Reverse aggregates nucleation induced by acids in liquid-liquid extraction processes

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Supporting Information

This section brings details regarding the following parts:

- Dynamic light scattering (page 1)
- Static light scattering (page 9)
- Activity coefficients (page 21)

1. Dynamic light scattering

The first step for exploiting DLS data was to adjust experimental correlation functions (averaged over 3 to 6 single measurements) with monoexponential decays. We have used equation (1):

$$G(t) = A.[1 + B.e^{-2D_t.q^2 t}] \quad (1)$$

where G(t) was the correlation function, D_t the translational diffusion coefficient, and q the normalized value of the wave vector. Measurements were realized at fixed angle (θ = 173°, backscattering), at fixed wavelength (λ = 633 nm), and always in heptane (refractive index n_s = 1.388). Therefore the q value was fixed by the experimental conditions and could be calculated using equation (2):

$$q = \frac{4\pi n_s \sin(\theta/2)}{\lambda} \quad (2)$$

The calculations gave $q = 2.73 \cdot 10^{-3}$ Å^{-1} and $q^2 = 756.415 \cdot 10^{-12}$ m^{-2} = 756.415 µm^{-2}

The fits were realized using the Origin software and afforded, for each experimental condition, the lateral diffusion coefficient. The results are reported in the following Table 1:

Table 1. Lateral diffusion coefficients obtained from adjustments of experimental correlation functions

3 M $LiNO_3$			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (µm²/s)**	**ΔDt,app (µm²/s)**
0.010	0.005	1270	200
0.015	0.008	1400	200
0.030	0.016	690	80
0.059	0.031	620	40
0.100	0.052	607	13
0.200	0.104	465	10
0.300	0.155	444	5
0.400	0.207	366	11
0.520	0.269	360	20
0.05 M HNO_3			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (µm²/s)**	**ΔDt,app (µm²/s)**
0.011	0.006	1400	200
0.014	0.007	1400	200
0.022	0.011	1500	200
0.033	0.017	950	100
0.107	0.055	751	20
0.128	0.066	580	15
0.307	0.159	461	10
0.424	0.220	400	25
1 M HNO_3			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (µm²/s)**	**ΔDt,app (µm²/s)**
0.010	0.005	2000	500
0.030	0.016	1200	200
0.080	0.041	1000	100
0.120	0.062	600	10
0.200	0.104	535	25
0.300	0.155	430	15
0.520	0.269	310	15
3 M HNO_3			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (µm²/s)**	**ΔDt,app (µm²/s)**
0.015	0.008	850	300
0.038	0.020	465	75

0.102	0.053	502	10
0.158	0.082	415	10
0.258	0.134	314	5
0.362	0.188	229	5
0.599	0.310	172	3
6 M HNO_3			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app ($\mu m^2/s$)**	**ΔDt,app ($\mu m^2/s$)**
0.010	0.005	1350	150
0.030	0.016	700	30
0.080	0.041	281	5
0.120	0.062	184	2
0.200	0.104	100	1
0.300	0.155	75	1
0.520	0.269	85.5	1
3 M HCl			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app ($\mu m^2/s$)**	**ΔDt,app ($\mu m^2/s$)**
0.010	0.005	2000	500
0.015	0.008	1300	300
0.030	0.016	1300	300
0.059	0.031	992	32
0.100	0.052	699	20
0.200	0.104	553	20
0.300	0.155	367	10
0.400	0.207	343	10
0.52	0.27	360	5
6 M HCl			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app ($\mu m^2/s$)**	**ΔDt,app ($\mu m^2/s$)**
0.010	0.005	1820	330
0.015	0.008	1400	400
0.030	0.016	1230	150
0.059	0.031	915	60
0.100	0.052	720	25
0.200	0.104	505	7
0.300	0.155	312	5
0.40	0.21	203	7
0.52	0.27	150	1
7 M HCl			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app ($\mu m^2/s$)**	**ΔDt,app ($\mu m^2/s$)**
0.010	0.005	1225	300
0.030	0.016	920	250
0.059	0.031	613	20
0.100	0.052	166	2
0.200	0.104	75	1
0.300	0.155	65	2
0.520	0.269	72	1
1 M $HClO_4$			

[diamide] (M)	Vol Fraction Φ	Dt,app ($\mu m^2/s$)	ΔDt,app ($\mu m^2/s$)
0.010	0.005	1500	500
0.015	0.008	1250	300
0.030	0.016	1190	150
0.059	0.031	848	30
0.100	0.052	450	50
0.200	0.104	285	10
0.300	0.155	182	5
0.400	0.207	140	2
0.520	0.269	129	2

3 M $HClO_4$

[diamide] (M)	Vol Fraction Φ	Dt,app ($\mu m^2/s$)	ΔDt,app ($\mu m^2/s$)
0.010	0.005	1325	200
0.015	0.008	407	15
0.030	0.016	276	5
0.059	0.031	189	2
0.100	0.052	87	1
0.200	0.104	21	1
0.300	0.155	14	1
0.400	0.207	17	1
0.520	0.269	32	1

6 M $HClO_4$

[diamide] (M)	Vol Fraction Φ	Dt,app ($\mu m^2/s$)	ΔDt,app ($\mu m^2/s$)
0.010	0.005	171	2
0.015	0.008	176	5
0.030	0.016	170	10
0.059	0.031	107	5
0.100	0.052	95	1
0.520	0.269	18	1

3 M HCOOH

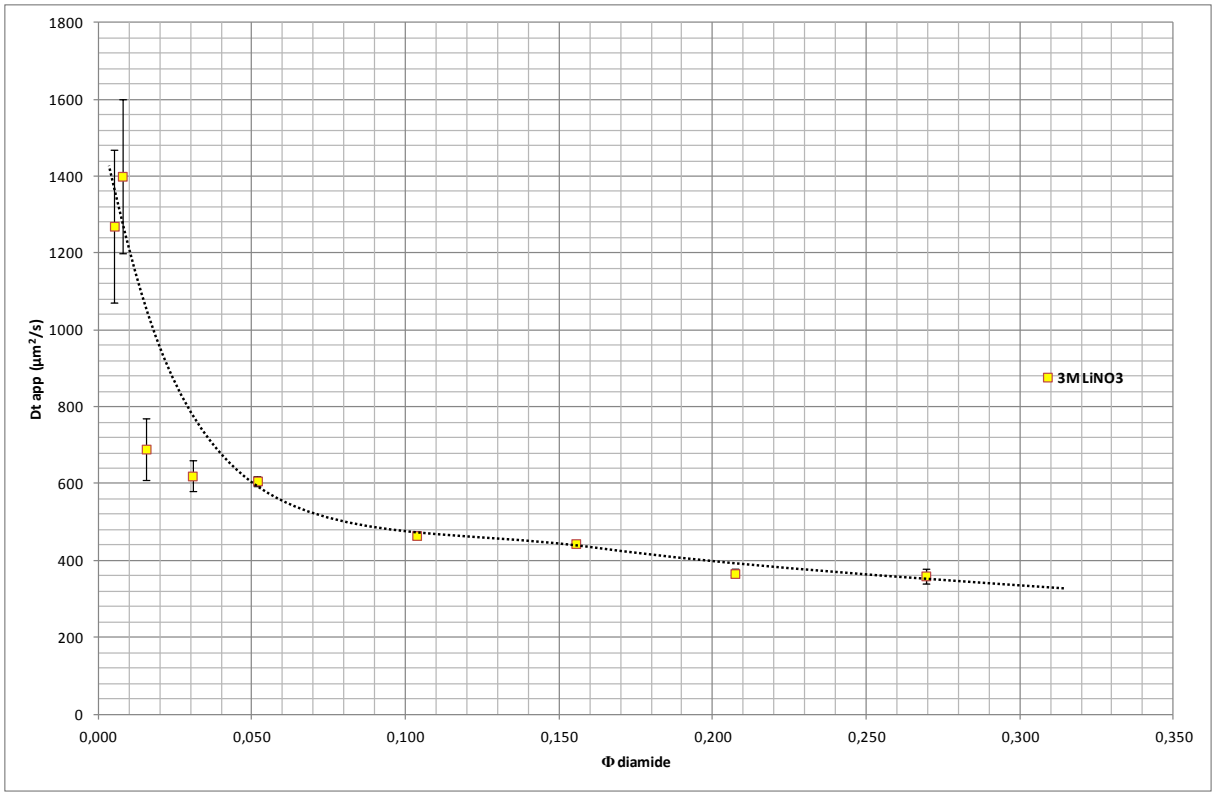
[diamide] (M)	Vol Fraction Φ	Dt,app ($\mu m^2/s$)	ΔDt,app ($\mu m^2/s$)
0.010	0.005	1500	200
0.015	0.008	1500	200
0.030	0.016	870	200
0.059	0.031	935	50
0.100	0.052	623	10
0.200	0.104	430	5
0.300	0.155	340	5
0.400	0.207	288	5
0.520	0.269	267	5

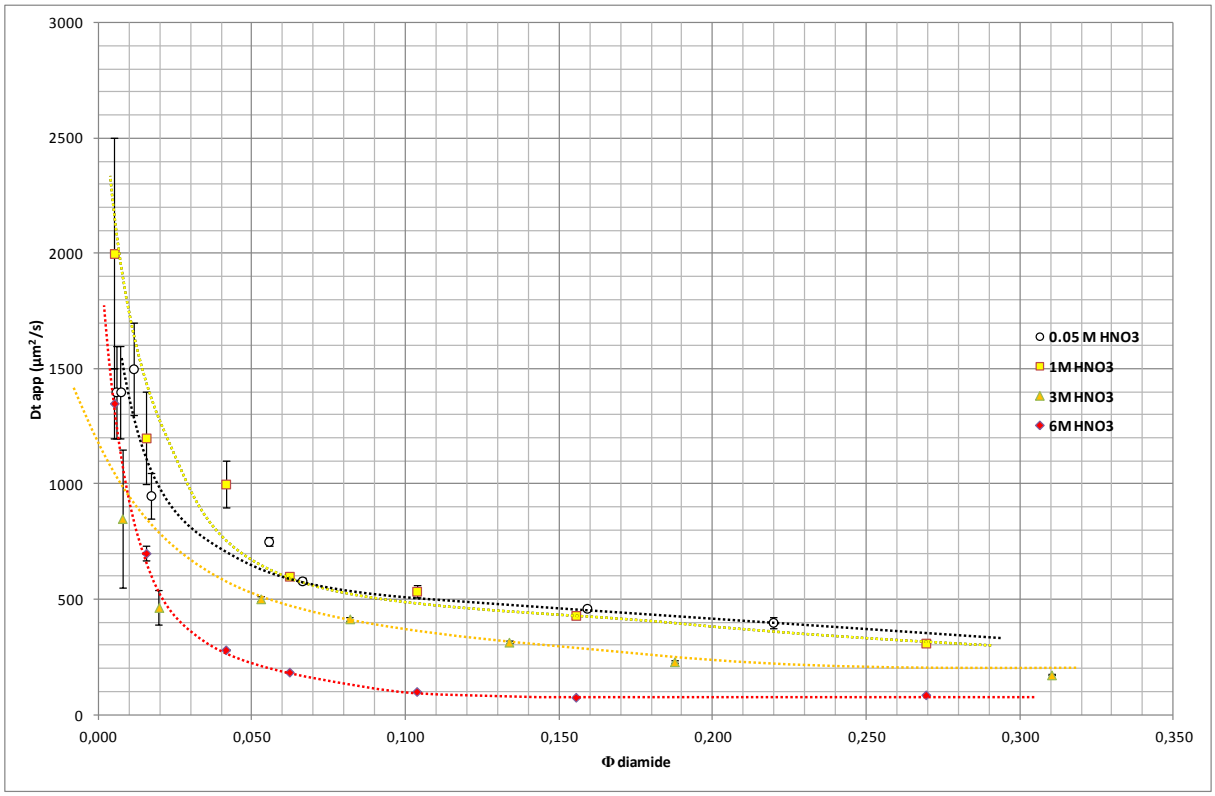
6 M HCOOH

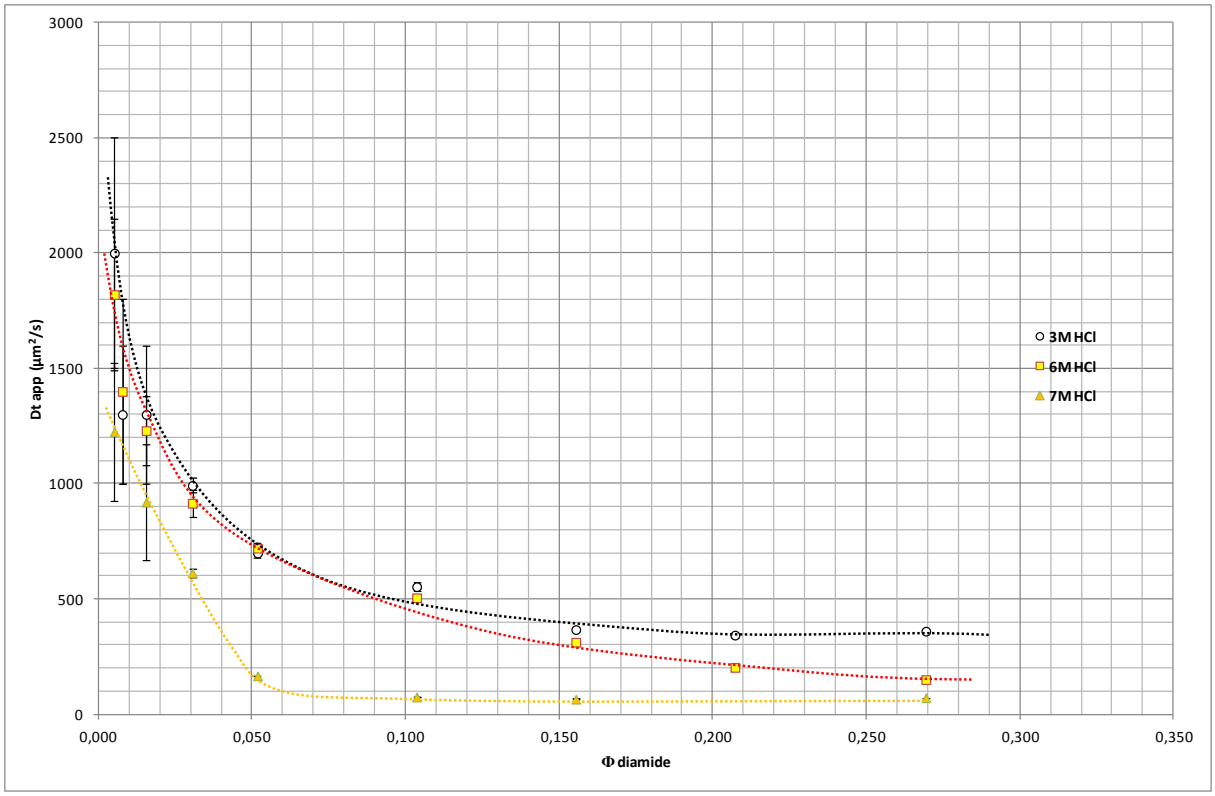
[diamide] (M)	Vol Fraction Φ	Dt,app ($\mu m^2/s$)	ΔDt,app ($\mu m^2/s$)
0.010	0.005	1300	500
0.015	0.008	1100	500

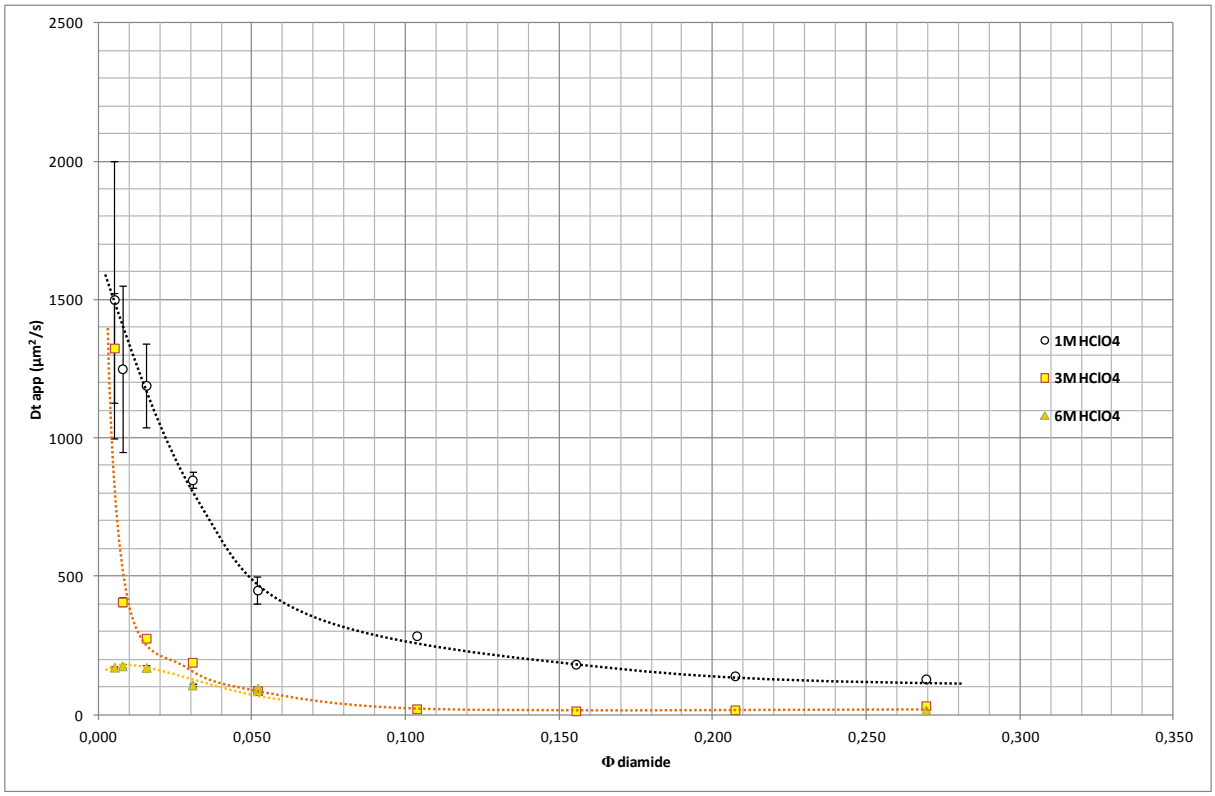
0.030	0.016	1200	250
0.059	0.031	725	40
0.100	0.052	538	5
0.200	0.104	351	3
0.300	0.155	282	3
0.520	0.269	222	2
HCOOH	**20 M**		
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (μm²/s)**	**ΔDt,app (μm²/s)**
0.010	0.005	2000	500
0.015	0.008	1200	500
0.030	0.016	1200	450
0.059	0.031	565	125
0.100	0.052	264	5
0.200	0.104	72	1
0.300	0.155	27.5	0.5
0.400	0.207	12.5	0.5
0.520	0.269	22	0.5
8 M H_3PO_4			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (μm²/s)**	**ΔDt,app (μm²/s)**
0.010	0.005	1300	250
0.055	0.028	450	50
0.100	0.052	475	25
0.200	0.104	210	10
0.300	0.155	135	5
0.400	0.207	110	5
0.500	0.259	85	5
6 M H_2SO_4			
[diamide] (M)	**Vol Fraction Φ**	**Dt,app (μm²/s)**	**ΔDt,app (μm²/s)**
0.015	0.008	700	100
0.030	0.016	400	50
0.055	0.028	550	50
0.100	0.052	57	1
0.200	0.104	41	1
0.300	0.155	37	1
0.400	0.207	44	1
0.500	0.259	55	2

These experimental results were then used to plot the lateral diffusion coefficients $D_{t,app}$ as a function of diamide volume fraction Φ. These plots are reported in Figure 1:


Dt app (µm²/s)
1800
1600
1400
1200
1000
800
600
400
200
0
0,000
0,050
0,100
0,150
0,200
0,250
0,300
0,350
Φ diamide
3M LiNO3


Dt app (µm²/s)
3000
2500
2000
1500
1000
500
0
0,000
0,050
0,100
0,150
0,200
0,250
0,300
0,350
Φ diamide
0.05 M HNO3
1M HNO3
3M HNO3
6M HNO3


3000
2500
2000
1500
1000
500
0
Dt app (µm²/s)
0,000
0,050
0,100
0,150
0,200
0,250
0,300
0,350
Φ diamide
3M HCl
6M HCl
7M HCl


2500
2000
1500
1000
500
0
Dt app (µm²/s)
0,000
0,050
0,100
0,150
0,200
0,250
0,300
0,350
Φ diamide
1M HClO4
3M HClO4
6M HClO4

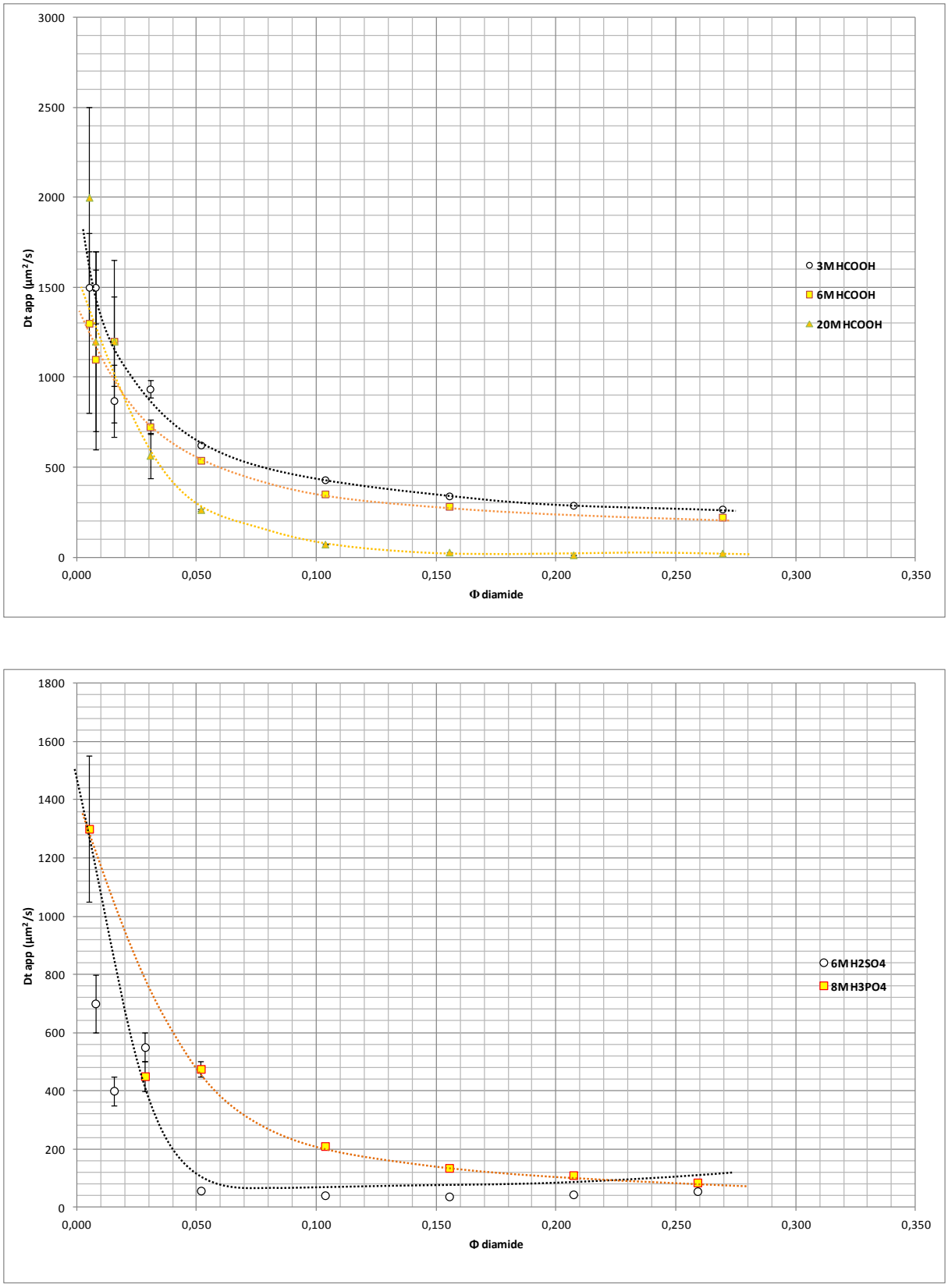


Figure 1. Variation of apparent lateral diffusion coefficients as a function of diamide volume fraction for each extracted solute series.

From Figure 1 the cac's were determined at the point where $D_{t,app}$ curves cross the 600 $\mu m^2/s$ threshold value (obtained from reference 3M $LiNO_3$).

Determination of D_0 and k_0 values was realized using linear regressions of $D_{t,app}=f(\Phi)$ curves for diamide volume fractions larger than the corresponding cac.

2. Static light scattering

This method was used to determine the apparent molecular weight (M_w) of the small aggregates using the Zimm equation:

$$\frac{K \cdot c}{R(\theta) \cdot P(\theta)} = \frac{1}{M_w} + 2A_2 \cdot c \qquad (3)$$

The Rayleigh ratio R(θ) is defined by equation (4) :

$$R(\theta) = \frac{I_A(\theta) \cdot n_0^2}{I_T(\theta) \cdot n_T^2} \cdot R_T \qquad (4)$$

The intensity scattered due to local fluctuations of optical index observed at one angle θ is $I_A(\theta)$, n_0 is the refractive index of the solvent, while I_T, n_T, and R_T are relative to toluene considered as a standard and correspond respectively to the scattered intensity, the refractive index, and the Rayleigh ratio of toluene ($R_T = 1.35x10^{-5}$ cm^{-1}).

The form factor P(θ) is expressed by the following equation (5) :

$$P(\theta) = 1 + \frac{16\pi^2 n_0^2 R_g^2}{3\lambda_0^2} \sin^2\left(\frac{\theta}{2}\right) \qquad (5)$$

where R_g is the radius of gyration, and λ the wavelength of the light source (a He-Ne laser with λ = 633nm). In our case θ = 173° and $R_g << \lambda_0$ so it was reasonable to consider the approximation P(θ)=1.

The scattering vector for vertically polarized light is expressed in equation (6) :

$$q = \frac{4\pi n_0 \sin(\frac{\theta}{2})}{\lambda} \qquad (6)$$

And finally the constant K is defined by equation (7):

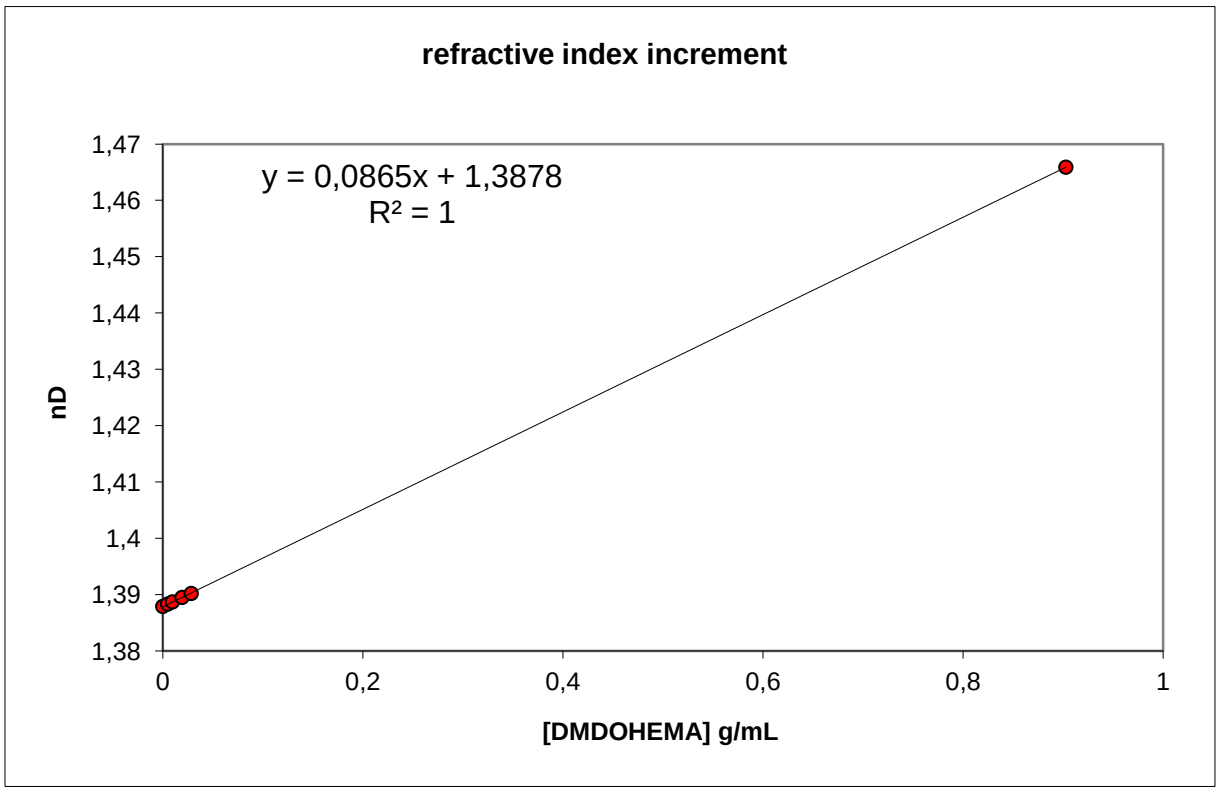
$$K = \frac{2\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2}{N_A \lambda^4} \qquad (7)$$

with dn/dc the refractive index increment of the solution and N_A the Avogadro number.

heptane refractive index, n_0	1.39
Wavelength, λ (cm)	6.33E-05

The determination of the differential refractive index of DMDOHEMA dn/dc was determined by measuring refractive indexes of diamide solutions in heptane at various concentrations:

[DMDOHEMA] mol/L	[DMDOHEMA] g/L	[DMDOHEMA] g/mL	refractive index nD
0	0	0	1.3879
0.01	4.828	0.00483	1.3883
0.02	9.656	0.00966	1.3887
0.04	19.312	0.01931	1.3895
0.059	28.485	0.02848	1.3902
1.87	902.817	0.90282	1.4659



It came out dn/dc = 0.0865 mL/g

Then the constant K could be calculated:

K ($cm^2.g^{-2}.mol^{-1}$)	**2.95E-08**

The Rayleigh ratio R(θ) and is defined by:

$$R(\theta) = \frac{I_A(\theta) \cdot n_0^2}{I_T(\theta) \cdot n_T^2} \cdot R_T$$

Using the following values:

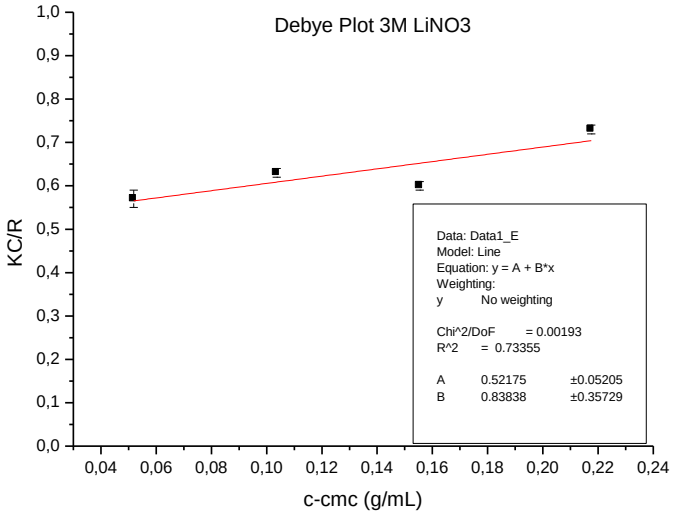
heptane refractive index, n_0	1.39
toluene refractive index, n_T	1.5
heptane scattering intensity, I_0 (kcps)	101.7
toluene scattering intensity, I_T (kcps)	283.4
toluene rayleigh ratio, R_T (cm^{-1})	1.35E-05

For each analyte, the residual scattering intensity I_A was obtained by subtracting the contribution of heptane I_0.

Debye plots were then realized for each sample, allowing determination of M_w and the aggregation number dividing M_w by the molecular weight of diamide (483 g/mol). The results are reported in the following tables and graphs.

$LiNO_3$ 3M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	$Kc/R_\theta P$	$\Delta Kc/R_\theta P$
0,010	0,0052	0,00483		10,1	1,8	4,1498E-07	7,171101E-08	0,34	0,06
0,015	0,0078	0,00724		6,3	1,6	2,5925E-07	6,476765E-08	0,82	0,21
0,030	0,0155	0,01448		17,3	0,3	7,0616E-07	1,221468E-08	0,61	0,01
0,059	0,0306	0,02848		42,0	3,7	1,7193E-06	1,525504E-07	0,49	0,04
0,100	0,0518	0,04828		46,3	2,2	1,8939E-06	8,999195E-08	0,75	0,04
0,200	0,1036	0,09656	0,05181	121,2	4,3	4,9578E-06	1,761880E-07	0,57	0,02
0,300	0,1554	0,14484	0,10361	165,2	2,3	6,7591E-06	9,587068E-08	0,63	0,01
0,400	0,2072	0,19312	0,15541	233,2	3,9	9,5378E-06	1,590164E-07	0,60	0,01
0,520	0,2694	0,25105	0,21757	248,3	2,6	1,0156E-05	1,079702E-07	0,73	0,01



For 3M $LiNO_3$:

$M_w^{-1} = 0.52 \pm 0.05\ kDa^{-1}$

$M_w = 1.92 \pm 0.18\ kDa$

$N_{agg} = 4.0 \pm 0.4$

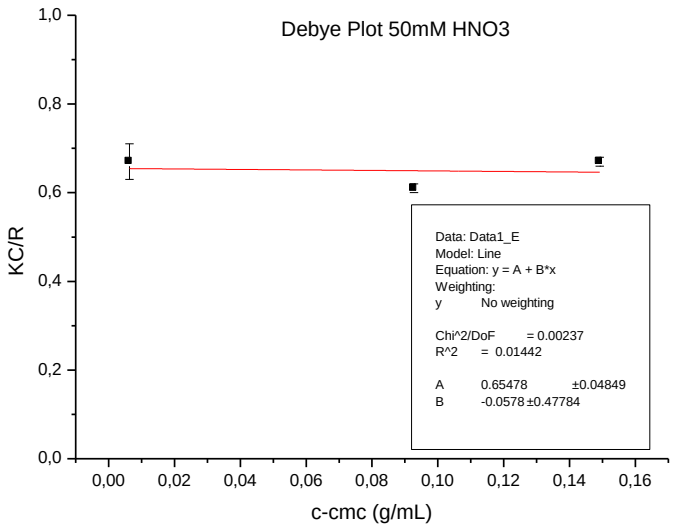
Second virial coefficient:

$A_2 = 0.4 \pm 0.2\ mL.g^{-1}$

HNO3 50mM

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R_0P	$\Delta Kc/R_0P$
0,011	0,005698	0,00531		2,86374	1,753093	1,1714E-07	7,171101E-08	1,34	0,82
0,014	0,007252	0,00676		5,10863	1,583351	2,0897E-07	6,476765E-08	0,95	0,30
0,022	0,011397	0,01062		5,94884	0,298608	2,4334E-07	1,221468E-08	1,29	0,06
0,033	0,017095	0,01593		16,4953	3,729343	6,7475E-07	1,525504E-07	0,70	0,16
0,107	0,055429	0,05166		47,9019	2,2	1,9594E-06	8,999195E-08	0,78	0,04
0,128	0,066307	0,06180	0,00630	66,6923	4,307203	2,7281E-06	1,761880E-07	0,67	0,04
0,307	0,159034	0,14822	0,09272	175,317	2,343715	7,1714E-06	9,587068E-08	0,61	0,01
0,424	0,219643	0,20470	0,14920	221,841	3,887416	9,0745E-06	1,590164E-07	0,67	0,01

For 50mM HNO_3:



$M_w^{-1} = 0.65 \pm 0.05\ kDa^{-1}$

$M_w = 1.54 \pm 0.12\ kDa$

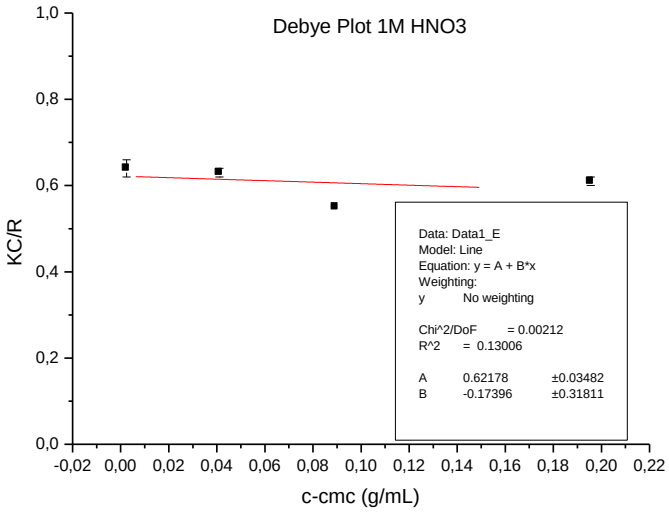
$N_{agg} = 3.2 \pm 0.3$

Second virial coefficient:

$A_2 = 0.0 \pm 0.5\ mL.g^{-1}$

HNO3 1M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R$_0$P	ΔKc/R$_0$P
0,01	0,00518	0,00483		4,80321	1,018823	1,9648E-07	4,167539E-08	0,73	0,15
0,03	0,015541	0,01448		12,3329	1,630951	5,0448E-07	6,671474E-08	0,85	0,11
0,08	0,041442	0,03862		33,8164	0,466905	1,3833E-06	1,909894E-08	0,82	0,01
0,12	0,062163	0,05793	0,0024348	64,9421	1,995829	2,6565E-06	8,164025E-08	0,64	0,02
0,2	0,103605	0,09656	0,041058	110,783	1,718527	4,5316E-06	7,029707E-08	0,63	0,01
0,3	0,155408	0,14484	0,089337	190,257	0,928978	7,7826E-06	3,800025E-08	0,55	0,00
0,52	0,269373	0,25105	0,1955508	295,621	4,174825	1,2093E-05	1,707730E-07	0,61	0,01



For 1M HNO_3:

$M_w^{-1} = 0.62 \pm 0.04$ kDa^{-1}

$M_w = 1.61 \pm 0.10$ kDa

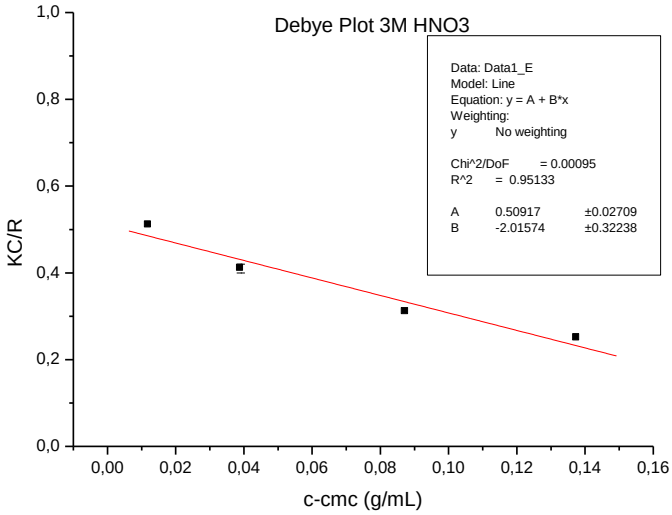
$N_{agg} = 3.3 \pm 0.2$

Second virial coefficient:

$A_2 = - 0.2 \pm 0.3$ mL.g^{-1}

HNO3 3M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R$_0$P	ΔKc/R$_0$P
0,015	0,00777	0,00724		5,62804	0,912871	2,3022E-07	3,734138E-08	0,93	0,15
0,038	0,019685	0,01835		13,7027	0,858487	5,6052E-07	3,511679E-08	0,97	0,06
0,102	0,052839	0,04924	0,01207458	69,0428	0,409878	2,8242E-06	1,676624E-08	0,51	0,00
0,158	0,081848	0,07628	0,03911082	135,378	1,665233	5,5377E-06	6,811707E-08	0,41	0,01
0,258	0,133651	0,12456	0,08738982	292,394	2,669644	1,1961E-05	1,092030E-07	0,31	0,00
0,362	0,187525	0,17477	0,13759998	501,863	1,094532	2,0529E-05	4,477230E-08	0,25	0,00
0,599	0,310297	0,28919	0,25202121	585,968	4,966085	2,3969E-05	2,031399E-07	0,36	0,00



For 3M HNO_3:

$M_w^{-1} = 0.51 \pm 0.03\ kDa^{-1}$

$M_w = 1.96 \pm 0.12\ kDa$

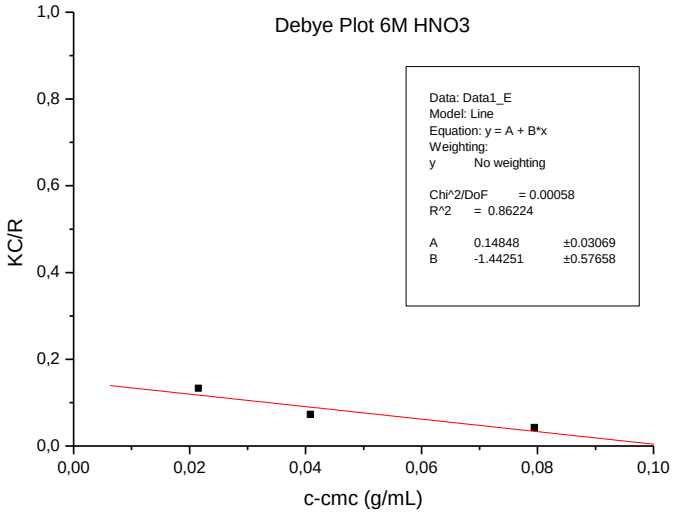
$N_{agg} = 4.0 \pm 0.3$

Second virial coefficient:

$A_2 = -\ 2.0 \pm 0.3\ mL.g^{-1}$

HNO_3 6M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	$Kc/R_\theta P$	$\Delta Kc/R_\theta P$
0,010	0,0052	0,00483		1,6	0,4	6,3607E-08	1,557633E-08	2,24	0,55
0,030	0,0155	0,01448		21,7	0,9	8,8881E-07	3,800025E-08	0,48	0,02
0,080	0,0414	0,03862	0,0217232	207,2	1,0	8,4755E-06	4,054593E-08	0,13	0,00
0,120	0,0622	0,05793	0,0410348	599,8	7,7	2,4537E-05	3,168653E-07	0,07	0,00
0,200	0,1036	0,09656	0,079658	1887,1	37,6	7,7192E-05	1,536764E-06	0,04	0,00
0,300	0,1554	0,14484	0,127937	2786,5	68,2	0,00011398	2,788137E-06	0,04	0,00
0,520	0,2694	0,25105	0,2341508	1585,0	30,9	6,4835E-05	1,261996E-06	0,11	0,00



For 6M HNO_3:

$M_w^{-1} = 0.15 \pm 0.03\ kDa^{-1}$

$M_w = 6.7 \pm 1.3\ kDa$

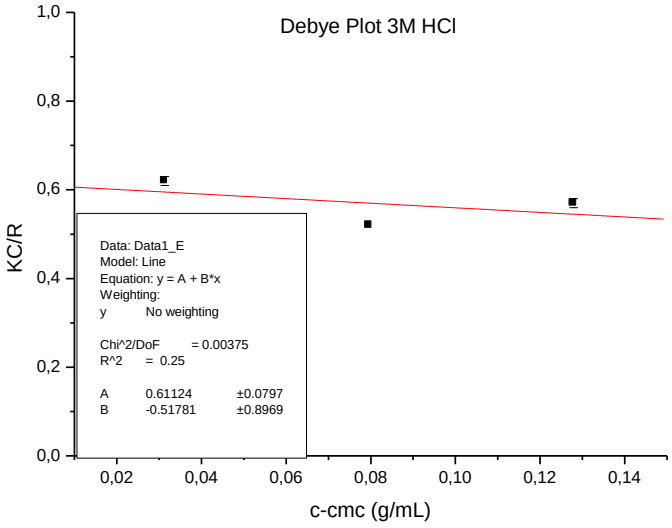
$N_{agg} = 14 \pm 3$

Second virial coefficient:

$A_2 = -\ 1.4 \pm 0.6\ mL.g^{-1}$

HCl 3M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R$_0$P	ΔKc/R$_0$P
0,010	0,0052	0,00483		1,1	0,8	4,4718E-08	3,189575E-08	3,19	2,27
0,015	0,0078	0,00724		3,4	0,7	1,3725E-07	2,956815E-08	1,56	0,34
0,030	0,0155	0,01448		10,4	0,8	4,2391E-07	3,272435E-08	1,01	0,08
0,059	0,0306	0,02848		21,2	1,0	8,6559E-07	4,207497E-08	0,97	0,05
0,100	0,0518	0,04828		46,0	0,9	1,8835E-06	3,777944E-08	0,76	0,02
0,200	0,1036	0,09656	0,031358	112,5	1,5	4,6018E-06	6,067256E-08	0,62	0,01
0,300	0,1554	0,14484	0,079637	200,9	1,5	8,216E-06	6,156234E-08	0,52	0,00
0,400	0,2072	0,19312	0,127916	244,9	4,2	1,0017E-05	1,710464E-07	0,57	0,01
0,520	0,2694	0,25105	0,1858508	243,2	1,7	9,9477E-06	6,881359E-08	0,74	0,01



For 3M HCl:

$M_w^{-1} = 0.61 \pm 0.08$ kDa^{-1}

$M_w = 1.64 \pm 0.22$ kDa

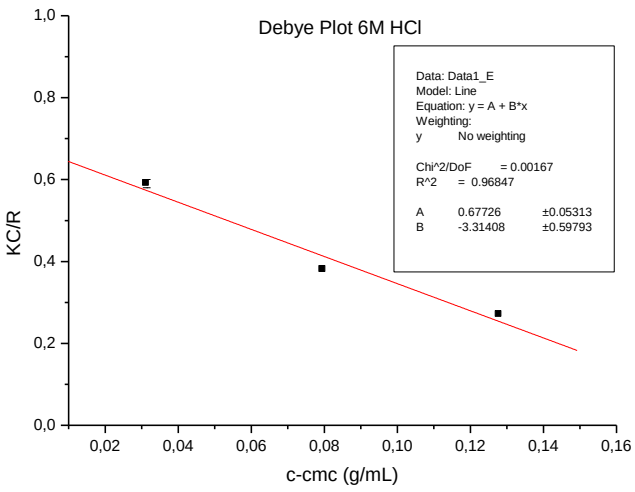
N_{agg} = 3.4 ± 0.5

Second virial coefficient:

$A_2 = - 0.6 \pm 0.9$ mL.g^{-1}

HCl 6M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R$_0$P	ΔKc/R$_0$P
0,010	0,0052	0,00483		-0,1	1,7	-6,0224E-09	6,836635E-08	-23,66	268,55
0,015	0,0078	0,00724		1,6	1,5	6,6659E-08	6,142629E-08	3,21	2,95
0,030	0,0155	0,01448		6,7	0,7	2,7496E-07	2,660426E-08	1,55	0,15
0,059	0,0306	0,02848		19,4	0,8	7,9431E-07	3,074718E-08	1,06	0,04
0,100	0,0518	0,04828		46,7	1,7	1,9111E-06	7,005466E-08	0,75	0,03
0,200	0,1036	0,09656	0,031358	117,7	1,4	4,8133E-06	5,707737E-08	0,59	0,01
0,300	0,1554	0,14484	0,079637	271,9	2,1	1,1124E-05	8,667706E-08	0,38	0,00
0,400	0,2072	0,19312	0,127916	510,5	3,4	2,088E-05	1,400974E-07	0,27	0,00
0,520	0,2694	0,25105	0,1858508	674,9	3,3	2,7606E-05	1,335423E-07	0,27	0,00



For 6M HCl:

$M_w^{-1} = 0.68 \pm 0.06\ kDa^{-1}$

$M_w = 1.47 \pm 0.13\ kDa$

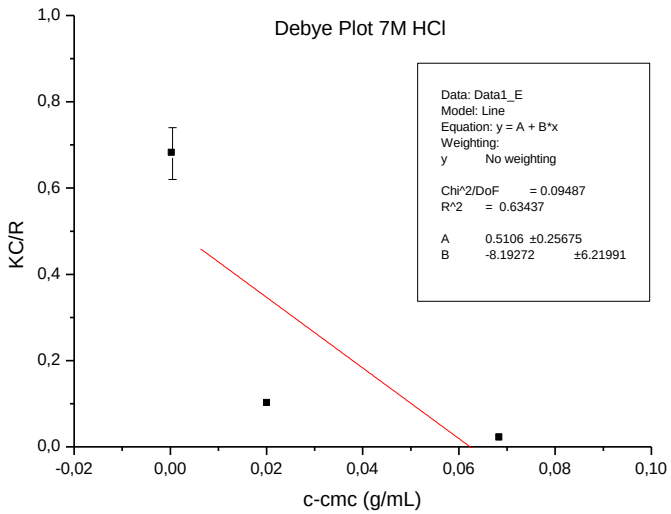
$N_{agg} = 3.0 \pm 0.3$

Second virial coefficient:

$A_2 = -\ 3.3 \pm 0.6\ mL.g^{-1}$

HCl 7M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R₀P	ΔKc/R₀P
0,010	0,0052	0,00483		-1,3	2,0	-5,1873E-08	8,237986E-08	-2,75	4,36
0,030	0,0155	0,01448		7,5	1,0	3,0492E-07	4,084403E-08	1,40	0,19
0,059	0,0306	0,02848	0,00048461	30,4	2,9	1,2445E-06	1,190973E-07	0,68	0,06
0,100	0,0518	0,04828	0,020279	335,2	1,0	1,371E-05	3,919244E-08	0,10	0,00
0,200	0,1036	0,09656	0,068558	2912,4	45,8	0,00011913	1,874082E-06	0,02	0,00
0,300	0,1554	0,14484	0,116837	3539,7	59,5	0,00014479	2,435898E-06	0,03	0,00
0,520	0,2694	0,25105	0,2230508	2003,8	38,2	8,1966E-05	1,563405E-06	0,09	0,00



For 7M HCl:

$M_w^{-1} = 0.51 \pm 0.26\ kDa^{-1}$

$M_w = 2.0 \pm 1.0\ kDa$

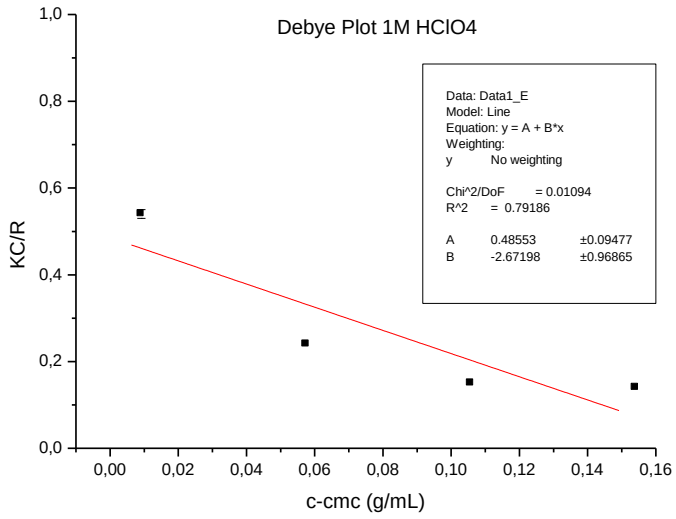
$N_{agg} = 4.0 \pm 2.0$

Second virial coefficient:

$A_2 = -\ 8 \pm 6\ mL.g^{-1}$

$HClO_4$ 1M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	$Kc/R_\theta P$	$\Delta Kc/R_\theta P$
0,010	0,0052	0,00483		6,2	0,6	2,5526E-07	2,331969E-08	0,56	0,05
0,015	0,0078	0,00724		7,3	1,1	2,9742E-07	4,542161E-08	0,72	0,11
0,030	0,0155	0,01448		12,3	0,3	5,031E-07	1,022636E-08	0,85	0,02
0,059	0,0306	0,02848		26,7	0,1	1,0907E-06	5,333416E-09	0,77	0,00
0,100	0,0518	0,04828	0,009179	64,9	1,5	2,6538E-06	6,242827E-08	0,54	0,01
0,200	0,1036	0,09656	0,057458	285,3	1,9	1,1669E-05	7,839556E-08	0,24	0,00
0,300	0,1554	0,14484	0,105737	699,8	7,0	2,8626E-05	2,856945E-07	0,15	0,00
0,400	0,2072	0,19312	0,154016	981,7	4,4	4,0156E-05	1,788976E-07	0,14	0,00
0,520	0,2694	0,25105	0,2119508	974,3	5,1	3,9856E-05	2,086097E-07	0,19	0,00



For 1M $HClO_4$:

$M_w^{-1} = 0.49 \pm 0.10$ kDa^{-1}

$M_w = 2.04 \pm 0.42$ kDa

$N_{agg} = 4.2 \pm 0.9$

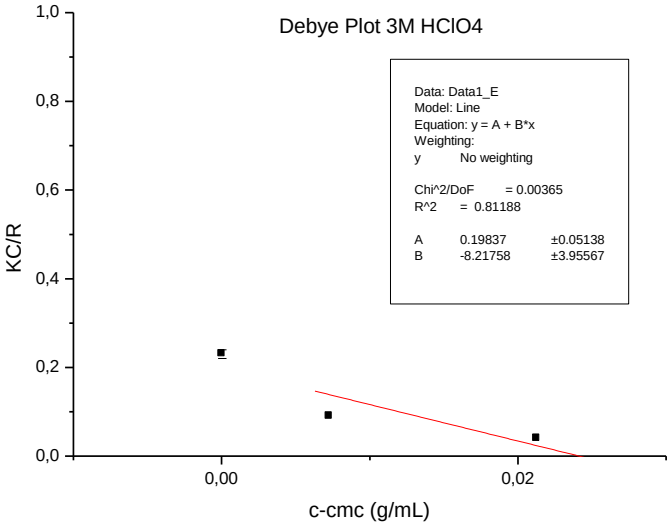
Second virial coefficient:

$A_2 = -2.7 \pm 1.0$ mL.g^{-1}

$HClO_4$ 3M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	$Kc/R_\theta P$	$\Delta Kc/R_\theta P$
0,010	0,0052	0,00483		5,6	0,9	2,2797E-07	3,535422E-08	0,62	0,10
0,015	0,0078	0,00724	4,185E-05	22,7	0,6	9,2815E-07	2,251657E-08	0,23	0,01
0,030	0,0155	0,01448	0,0072837	112,5	0,3	4,6036E-06	1,338052E-08	0,09	0,00
0,059	0,0306	0,02848	0,02128461	459,8	7,2	1,8807E-05	2,928898E-07	0,04	0,00
0,100	0,0518	0,04828	0,041079	2171,9	82,6	8,8842E-05	3,380322E-06	0,02	0,00
0,200	0,1036	0,09656	0,089358	10237,5	271,4	0,00041877	1,110209E-05	0,01	0,00
0,300	0,1554	0,14484	0,137637	10836,2	48,9	0,00044326	2,002157E-06	0,01	0,00
0,400	0,2072	0,19312	0,185916	8014,2	105,4	0,00032783	4,312619E-06	0,02	0,00
0,520	0,2694	0,25105	0,2438508	4119,4	52,8	0,00016851	2,158420E-06	0,04	0,00

For 3M $HClO_4$:



$M_w^{-1} = 0.20 \pm 0.05$ kDa^{-1}

$M_w = 5.0 \pm 1.3$ kDa

N_{agg} = 10 ± 3

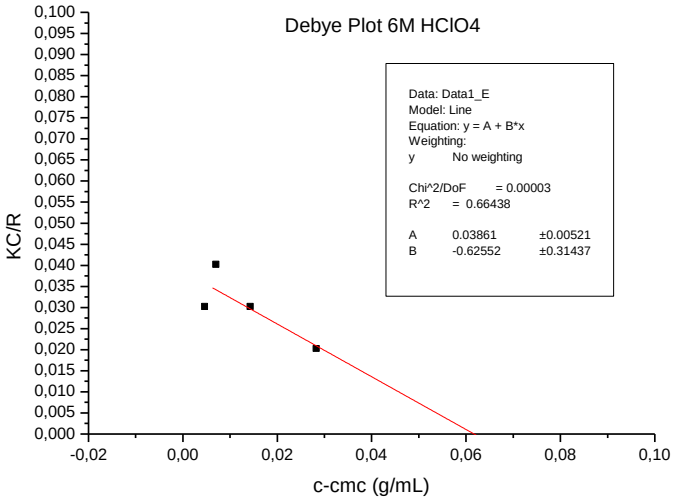
Second virial coefficient:

$A_2 = - 8 \pm 4$ mL.g^{-1}

$HClO_4$ 6M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R_0P	ΔKc/R_0P
0,010	0,0052	0,00483		100,0	2,6	4,0886E-06	1,070598E-07	0,03	0,00
0,015	0,0078	0,00724		144,0	9,6	5,8885E-06	3,912318E-07	0,04	0,00
0,030	0,0155	0,01448		345,1	16,4	1,4115E-05	6,693447E-07	0,03	0,00
0,059	0,0306	0,02848		1239,9	6,6	5,0718E-05	2,691161E-07	0,02	0,00
0,100	0,0518	0,04828		1532,7	28,6	6,2696E-05	1,168906E-06	0,02	0,00
0,520	0,2694	0,25105		5843,0	173,6	0,00023901	7,102161E-06	0,03	0,00

For 6M $HClO_4$:



$M_w^{-1} = 0.039 \pm 0.005$ kDa^{-1}

$M_w = 25.6 \pm 3.3$ kDa

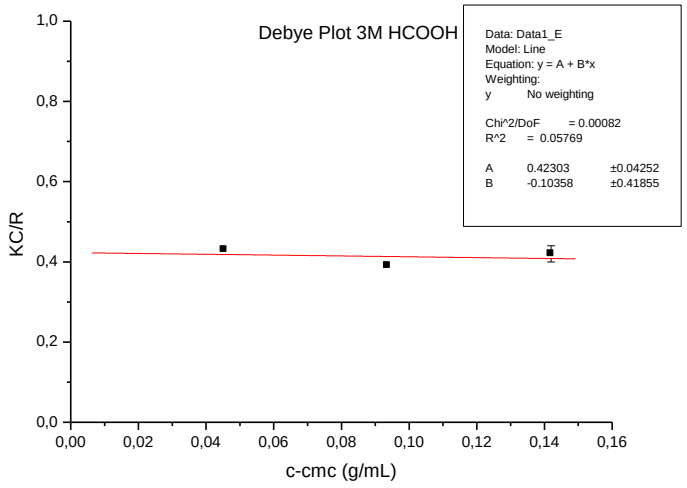
N_{agg} = 53 ± 7

Second virial coefficient:

$A_2 = - 0.6 \pm 0.3$ mL.g^{-1}

HCOOH 3M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R_0P	$\Delta Kc/R_0P$
0,010	0,0052	0,00483		2,0	0,7	8,187E-08	2,703062E-08	1,74	0,57
0,015	0,0078	0,00724		2,3	1,4	9,2757E-08	5,716525E-08	2,30	1,42
0,030	0,0155	0,01448		7,9	0,6	3,2245E-07	2,346869E-08	1,33	0,10
0,059	0,0306	0,02848		23,8	0,7	9,7315E-07	2,765280E-08	0,86	0,02
0,100	0,0518	0,04828		58,2	0,7	2,3818E-06	3,041890E-08	0,60	0,01
0,200	0,1036	0,09656	0,045358	163,2	0,9	6,6774E-06	3,594096E-08	0,43	0,00
0,300	0,1554	0,14484	0,093637	265,6	2,2	1,0866E-05	8,950722E-08	0,39	0,00
0,400	0,2072	0,19312	0,141916	331,5	14,1	1,3562E-05	5,749477E-07	0,42	0,02
0,520	0,2694	0,25105	0,1998508	338,1	1,1	1,3829E-05	4,348307E-08	0,54	0,00



For 3M HCOOH:

$M_w^{-1} = 0.42 \pm 0.05\ kDa^{-1}$

$M_w = 2.38 \pm 0.28\ kDa$

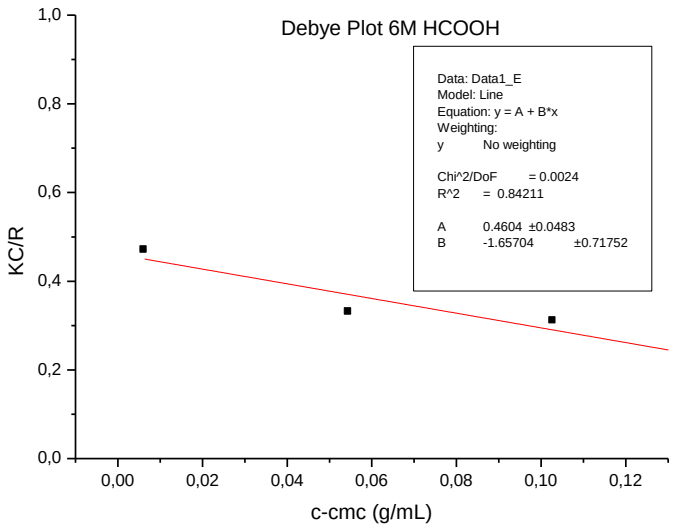
$N_{agg} = 4.9 \pm 0.6$

Second virial coefficient:

$A_2 = -0.1 \pm 0.4\ mL.g^{-1}$

HCOOH 6M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R_0P	$\Delta Kc/R_0P$
0,010	0,0052	0,00483		4,1	2,5	1,6577E-07	1,025631E-07	0,86	0,53
0,015	0,0078	0,00724		3,4	0,1	1,3823E-07	2,361676E-09	1,55	0,03
0,030	0,0155	0,01448		9,7	2,7	3,9764E-07	1,095548E-07	1,07	0,30
0,059	0,0306	0,02848		28,1	1,0	1,1477E-06	4,024563E-08	0,73	0,03
0,100	0,0518	0,04828	0,006279	73,5	0,6	3,0048E-06	2,577367E-08	0,47	0,00
0,200	0,1036	0,09656	0,054558	213,8	1,2	8,7459E-06	4,865649E-08	0,33	0,00
0,300	0,1554	0,14484	0,102837	341,1	1,4	1,3955E-05	5,670975E-08	0,31	0,00
0,520	0,2694	0,25105	0,2090508	400,0	2,5	1,6361E-05	1,018291E-07	0,45	0,00



For 6M HCOOH:

$M_w^{-1} = 0.46 \pm 0.05\ kDa^{-1}$

$M_w = 2.17 \pm 0.24\ kDa$

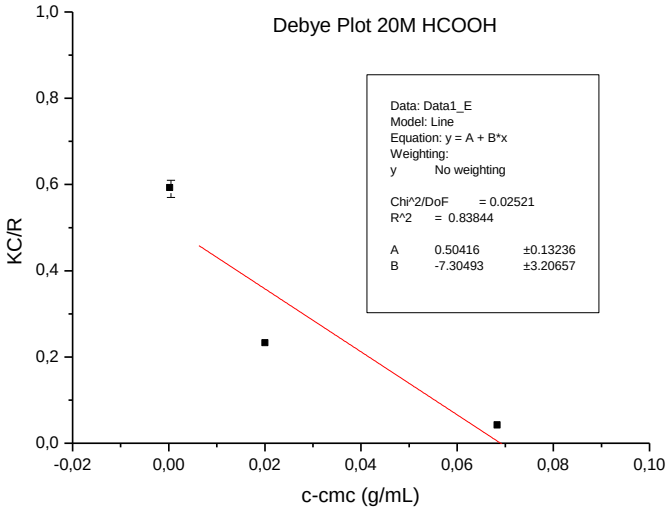
$\mathbf{N_{agg} = 4.5 \pm 0.5}$

Second virial coefficient:

$A_2 = -\ 1.7 \pm 0.7\ mL.g^{-1}$

HCOOH 20M

c diamide (M)	Φ	c (g/mL)	c-cmc (g/mL)	I (kcps)	ΔI (kcps)	R(θ)	ΔR(θ)	Kc/R_0P	$\Delta Kc/R_0P$
0,010	0,0052	0,00483		1,5	0,4	6,1766E-08	1,797048E-08	2,31	0,67
0,015	0,0078	0,00724		5,3	0,5	2,162E-07	1,887864E-08	0,99	0,09
0,030	0,0155	0,01448		10,0	1,1	4,0796E-07	4,503315E-08	1,05	0,12
0,059	0,0306	0,02848	0,00048461	34,9	1,3	1,4285E-06	5,249619E-08	0,59	0,02
0,100	0,0518	0,04828	0,020279	151,6	0,8	6,2009E-06	3,096409E-08	0,23	0,00
0,200	0,1036	0,09656	0,068558	1760,8	84,0	7,2027E-05	3,434989E-06	0,04	0,00
0,300	0,1554	0,14484	0,116837	5417,6	399,3	0,00022161	1,633313E-05	0,02	0,00
0,400	0,2072	0,19312	0,165116	9469,2	126,9	0,00038734	5,190682E-06	0,01	0,00
0,520	0,2694	0,25105	0,2230508	5393,7	52,7	0,00022063	2,154988E-06	0,03	0,00



For 20M HCOOH:

$M_w^{-1} = 0.50 \pm 0.13\ kDa^{-1}$

$M_w = 2.0 \pm 0.5\ kDa$

N_{agg} = 4.1 ± 1.0

Second virial coefficient:

A_2 = - 7.3 ± 3.2 mL.g^{-1}

3. Calculation of activity coefficients

Considering an electrolyte $\nu^+\nu^-$ dissociated in water in ν^+ cations and ν^- anions, the electrolyte activity coefficient γ_{salt} is usually derived from the following general equation of activity:

$$a = \nu_+^{\nu_+}\nu_-^{\nu_-}(m\gamma_{salt})^{(\nu_+ + \nu_-)}$$

where m is the molality in mol/kg, given by: m=1000C/(ρ(1000-CM/ρ).

This leads to a = m²·γ_{salt}^2 for monovalent acids (for which $\nu_+ = \nu_- = 1$), to a = 4m^3·γ_{salt}^3 for diacids such as H_2SO_4 ($\nu_+ = 2, \nu_- = 1$), and to a = 27m^4·γ_{salt}^4 for H_3PO_4 ($\nu_+ = 3, \nu_- = 1$). Nevertheless in this later case, and because of the very low pH value, we actually considered the convention $\nu_+ = \nu_- = 1$ for H_3PO_4, leading to a = m²·γ_{salt}^2. Indeed this convention corresponds to the choice of the experimental measurements (R. F. Platford, *J. Sol. Chem.* **1975**, *4*, 591-598; K. L. Elmore, C. M. Mason, J. H. Christensen, *J. Am. Chem. Soc.* **1946**, *68*, 2528-2532).

For each acid, the activity coefficient γ_{salt} was obtained from a fit of the experimental data found in literature (V. M. M. Lobo, "*Electrolyte solutions: data on thermodynamic and transport properties*", Coimbra Ed., Lisbon Portugal, **1984**; R. A. Robinson, R. H. Stokes, "Electrolyte solutions", Butterworths, **1970**; R. F. Platford, *J. Sol. Chem.* **1975**, *4*, 591-598; K. L. Elmore, C. M. Mason, J. H. Christensen, *J. Am. Chem. Soc.* **1946**, *68*, 2528-2532).

The following fitting equations have been considered:

$log_{10}\,\gamma_{salt} = -0.509m^{1/2} + Am + Bm^2$ for $HClO_4$, HCOOH, and H_3PO_4

$log_{10}\,\gamma_{salt} = -0.509\frac{m^{1/2}}{1+Cm^{1/2}} + Am + Bm^2$ for HNO_3 and HCl

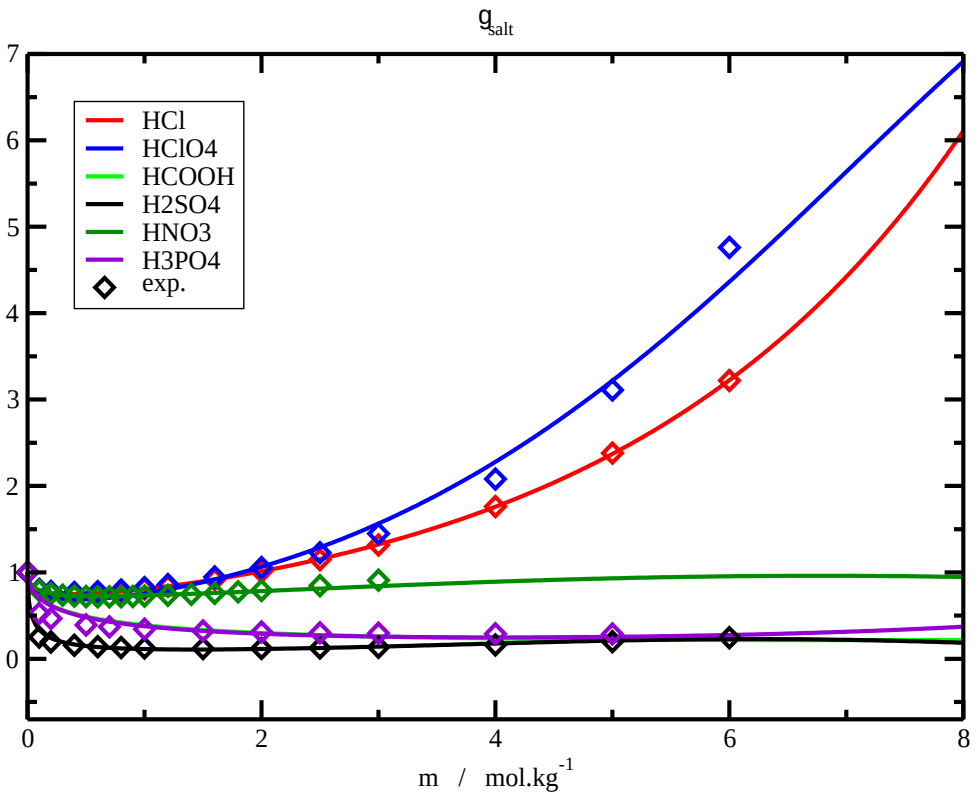
$log_{10}\,\gamma_{salt} = -1.763m^{1/2} + Am + Bm^2$ for H_2SO_4

These expressions are very classical expansions of activity coefficients in electrolyte theory (J. M. G. Barthel, H. Krienke, W. Kunz, "*Physical Chemistry of Electrolyte Solutions"*, Springer, **1998**) similar to the Specific Ion Theory (SIT) or Pitzer approaches (I. Grenthe, A. Plyasunov, *Pure Appl. Chem.* **1997**, *69*, 951-958; Hamer & Wu, *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047-1099). The first term corresponds to the Debye-Hückel limiting law, that can be cut by the *C* coefficient at high concentration if necessary. The next terms *A* and *B* represent specific interactions between the ions such as the effect of the size of the particles that can be modulated by the ionic association.

The following fitted coefficients were derived:

	A	B	C
HNO_3	0.06711	-0.0047	1.5905
HCl	0.128	0.00112	1.2895
$HClO_4$	0.403	-0.0148	
HCOOH	0.098	-0.0001	
H_2SO_4	0.855	-0.0404	
H_3PO_4	0.0793	0.005853	

Using these coefficients, the activity coefficients for each acid were determined as a function of the molality:



In this first approach, we consider that co-extracted water is always present, but does not interfere with the differences in nucleation by acids as evidenced. If this term is taken into account, one has:

$$nL + mH_2O + El \Leftrightarrow AElH_2O \qquad \text{(C1)}$$

instead of :

$$nL + El \Leftrightarrow AEl \qquad \text{(C2)}$$

The amount m of co-extracted water, typically around m=1, depends on the peculiar electrolyte under study, but does not interfere, as long as the activity of water a_{H_2O} is approximately constant whatever the concentration of acid. This is true for dilute solutions, with an asymptotic behavior where activity and mole fraction are assumed to be equal:

$a_{H_2O} = x^w_{H_2O}$

Typically, if C_{salt} = 6 mol/L and C_{H_2O} = 55 mol/L, then $x^w_{H_2O}$ = 0.9 (close to 1).

Therefore, the equilibrium constant $K^0 = \frac{a_{AElH_2O}}{(a_L)^n (a_{H_2O})^m (a_{El})^1}$ gives $K^0 (a_{H_2O})^m = \frac{a_{AElH_2O}}{(a_L)^n (a_{El})^1}$

and case (C2) becomes valid.