - Q_{II}^{G*} - L_2$ .

(bottom) 0wt% water. The temperature was scanned from 30 to 85°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c (1) - FI$ .

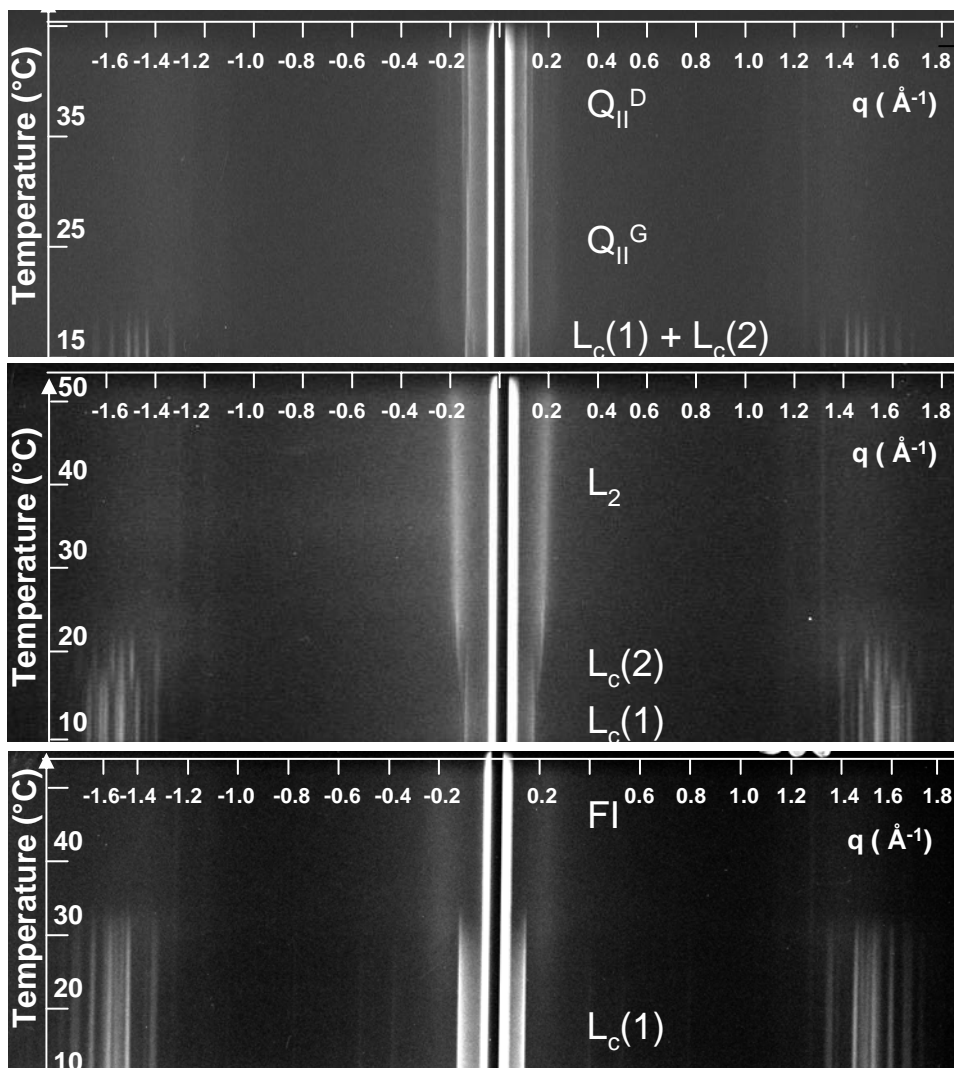


Figure S4: Representative temperature scans of diffraction data for the linoleoyl ethanolamide – water system with:

(top) 40 wt% water. The temperature was scanned from 15 to 45°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c(1) + L_c(2) - Q_{II}^G - Q_{II}^D$ .

(middle) 10wt% water. The temperature was scanned from 10 to 55°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c(1) - L_c(2) - L_2$ .

(bottom) 0wt% water. The temperature was scanned from 10 to 55°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c(1) - FI$ .

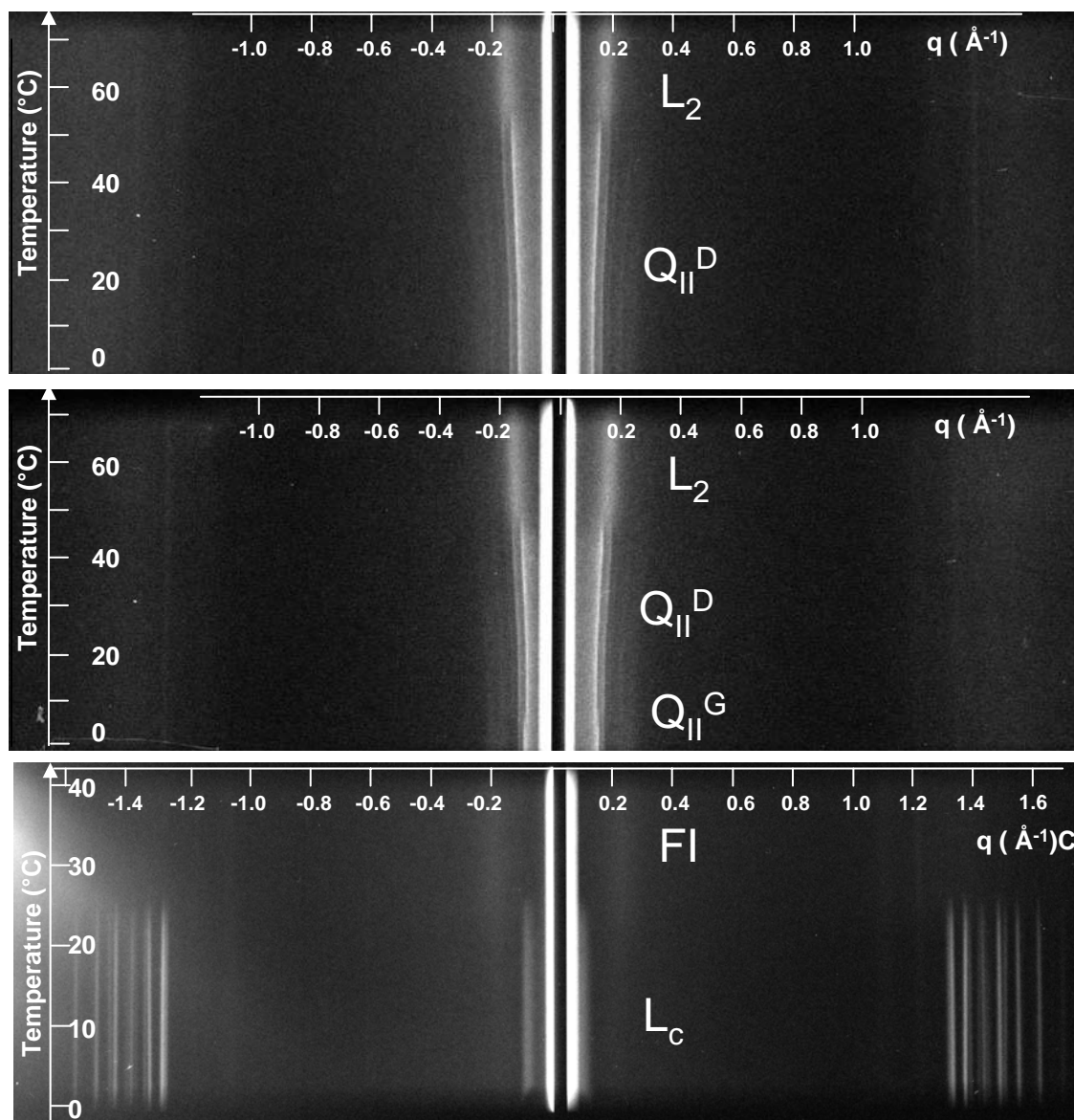


Figure S5: Representative temperature scans of diffraction data for the linolenoyl ethanolamide – water system with:

(top) 61 wt% water. The temperature was scanned from 1 to 71°C at a rate of 4°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $Q_{II}^D - L_2$ .

(middle) 53wt% water. The temperature was scanned from 1 to 71°C at a rate of 4°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $Q_{II}^G - Q_{II}^D - L_2$ .

(bottom) 0wt% water. The temperature was scanned from 0 to 40°C at a rate of 2°C/hr with a motor speed of 0.03mm/min. The phase sequence observed is  $L_c - FI$ .



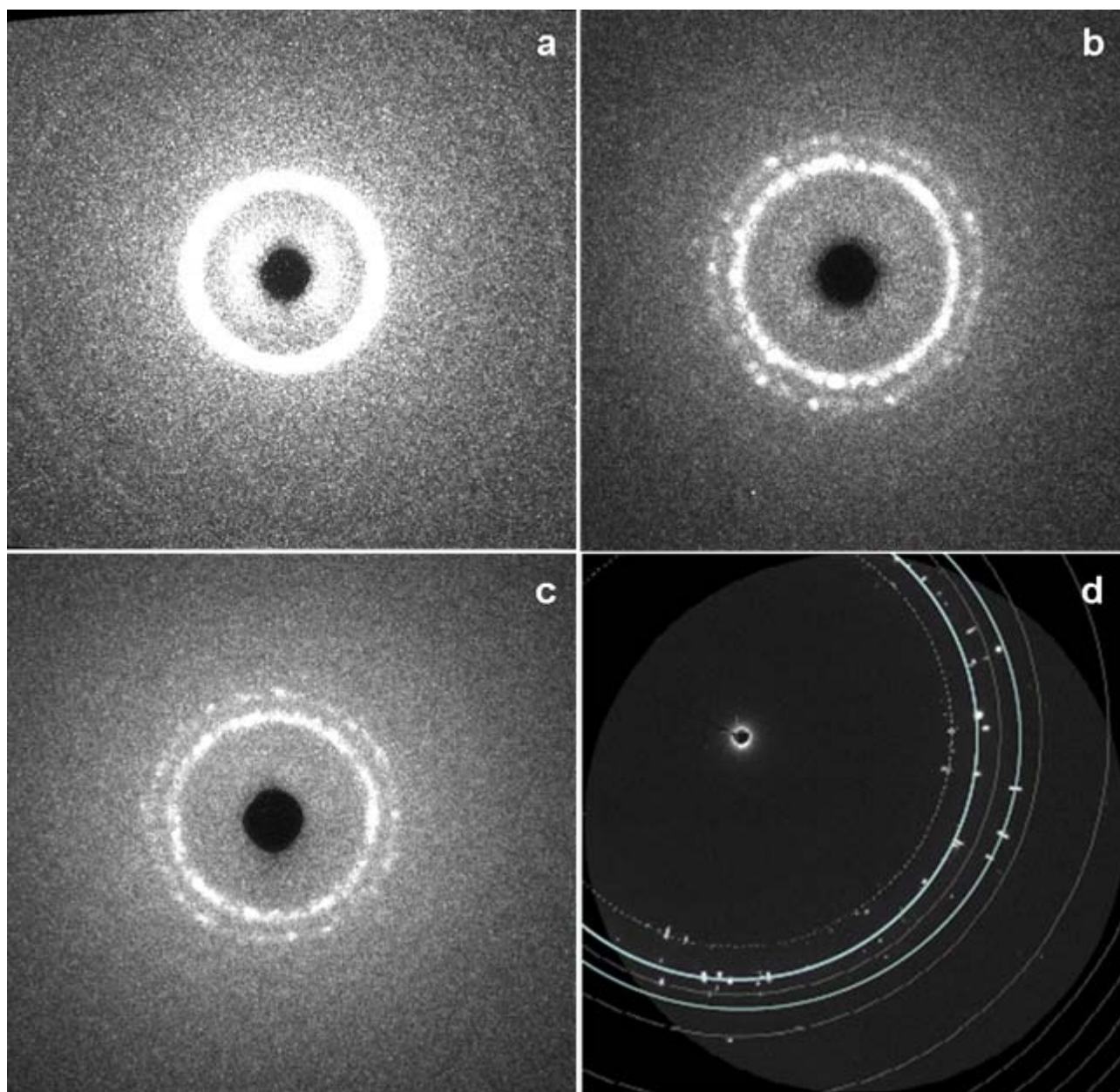


Figure S6: Representative small-angle x-ray diffraction patterns for a) oleoyl ethanolamide with 50wt% water at 25°C. The first and third order reflections of an Lc phase are seen b) oleoyl ethanolamide with 50wt% water at 45°C. The  $\sqrt{2}$ ,  $\sqrt{3}$ , and  $\sqrt{6}$  reflections of a  $Q_{II}^D$  phase are seen c) linoleoyl ethanolamide with 50wt% water at 45°C. The  $\sqrt{2}$ ,  $\sqrt{3}$ , and  $\sqrt{6}$  reflections of a  $Q_{II}^D$  phase are seen and d) co-existing  $Q_{II}^D$  and  $Q_{II}^G$  phases of linolenoyl ethanolamide with 35wt% water at 23°C. The  $\sqrt{2}$ ,  $\sqrt{3}$ ,  $\sqrt{4}$  and  $\sqrt{6}$  reflections of a  $Q_{II}^D$  phase and  $\sqrt{6}$  and  $\sqrt{8}$  reflections of a  $Q_{II}^G$  phase are seen.

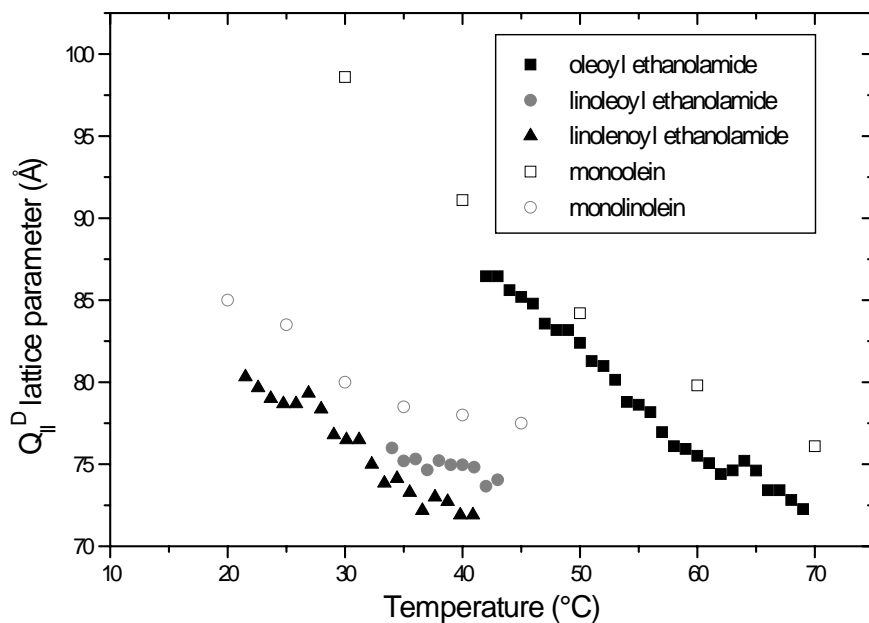


Figure S7: The lattice parameter of the  $Q_{II}^D$  phases of oleoyl ethanolamide, linoleoyl ethanolamide, linolenoyl ethanolamide, monoolein<sup>29</sup> and monolinolein<sup>25</sup> as a function of temperature are shown. Each sample had a water content of 40wt%. Note that whilst the monoolein data were extracted from tabulated data, the monolinolein data were read off a graph.