Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for:

Amorphous Phase State Diagrams and Viscosity of Ternary Aqueous Organic/Organic and Inorganic/Organic Mixtures

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S1. Water activity models.

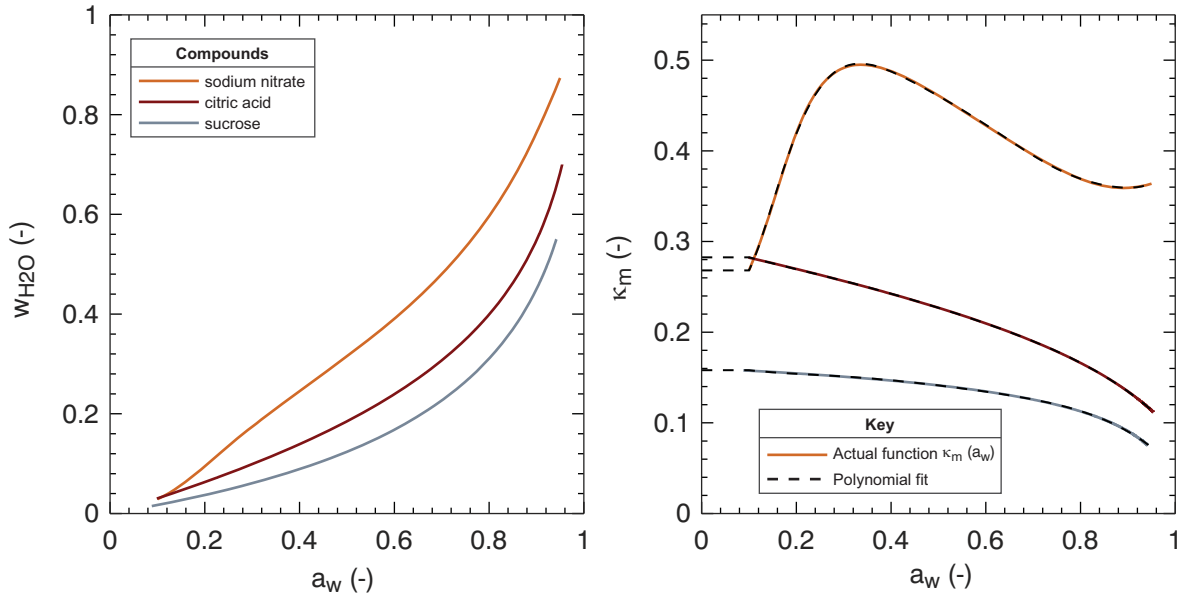

Figure S1.1 Water mass fraction (left) and hygroscopicity parameter (right) has a function of water activity for pure $NaNO_3$, citric acid, and sucrose. Dashed line corresponds to a polynomial representation of $\kappa_m(a_w)$.

Water content for $NaNO_3$, sucrose, citric acid and sodium nitrate are modeled as follows. First the relationship between a_w and w_{H2O} is obtained from literature models or parameterization. Water mass fractions for $NaNO_3$ are obtained from E-AIM Model III,[1] citric acid from the parameterization given in the supplement of Berkemeier et al.[2] and sucrose from the parameterization given by Zobrist et al. (Table A4).[3] The relationship between a_w and w_{H2O} was used to compute the mass based hygrosocpicity parameter κ_m via

$$\kappa_m = \left(\frac{1}{a_w} - 1\right)\left(\frac{w_{H2O}}{1 - w_{H2O}}\right)$$

Finally, $\kappa_m(a_w)$ is modeled using a polynomial with n+1 coefficients

$$\kappa_m(a_w) = \begin{cases} c_1 a_w^n + c_2 a_w^{n-1} + \cdots + c_n a_w + c_{n+1} & \text{for } [0.1 > a_w > 0.95] \\ \kappa_m(a_w = 0.1) & \text{for } a_w < 0.1 \end{cases}$$

Coefficients are provided in Table S1.1.

Table S1.1 Polynomial coefficients for binary aqueous-solute water activity models.

Mixtures	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9
$NaNO_3$	238.72	-1109.31	2173.98	-2327.82	1471.31	-549.24	111.93	-9.71	0.54
Citric acid	-0.56	1.19	-1.03	0.38	-0.19	0.30			
Sucrose	-1.00	2.21	-1.89	0.72	-0.15	0.17			

S.2. Surface tension models.

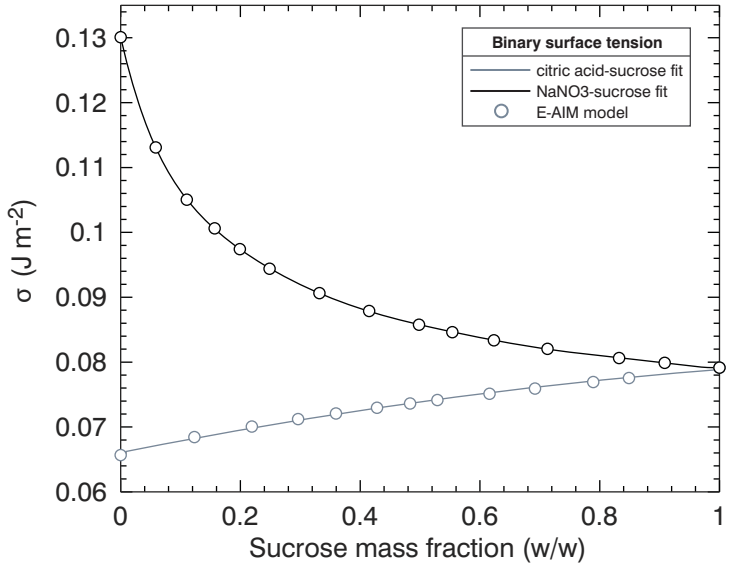

Figure 2.1 Binary surface tension for as a function of sucrose weight fraction for mixtures at a_w = 0.1 at 25 °C. Fitting represent polynomial fits presented in Table S2.1.

Surface tension was modeled using E-AIM Model III,[1] assuming a_w = 0.1. AIM predicts the surface tension for NaNO3.[1] Values for pure sucrose and citric acid were entered as 0.08 J m-2[4] and 0.065 J m^{-2} based on the value for concentrated solutions. E-AIM model calculations were performed for a series of sucrose weight fractions. Results were parameterized as using polynomial with n+1 coefficients

$$\sigma(w_s) = c_1 w_s^n + c_2 w_s^{n-1} + \cdots + c_n w_s + c_{n+1}$$

The relationship is only a weak function of aw for a_w < 0.5 and was used to define surface tension to infer viscosity from the mobility diameter data.

Coefficients are provided in Table S2.1.

Table S2.1 Polynomial coefficients for water binary surface tension models.

Mixtures	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9
$NaNO_3$	5.538	-24.627	45.937	-46.783	28.431	-10.656	2.515	-0.406	0.130
Citric acid	-0.0056	0.0184	0.0661						

S.3. HOT measurements

Table S3.1 Tabulated data points in Figure 4 of the main manuscript for sucrose-citric acid mixture weighted 60 % and 40 % by mass of each solute.

RH / %	log(viscosity) / Pa s	RH / %	log(viscosity) / Pa s
95	-2.215 ± 0.35	50	0.335 ± 0.72
83	-1.795 ± 0.01	40	2.523 ± 0.01
70	-0.617 ± 0.04	35	3.389 ± 0.19
60	0.0411 ± 0.18	35	3.251 ± 0.10
52	0.201 ± 0.65	26	4.011 ± 0.18

Table S3.2 Tabulated parametrisation of solution viscosity with associated uncertainties as shown in Figure 4 of main manuscript.

System	Parameterization
Aqueous sucrose-citric acid	$\log \eta = (8.02 \pm 1.79) + (-0.1556 \pm 0.029) \times RH + (4.52 \pm 1.10) \times 10^{-4} \times RH^2$
Aqueous citric acid	$\log \eta = (6.33 \pm 1.51) + (-0.156 \pm 0.024) \times RH + (6.28 \pm 0.842) \times 10^{-4} \times RH^2$
Aqueous sucrose	$\log \eta = (15.92 \pm 1.62) - (0.276 \pm 0.027) \times RH + (8.68 \pm 1.09) \times 10^{-4} \times RH^2$

Tabulated data is provided for the HOT data points underlying Figure 7, the measurements corresponding to 100 % citric acid and 60:40 Sucrose/Citric Acid correspond to parametrisations based on measurements as shown in Figure 4. Errors provided for these measurements are a result of the uncertainty associated with the parametrisation at a viscosity of ~5×10^6 Pa·s. The data underlying the binary aqueous-citric acid viscosity corresponds to work by Song et al.[5] The 60:40 Sucrose/Citric Acid viscosity and RH relationship was measured in this work. The remaining values of RH_R at sucrose and citric acid compositions of 80:20, 40:60 and 20:80 were also measured in this work. In these examples, coalescence measurements of viscosity were performed using the HOT for viscosities approaching ~5×10^6 Pa·s. Three viscosity measurements were performed and averaged to provide a final RH_r for comparison with the DCIC measurements.

Table S3.3 Tabulated RH_r for aqueous droplets containing mixtures of sucrose and citric acid from HOT measurements, at 22 °C (plotted in Figure 7 of the main manuscript).

Composition Suc/Cit	RH_r / %	± Error in RH_r / %	Log_{10} (viscosity)	±Error in Temperature /ºC
80:20	25.5	2	6.27474	2.5
60:40	8.8	8	6.6989	2.5
40:60	14	2	6.22607	2.5
20:80	9.5	2	6.15551	2.5
0:100[5]	6.22	2.4	6.6989	2.5

S.4. DCIC Measurements

Table S4.1 Tabulated values of sodium nitrate/sucrose DCIC temperature scans taken in this work. Where, w is the mass % of sucrose, T_c is the temperature where the viscosity is exactly 5×10^6 Pa·s, T_g is the glass transition temperature, T_{sys} is the system temperature, and σ is the surface tension of the mixture. T_r and k are as defined in Eq. (1) of the main text, ΔT is the 95% confidence interval of T_r. RH is the measured RH during the scan, ΔRH is the standard deviation of the during the scan, A, B, and T_0 are the VFT fit parameters as defined in Eq. (6) of the main text.

					Equation 2					Equation 7		
w [%]	T_c [°C]	T_g [°C]	T_{sys} [°C]	σ [J m^{-2}]	T_r [°C]	k [-]	ΔT [°C]	RH [%]	ΔRH [%]	A [-]	B [-]	T_0 [K]
90	80.0	67.4	36	0.082	80.3	0.65	1.1	0.4	0.1	0.72	160.77	326.33
70	66.9	45.0	20.9	0.084	67.2	0.38	2.4	1.86	1.85	0.70	280.10	293.35
60	61.8	41.1	32.7	0.081	62.0	0.40	0.8	0.78	0.31	0.79	257.96	291.29
80	74.8	59.6	32.0	0.082	75.1	0.54	1.5	0.93	0.75	0.70	195.25	315.48
70	68.6	48.9	33.4	0.080	68.8	0.41	1.1	0.52	0.25	0.84	242.81	300.33
60	62.4	47.6	36.2	0.084	62.5	0.56	0.9	-	-	0.72	188.18	304.11
50	54.6	32.9	37.4	0.086	54.7	0.37	2.0	0.76	0.00	1.05	252.13	283.15
55	54.1	33.3	38.1	0.085	54.3	0.38	4.0	0.87	0.15	1.21	232.62	284.95

Table S4.2 Tabulated values of citric acid/sucrose DCIC temperature scans taken in this work. Where, w is the mass % of sucrose, T_c is the temperature where the viscosity is exactly 5×10^6 Pa·s, T_g is the glass transition temperature, T_{sys} is the system temperature, and σ is the surface tension of the mixture. T_r and k are as defined in Eq. (1) of the main text, ΔT is the 95% confidence interval of T_r. RH is the measured RH during the scan, ΔRH is the standard deviation of the during the scan, A, B, and T_0 are the VFT fit parameters as defined in Eq. (6) of the main text. During these specific experiments, the RH sensor was offline.

					Equation 2					Equation 7		
w [%]	T_c [°C]	T_g [°C]	T_{sys} [°C]	σ [J m^{-2}]	T_r [°C]	k [-]	ΔT [°C]	RH [%]	ΔRH [%]	A [-]	B [-]	T_0 [K]
0	32.8	13.0	3.9	0.066	33.8	0.39	0.9	-	-	1.07	230.17	265.17
20	38.3	11.4	3.6	0.070	39.5	0.29	4.3	-	-	1.25	297.94	256.85
40	44.7	33.7	3.9	0.073	45.1	0.74	1.5	-	-	0.70	139.78	294.61
60	52.0	25.2	32.6	0.075	52.7	0.29	2.5	-	-	1.16	302.93	270.45
80	64.3	43.2	31.9	0.077	64.8	0.37	2.1	-	-	1.24	232.92	294.79
90	78.4	52.6	32.8	0.078	79.0	0.30	3.8	-	-	1.29	282.57	299.38

Table S4.3 Tabulated values of citric acid/sucrose DCIC RH scans taken in this work. Here, w is the mass % of sucrose, T is the temperature of the conditioning loop, RH_c is the RH where the viscosity is exactly 5×10^6 Pa·s, T_{sys} is the system temperature, σ is the surface tension of the mixture, RH_r and k are as defined in Eq. (1) of the main text, and ΔRH_r is the 95% confidence interval of the fitted RH_r. The ΔRH_R for the second row is omitted due to non-convergence of the confidence interval routine.

					Equation 2		
w [%]	T [°C]	RH_c [%]	T_{sys} [°C]	σ [J m^{-2}]	RH_r [%]	k [-]	ΔRH_r [%]
80	10.00	39.5	21.7	0.077	39.7	0.91	1.0
0	10.00	6.2	19.0	0.066	7.2	0.40	-
40	10.00	22.0	12.1	0.073	22.5	0.59	1.2
60	10.00	25.3	12.8	0.075	25.8	0.50	1.8
20	10.00	10.7	11.5	0.070	11.0	1.09	1.3
80	10.00	41.0	12.7	0.077	41.0	2.53	4.6
40	0.00	38.0	15.5	0.073	38.3	0.95	0.9
60	0.00	42.3	15.6	0.075	42.4	2.43	0.6
20	0.00	28.8	12.0	0.070	29.0	1.60	0.7
0	0.00	16.0	5.5	0.066	16.5	0.72	1.2

Table S4.4 Tabulated values of sodium nitrate/sucrose DCIC RH scans taken in this work Here, w is the mass % of sucrose, T is the temperature of the conditioning loop, RH_c is the RH where the viscosity is exactly 5×10^6 Pa·s, T_{sys} is the system temperature, σ is the surface tension of the mixture, RH_r and k are as defined in Eq. (1) of the main text, and ΔRH_r is the 95% confidence interval of the fitted RH_r.

					Equation 2		
w [%]	T [°C]	RH_c [%]	T_{sys} [°C]	σ [J m^{-2}]	RH_r [%]	k [-]	ΔRH_r [%]
100	5.2	42.8	20.0	0.079	43.1	0.46	1.7
90	5.0	35.6	19.9	0.080	35.8	0.96	0.7
80	5.0	30.5	19.9	0.081	30.6	1.27	0.9
70	5.0	24.2	20.0	0.082	24.4	1.00	0.5
90	10.0	34.9	19.7	0.080	35.0	1.07	0.4
80	10.0	27.1	18.6	0.081	27.2	1.21	0.4
70	10.0	20.6	20.8	0.082	20.7	1.71	0.5
60	10.0	14.7	20.8	0.084	14.8	0.75	0.7
60	5.0	18.3	21.7	0.084	18.4	1.16	0.6
70	0.0	24.7	12.4	0.082	24.9	0.41	3.0
60	0.0	24.1	12.3	0.084	24.1	1.14	1.4
90	0.0	41.9	12.2	0.080	42.0	3.80	5.6

S.5. References Cited

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