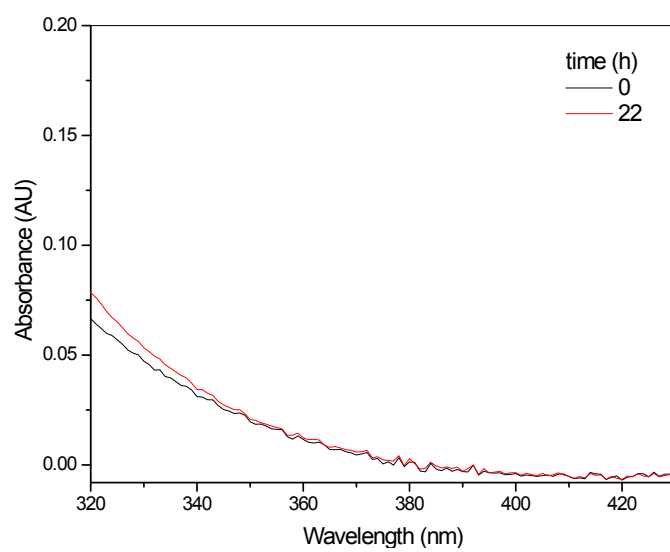# Supplementary Information

Protic Ionic Liquid when Entrapped in Cationic Reverse Micelles Can Be Used as Suitable Solvent for a Bimolecular Nucleophilic Substitution Reaction

Matías A. Crosio, N. Mariano Correa, Juana J. Silber, R. Darío Falcone*

Departamento de Química. Universidad Nacional de Río Cuarto. Agencia Postal # 3.

C.P. X5804BYA Río Cuarto. Argentina.

Figure S1. Absorption spectra of the reaction of Cl$^-$ (0.2 M) with S$^+$ in neat EAN at 30 °C. [S$^+$] = 5 x 10^{-5} M. T = 30 ºC.
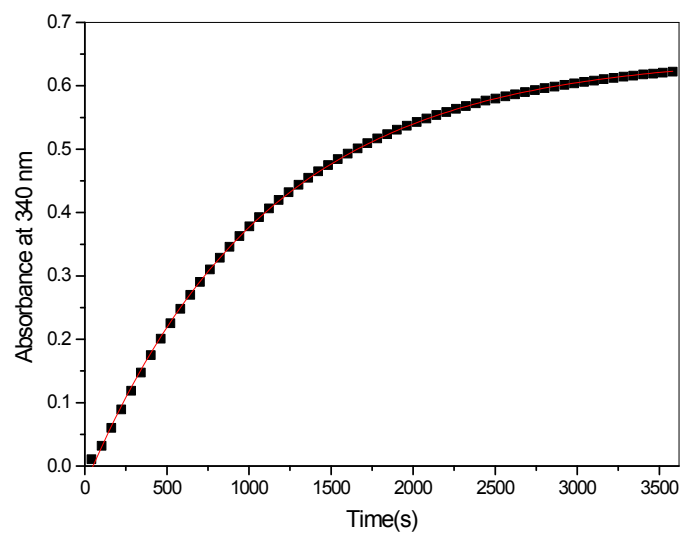
Figure S2. Absorbance at 340 nm as a function of time in the reaction shown in Figure 2. (■) experimental data and (—) first order reaction fit. $W_s = 0.05$. $[Cl^-] = 0.1$ M. $[S^+] = 5 \times 10^{-5}$ M. T = 30 °C. The spectra were recorded at 60 second intervals.

Table S1. k_{obs} values obtained in toluene/BHDC/EAN RMs, varying the total concentration of BHDC ([BHDC]$_{tot}$) at different W_s. T = 30 °C.

W_s	[BHDC]$_{tot}$ / M	k_{obs} / s^{-1}
0.02	0.01	8.4 x 10^{-5}
	0.07	7.4 x 10^{-4}
	0.09	8.4 x 10^{-4}
	0.10	8.7 x 10^{-4}
	0.15	9.5 x 10^{-4}
	0.20	9.9 x 10^{-4}
0.05	0.03	7.0 x 10^{-4}
	0.06	7.5 x 10^{-4}
	0.08	8.2 x 10^{-4}
	0.10	8.5 x 10^{-4}
	0.15	9.1 x 10^{-4}
	0.19	9.4 x 10^{-4}
0.11	0.03	5.9 x 10^{-4}
	0.06	7.3 x 10^{-4}
	0.10	8.0 x 10^{-4}
	0.15	9.0 x 10^{-4}
	0.19	9.4 x 10^{-4}
0.17	0.03	1.8 x 10^{-4}
	0.07	2.6 x 10^{-4}
	0.09	2.9 x 10^{-4}
	0.10	3.2 x 10^{-4}
	0.15	3.7 x 10^{-4}
	0.20	4.0 x 10^{-4}

Derivation of the rate equation

The reaction of the sulfonium S^+ with chloride ion presented in Scheme 2 is a bimolecular reaction, which follows the rate law descripted by equation S1:

$$rate = \frac{d[P]}{dt} = k_2[Cl^-][S^+] \qquad (S1)$$

If $[Cl^-] \gg [S^+]$, a pseudo first order behavior for the kinetics of the reaction is assumed in order to quantify the reaction rate. Thus, the expression for the observable rate constant (k_{obs}) can be defined as equation S2:

$$k_{obs} = k_2[Cl^-] \qquad (S2)$$

where k_2 is the second order rate constant and $[Cl^-]$ is the total nucleophile concentration.

As in the present work we used [BHDC] > critical micellar concentration (cmc) value (0.01 M)[1], S^+ is incorporated into the RMs (as is expressed by equation S3) favored by its low solubility in the aromatic solvent.

$$S_o^+ + BHDC_{RMs} \rightleftharpoons S_{RMs}^+ \qquad (S3)$$
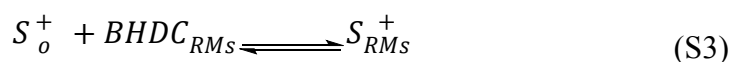
where S_o^+ and S_{RMs}^+ symbolize the substrate in the toluene and in the RMs pseudophases, respectively. $BHDC_{RMs}$ represents the cationic RMs. As it is conventional for micellar aggregates, the concentration of micellized[2] surfactant defined

as $[BHDC]_{RMs}$ (where $[BHDC]_{RMs}$ can be approximated to $[BHDC]_{tot}$ – cmc) can be calculated, and if the mass balance for S^+ ($[S^+]_{tot} = [S^+]_o + [S^+]_{RMs}$) is considered, the partition constant of the substrate (K_p) is defined as equation S4:

$$K_p = \frac{[S^+]_{RMs}}{[S^+]_o [BHDC]_{RMs}}$$

(S4)

The overall reaction rate can be expressed as the sum of the rate in the organic pseudophase and in the RMs, as equation S5:

$$rate = k_o'[S^+]_o + k_{RMs}'[S^+]_{RMs}$$

(S5)

where $[S^+]_o$ and $[S^+]_{RMs}$ are the concentration of S^+ in organic pseudophase and in the RMs, both referred to the total volume. k_o' and k_{RMs}' are the pseudo-first order rate constant values in the organic pseudophase and in BHDC RMs, respectively. Both rate constants are defined as equations S6 and S7, respectively.

$$k_o' = k_2^o [Cl^-]_o$$

(S6)

$$k_{RMs}' = k_2^{RMs} [Cl^-]_{RMs}$$

(S7)

Where k_2^o and k_2^{RMs} are the second order rate constants in the organic and RMs pseudophases. $[Cl^-]_{RMs}$ is the Cl⁻ concentration in the RMs referring to the volume of

the RMs (V_m). This concentration can be expressed also as the multiplication of the fraction of neutralized charge, β, and [BHDC][3,4] (equation S8).

$$k'_{RMs} = k_2^{RMs} \beta [BHDC]_{RMs}^{m}$$ (S8)

Additionally, the surfactant concentrations referred to the micellar phase volume ($[BHDC]_{RMs}^{m}$) can be expressed in concentrations referred to the total volume, ($[BHDC]_{RMs}$), taking into consideration the volume fraction occupied by the micellar phase, V_{tot}/V_m as equation S9 shows.

$$k'_{RMs} = k_2^{RMs} \beta \frac{V_{tot}}{V_m}[BHDC]_{RMs}$$ (S9)

The concentrations can be transformed into concentrations referred to the total volume of the system by taking into account just the phase volumes[5] (equation S10).

$$\frac{V_{tot}}{V_m} = \frac{1}{V_{BHDC}[BHDC]_{RMs}}$$ (S10)

where V_{BHDC} is the molar volume of BHDC. Thus, equation S7 can be rewritten as:

$$k'_{RMs} = k_2^{RMs} \beta \frac{1}{V_{BHDC}}$$ (S11)

When the BHDC RMs are formed, the rate constant in the organic pseudophase (toluene + BHDC surfactant monomers), $k_o^{'}$ in equation S5, can be assumed as the observed rate constant value in the cmc (k_{obs}^{cmc}). It must be recalled that above the cmc, the monomeric [BHDC] remains constant and the rate constant for the reaction in the organic solvent should be constant.

Taking into account the equations S3-11, the concentration of the substrate in the RMs can be expressed as equation S12:

$$[S^+]_{RMs} = \frac{K_p[BHDC]_{RMs}}{1 + K_p[BHDC]_{RMs}}[S^+]_{tot}$$

(S12)

Thus, in the toluene/BHDC/EAN RMs the observed rate constant k_{obs} can depicted as equation S13 (equation 5 in the main text):

$$k_{obs} = k_{obs}^{cmc} + \frac{k_2^{RMs} \beta}{V_{BHDC}} \frac{K_p[BHDC]_{RMs}}{1 + K_p[BHDC]_{RMs}}$$

(S13)

References

1- A. Jada, J. Lang, R. Zana, *J. Phys. Chem.* 1990, **94**, 381-387.

2- C. A. Bunton, F. Nome, F. H. Quina, L. S. Romsted, *Acc. Chem. Res.* 1991, **24**, 357-364.

3- D. Blach, M Pessêgo, J. J. Silber, N. M. Correa, L. García-Río, R. D. Falcone, *Langmuir*, 2014, **30**, 12130-12137.

4- E. Fernandez, L. Garcia-Rio, P. Rodriguez-Dafonte, *J. Colloid Int. Sci.* 2007, **316**, 1023-1026.

5- M. Andujar-Matalobos, L. Garcia-Rio, S. Lopez-Garcia, P. Rodriguez-Dafonte, *J. Colloid Int. Sci.* 2011, **363**, 261-267.