Comparative Effect of Physiological Salts upon Micellization of T1304 and T1307

(Master Thesis)

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Introduction

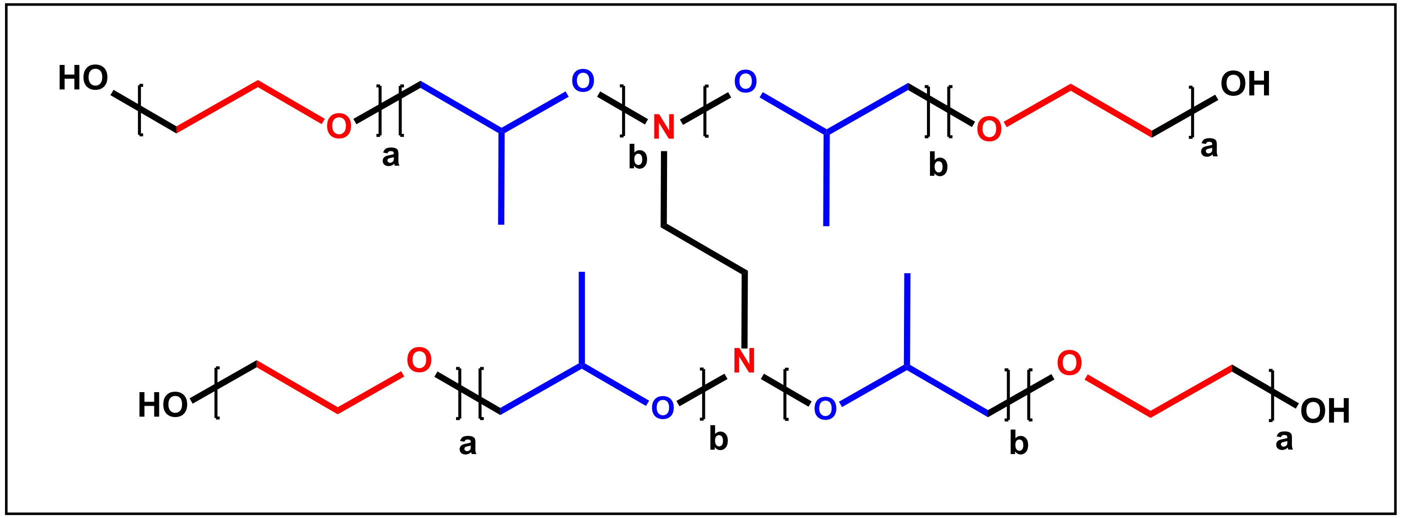


Fig. 1: Chemical structure of Tetronics: T1304, a = 24 and b = 27; T1307, a = 61 and b = 27

- **Dual behaviour -** thermo-responsive and pH-responsive
- **T1304** - micelles at ambient temperature – Hydrophobic / Low CMT/CMC
- **T1307** - unimers, micelles, clusters at ambient temperature – Hydrophilic / High CMT/CMC
- **Additives** - salts help to lower CMT/CMC

CMC = Critical micelle concentration, CMT = Critical micelle temperature

Physiological salts

- **Salts promoting micellization:**
  - Na_2CO_3 and NaH_2PO_4, KH_2PO_4 – maintain pH
  - NaCl - maintain isotonicity and the right balance of body fluid
- **Salts impeding micellization:**

  KI

Salting out effect : $CO_3^{2-} > SO_4^{2-} > H_2PO4^{-} > F^{-} > Cl^{-} > Br^{-} > I^{-}$

$NH^{4+} > Cs^{+} > K^{+} > Na^{+} > Ca^{2+} > Mg^{2+}$

Objectives

- To examine the effect of different physiological salts (NaH_2PO_4, KH_2PO_4, Na_2CO_3, NaCl and KI) on aggregation characteristics of T1304 and T1307.
- To estimate the effect of solution temperature and pH upon micellization characteristics
- To estimate and compare the dependence of micellization parameters (CMC, enthalpic changes, entropy and free energy) of T1304 and T1307 for over salt-type and concentration
- To study the structural characteristics of copolymer aggregates using scattering techniques

Method of preparation

Solution Preparation

1. 2% Aqueous stock solutions of block copolymers were prepared in Millipore water.
2. Different concentrations of salt were added to aqueous solutions of block copolymers namely, Na_2CO_3, NaH_2PO_4, KH_2PO_4, NaCl, and KI.

Characterizations

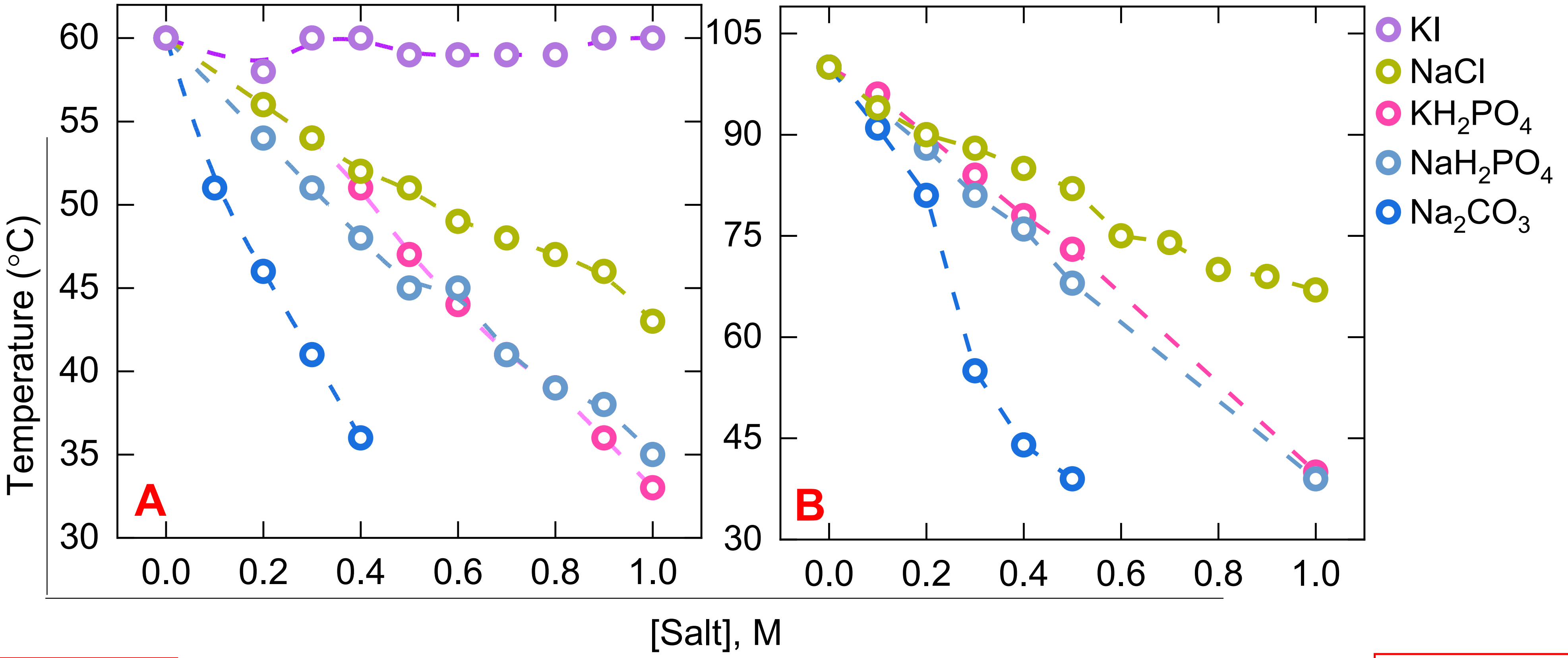
- **Thermodynamic studies** - Cloud point

  Isothermal titration calorimetry

- **Scattering techniques** - Dynamic light scattering

  Small-angle neutron scattering

Cloud point



2%T1304 - 60°C

Order : Na_2CO_3 > NaH_2PO_4 > KH_2PO_4 > NaCl > KI

2%T1307 - >100°C
KI - >100°C

Fig. 1. Changes in the cloud point of T1307 and T1304 at increasing salt concentrations. The concentration of tetronic was fixed at 2%.

ITC analysis

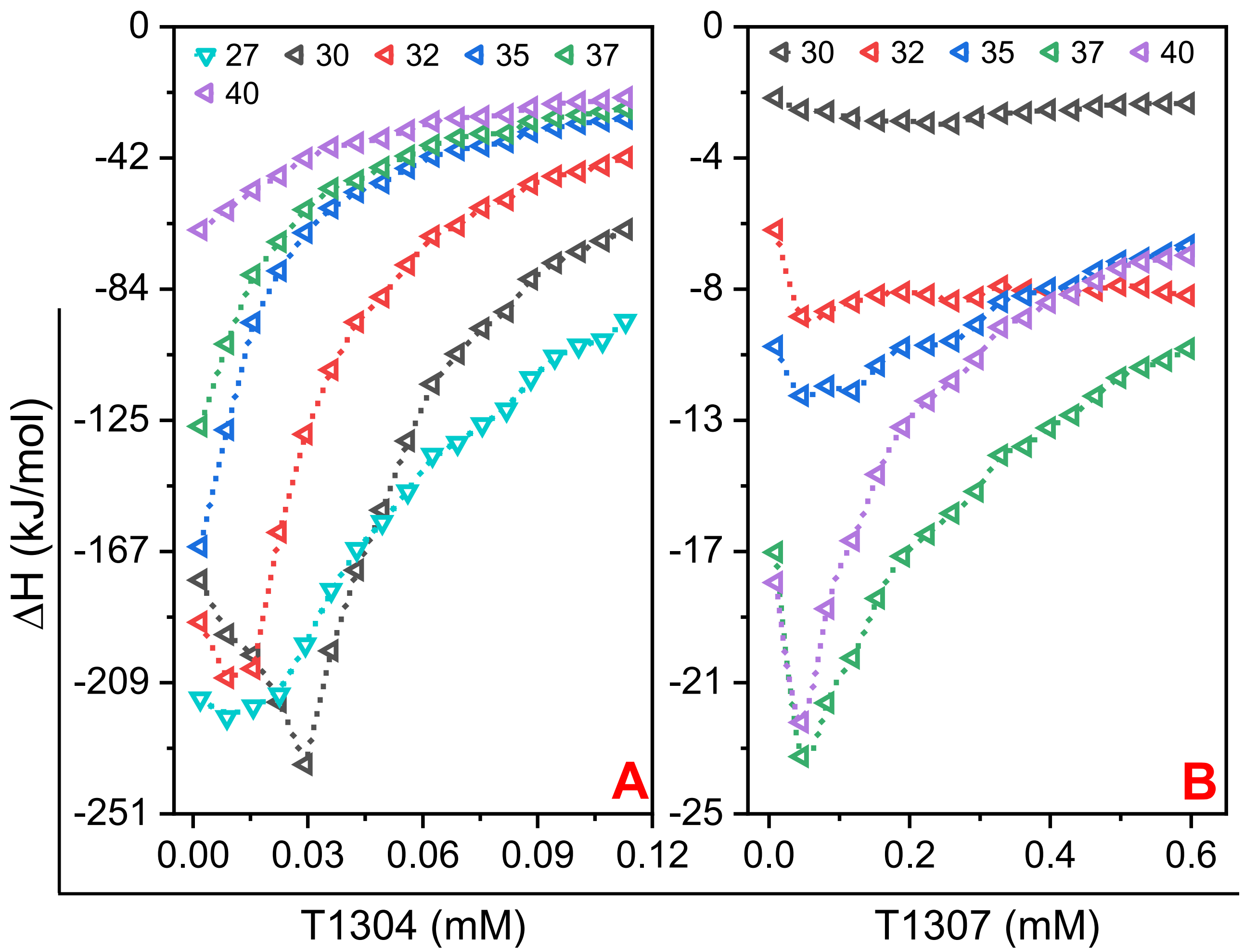


Fig. 2. ITC data of T1307 and T1304 aqueous solution at different temperatures.

ITC analysis

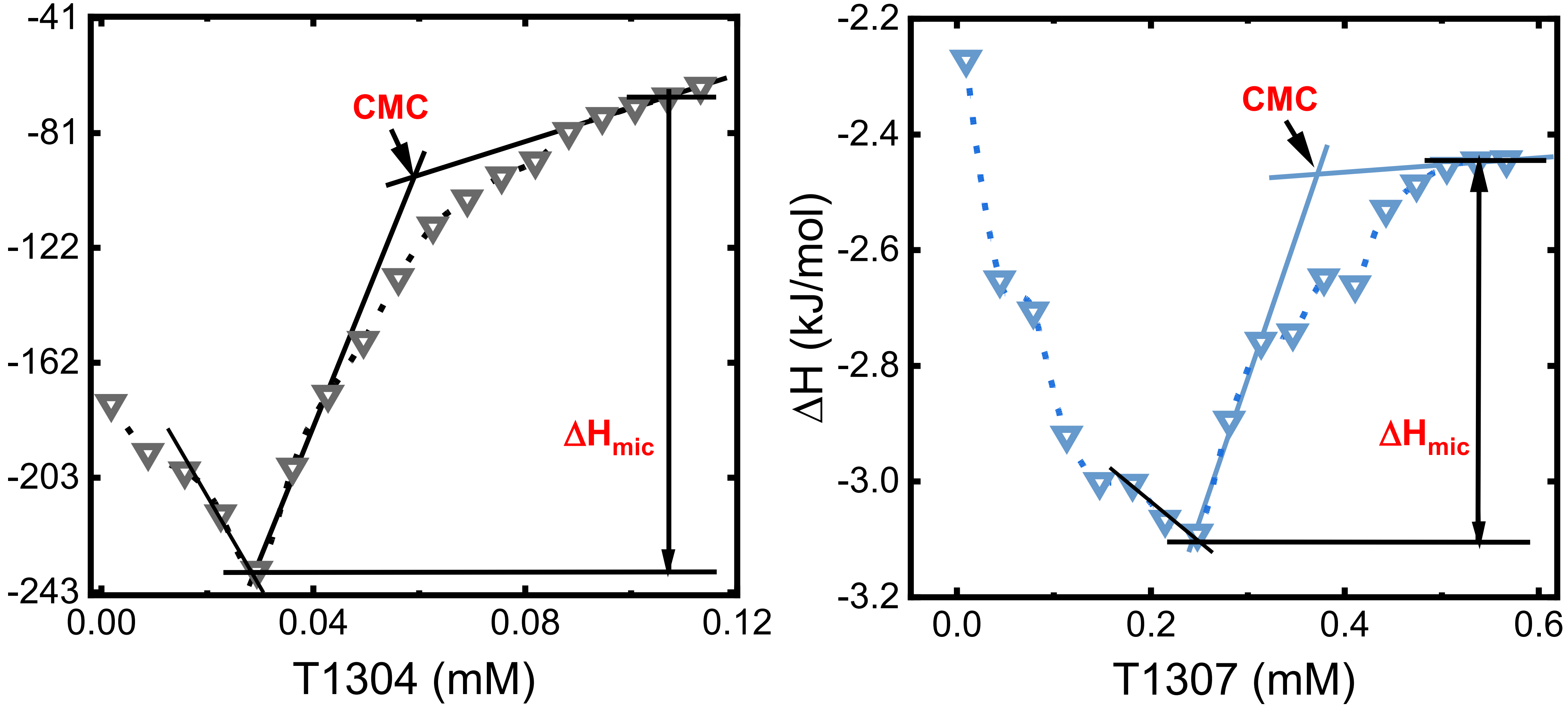
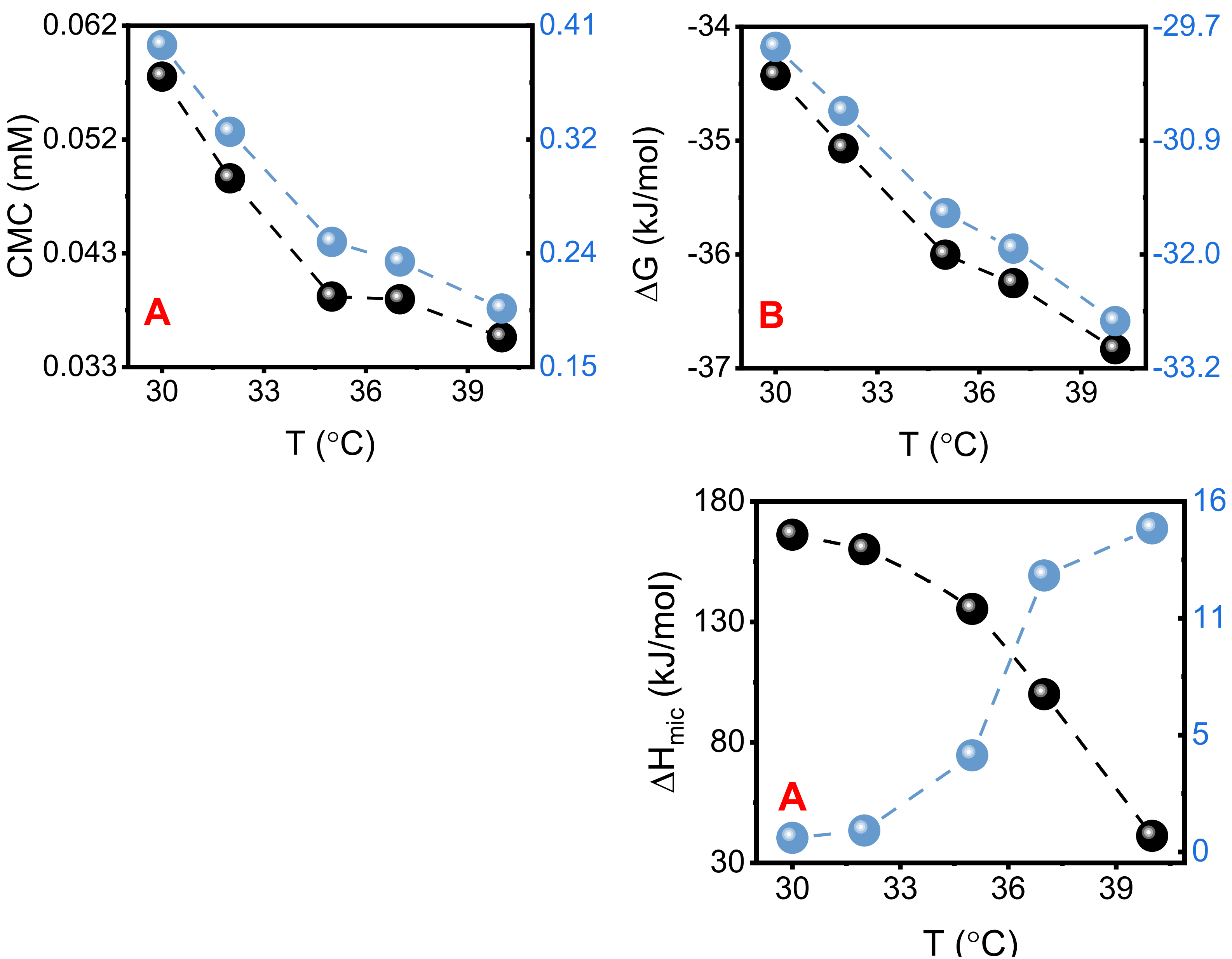


Fig. 3. Determination of CMC of aqueous T1307 and T1304 solution at different temperatures through ITC.



Black - T1304
Blue – T1307

Fig. 4. Micellization free energy, entropy, CMC and enthalpy of Tetronic T1304 and T1307 in water plotted as a function of salt type.

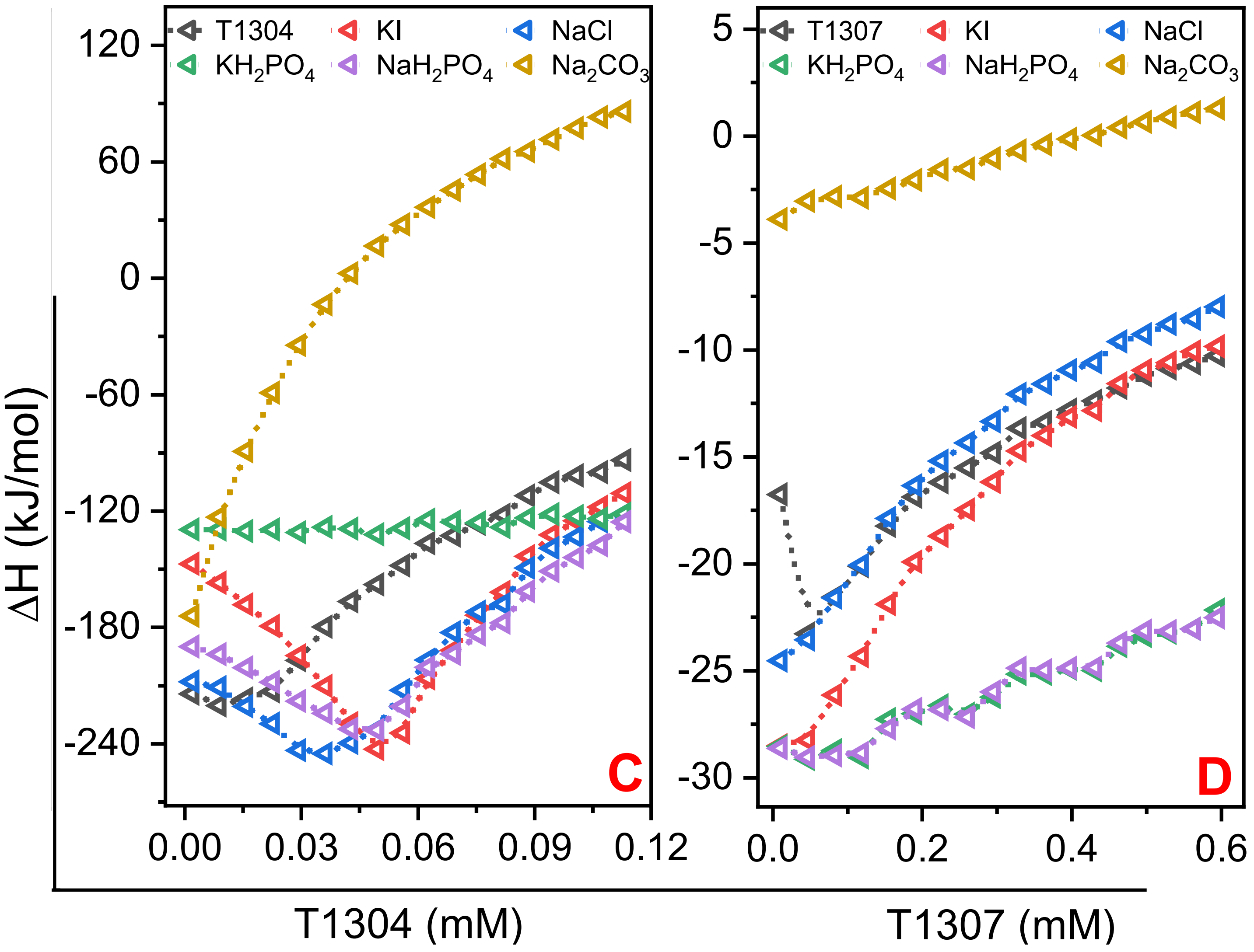
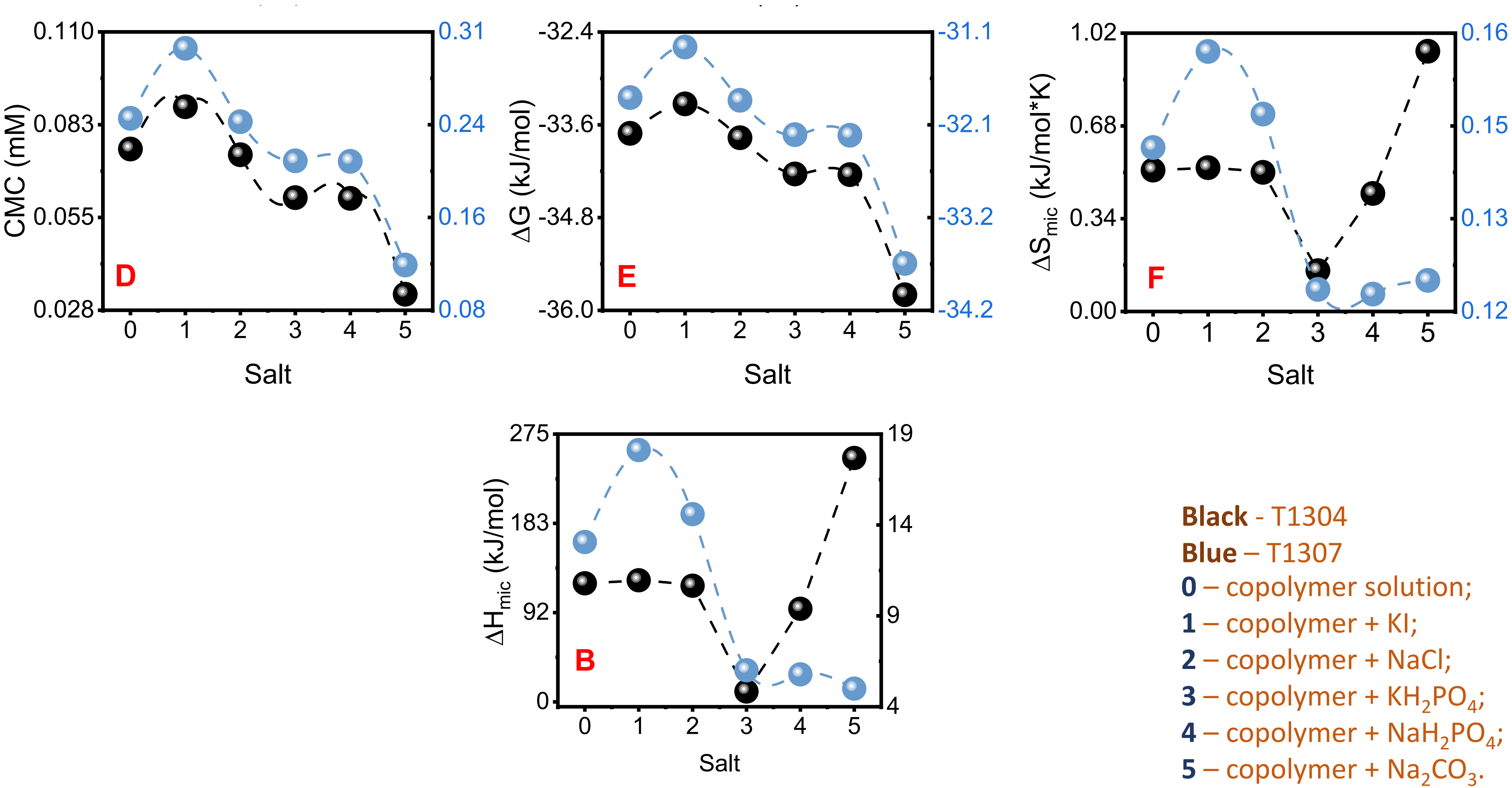


Fig. 5. ITC data of T1307 (27°C) and T1304 (37°C) aqueous solution at different salt type.



Black - T1304

Blue – T1307

0 – copolymer solution;

1 – copolymer + KI;

2 – copolymer + NaCl;

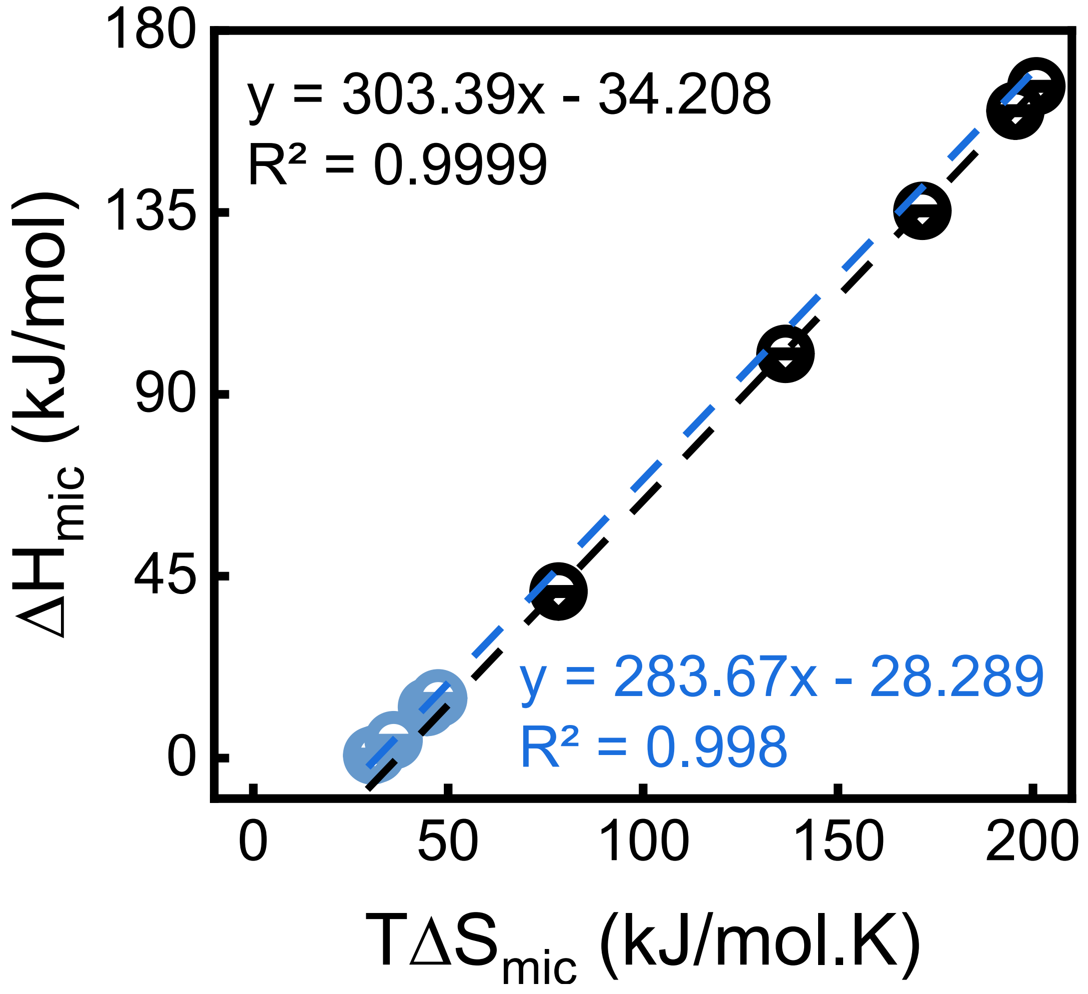
3 – copolymer + KH_2PO_4;

4 – copolymer + NaH_2PO_4;

5 – copolymer + Na_2CO_3.

Fig. 6. Micellization free energy, entropy, CMC and enthalpy of Tetronic T1304 and T1307 in water plotted as a function of salt type.

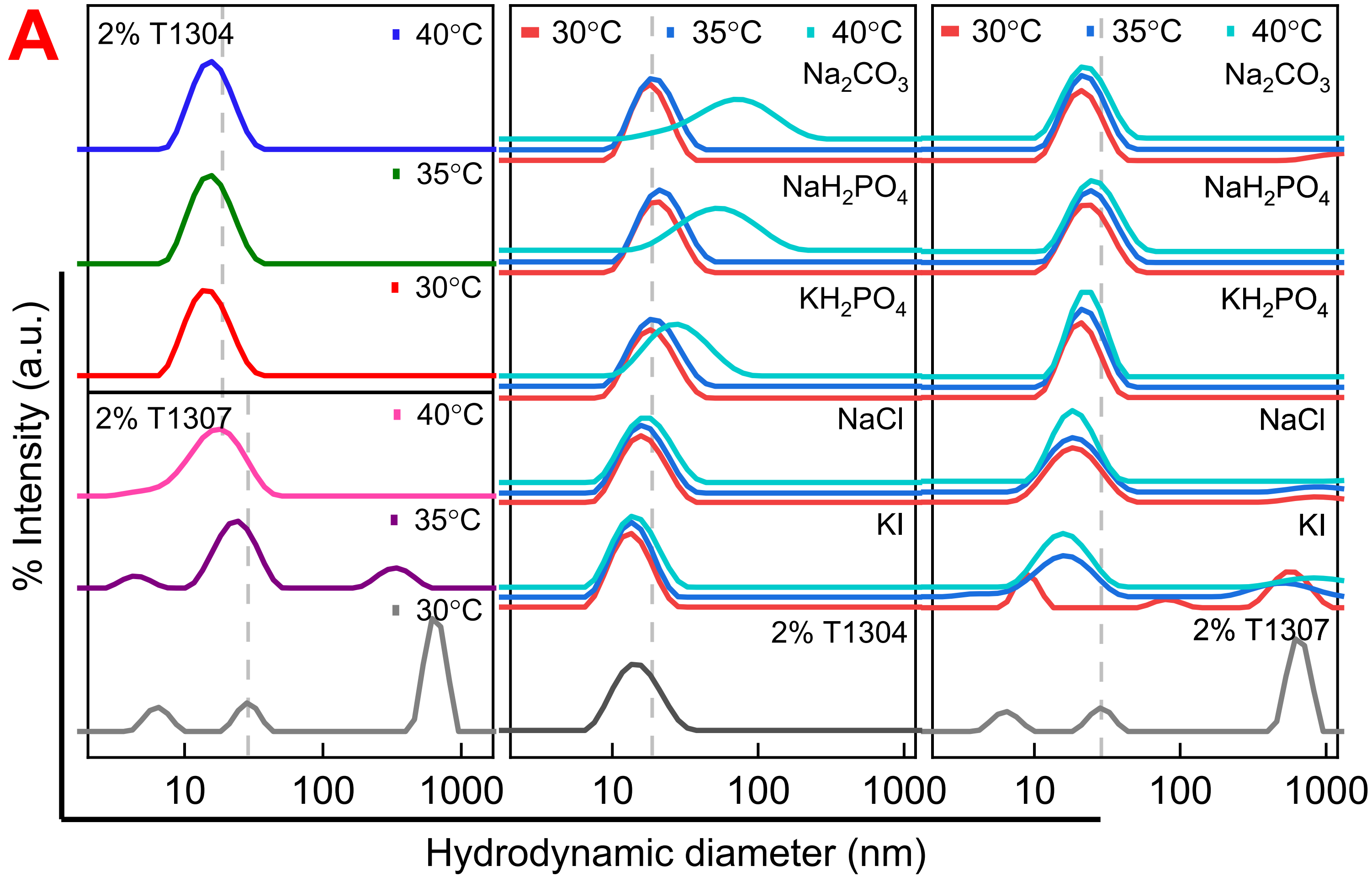
Enthalpy-Entropy compensation plot



$$\Delta H_{mic} = \Delta H_m + Tc\Delta S_{mic}$$

Fig. 7. The enthalpy-entropy compensation plot of 2 % T1304 and T1307 at different temperature.

Effect of temperature



Order :

Na$_2$CO$_3$ > NaH$_2$PO$_4$ > KH$_2$PO$_4$ > NaCl > KI

Fig. 8. DLS data of apparent hydrodynamic diameter of 2% T1304 and 2% T1307 in the absence and presence of the 0.7M and 0.3M (Na$_2$CO$_3$) salt concentrations carried at different temperatures.

Effect of concentration

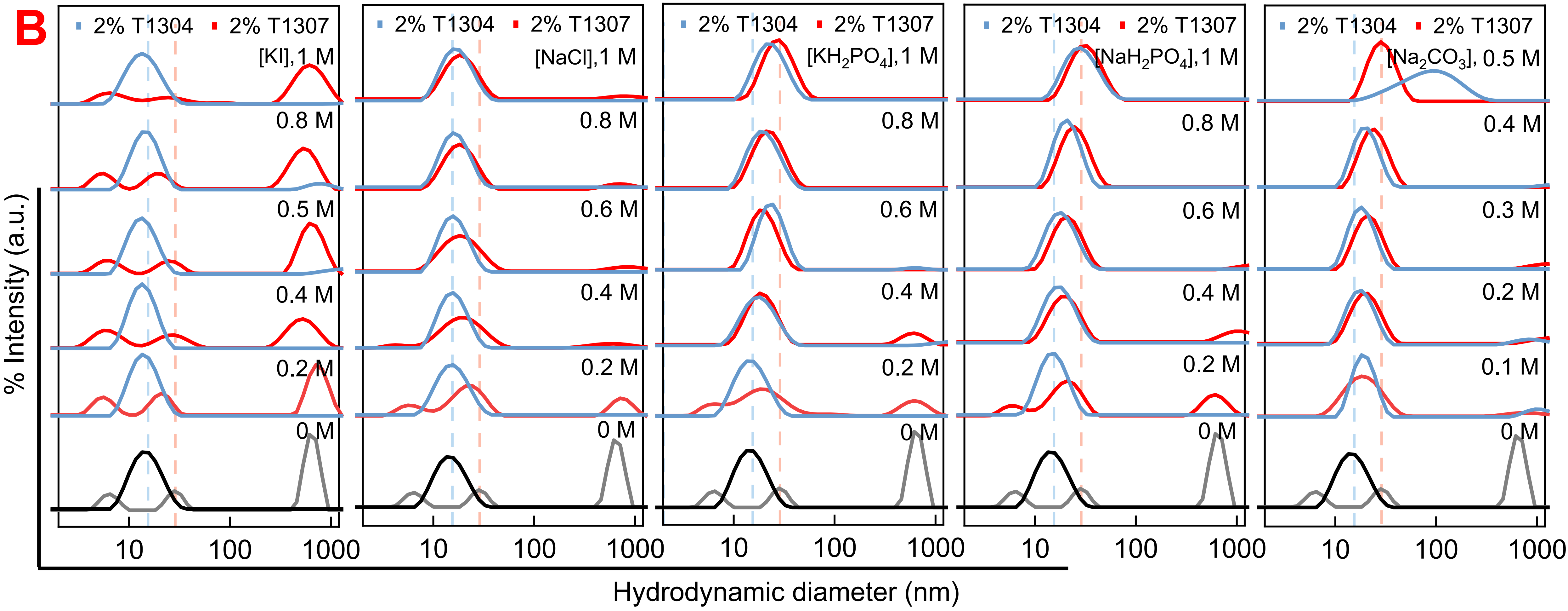
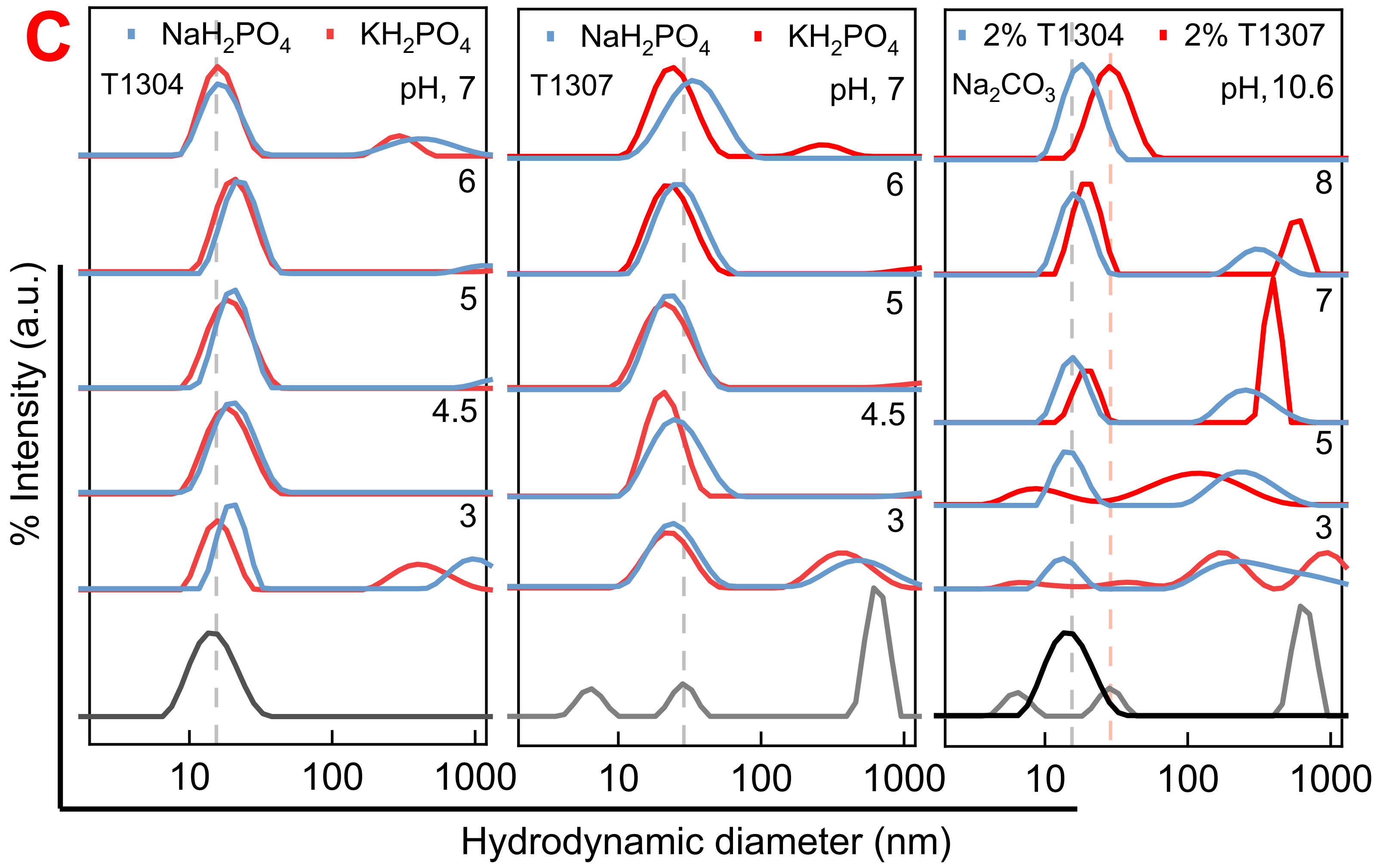


Fig. 9. DLS data of apparent hydrodynamic diameter of 2% T1304 and 2% T1307 at different concentration of salt

Effect of pH



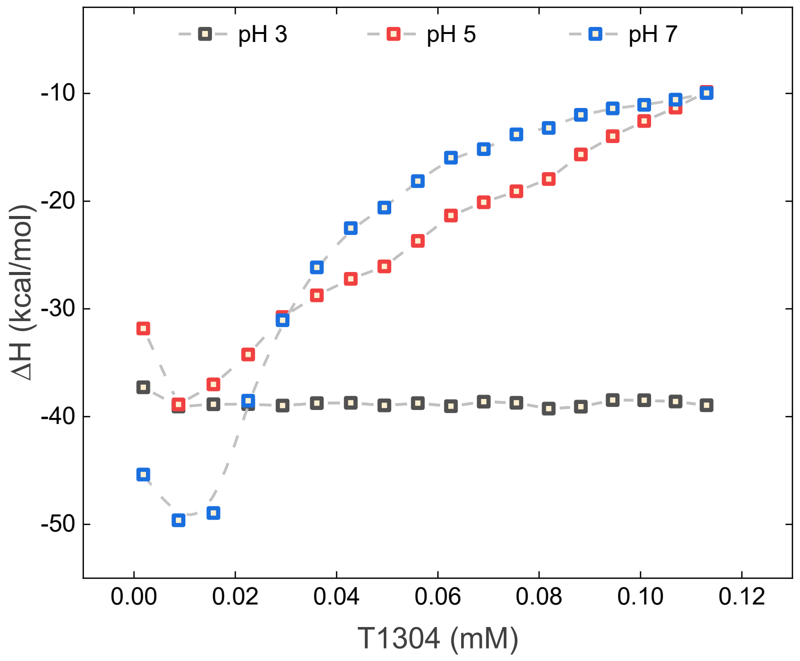


Fig. 10. DLS data of apparent hydrodynamic diameter of 2% T1304 and 2% T1307 at different pH in presence of 0.7M salt

SANS study

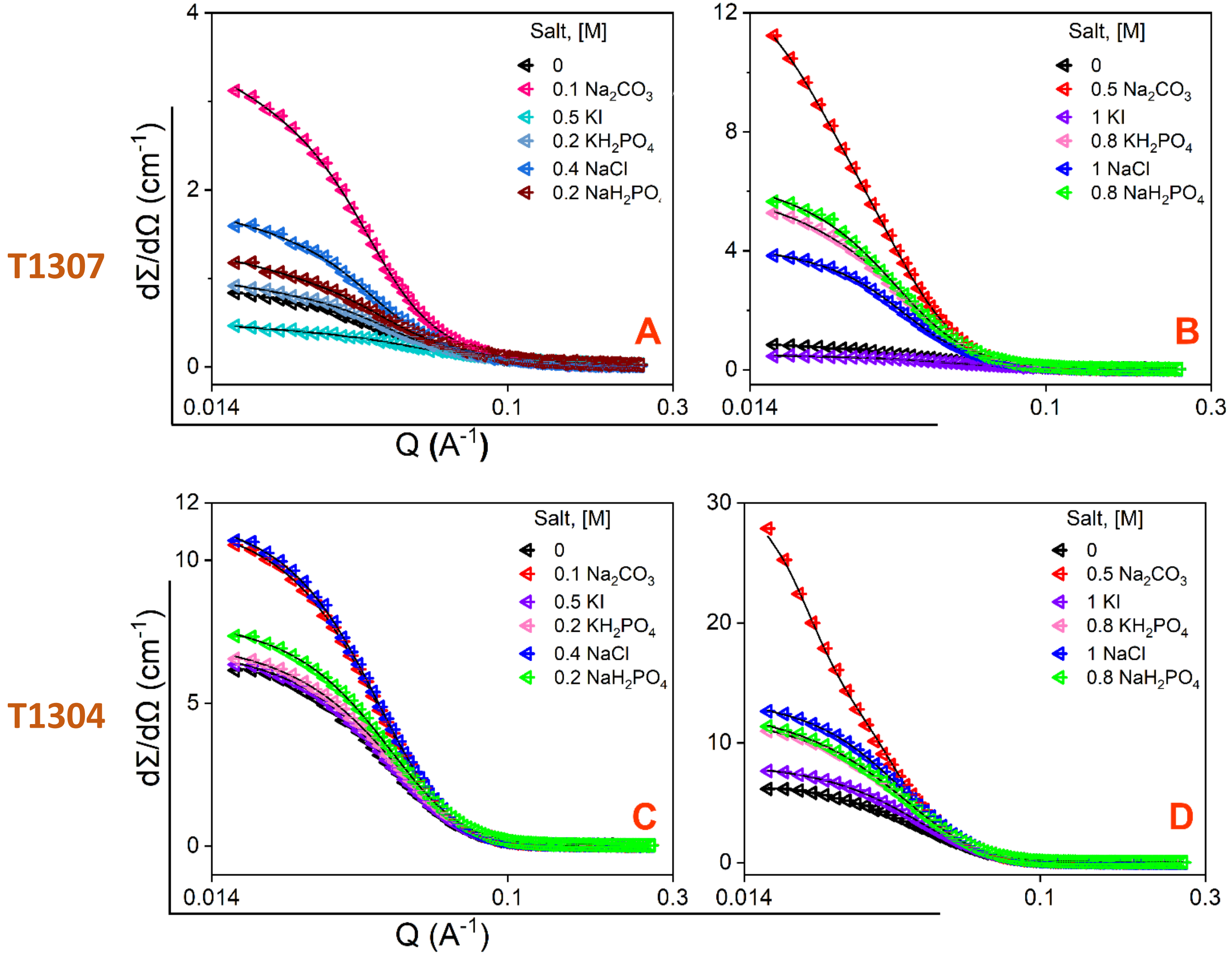


Fig. 11. SANS data of 2% T1304 and T1307 at different concentrations of salt

SANS table

Tetronics	Temperature (°C)	R_c (nm)	R_{hs} (nm)	Φ	PD	N_{agg}	Number density *10^{16}	SLD_{core}*10^{10} (cm^{-2})
T1307	30	Mostly unimers (R_g = 3.37 nm)						0.35
	35	4.28	7.87	0.051	0.36	36	2.49	0.38
	40	4.53	7.78	0.056	0.35	43	2.84	0.44
T1304	30	4.04	6.32	0.024	0.26	31	2.26	0.54
	35	4.27	6.73	0.022	0.23	36	1.72	0.96
	40	4.58	7.47	0.023	0.23	45	1.33	1.02

SANS data of T1307 and T1304 aqueous solution at different temperature.

SANS table

Tetronics	Salt concentration	R_c (nm)	R_{hs} (nm)	Φ	PD	N_{agg}	Number density *10^{16}
2% T1307	0M	Mostly unimers, R_g = 3.37					
	0.5M KI	Mostly unimers, R_g = 3.37					
	1M KI	Mostly unimers, R_g = 3.37					
	0.4M NaCl	2.96	7.40	0.064	0.55	11	1.54
	1M NaCl	4.45	7.65	0.056	0.36	41	1.10
	0.2M KH_2PO_4	4.06	6.79	0.053	0.36	31	3.34
	0.8M KH_2PO_4	4.62	6.74	0.051	0.35	46	1.49
	0.2M NaH_2PO_4	3.99	6.61	0.047	0.37	30	1.98
	0.8M NaH_2PO_4	4.65	7.32	0.045	0.35	47	1.75
	0.1M Na_2CO_3	4.34	7.25	0.056	0.38	38	1.51
	0.5M Na_2CO_3	5.44	7.50	0.055	0.35	57	1.33
2% T1304	0M	4.04	6.31	0.024	0.26	26	2.26
	0.5M KI	4.02	5.90	0.029	0.27	26	2.32
	1M KI	4.19	6.57	0.025	0.25	30	2.08
	0.4M NaCl	4.42	7.27	0.025	0.24	35	3.80
	1M NaCl	4.65	7.71	0.021	0.22	40	2.98
	0.2M KH_2PO_4	3.93	5.66	0.025	0.27	24	4.04
	0.8M KH_2PO_4	4.44	6.83	0.020	0.23	35	3.97
	0.2M NaH_2PO_4	3.99	6.50	0.023	0.26	25	3.88
	0.8M NaH_2PO_4	4.53	6.48	0.020	0.24	37	2.74
	0.1M Na_2CO_3	4.44	7.13	0.023	0.23	35	3.50
	0.5M Na_2CO_3	5.23	7.10	0.020	0.33	75	3.11

Order :

Na_2CO_3 >> NaH_2PO_4 > KH_2PO_4 > NaCl >> KI

R_c = Core radius (A°),
R_{hs} = Hard sphere radius (A°),
Φ = Volume fraction,
PD = Polydispersity,
N_{agg} = Aggregation no.

SANS data of T1307 and T1304 aqueous solution at 30 ºC in presence of different concentration of salt.

Conclusions

- T1304, being more hydrophobic, formed micelles spontaneously in comparison to T1307.
- Micelles exhibited dissociation at pH below 3 and more than 7.
- Micellization of T1304 and 1307 was found to be endothermic.
- A decrease in CMC was observed with an increase in temperature and salt addition.
- The correlation of enthalpy and entropy of micelle formation exhibited linearity.
- KI triggered crowding of water molecules around the micelles which was followed by de-aggregation.
- Salt-induced micellization followed the trend: **Na_2CO_3 >> NaH_2PO_4 > KH_2PO_4 > NaCl >> KI.**

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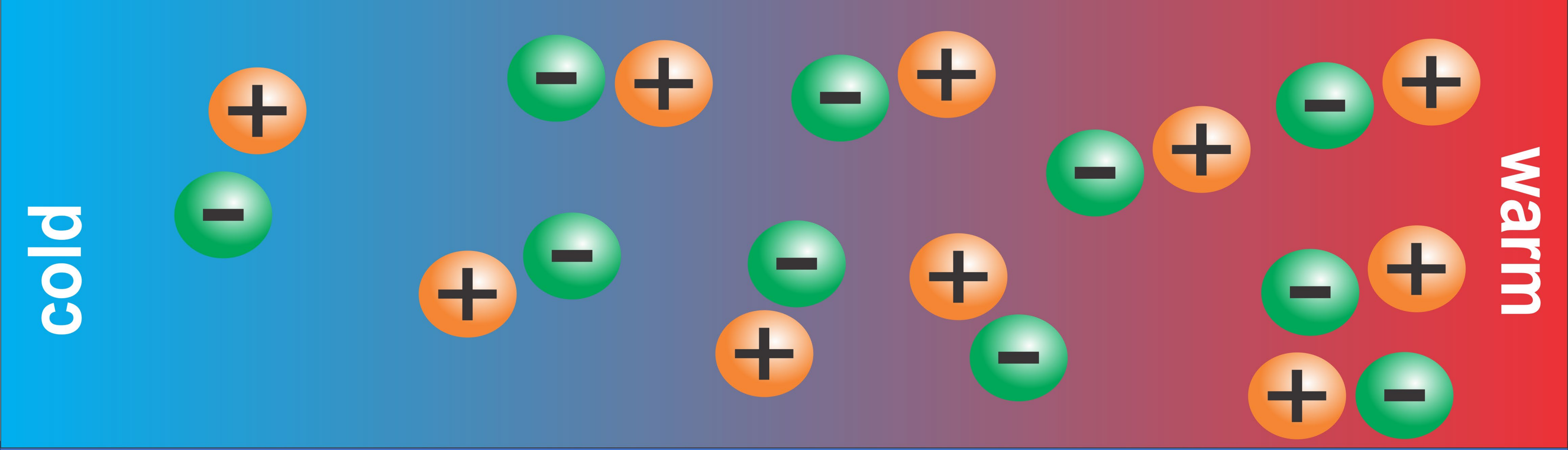


THERMOPHORESIS OF (BIO)-COMPOUNDS AND CHELATING AGENTS

BINNY RUDANI

MOTIVATION

Thermophoresis

- Motion of solute particles induced by thermal gradient.
- Tendency of a mixture to separate under thermal gradient is quantified by *Soret coefficient*.
- Sensitive tool for probing molecular interactions.

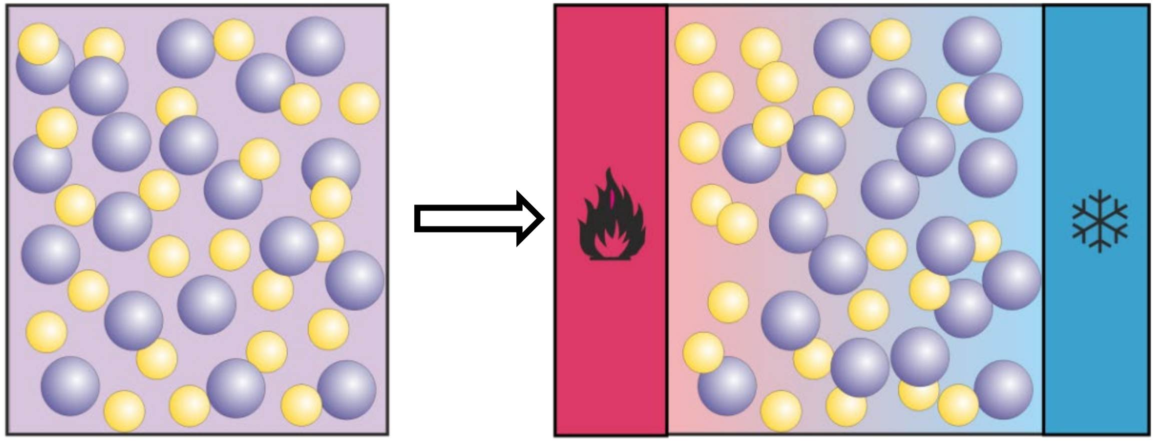
$$\vec{j} = -D\vec{\nabla}c - c(1-c)D_{\mathrm{T}}\vec{\nabla}T$$

steady state: $\vec{j} = 0$

$$\frac{D_{\mathrm{T}}}{D} = -\frac{\vec{\nabla}c}{c(1-c)\ \vec{\nabla}T}$$

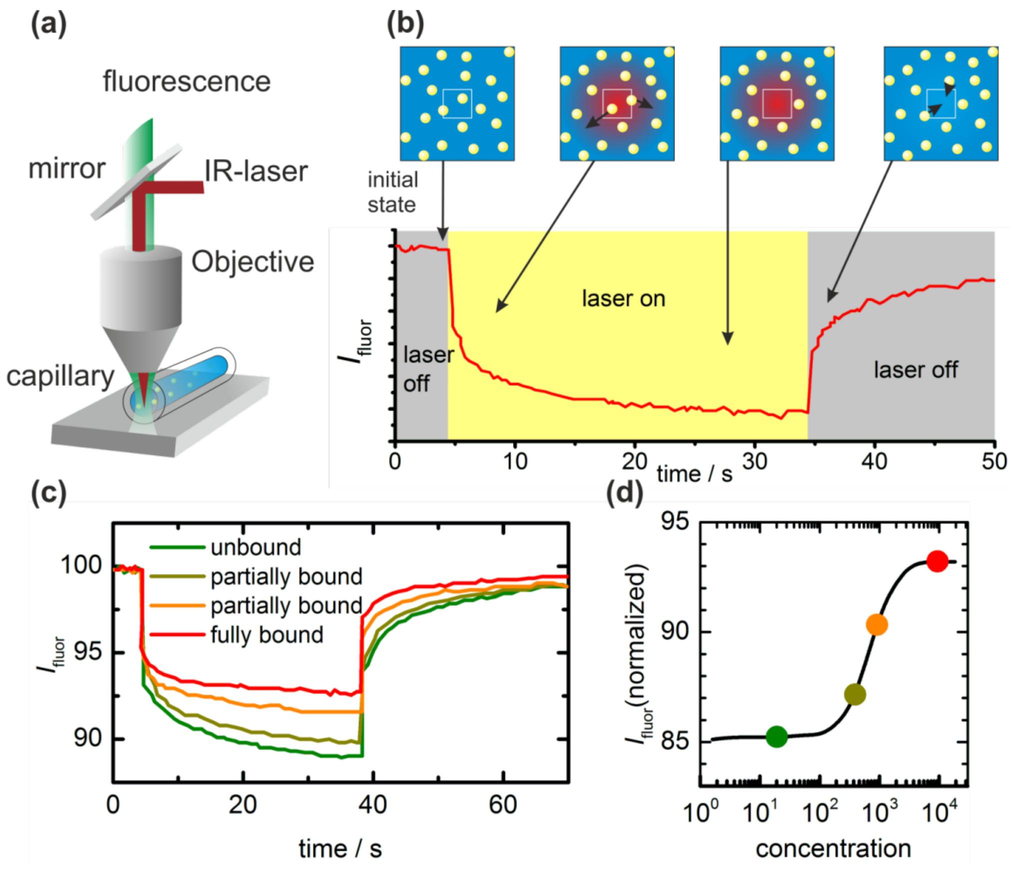
$$S_{\mathrm{T}} = \frac{D_{\mathrm{T}}}{D} \propto \frac{\Delta c}{\Delta T}$$

$\vec{j}$	mass flux
c	concentration
D	diffusion coefficient
D_{T}	thermodiffusion coefficient
T	temperature
S_{T}	Soret coefficient



THERMOPHORESIS

Application in biotechnology + challenge



Various contributions :

- Ionic
- Hydrophobic
- Hydrogen bonds
- Van der Waal’s

Microscopic understanding still missing

THERMOPHORESIS

Objectives

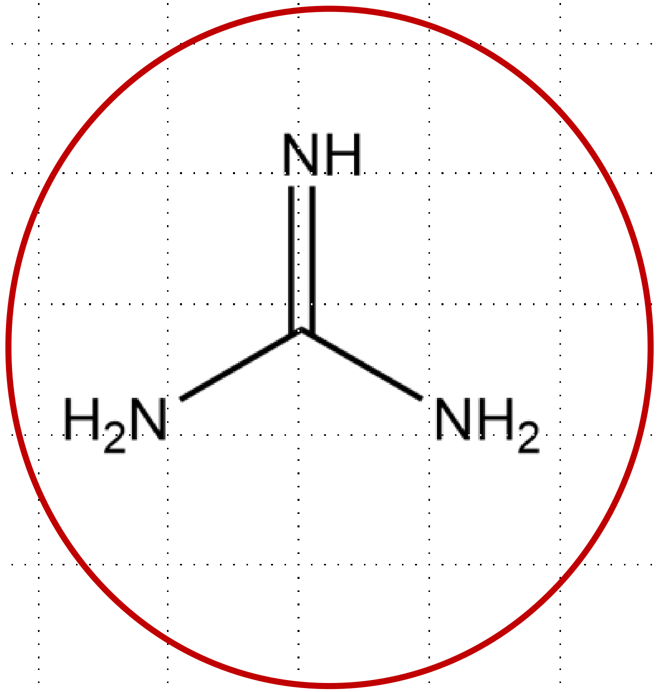
Systematic study of various components:

- Salts with non-ionic groups (TDFRS)
- Salts + chelating agents (TDFRS+ITC)
- Proteins (TDFRS, ITC and SANS)

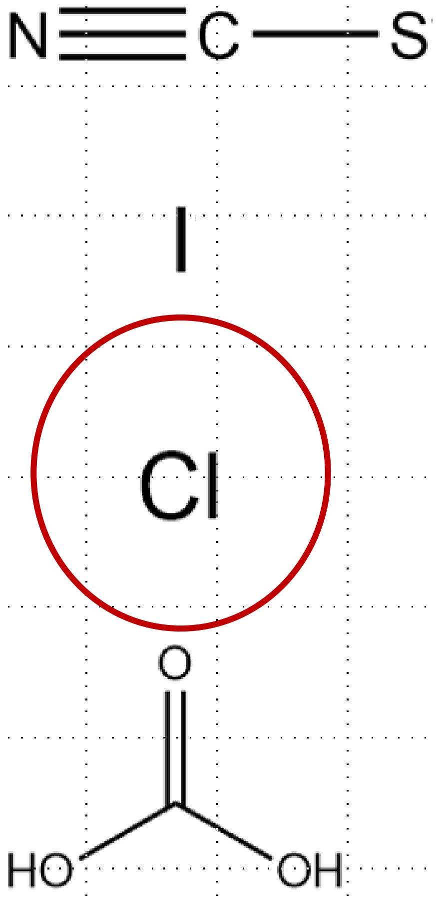
Thermophoresis of aqueous solutions of guanidinium salts:

Ongoing project

Guanidinium cation (+)



different anions (-)

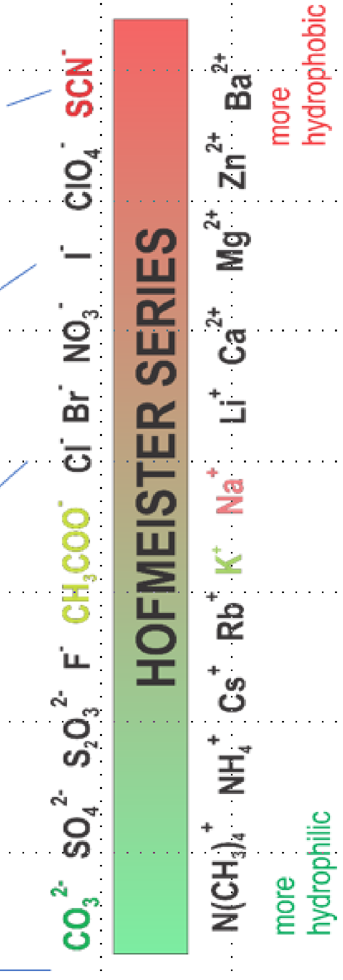


Guanidinium thiocyanate

Guanidinium iodide

Guanidinium choride

Guanidinium carbonate



THANK YOU