

# Catalysed quaternization of coordinated triethylamine by ethyl iodide: further developments in the kinetic analysis

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## Abstract

A new approach in the kinetic analysis of the joint homogeneous–heterogeneous catalysis of the quaternization of silver(I) coordinated triethylamine by ethyl iodide in toluene is presented. This complex competitive process was thoroughly scrutinized and the set of solution and surface rate equations were integrated under a novel perspective thus leading to the calculation of solution rate constants as well as guesstimates of the superficial quaternization rate. Testing the rate equations developed herein also required the performance of kinetic runs over a wider range of experimental conditions, than those previously reported.

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## 1. Introduction

Over the last 25 years, and in particular after Moroz et al.'s [1] synthesis of active sites over catalytic supports, the significance of the three-dimensional molecular architecture in catalysis has been growing in chemical, pharmaceutical and materials science [2]. In fact, ever since the early 1980s several joint homogeneous–heterogeneous catalytic processes [3–5] have been rationalized in terms of molecular tailoring construction processes over surfaces. Cooperative homogeneous–heterogeneous catalysis for the Menshutkin reaction in benzene [5] and toluene has been reported before and a preliminary analysis of the kinetic data exposed a new competitive reaction between uncoordinated silver nitrate and ethyl iodide [6].

A thorough comprehension of this biphasic catalytic quaternization of silver coordinated triethylamine by ethyl iodide implies the description of this complex process in terms of appropriate rate equations. In this work, a set of differential rate equations, based on the superficial molecular arrangement previously proposed [6], was developed and integrated over extended time periods, after a set of adequate approximations.

In order to thoroughly test the rate equations obtained, as well as the underlying simplifications, a new set of kinetic runs was carried out, extending those previously reported, over a wider range of experimental conditions. This kinetic analysis was successfully accomplished and allowed the calculation of solution rate constant as well as guesstimates of the superficial rate constant for the quaternization process, apart from providing estimates for the rate constant of the competitive solution process, previously reported [6].

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## 2. Materials and methods

### 2.1. Reagents and solutions

Toluene *Aristar* grade (purity  $\geq 99.95\%$ ) was supplied by BDH and was used without further purification. Triethylamine, Merck-p. synthesis and ethyl iodide BDH-GPR grade (purity  $\geq 99\%$ ), were purified as previously described [6,7]. The purity of the solvent and reagents was checked by GC, being 99.98% for the solvent toluene, 99.94% for triethylamine and 99.75% for ethyl iodide.

Silver nitrate GPR grade (purity  $\geq 99.8\%$ ) was supplied by BDH and was used without further purification. Silver iodide was synthesised before each run according to a procedure formerly described [8,9]. The polycrystalline solid obtained was predominantly composed of  $\beta$ -AgI and had a BET ( $N_2$ ) specific surface area of  $0.407 \pm 0.003 \text{ m}^2 \text{ g}^{-1}$ .

The amine and ethyl iodide solutions in toluene were prepared, by weight, in volumetric flasks and under a light  $N_2$  flux as previously described [10,11].

### 2.2. Kinetic runs

The kinetic experiments were performed at  $25.0 \pm 0.05^\circ\text{C}$  and under constant stirring with the previously described set up. The experimental procedure being also identical to the one described before.

The kinetic runs were monitored collecting reaction mixture samples and the amine content as well as the silver content determined by potentiometric back-titration, a procedure that ensured the reaction under study was simultaneously interrupted in the collected sample mixture [6] and simultaneously no interferences in the analytical method [12,13]. The almost simultaneous analysis of the reaction mixtures, in terms of the amine and silver content was accomplished using a specifically built computer-controlled multi-electrode switch to command two automatic titration assemblies and a Radiometer PHM64 pH Meter [14].

#### 2.2.1. Amine titration

The usual acid–base titration, in anhydrous acetic acid, proved to be inappropriate due to the interference of silver ions while the acid–base titration, in aqueous media showed to be accurate [6]. The

amine concentration in sample reaction mixtures was determined by potentiometric back-titration, of an excess of perchloric acid ( $\approx 0.01 \text{ M}$ ) with standardised sodium hydroxide ( $\approx 0.04 \text{ M}$ ) and the titration monitored using a Radiometer G2040C glass electrode and a Radiometer K4040 reference calomel electrode.

#### 2.2.2. Silver titration

Difficulties have been reported for the silver titration, in the presence of solids, while iodide titration did not show interferences [6], so after carefully checking the reliability of the procedure, the silver concentration in solution was determined by potentiometric back-titration of an excess of standardised potassium iodide with silver nitrate. This titration was monitored using a Radiometer P4040 silver electrode and as reference a Radiometer K6040 modified calomel electrode ( $\text{Hg}|\text{Hg}_2\text{SO}_4||\text{K}_2\text{SO}_4(\text{sat})||$ ).

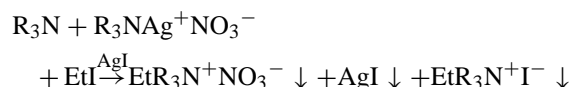
#### 2.2.3. Reaction products

The solid reaction products for the quaternization reaction of triethylamine with ethyl iodine, in toluene, in the presence of soluble silver nitrate were analysed and are composed of tetraethylammonium nitrate and silver iodide [6].

## 3. Experimental results

The experimental data, obtained in six independent runs for the quaternization of triethylamine, coordinated and uncoordinated, by ethyl iodide in the presence or absence of solid silver iodide, are presented in Fig. 1. These plots clearly evidence the effect of coordination on the rate of amine consumption as well as the surface effect on the quaternization rate.

These data confirm previous studies [6] on the reaction system



which lead to the proposal of reaction in Scheme 1 to represent the overall solution and surface process. In this model,  $k_Q$  and  $k'_Q$  are, respectively, the rate constants for the solution and surface catalysed quaternization of the coordinated amine by the ethyl iodide,  $k_M$  and  $k'_M$  the solution and surface rate constants

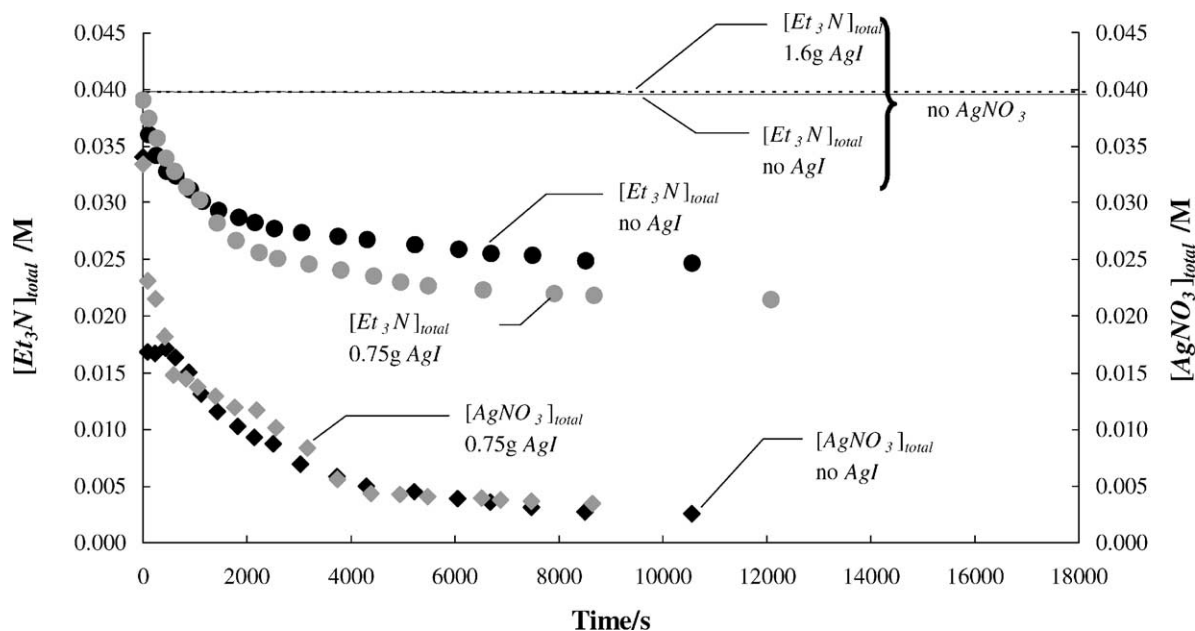
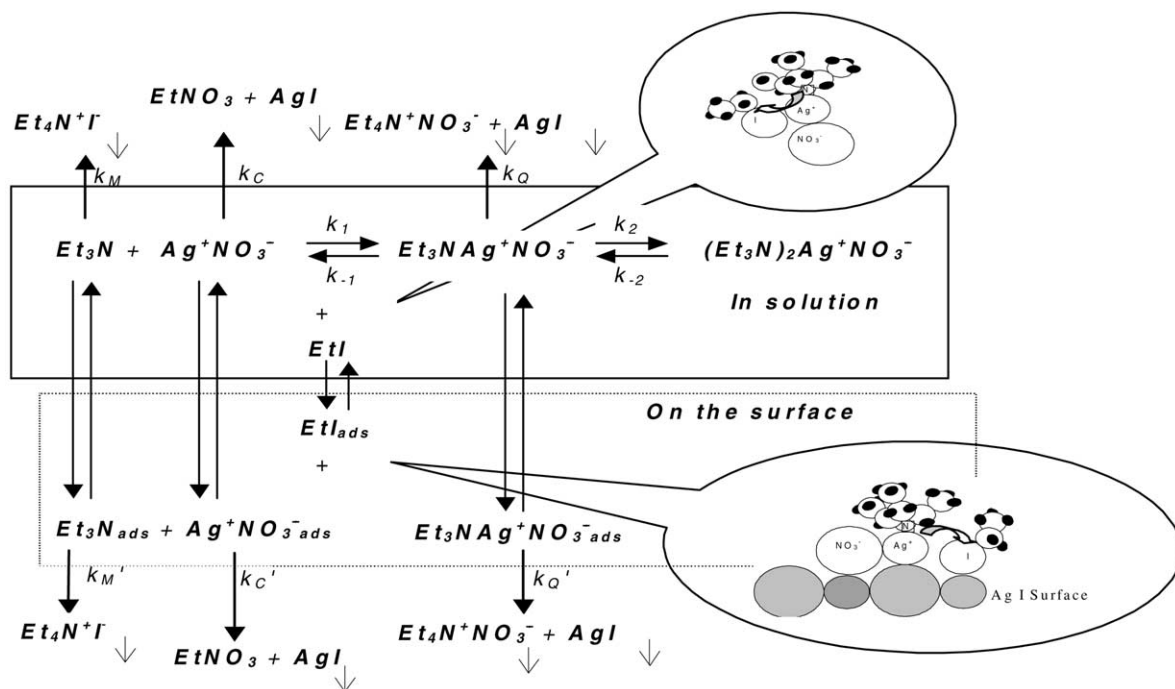


Fig. 1. Plots of kinetic runs for the quaternization of coordinated (runs 1 and 4) and uncoordinated triethylamine by ethyl iodide in the presence and absence of silver iodide.



Scheme 1. Schematic representation of the molecular model proposed to interpret the silver iodide catalysed quaternization of coordinated triethylamine by ethyl iodide in toluene.

Table 1

Set of initial experimental conditions of the kinetic runs used to test the novel approach in the calculation of kinetic parameters

Run	Initial conditions			
	Reagents	[Et <sub>3</sub> N]AgNO <sub>3</sub> ] (M)	[EtI] (M)	$m_{\text{AgI}}^0$ (g)
1 <sup>a</sup>	[Et <sub>3</sub> N]/M = 0.0390 <sub>4</sub> [AgNO <sub>3</sub> ]/M = 0.0340 <sub>3</sub>	0.0335 <sub>7</sub>	0.0399 <sub>1</sub>	0.00
2 <sup>a</sup>	[Et <sub>3</sub> N]/M = 0.0390 <sub>4</sub> [AgNO <sub>3</sub> ]/M = 0.0168 <sub>6</sub>	0.0159 <sub>5</sub>	0.0399 <sub>0</sub>	0.00
3 <sup>a</sup>	[Et <sub>3</sub> N]/M = 0.0385 <sub>4</sub> [AgNO <sub>3</sub> ]/M = 0.0341 <sub>3</sub>	0.0337 <sub>2</sub>	0.0384 <sub>0</sub>	1.5 <sub>0</sub>
4	[Et <sub>3</sub> N]/M = 0.0390 <sub>4</sub> [AgNO <sub>3</sub> ]/M = 0.0333 <sub>9</sub>	0.0329 <sub>2</sub>	0.0399 <sub>1</sub>	0.7 <sub>5</sub>
5	[Et <sub>3</sub> N]/M = 0.0375 <sub>5</sub> [AgNO <sub>3</sub> ]/M = 0.0167 <sub>9</sub>	0.0159 <sub>0</sub>	0.0400 <sub>7</sub>	1.5 <sub>3</sub>
6	[Et <sub>3</sub> N]/M = 0.0400 <sub>2</sub> [AgNO <sub>3</sub> ]/M = 0.0332 <sub>4</sub>	0.0326 <sub>2</sub>	0.1570 <sub>8</sub>	0.00
7	[Et <sub>3</sub> N]/M = 0.0400 <sub>2</sub> [AgNO <sub>3</sub> ]/M = 0.0327 <sub>7</sub>	0.0322 <sub>0</sub>	0.1570 <sub>8</sub>	1.5 <sub>6</sub>
8	[Et <sub>3</sub> N]/M = 0.0400 <sub>0</sub> [AgNO <sub>3</sub> ]/M = 0.0302 <sub>1</sub>	0.0294 <sub>5</sub>	0.1561 <sub>2</sub>	0.00
9	[Et <sub>3</sub> N]/M = 0.0400 <sub>0</sub> [AgNO <sub>3</sub> ]/M = 0.0299 <sub>3</sub>	0.0291 <sub>3</sub>	0.1588 <sub>8</sub>	1.5 <sub>4</sub>
10	[Et <sub>3</sub> N]/M = 0.0212 <sub>5</sub> [AgNO <sub>3</sub> ]/M = 0.0096 <sub>7</sub>	0.0094 <sub>0</sub>	0.1585 <sub>0</sub>	1.5 <sub>7</sub>
11	[Et <sub>3</sub> N]/M = 0.0113 <sub>6</sub> [AgNO <sub>3</sub> ]/M = 0.0047 <sub>4</sub>	0.0046 <sub>1</sub>	0.1585 <sub>0</sub>	0.00
12	[Et <sub>3</sub> N]/M = 0.0113 <sub>6</sub> [AgNO <sub>3</sub> ]/M = 0.0047 <sub>4</sub>	0.0159 <sub>5</sub>	0.1585 <sub>0</sub>	1.5 <sub>4</sub>

<sup>a</sup> Experimental data set presented previously [6].

for the Menshutkin reaction,  $k_C$  the rate constant for the competitive solution reaction between silver nitrate and the ethyl iodide and  $K_1 = k_1/k_{-1}$  and  $K_2 = k_2/k_{-2}$  are the equilibrium constants for the formation of the 1:1 and 1:2 silver–amine complexes.

Assessing the relevance of coordination and its consequences in terms of the resulting superficial molecular arrangement, within the overall quaternization process involved a meticulous mathematical analysis of Scheme 1, in terms of the rate equations for all the species implicated. Finally, the kinetic data obtained under various experimental conditions, namely in the presence and absence of an initial amount of solid, and for different amine/silver nitrate ratios as well as with various ethyl iodide concentrations was used to test the rate developed and to extract relevant kinetic parameters. In Table 1 the initial experimental conditions for the 12 kinetic runs considered in the novel kinetic analysis are presented, while in Table 2, only the experimental data pertaining to 9 runs, not reported previously, were included.

#### 4. Evaluation of kinetic parameters: a new approach

The overall consumption of the reactants involved in Scheme 1, ethyl iodide, triethylamine and silver nitrate, includes solution and superficial components, so the global rates of reaction must include solution and surface terms that when expressed in terms of the moles transformed per unit time may be written as

$$-V \frac{d[\text{EtI}]_{\text{total}}}{dt} = -\left( V \frac{d[\text{EtI}]_{\text{tot}}}{dt} + a_s m \frac{d[\text{EtI}]_{\text{ads}}}{dt} \right) \quad (1)$$

$$-V \frac{d[\text{Et}_3\text{N}]_{\text{total}}}{dt} = -\left( V \frac{d[\text{Et}_3\text{N}]_{\text{tot}}}{dt} + a_s m \frac{d[\text{Et}_3\text{N}]_{\text{tot,ads}}}{dt} \right) \quad (2)$$

$$-V \frac{d[\text{AgNO}_3]_{\text{total}}}{dt} = -\left( V \frac{d[\text{AgNO}_3]_{\text{tot}}}{dt} + a_s m \frac{d[\text{AgNO}_3]_{\text{tot,ads}}}{dt} \right) \quad (3)$$

Table 2

Set of experimental data, fitted and calculated values for kinetic runs 4–12<sup>a</sup>

Time (s)	[AgNO <sub>3</sub> ] <sub>total</sub> (M)	[AgNO <sub>3</sub> ] <sub>corr</sub> (M)	Time (s)	[Et <sub>3</sub> N] <sub>total</sub> (M)	[Et <sub>3</sub> N] <sub>corr</sub> (M)	[AgNO <sub>3</sub> ] <sub>fit</sub> (M)	[Comp1:1] (M)	[Et <sub>3</sub> N] (M)	[EtI] (M)
Run 4 (0.75 g AgI)									
0	0.03339	0.03339	0	0.03904	0.03904	0.03339	0.03292	0.00512	0.03991
86	0.02303	0.02310	116	0.03731	0.03742	0.02590	0.02514	0.01074	0.03242
241	0.02142	0.02150	275	0.03556	0.03568	0.02160	0.02082	0.01332	0.02812
420	0.01815	0.01822	446	0.03381	0.03394	0.01890	0.01817	0.01427	0.02542
582	0.01476	0.01483	611	0.03258	0.03273	0.01700	0.01631	0.01501	0.02352
821	0.01441	0.01448	845	0.03118	0.03134	0.01530	0.01466	0.01536	0.02182
1050	0.01370	0.01377	1087	0.02996	0.03012	0.01430	0.01371	0.01521	0.02082
1397	0.01289	0.01297	1424	0.02803	0.02819	0.01310	0.01258	0.01458	0.01962
1762	0.01188	0.01196	1793	0.02645	0.02662	0.01190	0.01144	0.01424	0.01842
2182	0.01164	0.01172	2234	0.02540	0.02557	0.01080	0.01038	0.01438	0.01732
2556	0.01012	0.01020	2593	0.02488	0.02506	0.00980	0.00940	0.01490	0.01632
3161	0.00831	0.00837	3193	0.02435	0.02454	0.00820	0.00785	0.01595	0.01472
3736	0.00556	0.00560	3803	0.02382	0.02402	0.00680	0.00649	0.01689	0.01332
4379	0.00430	0.00434	4435	0.02330	0.02350	0.00550	0.00524	0.01774	0.01202
4942	0.00425	0.00428	4963	0.02277	0.02297	0.00480	0.00457	0.01797	0.01132
5470	0.00404	0.00408	5495	0.02242	0.02263	0.00440	0.00419	0.01799	0.01092
6508	0.00391	0.00395	6548	0.02207	0.02228	0.00380	0.00361	0.01831	0.01032
6872	0.00376	0.00380	7917	0.02172	0.02194	0.00350	0.00333	0.01823	0.01002
7473	0.00363	0.00367	8672	0.02155	0.02177	0.00330	0.00314	0.01834	0.00982
8642	0.00342	0.00346	12086	0.02120	0.02142	0.00320	0.00000	0.02140	0.00972
Run 5 (1.53 g AgI)									
0	0.01679	0.01679	0	0.03755	0.03755	0.01679	0.01590	0.01990	0.04007
146	0.01002	0.01007	163	0.03288	0.03305	0.01170	0.01105	0.02075	0.03498
256	0.00898	0.00904	287	0.03073	0.03091	0.01000	0.00946	0.02036	0.03328
437	0.00830	0.00835	459	0.02929	0.02948	0.00880	0.00832	0.02022	0.03208
678	0.00772	0.00777	690	0.02876	0.02895	0.00780	0.00737	0.02077	0.03108
854	0.00680	0.00685	876	0.02840	0.02860	0.00700	0.00660	0.02120	0.03028
1154	0.00598	0.00602	1167	0.02804	0.02825	0.00620	0.00584	0.02164	0.02948
1395	0.00514	0.00518	1411	0.02768	0.02790	0.00550	0.00518	0.02208	0.02878
1710	0.00441	0.00445	1723	0.02732	0.02754	0.00470	0.00442	0.02252	0.02798
2102	0.00367	0.00370	2117	0.02697	0.02719	0.00390	0.00366	0.02306	0.02718
2526	0.00286	0.00289	2539	0.02661	0.02684	0.00330	0.00310	0.02330	0.02658
3022	0.00240	0.00242	3043	0.02643	0.02667	0.00270	0.00253	0.02383	0.02598
3523	0.00198	0.00200	3539	0.02625	0.02650	0.00230	0.00215	0.02405	0.02558
4125	0.00171	0.00173	4140	0.02618	0.02643	0.00190	0.00178	0.02438	0.02518
4817	0.00148	0.00150	4827	0.02607	0.02633	0.00150	0.00140	0.02470	0.02478
5487	0.00122	0.00123	5501	0.02596	0.02623	0.00130	0.00121	0.02481	0.02458
6175	0.00102	0.00104	6190	0.02589	0.02617	0.00110	0.00103	0.02503	0.02438
7195	0.00083	0.00084	7207	0.02582	0.02611	0.00090	0.00084	0.02514	0.02418
8250	0.00068	0.00069	8303	0.02571	0.02601	0.00060	0.00056	0.02536	0.02388
9230	0.00041	0.00042	9245	0.02561	0.02591	0.00040	0.00000	0.02590	0.02368
Run 6 (no AgI)									
0	0.03324	0.03324	0	0.04002	0.04002	0.03324	0.03262	0.00623	0.15708
77	0.00985	0.00988	113	0.02972	0.02980	0.01680	0.01623	0.01243	0.14064
193	0.00916	0.00918	209	0.02898	0.02907	0.01150	0.01097	0.01707	0.13534
318	0.00820	0.00823	331	0.02698	0.02708	0.00880	0.00838	0.01788	0.13264
457	0.00767	0.00770	469	0.02532	0.02542	0.00710	0.00676	0.01796	0.13094
585	0.00574	0.00577	597	0.02415	0.02426	0.00590	0.00561	0.01811	0.12974
706	0.00501	0.00503	720	0.02332	0.02343	0.00470	0.00447	0.01847	0.12854
902	0.00181	0.00182	918	0.02265	0.02277	0.00310	0.00294	0.01954	0.12694

Table 2 (Continued)

Time (s)	[AgNO <sub>3</sub> ] <sub>total</sub> (M)	[AgNO <sub>3</sub> ] <sub>corr</sub> (M)	Time (s)	[Et <sub>3</sub> N] <sub>total</sub> (M)	[Et <sub>3</sub> N] <sub>corr</sub> (M)	[AgNO <sub>3</sub> ] <sub>fit</sub> (M)	[Comp1:1] (M)	[Et <sub>3</sub> N] (M)	[EtI] (M)
1049	0.00139	0.00140	1076	0.02232	0.02244	0.00220	0.00208	0.02008	0.12604
1206	0.00097	0.00098	1218	0.02199	0.02211	0.00160	0.00151	0.02041	0.12544
1379	0.00062	0.00062	1407	0.02182	0.02195	0.00100	0.00094	0.02084	0.12484
1636	0.00016	0.00016	1649	0.02165	0.02178	0.00060	0.00057	0.02117	0.12444
2042	0.00010	0.00010	2061	0.02149	0.02162	0.00030	0.00028	0.02128	0.12414
2669	0.00006	0.00006	2682	0.02132	0.02146	0.00010	0.00009	0.02139	0.12394
3305	0.00004	0.00004	3319	0.02115	0.02129	0.00000	0.00000	0.02130	0.12384
4040	0.00002	0.00002	4051	0.02115	0.02130	–	–	–	–
4820	0.00000	0.00000	4839	0.02099	0.02114	–	–	–	–
Run 7 (1.56 g AgI)									
0	0.03277	0.03277	0	0.04002	0.04002	0.03277	0.03220	0.00660	0.15708
83	0.01026	0.01033	105	0.03151	0.03172	0.01730	0.01665	0.01375	0.14162
182	0.00922	0.00928	198	0.03017	0.03039	0.01170	0.01123	0.01803	0.13602
333	0.00761	0.00767	348	0.02884	0.02906	0.00840	0.00794	0.02024	0.13272
437	0.00653	0.00658	455	0.02760	0.02783	0.00700	0.00671	0.02041	0.13132
613	0.00523	0.00527	629	0.02633	0.02656	0.00520	0.00510	0.02100	0.12952
747	0.00395	0.00479	761	0.02517	0.02540	0.00410	0.00405	0.02135	0.12842
882	0.00228	0.00277	896	0.02416	0.02440	0.00300	0.00311	0.02161	0.12732
1001	0.00090	0.00108	1015	0.02333	0.02357	0.00210	0.00226	0.02116	0.12642
1132	0.00039	0.00048	1145	0.02266	0.02290	0.00140	0.00160	0.02130	0.12572
1241	0.00018	0.00021	1256	0.02226	0.02250	0.00100	0.00113	0.02133	0.12532
1404	0.00009	0.00011	1420	0.02183	0.02207	0.00060	0.00075	0.02125	0.12492
1634	0.00006	0.00007	1653	0.02149	0.02174	0.00030	0.00047	0.02117	0.12462
2086	0.00004	0.00005	2098	0.02116	0.02141	0.00010	0.00019	0.02119	0.12442
2612	0.00003	0.00003	2625	0.02083	0.02108	0.00000	0.00000	0.02110	0.12432
3323	0.00003	0.00003	3339	0.02066	0.02092	–	–	–	–
4024	0.00001	0.00001	4039	0.02049	0.02076	–	–	–	–
4777	0.00001	0.00001	4792	0.02049	0.02077	–	–	–	–
Run 8 (no AgI)									
0	0.03021	0.03021	0	0.04000	0.04000	0.03021	0.02945	0.00905	0.15612
72	0.01178	0.01180	85	0.03074	0.03081	0.01600	0.01538	0.01418	0.14191
144	0.00690	0.00691	164	0.02943	0.02952	0.01040	0.00988	0.01858	0.13631
244	0.00582	0.00584	275	0.02865	0.02874	0.00700	0.00660	0.02130	0.13291
362	0.00505	0.00507	380	0.02787	0.02797	0.00560	0.00527	0.02207	0.13151
474	0.00499	0.00501	489	0.02735	0.02745	0.00480	0.00451	0.02241	0.13071
606	0.00489	0.00491	619	0.02709	0.02720	0.00380	0.00357	0.02317	0.12971
693	0.00321	0.00322	706	0.02683	0.02694	0.00310	0.00291	0.02361	0.12901
840	0.00110	0.00111	854	0.02657	0.02669	0.00200	0.00187	0.02457	0.12791
957	0.00075	0.00075	970	0.02631	0.02643	0.00160	0.00150	0.02470	0.12751
1106	0.00050	0.00050	1116	0.02605	0.02618	0.00130	0.00121	0.02481	0.12721
1268	0.00031	0.00032	1280	0.02579	0.02592	0.00070	0.00065	0.02515	0.12661
1518	0.00007	0.00007	1532	0.02553	0.02567	0.00040	0.00037	0.02527	0.12631
1840	0.00009	0.00009	1858	0.02527	0.02541	0.00030	0.00028	0.02508	0.12621
2389	–0.00002	–0.00002	2402	0.02501	0.02515	0.00010	0.00000	0.02520	0.12601
Run 9 (1.54 g AgI)									
0	0.02993	0.02993	0	0.04000	0.04000	0.02993	0.02913	0.00933	0.15889
62	0.01140	0.01147	75	0.03178	0.03198	0.01690	0.01624	0.01444	0.14586
149	0.00881	0.00887	166	0.02813	0.02834	0.01020	0.00972	0.01762	0.13916
227	0.00587	0.00592	240	0.02761	0.02783	0.00710	0.00671	0.02031	0.13606
323	0.00368	0.00371	337	0.02501	0.02522	0.00480	0.00454	0.02014	0.13376
435	0.00203	0.00205	450	0.02396	0.02418	0.00300	0.00283	0.02103	0.13196
545	0.00113	0.00114	561	0.02266	0.02288	0.00200	0.00189	0.02079	0.13096

Table 2 (Continued)

Time (s)	[AgNO <sub>3</sub> ] <sub>total</sub> (M)	[AgNO <sub>3</sub> ] <sub>corr</sub> (M)	Time (s)	[Et <sub>3</sub> N] <sub>total</sub> (M)	[Et <sub>3</sub> N] <sub>corr</sub> (M)	[AgNO <sub>3</sub> ] <sub>fit</sub> (M)	[Comp1:1] (M)	[Et <sub>3</sub> N] (M)	[EtI] (M)
702	0.00099	0.00100	717	0.02240	0.02262	0.00120	0.00113	0.02133	0.13016
812	0.00084	0.00085	827	0.02222	0.02244	0.00090	0.00085	0.02145	0.12986
961	0.00066	0.00066	974	0.02204	0.02227	0.00060	0.00057	0.02167	0.12956
1100	0.00049	0.00050	1113	0.02188	0.02212	0.00040	0.00038	0.02168	0.12936
1259	0.00016	0.00017	1278	0.02172	0.02196	0.00030	0.00028	0.02168	0.12926
1463	0.00006	0.00006	1479	0.02157	0.02181	0.00010	0.00000	0.02180	0.12906
1839	−0.00018	−0.00019	1858	0.02144	0.02169	—	—	—	—
Run 10 (1.57 g AgI)									
0	0.00967	0.00967	0	0.02125	0.02125	0.00967	0.00940	0.01120	0.15850
65	0.00404	0.00406	85	0.01669	0.01678	0.00530	0.00514	0.01134	0.15413
132	0.00348	0.00350	146	0.01641	0.01650	0.00410	0.00396	0.01226	0.15293
251	0.00238	0.00239	276	0.01614	0.01623	0.00280	0.00270	0.01330	0.15163
349	0.00212	0.00213	370	0.01587	0.01596	0.00190	0.00183	0.01403	0.15073
444	0.00150	0.00151	463	0.01559	0.01569	0.00140	0.00135	0.01425	0.15023
562	0.00056	0.00056	578	0.01532	0.01542	0.00090	0.00086	0.01446	0.14973
668	0.00048	0.00048	692	0.01504	0.01515	0.00060	0.00058	0.01448	0.14943
804	0.00008	0.00008	823	0.01477	0.01487	0.00030	0.00029	0.01459	0.14913
948	0.00006	0.00006	963	0.01450	0.01460	0.00010	0.00000	0.01460	0.14893
1150	0.00006	0.00006	1166	0.01444	0.01455	0.00000	0.00000	0.01455	0.14883
1409	0.00004	0.00004	1430	0.01433	0.01444	—	—	—	—
1709	−0.00002	−0.00002	1726	0.01422	0.01434	—	—	—	—
Run 11 (no AgI)									
0	0.00474	0.00474	0	0.01136	0.01136	0.00474	0.00461	0.00661	0.15852
59	0.00250	0.00251	78	0.01012	0.01012	0.00260	0.00255	0.00745	0.15638
144	0.00086	0.00086	168	0.00930	0.00931	0.00140	0.00137	0.00787	0.15518
225	0.00043	0.00043	241	0.00922	0.00922	0.00080	0.00078	0.00838	0.15458
330	0.00021	0.00021	353	0.00911	0.00912	0.00040	0.00039	0.00869	0.15418
450	0.00014	0.00014	467	0.00903	0.00903	0.00020	0.00020	0.00880	0.15398
553	0.00012	0.00012	566	0.00892	0.00892	0.00010	0.00010	0.00880	0.15388
682	0.00008	0.00008	704	0.00884	0.00884	0.00010	0.00010	0.00870	0.15388
873	0.00004	0.00004	889	0.00875	0.00876	0.00000	0.00000	0.00880	0.15378
981	−0.00000	−0.00000	996	0.00870	0.00871	—	—	—	—
Run 12 (1.54 g AgI)									
0	0.00513	0.00513	0	0.01136	0.01136	0.00513	0.00501	0.00621	0.15850
72	0.00240	0.00241	88	0.00903	0.00907	0.00270	0.00265	0.00635	0.15607
154	0.00090	0.00090	178	0.00848	0.00852	0.00130	0.00127	0.00717	0.15467
232	0.00032	0.00032	252	0.00826	0.00830	0.00080	0.00078	0.00748	0.15417
327	0.00016	0.00016	343	0.00815	0.00820	0.00040	0.00039	0.00779	0.15377
436	0.00012	0.00012	466	0.00796	0.00800	0.00020	0.00020	0.00780	0.15357
592	0.00008	0.00008	625	0.00788	0.00792	0.00020	0.00020	0.00770	0.15357
737	0.00006	0.00006	761	0.00777	0.00781	0.00010	0.00000	0.00780	0.15347
913	0.00004	0.00004	937	0.00766	0.00771	0.00000	0.00000	0.00780	0.15337
1164	0.00002	0.00002	1180	0.00760	0.00765	—	—	—	—
1316	−0.00002	−0.00002	1338	0.00752	0.00757	—	—	—	—

<sup>a</sup> The experimental data for runs 1–3 was presented before [6] in a preliminary analysis of the reaction mechanism.

where the subscript total refers to the overall concentration, the first terms refer to the global concentration in solution, including the various solution species (subscript tot), and the second terms refer to the

corresponding global surface concentration (subscript tot, ads).

Eqs. (2) and (3) must be further specified in terms of the species involved, free and coordinated, and

therefore

$$\begin{aligned}
 & -V \frac{d[\text{Et}_3\text{N}]_{\text{total}}}{dt} \\
 & = -V \left( \frac{d[\text{Et}_3\text{N}]}{dt} + \frac{d[\text{Et}_3\text{NAgNO}_3]}{dt} \right. \\
 & \quad \left. + \frac{d[(\text{Et}_3\text{N})_2\text{AgNO}_3]}{dt} \right) \\
 & \quad - a_s m \left( \frac{d[\text{Et}_3\text{N}]_{\text{ads}}}{dt} + \frac{d[\text{Et}_3\text{NAgNO}_3]_{\text{ads}}}{dt} \right) \quad (4)
 \end{aligned}$$

and

$$\begin{aligned}
 & -V \frac{d[\text{AgNO}_3]_{\text{total}}}{dt} \\
 & = -V \left( \frac{d[\text{AgNO}_3]}{dt} + \frac{d[\text{Et}_3\text{NAgNO}_3]}{dt} \right) \\
 & \quad - a_s m \left( \frac{d[\text{AgNO}_3]_{\text{ads}}}{dt} + \frac{d[\text{Et}_3\text{NAgNO}_3]_{\text{ads}}}{dt} \right) \quad (5)
 \end{aligned}$$

as on one hand steric hindrance is likely to inhibit the adsorption of the silver amine 1:2 complex and on the other this species' consumption, intrinsic to the equilibrium shifts, does not lead to any change in the overall silver nitrate solution concentration.

Further development of these equations, bearing in mind the bimolecular character of quaternization reactions, involves the identification of the contributions for all the species and therefore Eq. (1) should be rewritten as

$$\begin{aligned}
 & -V \frac{d[\text{EtI}]_{\text{total}}}{dt} \\
 & = V k_Q [\text{EtI}] [\text{R}_3\text{NAgNO}_3] \\
 & \quad + V k_C [\text{EtI}] [\text{AgNO}_3] \\
 & \quad + V k_M [\text{EtI}] [\text{R}_3\text{N}] \\
 & \quad + a_s m k'_Q [\text{EtI}]_{\text{ads}} [\text{Et}_3\text{NAgNO}_3]_{\text{ads}} \\
 & \quad + k'_C a_s m [\text{EtI}]_{\text{ads}} [\text{AgNO}_3]_{\text{ads}} \\
 & \quad + k'_M a_s m [\text{EtI}]_{\text{ads}} [\text{Et}_3\text{N}]_{\text{ads}} \quad (6)
 \end{aligned}$$

an equation that can be simplified whenever the coordination equilibria are rapidly re-established and, upon rearrangement leads to

$$\begin{aligned}
 -\frac{d[\text{EtI}]_{\text{total}}}{dt} & = \left( k_Q + \frac{k_C}{K_1 [\text{Et}_3\text{N}]} + \frac{k_M}{K_1 [\text{AgNO}_3]} \right) \\
 & \quad \times [\text{EtI}] [\text{Et}_3\text{NAgNO}_3]
 \end{aligned}$$

$$\begin{aligned}
 & + \frac{a_s m}{V} k'_Q [\text{EtI}]_{\text{ads}} [\text{Et}_3\text{NAgNO}_3]_{\text{ads}} \\
 & + k'_C \frac{a_s m}{V} [\text{EtI}]_{\text{ads}} [\text{AgNO}_3]_{\text{ads}} \\
 & + \frac{a_s m}{V} k'_M [\text{EtI}]_{\text{ads}} [\text{Et}_3\text{N}]_{\text{ads}} \quad (7)
 \end{aligned}$$

Likewise, the rate equations for the consumption of triethylamine and silver nitrate may also be rewritten in an identical form.

These equations are rather complex but a look at the experimental data plots, presented in Fig. 1, make possible a few simplifications namely

- neglecting the contribution of the terms referring to the Menschutkin reactions ( $k_M = 3.3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  [15,16] and  $k'_M \leq k_M$ ), which are very slow,
- neglecting the superficial term of the reaction between free silver nitrate and ethyl iodide that on a first approach may be disregarded versus its solution counterpart.

Therefore, one may write

$$\frac{d[\text{EtI}]_{\text{total}}}{dt} \cong \frac{d[\text{AgNO}_3]_{\text{total}}}{dt} > \frac{d[\text{Et}_3\text{N}]_{\text{total}}}{dt} \quad (8)$$

The integration of Eq. (7), or any of the corresponding rate equations for  $[\text{AgNO}_3]_{\text{total}}$  or  $[\text{Et}_3\text{N}]_{\text{total}}$ , involves variable transformations to interrelate the consumption of all the species involved. These relationships can be obtained from the solution mass balance and equilibrium equations as, due to the low surface area of the solid silver iodide [8,9,17], the fraction of molecules adsorbed can be disregarded when compared with the corresponding quantities in solution.

In the experimental range of conditions studied, specifically for an excess of amine relative to silver nitrate and for concentrations larger than  $10^{-5} \text{ M}$  one may write (see Appendix A)

$$\begin{aligned}
 \Delta[\text{EtI}]_{\text{tot}} & = [\text{EtI}]_{\text{tot},t+\Delta t} - [\text{EtI}]_{\text{tot},t} \\
 & = \Delta[\text{AgNO}_3]_{\text{tot}} = x = [\text{AgNO}_3]_t \\
 & \quad + x_5 \left( 1 + \frac{K_2 [\text{Et}_3\text{N}]_t}{1 + K_2 ([\text{Et}_3\text{NAgNO}_3]_t - x_5)} \right) \quad (9)
 \end{aligned}$$

where  $x$  is the overall change in the ethyl iodide and silver nitrate concentration and  $x_5$  represents the



corresponding decrease in the concentration of the coordinated species,  $\text{Et}_3\text{NAgNO}_3$ .

Correspondingly, and designating the overall change in the amine concentration  $x_1$

$$\begin{aligned}\Delta[\text{Et}_3\text{N}]_{\text{tot}} &= [\text{Et}_3\text{N}]_{\text{tot},t+\Delta t} - [\text{Et}_3\text{N}]_{\text{tot},t} = x_1 \\ &= x_5 + \frac{K_2[\text{Et}_3\text{N}]_t x_5}{1 + K_2([\text{Et}_3\text{NAgNO}_3]_t - x_5)}\end{aligned}\quad (10)$$

Eq. (10) clearly evidences the underlying hypothesis that through equilibrium shifts the decrease in concentration of the complex species, due to its reaction with ethyl iodide, is partially compensated with a corresponding increase in the free amine concentration ( $\Delta[\text{Et}_3\text{N}] < \Delta[\text{Et}_3\text{NAgNO}_3]$ ).

Further simplifications of relationships (9) and (10) are possible under the experimental conditions used, as  $[\text{Et}_3\text{NAgNO}_3]_t \cong 10^{-2} \text{ M}$  the second term can be neglected ( $1 + K_2([\text{Et}_3\text{NAgNO}_3]_t - x_5) \approx 1$ ) and therefore

$$x \approx [\text{AgNO}_3]_t + x_5(1 + K_2[\text{Et}_3\text{N}]_t) \quad (11)$$

and

$$x_5 \approx \frac{x_1}{1 + K_2[\text{Et}_3\text{N}]_t} \quad (12)$$

Consequently

$$x_1 \approx x - [\text{AgNO}_3]_t \quad (13)$$

Expressions (11)–(13) involve simple functions that can be readily introduced in differential Eq. (7), as well as in the corresponding equations for the rates of reaction of  $[\text{AgNO}_3]_{\text{total}}$  and  $[\text{Et}_3\text{N}]_{\text{total}}$ . And accordingly, using the common simplified notation where the index  $t$  is dropped, one may write

$$\begin{aligned}-\frac{d[\text{EtI}]}{dt} = \frac{dx}{dt} &\approx \left( k_Q + \frac{k_C}{K_1[\text{Et}_3\text{N}]} \right) \\ &\times \left( [\text{EtI}] - x - \frac{a_s m}{V} [\text{EtI}]_{\text{ads}} \right) \\ &\times \left( [\text{Et}_3\text{NAgNO}_3] - \frac{x - [\text{AgNO}_3]}{1 + K_2[\text{Et}_3\text{N}]} \right. \\ &\quad \left. - \frac{a_s m}{V} [\text{Et}_3\text{NAgNO}_3]_{\text{ads}} \right) \\ &+ k'_Q \frac{a_s m}{V} [\text{EtI}]_{\text{ads}} [\text{Et}_3\text{NAgNO}_3]_{\text{ads}}\end{aligned}\quad (14)$$

where the amounts adsorbed  $[\text{EtI}]_{\text{ads}}$  and  $[\text{Et}_3\text{NAgNO}_3]_{\text{ads}}$  shall be given by the appropriate adsorption isotherms.

This equation evidences the dependency of the quaternization rate on the concentration of uncoordinated amine, a characteristic previously pointed out in the preliminary analysis of this complex mechanism [6], that was further checked by the analysis of the kinetic runs presented in Table 2.

In Fig. 2 plots for the calculated concentrations of coordinated and free amine for runs 2 and 7, determined as previously reported [6], show that it is possible to identify extended periods of time where the free amine concentration in solution remains almost constant ( $[\text{Et}_3\text{N}] \approx \text{constant} = [\overline{\text{Et}_3\text{N}}] \pm 5\%$ ) and therefore one may resort to an invariable average value for the solution contribution, which allows the integration of the differential rate equations.

Adsorption isotherms in solid–liquid systems usually follow Langmuir or Freundlich type isotherms and for silver iodide in particular previous studies point to Langmuir type adsorption [17–20]. Competition between the triethylamine and ethyl iodide has been reported [5] thus one may write for the surface coverage of ethyl iodide

$$\begin{aligned}\theta_{\text{EtI}} &= \frac{[\text{EtI}]}{1 + b_{\text{EtI}}[\text{EtI}] + b_{\text{Et}_3\text{N}}[\text{Et}_3\text{N}]} \\ &\approx \frac{[\text{EtI}] - x}{(1/b_{\text{EtI}}) + [\text{EtI}] - x + \varphi[\overline{\text{Et}_3\text{N}}]}\end{aligned}\quad (15)$$

where  $\varphi$  is the ratio of adsorption coefficients ( $\varphi = b_{\text{Et}_3\text{N}}/b_{\text{EtI}}$ ). Likewise competition between silver nitrate and coordinated silver is expected so, for the surface coverage of coordinated silver

$$\begin{aligned}\theta_{\text{R}_3\text{NAgNO}_3} &= \frac{b_{\text{Et}_3\text{NAgNO}_3} [\text{Et}_3\text{NAgNO}_3]}{1 + b_{\text{AgNO}_3} [\text{AgNO}_3] + b_{\text{Et}_3\text{NAgNO}_3} [\text{Et}_3\text{NAgNO}_3]} \\ &\approx \frac{b_{\text{Et}_3\text{NAgNO}_3} ([\text{Et}_3\text{NAgNO}_3] - x_5)}{1 + b_{\text{Et}_3\text{NAgNO}_3} ([\text{Et}_3\text{NAgNO}_3] - x_5)} \\ &= \frac{b_{\text{Et}_3\text{NAgNO}_3} ([\text{Et}_3\text{NAgNO}_3] - \phi x_1)}{1 + b_{\text{Et}_3\text{NAgNO}_3} ([\text{Et}_3\text{NAgNO}_3] - \phi x_1)}\end{aligned}\quad (16)$$

where the term referring to the silver nitrate adsorption was disregarded due to the minute concentration of this species, when compared with the concentration of coordinated silver ( $[\text{AgNO}_3] \approx 10^{-4} \times [\text{Et}_3\text{NAgNO}_3]$ ),

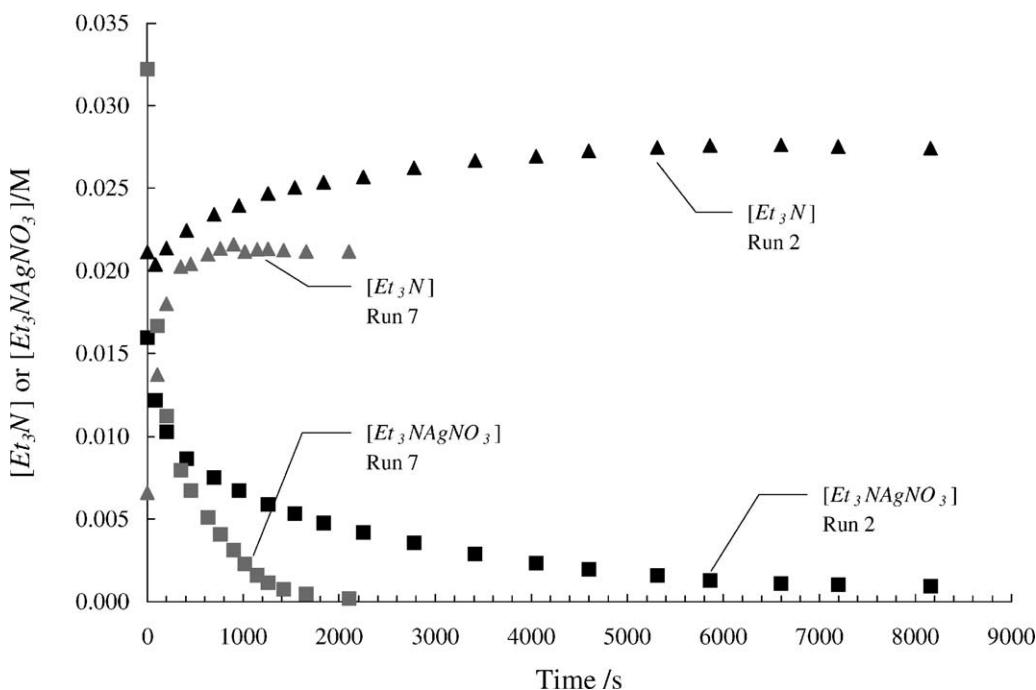


Fig. 2. Plots of calculated concentration of coordinated and free triethylamine during kinetic runs 2 and 7.

and simultaneously resorting to Eq. (12) expressed using the notation,  $\phi = 1/(1 + K_2[\text{Et}_3\text{N}])$ .

The introduction of the expressions for the surface coverage leads to rather complex differential rate equations for all the reactants involved, namely for ethyl iodide

$$\begin{aligned} \frac{dx}{dt_{\geq t_{ac}}} &= \left( k_Q + \frac{k_C}{K_1[\text{Et}_3\text{N}]} \right) ([\text{Et}_3\text{NAgNO}_3]_{t_{ac}} \\ &+ \phi[\text{AgNO}_3]_{t_{ac}} - \phi x)([\text{EtI}]_{t_{ac}} - x) \\ &+ k'_Q \frac{a_s m}{V} \left( \frac{([\text{EtI}]_{t_{ac}} - x)}{(1/b_{R1}) + ([\text{EtI}]_{t_{ac}} - x) + \phi[\text{Et}_3\text{N}]} \right) \\ &\times c_{\text{monoEtI}} \times b_{\text{Et}_3\text{NAgNO}_3} ([\text{Et}_3\text{NAgNO}_3]_{t_{ac}} \\ &+ \phi[\text{AgNO}_3]_{t_{ac}} - \phi x) c_{\text{monoEt}_3\text{NAgNO}_3} \end{aligned} \quad (17)$$

Despite their complexity, the onset of a period with an almost constant free amine concentration in solution ( $[\text{Et}_3\text{N}] \cong [\text{Et}_3\text{N}]_t$  for  $t \geq t_{ac}$ ), previously mentioned, allows the integration of these equations

leading to:

$$\begin{aligned} \ln \left( \frac{e - \phi x(t)}{a - x(t)} \right) &= \ln \left( \frac{e - \phi x(t_{ac})}{a - x(t_{ac})} \right) \\ &- \left( k_Q + \frac{k_C}{K_1[\text{Et}_3\text{N}]} \right) \\ &\times (\phi a - e)(1 + P)(t - t_{ac}) \end{aligned} \quad (18)$$

where, for the sake of simplicity, a shortened notation was used, namely:  $a$  is the initial ( $t = t_{ac}$ ) ethyl iodide concentration,  $e = [\text{Et}_3\text{NAgNO}_3]_{t_{ac}} - \phi[\text{AgNO}_3]_{t_{ac}}$  and  $P$  is given by:

$$\begin{aligned} P &= \frac{k'_Q}{(k_Q + (k_C/K_1[\text{Et}_3\text{N}]))} \frac{a_s m}{V} \\ &\times \frac{b_{\text{Et}_3\text{NAgNO}_3} c_{\text{monoEt}_3\text{NAgNO}_3} c_{\text{monoEtI}}}{(1/b_{\text{EtI}}) + [\text{EtI}]_{t_{ac}} + \phi[\text{Et}_3\text{N}]} \end{aligned} \quad (19)$$

Eq. (18) clearly predicts a surface effect on the ethyl iodide rate of consumption as the slope contains the multiplying factor  $(1 + P)$  where  $P$  is directly dependent on the mass of solid ( $m$ ). It should also be noted

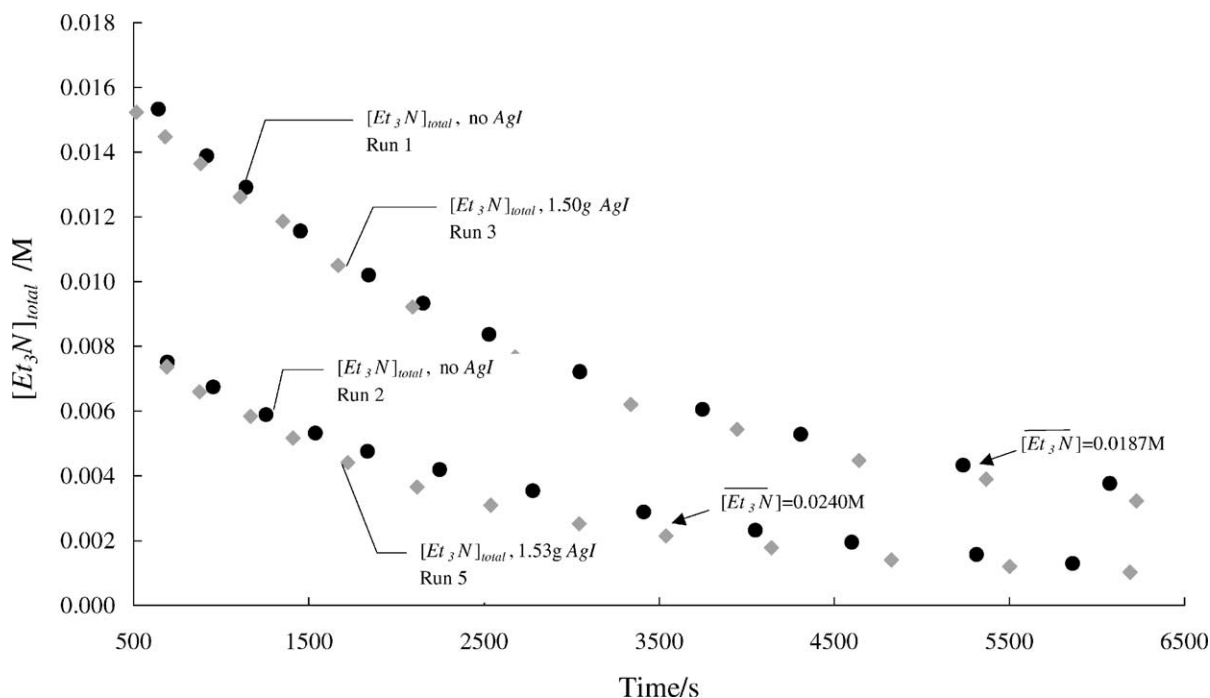


Fig. 3. Dependence of the rate of amine quaternization on the free amine concentration and on the mass of AgI (runs 3 vs. 5 and 1 vs. 3; 2 vs. 5).

that this surface effect is also dependent on the free amine concentration a feature that is also evident in the experimental data plotted in Fig. 3.

Similarly, a differential rate equation for the amine consumption may be written as:

$$\begin{aligned}
 & -\frac{d[\text{Et}_3\text{NAgNO}_3]}{dt} \\
 &= \frac{dx_1}{dt_{t \geq t_{ac}}} \approx k_Q ([\text{Et}_3\text{NAgNO}_3]_{t_{ac}} - \phi x_1) ([\text{EtI}]_{t_{ac}} \\
 & \quad - [\text{AgNO}_3]_{t_{ac}} - x_1) \\
 & \quad + k'_Q \frac{a_s m}{V} \left( \frac{([\text{EtI}]_{t_{ac}} - [\text{AgNO}_3]_{t_{ac}} - x_1)}{(1/b_{\text{EtI}}) + [\text{EtI}]_{t_{ac}} - [\text{AgNO}_3]_{t_{ac}} - x_1 + \phi [\text{Et}_3\text{N}]} \right) \\
 & \quad \times c_{\text{monoEtI}} \times b_{\text{Et}_3\text{NAgNO}_3} ([\text{Et}_3\text{NAgNO}_3]_{t_{ac}} - \phi x_1) \\
 & \quad \times c_{\text{monoEt}_3\text{NAgNO}_3} \quad (20)
 \end{aligned}$$

which for the same period,  $t \geq t_{ac}$ , can also be integrated leading to:

$$\begin{aligned}
 \ln \left( \frac{c - \phi x_1(t)}{g - x_1(t)} \right) &= \ln \left( \frac{c - \phi x_1(t_{ac})}{g - x_1(t_{ac})} \right) \\
 & \quad - k_Q (\phi g - c) (1 + N) (t - t_{ac}) \quad (21)
 \end{aligned}$$

where  $c$  is the concentration of coordinated amine at the onset of the integration period ( $t_{ac}$ ),  $g$  is given by the difference between the alkyl iodide and free silver nitrate concentration at  $t_{ac}$  ( $g = [\text{EtI}]_{t_{ac}} - [\text{AgNO}_3]_{t_{ac}}$ ) and  $N$  is:

$$N = \frac{k'_Q}{k_Q} \frac{a_s m}{V} \frac{b_{\text{Et}_3\text{NAgNO}_3} c_{\text{monoEt}_3\text{NAgNO}_3} c_{\text{monoEtI}}}{(1/b_{\text{EtI}}) + [\text{EtI}]_{t_{ac}} + \phi [\text{Et}_3\text{N}]} \quad (22)$$

Eq. (21) predicts plots with trends identical to those of Eq. (18) but with a smaller slope, due to the larger denominator of the surface term. The plots corresponding to Eqs. (18) and (21), for run 3 are presented in Fig. 4 and clearly demonstrate that the rates of ethyl iodide and amine consumption are different and obey the equations predicted for extended periods of time (2000–4000 s for run 3) after an initial

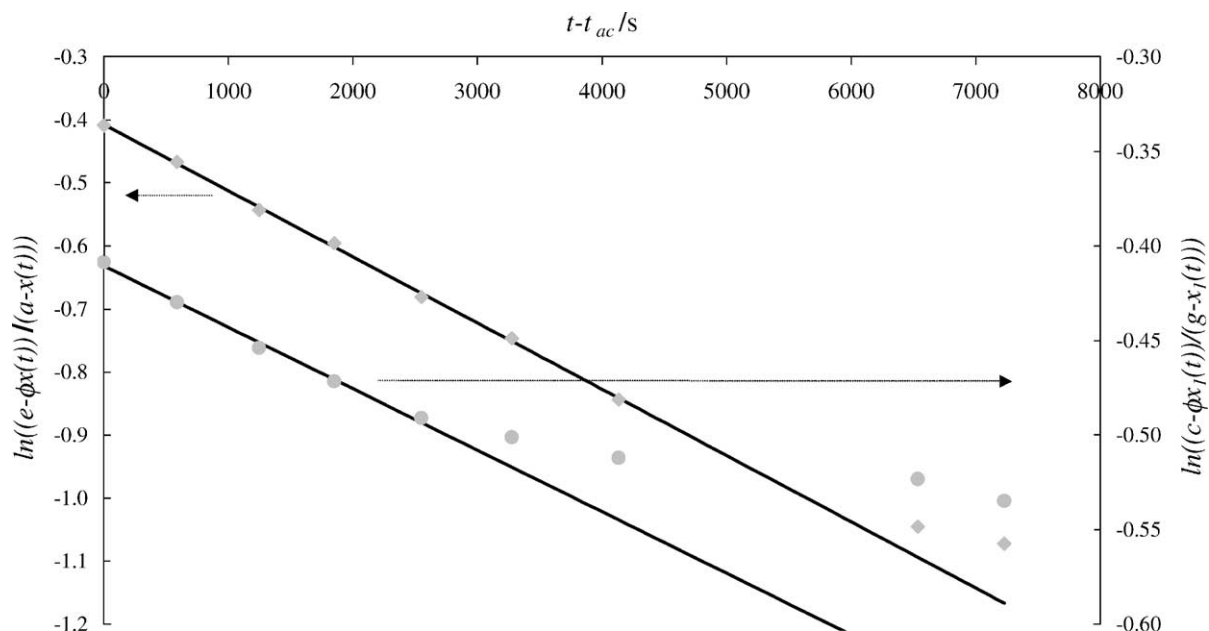


Fig. 4. Plots of Eqs. (18) and (21) for kinetic run 3.

period  $t_{ac}$ . Identical plots were obtained for several kinetic runs performed under different experimental conditions.

A quantitative evaluation of the solution and surface contributions in the quaternization reaction from the slopes of Eq. (21) is not straightforward. However, the introduction of coefficient  $Q_1$

$$Q_1 = k_Q(1 + N) = k_Q + k'_Q \frac{a_s m b_{Et_3N} a_{AgNO_3} c_{monoEt_3N} c_{monoEtI}}{V((1/b_{EtI}) + [EtI]_{t_{ac}} + \phi[Et_3N])} \quad (23)$$

allows the direct inter-comparison of the dependence on the mass of solid for experimental data sets obtained under different initial conditions. In fact, a linear dependence of this coefficient on the average mass of solid average present ( $\overline{m_{AgI}}$ ), within the period considered, allows the direct determination of  $k_Q$ , from the intercept, and of  $k'_Q$  from the slope and literature data on adsorption for these species.

Likewise, a coefficient  $Q_2$ , containing the contributions of the quaternization and competitive reaction,

can be identified in Eq. (18):

$$Q_2 = \left( k_Q + \frac{k_C}{K_1[Et_3N]} \right) (1 + P) = \left( k_Q + \frac{k_C}{K_1[Et_3N]} \right) + k'_Q \frac{a_s m b_{Et_3N} a_{AgNO_3} c_{monoEt_3N} c_{monoEtI}}{V((1/b_{EtI}) + [EtI]_{t_{ac}} + \phi[Et_3N])} \quad (24)$$

The extension of this type of reasoning to experimental data obtained under an excess of ethyl iodide leads to Eqs. (25) and (26) for the corresponding plots under pseudo-first order conditions

$$\ln(c - \phi x_1(t)) = \ln(c - \phi x_1(t_{ac})) - \phi[EtI]_{t_{ac}} k_Q (1 + T)(t - t_{ac}) \quad (25)$$

and

$$\begin{aligned} \ln(e - \phi x(t)) &= \ln(e - \phi x(t_{ac})) - \phi[EtI]_{t_{ac}} \left( k_Q + \frac{k_C}{K_1[Et_3N]} \right) \\ &\times (1 + U)(t - t_{ac}) \end{aligned} \quad (26)$$

where another set of coefficients  $Q_3$  and  $Q_4$ , related

to the corresponding slopes, can be defined namely

$$Q_3 = k_Q(1 + T) = k_Q + k'_Q \frac{a_s m}{V} \times \frac{b_{\text{Et}_3\text{NAgNO}_3} c_{\text{monoEt}_3\text{NAgNO}_3} \theta_{\text{EtI}} c_{\text{monoEtI}}}{[\text{EtI}]_{t_{\text{ac}}}} \quad (27)$$

and likewise for  $Q_4$ .

The dependence of  $Q_3$  on  $m$  also allows the determination of solution and surface quaternization reaction rates, from an independent set of kinetic runs obtained under pseudo-first order conditions.

The relationships between  $Q_1$  and  $Q_2$  or  $Q_3$  and  $Q_4$ , as well as the intercept of linear plots of  $Q_2$  and  $Q_4$  versus the average solid mass present ( $\overline{m_{\text{AgI}}}$ ) also enables the calculation of guess estimates for the competitive solution rate constant between non-coordinated silver and ethyl iodide.

## 5. Kinetic analysis of the experimental data

The calculated coefficients  $Q_1$ – $Q_4$ , as well as the average free amine concentration in the period under study ( $t \geq t_{\text{ac}}$ ) are presented in Table 3. This data evidences that both  $t_{\text{ac}}$ , and the superficial contribution decrease with the initial excess of amine versus silver nitrate concentration, and allows the estimate of the rate constants for the solution quaternization and competitive reactions as well as for the surface catalysed quaternization.

Guess estimates for the competitive solution rate constant between non-coordinated silver and ethyl iodide obtained by direct calculation, namely through  $k_C = K_1[\text{Et}_3\text{N}](Q_2 - Q_1)$  and  $k_C = K_1[\text{Et}_3\text{N}](Q_4 - Q_3)$ , are presented in Table 4 where only the estimates obtained from the runs initiated in the absence of solid, conditions that minimize the errors associated with the different estimates of the superficial term, are presented. This methodology leads, necessarily, to overestimates and a wide dispersion of data but the values obtained clearly point towards a dependency of  $k_C$  on the average free amine concentration in the period  $t$ – $t_{\text{ac}}$ . These data suggest an unaccounted for contribution to  $k_C$ , which decreases with the increase in concentration of the free amine in solution, a contribution that may be associated with a superficial counterpart of the competitive reaction, which was not considered in the model, due to the minute free silver concentration.

The analysis of plots of  $Q_2$  and  $Q_4$  versus  $\overline{m_{\text{AgI}}}$  presented in Fig. 5, further substantiates this hypothesis as the intercepts ( $k_Q + (k_C/K_1[\text{Et}_3\text{N}])$ ) show the predicted dependency on the average free amine concentration, and apart from it  $k_C$  values, determined by extrapolation to  $m = 0$  (Table 4), also present the same trend thus corroborating the hypothesis of a competitive superficial reaction between ethyl iodide and free silver nitrate. It should be pointed out that experimental runs 11 and 12, corresponding to the most favourable conditions for a competitive surface reaction: an excess of alkyl halide and also a minute amine concentration, do in fact lead to the higher estimates of

Table 3

Calculated  $Q_1$ – $Q_4$  coefficients as well as the corresponding free amine concentration for the reaction period under study ( $t \geq t_{\text{ac}}$ )

Run	$t_{\text{ac}}$ (s)	$[\text{Et}_3\text{N}] \pm \sigma$ (M)	$Q_1 \pm \sigma$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$Q_2 \pm \sigma$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$Q_3 \pm \sigma$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$Q_4 \pm \sigma$ ( $\text{M}^{-1} \text{s}^{-1}$ )
1 <sup>a</sup>	1842	$0.020 \pm 0.001$	$0.0043 \pm 0.0001$	$0.0183 \pm 0.0005$		
2 <sup>a</sup>	408	$0.026 \pm 0.001$	$0.0384 \pm 0.00007$	$0.0130 \pm 0.0001$		
3 <sup>a</sup>	2093	$0.017 \pm 0.001$	$0.0081 \pm 0.0003$	$0.0261 \pm 0.0006$		
4	2234	$0.016 \pm 0.001$	$0.0065 \pm 0.0002$	$0.0223 \pm 0.0006$		
5	459	$0.022 \pm 0.001$	$0.0066 \pm 0.0003$	$0.0171 \pm 0.0002$		
6	918	$0.0207 \pm 0.0006$			$0.0043 \pm 0.0006$	$0.0171 \pm 0.0007$
7	348	$0.0211 \pm 0.0003$			$0.0107 \pm 0.0005$	$0.0203 \pm 0.0006$
8	380	$0.0236 \pm 0.0009$			$0.0040 \pm 0.0002$	$0.0170 \pm 0.0007$
9	450	$0.0214 \pm 0.0006$			$0.00864 \pm 0.00007$	$0.0238 \pm 0.0006$
10	276	$0.0142 \pm 0.0003$			$0.0086 \pm 0.0002$	$0.027 \pm 0.001$
11	78	$0.0084 \pm 0.0004$			$0.0037 \pm 0.0001$	$0.0431 \pm 0.0008$
12	178	$0.0076 \pm 0.0002$			$0.009 \pm 0.001$	$0.047 \pm 0.002$

<sup>a</sup> Experimental data set presented previously [6].

Table 4

Calculated  $k_C$  and  $k_Q$  for independent analysis of the experimental data sets

Run (s)	$[\text{Et}_3\text{N}] \pm \sigma$ (M)	$\overline{m}_{\text{AgI}}$ (g)	$k_C \pm \sigma$ ( $\text{M}^{-1} \text{s}^{-1}$ )		$k_Q \pm \sigma$ ( $\text{M}^{-1} \text{s}^{-1}$ )
			$k_C = \frac{K_1[\text{Et}_3\text{N}](Q_{2n} - Q_{2n-1})}{K_1[\text{Et}_3\text{N}](Q_{2n} - k_Q)}$	$k_C(Q_{2n \rightarrow 0}) = \frac{K_1[\text{Et}_3\text{N}](Q_{2n} - k_Q)}{K_1[\text{Et}_3\text{N}](Q_{2n} - k_Q)}$	$k_Q = Q_{2n-1(n \rightarrow 0)}$
1 <sup>a</sup>	$0.020 \pm 0.001$	0.383	$8.1 \times 10^3 \pm 7 \times 10^2$		
2 <sup>a</sup>	$0.026 \pm 0.001$	0.163	$6.9 \times 10^3 \pm 5 \times 10^2$		
6	$0.0207 \pm 0.0006$	0.213	$7.7 \times 10^3 \pm 1 \times 10^3$		
8	$0.0236 \pm 0.0009$	0.377	$7.6 \times 10^3 \pm 6 \times 10^2$		
11	$0.0084 \pm 0.0004$	0.033	$9.6 \times 10^3 \pm 8 \times 10^2$		
1 <sup>a</sup> , 3 <sup>a</sup> –4	$0.0187 \pm 0.0006$	0.383–1.890		$6.6 \times 10^3 \pm 7 \times 10^2$	$3.5 \times 10^{-3} \pm 3 \times 10^{-4}$
2 <sup>a</sup> , 5	$0.0240 \pm 0.0007$	0.163–1.675		$6.4 \times 10^3 \pm 6 \times 10^2$	$3.5 \times 10^{-3} \pm 1 \times 10^{-4}$
6–9	$0.0211 \pm 0.0002$	0.213–1.962		$8 \times 10^3 \pm 2 \times 10^3$	$3.2 \times 10^{-3} \pm 4 \times 10^{-4}$
11–12	$0.0078 \pm 0.0002$	0.033–1.600		$8.9 \times 10^3 \pm 9 \times 10^2$	$3.6 \times 10^{-3} \pm 1 \times 10^{-4}$

<sup>a</sup> Experimental data set presented previously [6].

$k_C$ , thus the best estimates being those obtained from runs 1 through 5.

Solution and surface quaternization reaction rates were determined resorting to coefficients  $Q_1$  and  $Q_3$ , obtained from the plots of Eqs. (23) and (27), which do not contain explicitly any underlying dependencies on the eventual competitive surface reaction. Nonetheless,

indirect consequences of such a hypothesis must also be considered, and in fact the adsorption isotherm for the coordinated amine contains a competitive term, due to the adsorption of the free silver nitrate, however it is believed this term rapidly becomes neglectful versus the unitary term in the denominator of the adsorption isotherm.

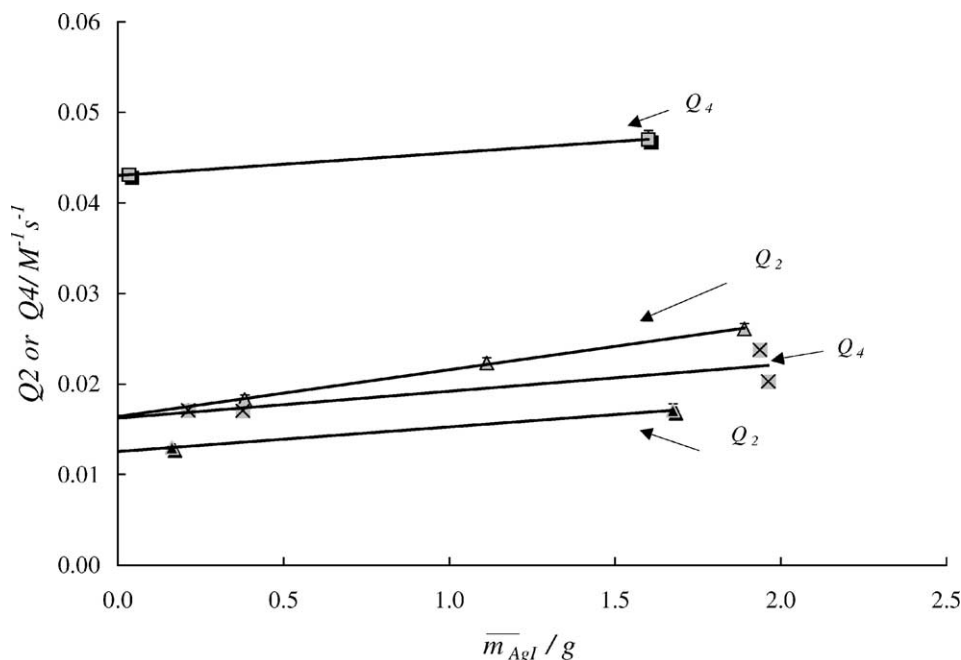


Fig. 5. Dependence of  $Q_2$  and  $Q_4$  (runs 1–9, 11 and 12) on the average mass of solid during the reaction period under study ( $t \geq t_{ac}$ ).

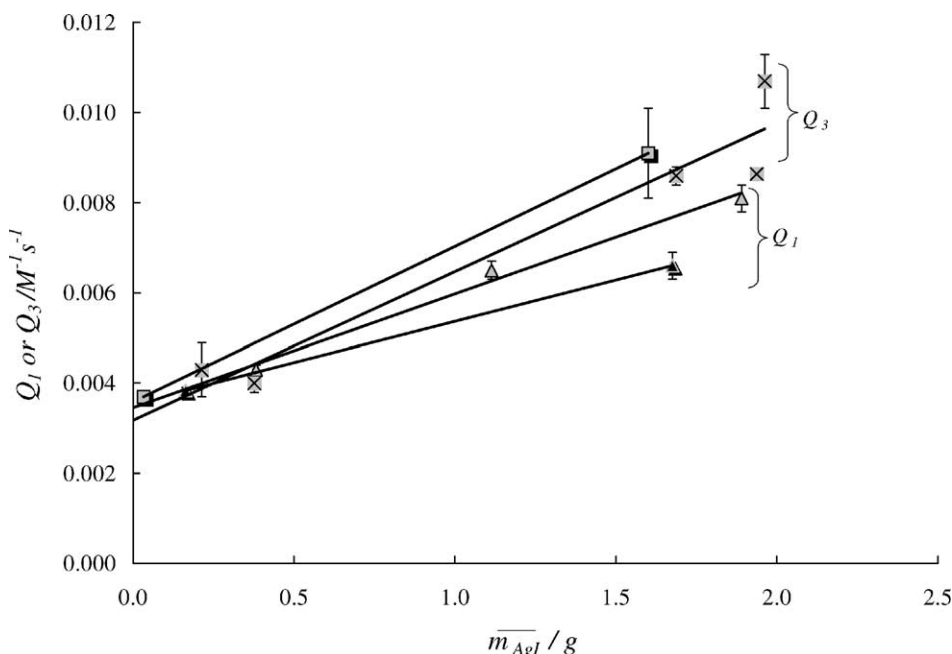


Fig. 6. Dependence of  $Q_1$  and  $Q_3$  (runs 1–12) on the average mass of solid during the reaction period under study ( $t \geq t_{ac}$ ).

In Fig. 6,  $Q_1$  and  $Q_3$  values are plotted as a function of the average mass of solid within the period,  $t-t_{ac}$ , considered, with the data sets subdivided in terms of the average free amine concentration. The extrapolation of  $Q_1$  and  $Q_3$  to zero mass leads to the solution quaternization rate constant for the coordinated amine and the plots show a good agreement between all data. The slopes of these plots reflect the surface dependence and show, as expected, that the rate of reaction decreases with the increase of free amine but increases with the ethyl iodide concentration. In fact, if ethyl iodide and the amine compete for the same surface sites an increase in the free amine concentration will necessarily be accompanied by a decrease in the amount of adsorbed alkyl halide thus leading to a decrease in the surface contribution of the quaternization reaction; likewise it is expected that an excess of alkyl halide in solution will lead to an increase in the superficial contribution as this species does not compete with coordinated amine for the same sites.

The resemblance between the magnitude of the slopes of the plots of  $Q_1$  and  $Q_3$  versus  $\bar{m}_{AgI}$  allows a guess estimate of the adsorption coefficient for ethyl

iodide in this media. A close look at Eqs. (23) and (27) demonstrates that this condition can only be satisfied if

$$\frac{1}{b_{EtI}} + [EtI]_{l_{ac}} + \varphi[\overline{Et_3N}] \approx [EtI]_{l_{ac}} \quad (\text{excess halide})$$

and therefore the left hand term must be dominated by  $1/b_{EtI}$ ,  $\varphi[\overline{Et_3N}]$  or both. Consequently, either  $\varphi \cong 10$  or  $1/b_{EtI} \cong 10^{-1}$ , hence as  $b_{Et_3N} = 618$  [17] one may conclude that  $b_{EtI}$  must be either between 70 and 100 or  $b_{EtI} \cong 8$ . The first estimate is likely to be very reliable bearing in mind the data reported by Austin et al. [20] for the adsorption of ethyl iodide on silver iodide in aqueous media ( $b_{EtI(H_2O)} = 60$ ) and the fact that in toluene the affinity of the alkyl halide for the surface should be slightly higher than in water.

The superficial contribution to the quaternization reaction, though clear cannot be quantified in terms of the specific rate constant for the surface reaction,  $k'_Q$ , as there is no data available for the adsorption coefficient of the coordinated silver nitrate. However, considering the adsorption parameters for  $Et_3N$  [17] ( $a_s = 1.08 \text{ m}^2 \text{ g}^{-1}$  and  $c_{\text{monoEt}_3N} = 4.2 \times 10^{-6} \text{ mol m}^{-2}$ ), that  $V = 60 \text{ cm}^3$ , and  $c_{\text{monoEt}_3N\text{AgNO}_3} \approx c_{\text{monoEtI}} \approx$



$c_{\text{monoEt}_3\text{N}}$  one may conclude that  $k'_Q b_{\text{Et}_3\text{NAgNO}_3} \cong 1.5 \times 10^7 \text{ m}^2 (\text{mol s})^{-1}$ , a value that upon consideration of the reported data for  $b_{\text{AgNO}_3}$  in water [20] allows the determination of a magnitude for  $k'_Q$  of  $10^5 \text{ m}^2 (\text{mol s})^{-1}$ .

## 6. Conclusions

A novel mathematical approach for the analysis of the kinetic data for the catalysed quaternization of coordinated triethylamine, based on a set of adequate approximations, allowed the analysis of integrated rate equations, valid for clearly defined extended time periods, and further substantiated the reaction mechanism previously proposed [6]. Beyond it a method to calculate precise solution quaternization rate was developed and methodologies to define clear boundaries in the estimated rates constants of the solution reaction of silver nitrate with ethyl iodide in toluene, and of the surface catalysed quaternization of the coordinated amine are presented.

The best estimates for the solution reaction rate constants between ethyl iodide and free silver nitrate are obtained, as discussed in the previous section, from the extrapolation to  $m = 0$  of  $Q_2$ , in particular from runs 2 and 5, or in other words  $k_C$  will be  $6.4 \times 10^3 \pm 6 \times 10^2 \text{ dm}^3 (\text{mol s})^{-1}$ , a range that agrees well with the first estimate of  $5.8 \times 10^3 \text{ dm}^3 (\text{mol s})^{-1}$  previously proposed [6].

The preliminarily estimate for the rate of the solution reaction of coordinated triethylamine by ethyl iodide [6] was clearly improved resorting to the values obtained by extrapolation of  $Q_1$  and  $Q_3$ , to zero mass of silver iodide. The good agreement found for all data sets:  $k_Q(Q_{1,m \rightarrow 0}) = 3.5 \times 10^{-3} \pm 3 \times 10^{-4} \text{ dm}^3 (\text{mol s})^{-1}$  and  $k_Q(Q_{3,m \rightarrow 0}) = 3.4 \times 10^{-3} \pm 4 \times 10^{-4} \text{ dm}^3 (\text{mol s})^{-1}$  allows the proposal of a very reliable value of  $3.5 \times 10^{-3} \pm 2 \times 10^{-4} \text{ dm}^3 (\text{mol s})^{-1}$  that, as expected, is lower than the previously overestimate of  $4.0 \times 10^{-3} \text{ dm}^3 (\text{mol s})^{-1}$ , put forward before [6].

The slopes of the plots of  $Q_1$  and  $Q_3$ , versus the mass of silver iodide demonstrate the surface effect, and allowed the proposal of the magnitude of a surface quaternization rate constant ( $k'_Q$ ), namely  $10^5 \text{ m}^2 (\text{mol s})^{-1}$ .

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## Appendix A

For any moment  $t + \Delta t$  after the addition of ethyl iodide, and considering that  $n_1$  moles of the silver–amine complex and  $n_2$  moles of ethyl iodide have been consumed in the period  $\Delta t$ , one may write, according to the proposed reaction scheme, and neglecting the amounts adsorbed for the reasons previously mentioned

$$\begin{aligned} [\text{R}_3\text{N}]_{\text{tot},t+\Delta t} &= [\text{R}_3\text{N}]_{t+\Delta t} + [\text{R}_3\text{NAgNO}_3]_{t+\Delta t} \\ &\quad + 2[(\text{R}_3\text{N})_2\text{AgNO}_3]_{t+\Delta t} \\ &= [\text{R}_3\text{N}]_{\text{tot},t+\Delta t} - x_1 = ([\text{R}_3\text{N}]_t + x_3 + x_4) \\ &\quad + ([\text{R}_3\text{NAgNO}_3]_t - x_1 - x_3 + x_4) \\ &\quad + 2([(R_3N)_2\text{AgNO}_3]_t - x_4) \end{aligned} \quad (\text{A.1})$$

and

$$\begin{aligned} [\text{AgNO}_3]_{\text{tot},t+\Delta t} &= [\text{AgNO}_3]_{t+\Delta t} + [\text{R}_3\text{NAgNO}_3]_{t+\Delta t} \\ &\quad + [(\text{R}_3\text{N})_2\text{AgNO}_3]_{t+\Delta t} \\ &= [\text{AgNO}_3]_{\text{tot},t} - x_1 - x_2 = ([\text{AgNO}_3]_t - x_2 + x_3) \\ &\quad + ([\text{R}_3\text{NAgNO}_3]_t - x_1 - x_3 + x_4) \\ &\quad + ([(\text{R}_3\text{N})_2\text{AgNO}_3]_t - x_4) \end{aligned} \quad (\text{A.2})$$

where  $x_3$  and  $x_4$  are the concentration changes associated with  $K_1$  and  $K_2$  equilibrium shifts, namely the reaction of  $n_3$  moles of the 1:1 silver–amine complex and the corresponding formation of  $n_3$  moles of silver nitrate and free amine. The consequent shift in the second equilibria with consumption of  $n_4$  moles of the 1:2 silver–amine complex, leads to the formation of the same amount of 1:1 complex and free amine in the same period  $\Delta t$ .

Introducing  $x$  and  $x_5$  corresponding to

$$x = x_1 + x_2 \quad (\text{A.3})$$

$$x_5 = x_1 + x_3 - x_4 \approx x_1 - x_4 \quad (\text{A.4})$$



or in other words the overall change in terms of the total silver (or ethyl iodide) content and the 1:1 coordination compound during the period  $\Delta t$ . In the expression (A.4), for the 1:1 complex mass balance, the term  $x_3$  was neglected due to the magnitude of  $K_1$ .

Expressing  $x_5$  in terms of the quantities determined experimentally ( $x_1$  and  $x$ ) involves knowing  $x_2$  and  $x_4$  and therefore solving a set of five equations corresponding to the equilibrium and mass balance equations, for any instant  $t$ , in terms of silver and amine.

$$\left\{ \begin{array}{l} K_1 = \frac{[\text{R}_3\text{NAgNO}_3]_t - x_1 + x_4}{([\text{R}_3\text{N}]_t + x_4)([\text{AgNO}_3]_t - x_2)} \\ K_2 = \frac{[(\text{R}_3\text{N})_2\text{AgNO}_3]_t - x_4}{([\text{R}_3\text{N}]_t + x_4)([\text{R}_3\text{NAgNO}_3]_t - x_1 + x_4)} \\ x = x_1 + x_2 \\ [\text{R}_3\text{N}]_{\text{tot},t} - x_1 = ([\text{R}_3\text{N}]_t + x_3 + x_4) \\ \quad + ([\text{R}_3\text{NAgNO}_3]_t - x_1 - x_3 + x_4) \\ \quad + 2([(\text{R}_3\text{N})_2\text{AgNO}_3]_t - x_4) \\ [\text{AgNO}_3]_{\text{tot},t} - x = ([\text{AgNO}_3]_t - x_2) \\ \quad + ([\text{R}_3\text{NAgNO}_3]_t - x_1 + x_4) \\ \quad + ([(\text{R}_3\text{N})_2\text{AgNO}_3]_t - x_4) \end{array} \right. \quad (\text{A.5})$$

The five solutions of the set of Eq. (A.5) are:

$$x_1 = [\text{R}_3\text{NAgNO}_3]_t - \frac{[(\text{R}_3\text{N})_2\text{AgNO}_3]_t - x_4}{([\text{R}_3\text{N}]_t + x_4)K_2} + x_4 \quad (\text{A.6})$$

$$x_2 = [\text{AgNO}_3]_t - \frac{[(\text{R}_3\text{N})_2\text{AgNO}_3]_t - x_4}{([\text{R}_3\text{N}]_t + x_4)^2 K_1 K_2} \quad (\text{A.7})$$

$$x_4 = \frac{K_2[\text{R}_3\text{N}]_t x_5}{1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5)} \quad (\text{A.8})$$

$$x = [\text{R}_3\text{NAgNO}_3]_t + [\text{AgNO}_3]_t + x_4 - \frac{([\text{R}_3\text{NAgNO}_3]_t - x_4)(([\text{R}_3\text{N}]_t + x_4)K_1 + 1)}{([\text{R}_3\text{N}]_t + x_4)^2 K_1 K_2}$$

and as

$$[\text{R}_3\text{N}]_{t+\Delta t} K_1 = ([\text{R}_3\text{N}]_t + x_4) K_1 \gg 1$$

$$x \approx [\text{R}_3\text{NAgNO}_3]_t + [\text{AgNO}_3]_t + x_4 - \frac{[\text{R}_3\text{NAgNO}_3]_t - x_4}{([\text{R}_3\text{N}]_t + x_4)K_2} \quad (\text{A.9})$$

or upon rearrangement

$$x = [\text{AgNO}_3]_t + \frac{x_5(1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5) + K_2[\text{R}_3\text{N}]_t)}{1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5)} \quad (\text{A.10})$$

Consequently

$$x_5 = \frac{-(K_2([\text{AgNO}_3]_t - x - [\text{R}_3\text{N}]_t) - [\text{R}_3\text{NAgNO}_3]_t - 1) \pm \sqrt{\text{Fact}}}{2K_2} \quad (\text{A.11})$$

where

$$\begin{aligned} \text{Fact} = & (K_2([\text{AgNO}_3]_t - x - [\text{R}_3\text{N}]_t) \\ & - [\text{R}_3\text{NAgNO}_3]_t)^2 \\ & - 4(x - [\text{AgNO}_3]_t)(K_2[\text{R}_3\text{NAgNO}_3]_t + 1)K_2 \end{aligned} \quad (\text{A.11a})$$

A rearrangement of (A.10) in terms of

$$x = [\text{AgNO}_3]_t + x_5 \left( 1 + \frac{K_2[\text{R}_3\text{N}]_t}{1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5)} \right) \quad (\text{A.10a})$$

evidences that in the concentration range studied  $1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5) \approx 1$  and therefore

$$x \approx [\text{AgNO}_3]_t + x_5(1 + K_2([\text{R}_3\text{N}]_t)) \quad (\text{A.12})$$

or when expressing  $x_5$  in terms of the total amine concentration in solution

$$x_5 = x_1 - \frac{K_2[\text{R}_3\text{N}]_t x_5}{1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5)} \quad (\text{A.13})$$

thus showing that the concentration change observed for the 1:1 silver–amine complex is slightly smaller than the consumption associated with its reaction with the alkyl iodide ( $x_1$ ). Resorting to the previously mentioned approximation  $1 + K_2([\text{R}_3\text{NAgNO}_3]_t - x_5) \approx 1$  one may write:

$$x_5 \approx \frac{x_1}{1 + K_2[\text{R}_3\text{N}]_t} \quad (\text{A.14})$$

or expressing  $x_1$  in terms of  $x$

$$x_1 \approx x - [\text{AgNO}_3]_t \quad (\text{A.15})$$

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