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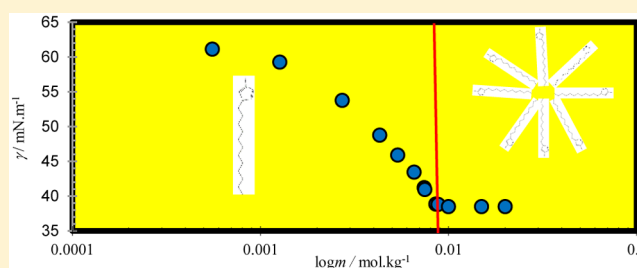
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Surface and Micellar Properties of Ionic Liquid 1-Dodecyl-3-methylimidazolium Bromide in Aqueous Solution in the Absence and Presence of a Series of Organic Electrolytes

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ABSTRACT: The surface and micellar properties (including critical micelle concentration (cmc), surface tension at the cmc (γ_{cmc}), adsorption efficiency (pC_{20}), effectiveness of surface tension reduction (Π_{cmc}), the maximum surface excess concentration (Γ_{max}), and minimum surface area per molecule (A_{min}) at the air–liquid interface) of 1-dodecyl-3-methylimidazolium bromide ($[\text{C}_{12}\text{mim}][\text{Br}]$) ionic liquid in aqueous solutions were studied in the absence and presence of a series of organic electrolytes by surface tensiometry at 298.15 K and 308.15 K. The electrolytes studied include tetraalkylammonium halides, namely, $(\text{CH}_3)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, $(\text{C}_3\text{H}_7)_4\text{NBr}$, $(\text{C}_4\text{H}_9)_4\text{NBr}$, $(\text{CH}_3)_4\text{NCl}$, and $(\text{CH}_3)_4\text{NI}$. The results show that the surface tensions as well as the cmc values decrease in the presence of the added electrolytes. Therefore, the electrolytes have a salting-out effect on the aggregation of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solutions. It was also found that the salting-out-inducing anions are predominately responsible for the observed effect, while the cations have a very small effect on the salting-out strength. The ability of the anions and cations to promote the aggregation of $[\text{C}_{12}\text{mim}][\text{Br}]$ decreases in the order of $\text{I}^- > \text{Br}^- > \text{Cl}^-$, and $(\text{C}_4\text{H}_9)_4\text{N}^+ > (\text{C}_3\text{H}_7)_4\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > (\text{CH}_3)_4\text{N}^+$, respectively.



1. INTRODUCTION

Ionic liquids (ILs), as a class of environmentally friendly solvents, have been significantly developed recently because of their extraordinary properties such as nonvolatility, nonflammability, high stability, high ionic conductivity, and easy recyclability.^{1,2} Their physicochemical properties can be easily modulated by a suitable selection of cations and anions.³ Many of the ILs are emerging as novel surfactants because of the amphiphilic nature of their cations or anions and because of their inherent amphiphilic nature, this class of ILs has been named surface active ionic liquids (SAILs) and they can form aggregates in aqueous solutions. Because of the possibility of fine-tuning the amphiphilicity of ILs by changing the alkyl chain length, the type of cations, and the nature of the counterions, one can change the structures of these aggregates. The ability to form the self-assembled structures may have consequences in a number of areas such as the extraction of products from IL-containing systems, the synthesis and purification of bulk ILs, the solvation properties of the IL molecules by simple solutes, and the formation of dispersed or phase-separated systems.^{4–7} Imidazolium-based SAILs have been the most studied in the field of colloid and interface chemistry. In this respect, Bowers et al.⁸ reported the aggregation behavior of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$), 1-octyl-3-methylimidazolium chloride ($[\text{C}_8\text{mim}][\text{Cl}]$), and 1-octyl-3-methylimidazolium iodide ($[\text{C}_8\text{mim}][\text{I}]$) in aqueous solution and they studied the role of the alkyl chain length and counterions on the aggregation behavior of these SAILs. A literature survey indicates that we can control the aggregation

behavior of SAILs in aqueous solutions by altering the alkyl chain length, cationic ring structure, and anionic type, as well as salts and organic additives. Dong et al.⁹ reported the effect of inorganic electrolytes with different anions (Cl^- , Br^- , I^-) on the surface activity of 1-dodecyl-3-methylimidazolium bromide ($[\text{C}_{12}\text{mim}][\text{Br}]$) and 1-dodecyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_{12}\text{mim}][\text{BF}_4]$), which was similar to that of the traditional ionic surfactants. Rafati et al.¹⁰ studied the aggregation behavior and surface activity of 1-hexyl-3-methylimidazolium chloride ($[\text{C}_6\text{mim}][\text{Cl}]$) in the presence of sodium halides. It is known that the long-range electrostatic interactions dominate the structure and stability of aggregates in ionic surfactant systems.^{11,12} Normally, the addition of organic and inorganic electrolytes reduces cmc, induces the formation of larger aggregates, and enhances the surface activity of surfactants.^{13,14} Rebelo et al.¹⁵ found that the cmc values of 1-alkyl-3-methylimidazolium chloride ($[\text{C}_n\text{mim}][\text{Cl}]$, $n = 10, 12$) in aqueous solutions were decreased significantly upon the addition of electrolytes (NaCl , Na_2SO_4 , $(\text{C}_4\text{H}_9)_4\text{NBr}$). Wang et al.¹⁶ studied the aggregation behavior of 1-decyl-3-methylimidazolium bromide ($[\text{C}_{10}\text{mim}][\text{Br}]$) in the presence of 15 inorganic/organic electrolytes with different hydrophobicity. They found that the effect of the added sodium electrolytes on the micellar properties basically followed the Hofmeister series of the anions. Jiao et al.¹⁷ studied the effect of the inorganic/

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organic electrolytes (LiCl , NaCl , MgCl_2 , $(\text{CH}_3)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, $(\text{C}_3\text{H}_7)_4\text{NBr}$, and $(\text{C}_4\text{H}_9)_4\text{NBr}$) on the aggregation behavior of 1-butyl-3-methylimidazolium dodecylsulfate ($[\text{C}_{12}\text{mim}][\text{C}_{12}\text{SO}_4]$), in aqueous solution. The results showed that all the electrolytes investigated have a salting-out effect, which promote aggregate formation of $[\text{C}_{12}\text{mim}][\text{C}_{12}\text{SO}_4]$. In recent years Levin and co-worker's developed some theoretical methods to calculate the critical micelle concentrations of ionic surfactants in the presence of different salts,¹⁸ the excess interfacial tension of an electrolyte–oil interface,¹⁹ the surface tensions, and the surface potentials of electrolyte solutions.²⁰

Previously, we reported the effects of salt additives on the aggregation behavior of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solutions by conductometric, volumetric, and vapor-pressure osmometry techniques.^{21,22} In continuation of our previous studies,^{21,22} in the present work we study the aggregation behavior and surface adsorption of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solution by surface tension measurements. Our intention is the study of the effect of hydrophobicity, size, and concentration of organic additives on the aggregation and surface behavior of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solution. For this purpose, six organic electrolytes, with a wide range of physicochemical properties including tetramethylammonium bromide ($(\text{CH}_3)_4\text{NBr}$), tetraethylammonium bromide ($(\text{C}_2\text{H}_5)_4\text{NBr}$), tetrapropylammonium bromide ($(\text{C}_3\text{H}_7)_4\text{NBr}$), tetrabutylammonium bromide ($(\text{C}_4\text{H}_9)_4\text{NBr}$), tetramethylammonium chloride ($(\text{CH}_3)_4\text{NCl}$), and tetramethylammonium iodide ($(\text{CH}_3)_4\text{NI}$) were selected, and the surface tensions of $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions were measured in the presence of (0.00, 0.010, 0.020, and 0.035) $\text{mol}\cdot\text{kg}^{-1}$ of these electrolytes at 298.15 K and 308.15 K. That is to say although the surface tension measurement is a very useful and important technique for the study of surfactant solutions and provides one of the popular means for determining and understanding surface and bulk properties of solutions, very limited surface tension data have been reported in the literature for these systems. Furthermore, as far as we know there is not any information in the literature about the surface properties of the systems studied in this work.

2. EXPERIMENTAL SECTION

2.1. Materials. The properties of chemicals used in this work are listed in Table 1. Prior to use, $[\text{C}_{12}\text{mim}][\text{Br}]$ was

Table 1. Specification of the Used Chemicals

chemical	source	country	purity (mass fraction %)
$(\text{CH}_3)_4\text{NBr}$	Merck	Germany	$\geq 99.0\%$
$(\text{C}_2\text{H}_5)_4\text{NBr}$	Merck	Germany	$\geq 99.0\%$
$(\text{C}_3\text{H}_7)_4\text{NBr}$	Merck	Germany	$\geq 99.0\%$
$(\text{C}_4\text{H}_9)_4\text{NBr}$	Merck	Germany	$\geq 99.0\%$
$(\text{CH}_3)_4\text{NCl}$	Merck	Germany	$\geq 98.0\%$
$(\text{CH}_3)_4\text{NI}$	Merck	Germany	$\geq 99.0\%$
$[\text{C}_{12}\text{mim}][\text{Br}]$	Iolitec GmbH	Germany	$\geq 98.0\%$

purified by using the procedure described in the literature.⁹ Briefly, the sample was recrystallized three times from ethyl acetate and ethyl acetate/acetonitrile (3:2 by volume), respectively, to remove any unreacted reagents and then dried under vacuum for 1 day. Other chemicals were used without further purification and double distilled and deionized water was used for the preparation of the solutions.

2.2. Methods. The surface tension was measured on a Tensiometer-K100MK2 processor (Krüss Company), equipped

with thermostatable vessel holder, using the plate method. The instrument was connected to a Julabo F32 circulating thermostat to maintain a constant temperature at 298.15 K or 308.15 K with a precision of 0.01 K. To ensure removal of surface-active contaminants, all glassware in contact with the sample was cleaned in acetone and rinsed with double distilled water. The platinum plate was thoroughly cleaned and flame-dried before each measurement. The SAIL solutions were kept in the sample cells for 15 min until the surface tension did not change with time. All measurements were repeated thrice and average values were reported.

3. RESULTS AND DISCUSSION

Surface tension has historically provided one of the popular means for determining and understanding surface and bulk properties of solution. In this study, the surface tensions of $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions were measured in the presence of (0.00, 0.010, 0.020, and 0.035) $\text{mol}\cdot\text{kg}^{-1}$ electrolytes $(\text{CH}_3)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, $(\text{C}_3\text{H}_7)_4\text{NBr}$, $(\text{C}_4\text{H}_9)_4\text{NBr}$, $(\text{CH}_3)_4\text{NCl}$, and $(\text{CH}_3)_4\text{NI}$ at 298.15 K and 308.15 K in order to investigate the surface and aggregation behavior of $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions, and the measured data are given in Table 2. As an example, Figure 1 shows the surface tension curves (log scale) of $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solution in the absence and presence of 0.035 $\text{mol}\cdot\text{kg}^{-1}$ electrolytes $(\text{CH}_3)_4\text{NCl}$, $(\text{CH}_3)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, $(\text{C}_3\text{H}_7)_4\text{NBr}$, $(\text{C}_4\text{H}_9)_4\text{NBr}$, and $(\text{CH}_3)_4\text{NI}$ at 298.15 K. The surface tension decreases initially with increasing concentration of $[\text{C}_{12}\text{mim}][\text{Br}]$, suggesting that the SAIL molecules are adsorbed at the air/solution interface. Then a plateau appears in the $(\gamma-m)$ plot, indicating that the micelles have been formed. The values of cmc and the surface tension at the cmc (γ_{cmc}) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension curves ($\gamma-\log m$ curves) using a linear regression analysis method.²³ Besides, the presence of a small amount of impurities may create characteristic minimum in the plot of γ versus log concentration of SAIL. Figure 2 shows the surface tension curve for the aqueous solutions of purified and unpurified samples of $[\text{C}_{12}\text{mim}][\text{Br}]$ at 298.15 K. The impurities are usually more surface active but slower adsorbing than the SAIL, thus they will lower the surface tension below that of the pure SAIL. By increasing concentration, the amounts of micelles increase and they begin to solubilize the impurities or withdraw them from the surface. Therefore, the rate of decreasing of the surface tension declines until it reaches the minimum. The minimum shows that the enough micelles have formed to be in equilibrium with the maximum concentration of the impurities. Generally, cmc may be affected by such impurities. As can be seen, in the present investigation, we could get rid of the surface tension minimum by using the above purification method. However, in the case of aqueous electrolyte- $[\text{C}_{12}\text{mim}][\text{Br}]$ solutions, because of existence of the electrolytes, the surface tension curves show a minimum. Kim et al.²⁴ investigated the surface behavior of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$) + water mixture using surface tension measurement and sum-frequency generation spectroscopy and proposed another model to explain the brief minimum near cmc. They explained that the liquid surface is mostly covered by the $[\text{BMIM}]^+$ cations at very low bulk concentration leading to rapid decreasing in surface tension until it reaches the minimum at 0.016 (mole fraction of ionic liquid). An unusual increase in surface tension from mole

Table 2. Surface Tension of Solutions of $[\text{C}_{12}\text{mim}][\text{Br}]$ in Water and in Aqueous Solution of Different Concentrations of Tetraalkylammonium Halide Salts at $T = 298.15\text{ K}$ and 308.15 K and Atmospheric Pressure (m_{IL} is the Moles of $[\text{C}_{12}\text{mim}][\text{Br}]$ per Kilogram of Salt Aqueous Solution)^a

$m_s = 0.01\text{ mol}\cdot\text{kg}^{-1}$			$m_s = 0.02\text{ mol}\cdot\text{kg}^{-1}$			$m_s = 0.035\text{ mol}\cdot\text{kg}^{-1}$		
m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$		m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$		m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$	
$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K	$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K	$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K
$(\text{CH}_3)_4\text{NBr}$								
0.00183	45.645	44.320	0.00120	44.255	43.118	0.00059	47.422	46.617
0.00302	42.992	41.507	0.00155	43.452	42.573	0.00113	45.412	44.813
0.00389	40.171	39.528	0.00180	42.661	41.985	0.00141	43.986	43.007
0.00423	38.894	37.996	0.00247	41.548	40.848	0.00159	41.466	40.789
0.00432	38.657	37.900	0.00304	40.245	39.207	0.00184	39.179	39.107
0.00491	37.920	37.227	0.00328	39.801	38.807	0.00212	38.275	37.908
0.00513	37.689	36.977	0.00439	38.003	37.324	0.00243	37.739	37.128
0.00558	37.086	36.570	0.00458	37.695	37.092	0.00256	37.657	36.920
0.00580	36.884	36.375	0.00548	36.705	36.203	0.00288	37.315	36.450
0.00595	36.689	36.256	0.00613	36.706	36.327	0.00315	36.909	36.115
0.00646	36.674	36.369	0.00671	37.121	36.665	0.00353	36.323	35.677
0.00663	37.146	36.590	0.00747	37.658	37.127	0.00370	36.380	35.770
0.00708	37.863	37.262	0.00891	37.536	37.217	0.00391	36.589	35.995
0.00758	37.852	37.569	0.01129	37.428	37.180	0.00429	36.846	36.340
0.00877	37.766	37.705	0.01517	37.583	37.198	0.00500	36.962	36.693
0.01037	38.170	37.892	0.02137	37.495	37.327	0.00758	37.158	36.890
0.01379	38.135	37.924				0.01102	37.047	36.894
0.01730	38.021	37.845						
$(\text{C}_2\text{H}_5)_4\text{NBr}$								
0.00139	46.204	45.567	0.00063	49.924	47.501	0.00059	47.020	46.123
0.00208	44.159	43.752	0.00124	45.440	44.582	0.00120	44.706	42.800
0.00303	42.527	41.518	0.00180	44.259	43.493	0.00147	43.047	41.194
0.00356	40.813	40.298	0.00225	42.652	41.927	0.00183	41.969	39.183
0.00448	38.304	37.183	0.00306	41.149	40.249	0.00242	40.223	37.046
0.00476	37.665	36.607	0.00378	38.806	37.613	0.00267	38.243	36.004
0.00503	36.992	35.995	0.00394	37.695	36.512	0.00285	37.202	35.592
0.00544	35.885	35.196	0.00416	36.947	35.906	0.00309	35.600	34.900
0.00571	35.726	35.354	0.00451	35.888	35.009	0.00317	34.736	34.690
0.00581	36.375	35.980	0.00480	35.159	34.622	0.00347	34.138	33.950
0.00595	37.250	36.768	0.00498	35.536	35.006	0.00352	34.211	34.021
0.00608	37.863	37.613	0.00552	36.264	35.806	0.00382	34.525	34.493
0.00706	37.992	37.670	0.00593	37.001	36.540	0.00422	35.732	35.290
0.00805	38.244	37.940	0.00743	37.191	36.880	0.00450	36.631	36.170
0.00933	38.042	37.755	0.00922	37.336	37.256	0.00510	36.556	36.182
			0.01248	37.593	37.046	0.00750	36.966	36.540
						0.01023	37.045	36.713
$(\text{C}_3\text{H}_7)_4\text{NBr}$								
0.00173	44.230	43.870	0.00061	53.867	47.462	0.00060	46.714	45.841
0.00296	41.683	41.270	0.00120	44.038	43.781	0.00119	43.023	41.768
0.00398	40.499	39.953	0.00182	41.601	41.555	0.00183	40.227	38.683
0.00430	39.380	38.800	0.00243	40.956	39.902	0.00236	38.870	36.849
0.00473	37.880	37.194	0.00335	39.601	38.650	0.00264	36.514	35.580
0.00491	37.250	36.800	0.00378	38.294	37.307	0.00279	35.455	34.900
0.00494	37.150	36.680	0.00401	37.626	36.709	0.00299	34.586	34.162
0.00521	36.352	36.019	0.00438	36.532	36.098	0.00303	34.441	34.058
0.00536	36.506	36.330	0.00467	35.987	35.650	0.00330	34.094	33.790
0.00554	36.696	36.740	0.00502	36.645	36.181	0.00346	34.194	33.933
0.00581	37.315	37.303	0.00549	37.591	37.026	0.00354	34.170	34.045
0.00614	37.813	37.509	0.00707	37.569	37.434	0.00387	34.603	34.465
0.00700	37.702	37.473	0.00995	37.764	37.635	0.00438	35.495	35.067
0.00751	37.514	37.299	0.01452	37.578	37.334	0.00452	36.076	35.341
0.01022	37.585	37.411				0.00547	36.586	36.120
						0.00763	36.489	36.039
						0.01042	36.932	36.582

Table 2. continued

$m_s = 0.01 \text{ mol}\cdot\text{kg}^{-1}$			$m_s = 0.02 \text{ mol}\cdot\text{kg}^{-1}$			$m_s = 0.035 \text{ mol}\cdot\text{kg}^{-1}$		
m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$		m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$		m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$	
$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K	$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K	$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K
(C ₄ H ₉) ₄ NBr								
0.00193	42.981	41.990	0.00060	43.672	42.691	0.00072	45.272	43.450
0.00296	41.687	41.208	0.00121	42.989	41.779	0.00120	43.099	41.997
0.00393	40.777	40.244	0.00178	42.069	41.308	0.00180	40.986	39.499
0.00423	39.599	38.718	0.00238	41.238	40.953	0.00209	38.709	37.653
0.00444	39.001	37.307	0.00325	40.296	39.994	0.00241	36.729	36.016
0.00453	38.287	36.900	0.00386	38.941	38.032	0.00253	36.050	35.440
0.00476	36.531	35.805	0.00423	37.333	36.890	0.00272	35.942	35.024
0.00486	35.863	35.463	0.00440	36.521	36.293	0.00293	35.621	34.940
0.00497	35.912	35.567	0.00456	35.885	35.960	0.00329	35.704	35.076
0.00518	36.361	35.943	0.00483	36.258	36.000	0.00340	35.881	35.157
0.00535	36.803	36.282	0.00498	36.583	36.235	0.00365	35.998	35.469
0.00545	37.045	36.589	0.00522	37.213	36.777	0.00390	36.526	35.596
0.00570	37.806	37.243	0.00705	37.550	37.023	0.00411	36.509	35.666
0.00629	37.996	37.508	0.00967	37.448	37.148	0.00444	36.568	36.052
0.00711	38.162	37.618	0.01469	37.003	36.962	0.00518	36.598	36.403
0.00829	38.229	37.564				0.00748	36.870	36.790
0.01031	37.959	37.621				0.01020	36.873	36.746
(CH ₃) ₄ NCl								
0.00302	47.685	46.098	0.00197	47.642	46.551	0.00053	52.121	51.544
0.00402	44.850	43.336	0.00294	46.273	45.531	0.00117	50.272	49.337
0.00456	43.435	42.345	0.00360	44.963	43.890	0.00184	49.502	48.100
0.00515	41.500	40.300	0.00393	43.482	43.007	0.00245	47.208	46.166
0.00530	40.912	39.965	0.00450	41.687	41.571	0.00279	45.258	43.989
0.00605	39.717	39.006	0.00465	41.432	41.027	0.00319	42.842	41.115
0.00635	39.290	38.654	0.00524	40.501	39.785	0.00390	40.873	39.603
0.00652	38.977	38.524	0.00556	39.953	39.199	0.00455	39.658	38.352
0.00699	38.261	38.195	0.00594	39.372	38.900	0.00483	38.820	37.666
0.00733	38.409	38.205	0.00643	39.154	38.669	0.00523	38.092	36.907
0.00743	38.701	38.327	0.00695	39.442	39.078	0.00595	36.887	36.247
0.00763	39.004	38.993	0.00749	40.000	39.527	0.00662	37.115	36.998
0.00848	39.300	39.147	0.01017	39.984	39.549	0.00742	37.989	37.637
0.01081	38.542	38.367	0.01353	39.740	39.362	0.00824	38.999	38.633
0.01281	38.331	38.052				0.00945	39.201	38.907
						0.01403	39.050	38.748
						0.01598	38.944	38.701
(CH ₃) ₄ NI								
0.00058	36.968	37.076	0.00038	37.734	37.218	0.00031	35.828	35.034
0.00081	35.384	34.876	0.00060	36.073	36.521	0.00045	32.902	32.378
0.00120	33.022	33.173	0.00096	34.000	32.907	0.00067	31.795	30.567
0.00147	32.190	31.450	0.00107	32.847	32.458	0.00075	31.002	30.123
0.00179	31.494	30.993	0.00121	31.755	31.990	0.00093	30.295	29.758
0.00209	30.845	30.545	0.00146	31.121	30.662	0.00120	30.030	29.308
0.00233	30.526	30.231	0.00162	30.815	30.347	0.00131	29.900	29.130
0.00260	30.740	30.523	0.00178	30.572	30.202	0.00153	29.748	29.070
0.00298	31.280	31.063	0.00201	30.704	30.230	0.00169	29.933	29.290
0.00341	31.842	31.757	0.00242	30.876	30.523	0.00187	30.224	29.470
0.00387	32.011	31.920	0.00322	31.328	30.966	0.00212	30.536	29.801
0.00455	32.015	31.984	0.00391	31.497	31.099	0.00272	30.804	30.478
0.00514	32.108	32.000	0.00444	31.475	31.192	0.00300	30.884	30.657
0.00550	32.051	32.035	0.00480	31.504	31.237	0.00328	30.969	30.879
0.00760	32.044	32.003	0.00533	31.549	31.337	0.00345	31.077	30.972
			0.00741	31.513	31.402	0.00495	31.262	31.200
			0.00966	31.567	31.450	0.00748	31.215	31.300
						0.01050	31.233	31.380

Table 2. continued

$m_s = 0 \text{ mol}\cdot\text{kg}^{-1}$		
m_{IL}	$\gamma/(\text{mN}\cdot\text{m}^{-1})$	
$\text{mol}\cdot\text{kg}^{-1}$	298.15 K	308.15 K
	pure water	
0.00056	61.126	59.884
0.00127	59.258	57.723
0.00272	53.769	52.443
0.00431	48.750	47.506
0.00538	45.875	44.872
0.00658	43.437	42.340
0.00743	41.201	40.273
0.00749	40.937	39.718
0.00856	38.827	38.162
0.00882	38.800	38.163
0.01035	38.482	37.911
0.01463	38.488	37.915
0.02015	38.462	37.900

^aThe expanded uncertainties for surface tension, ionic liquid molality, and temperature at 0.95 confidence level were estimated to be $1 \text{ mN}\cdot\text{m}^{-1}$, $5 \cdot 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$, and 10^{-2} K , respectively.

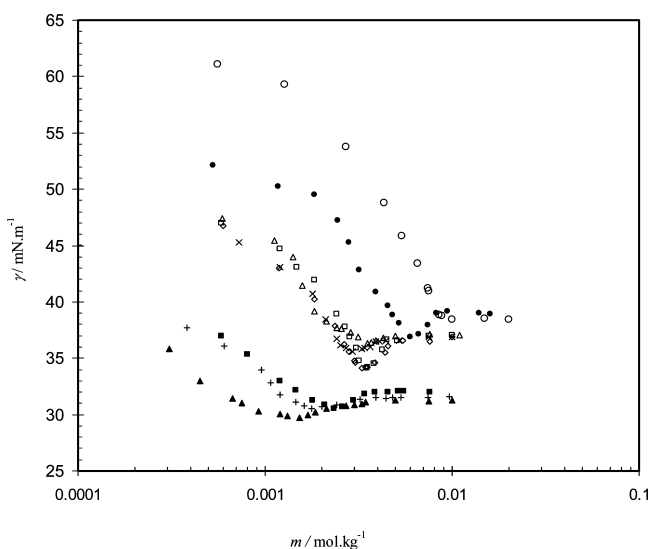


Figure 1. Surface tension as a function of m (log scale) for aqueous solutions of $[\text{C}_{12}\text{mim}][\text{Br}]$ in the absence and presence of $0.035 \text{ mol}\cdot\text{kg}^{-1}$ tetraalkylammonium bromide salts at 298.15 K: \circ , pure water; \triangle , $(\text{CH}_3)_4\text{NBr}$; \square , $(\text{C}_2\text{H}_5)_4\text{NBr}$; \diamond , $(\text{C}_3\text{H}_7)_4\text{NBr}$; \times , $(\text{C}_4\text{H}_9)_4\text{NBr}$; \bullet , $(\text{CH}_3)_4\text{NCl}$; \blacktriangle , $(\text{CH}_3)_4\text{NI}$; \blacksquare , $(\text{CH}_3)_4\text{NI}$ ($0.01 \text{ mol}\cdot\text{kg}^{-1}$); $+$, $(\text{CH}_3)_4\text{NI}$ ($0.02 \text{ mol}\cdot\text{kg}^{-1}$).

fraction 0.016 up to 0.05 suggested that BF_4^- anions start to appear at the surface from 0.016 until the anions and cations are equally populated at 0.05 or higher. In Figure 3, a comparison between the experimental surface tension data for $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions measured in this work and those taken from the literature^{25,26} has been shown at 298.15 K. As can be seen, there is a good agreement between our data and those taken from the literatures. Figure 1 shows that the surface tension values of $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions in the presence of electrolytes follow the orders: pure water > $(\text{CH}_3)_4\text{NCl}$ > $(\text{C}_4\text{H}_9)_4\text{NBr} \approx (\text{C}_3\text{H}_7)_4\text{NBr} \approx (\text{C}_2\text{H}_5)_4\text{NBr} \approx (\text{CH}_3)_4\text{NBr}$ > $(\text{CH}_3)_4\text{NI}$ and $(\text{CH}_3)_4\text{NCl}$ > pure water > $(\text{C}_4\text{H}_9)_4\text{NBr} \approx (\text{C}_3\text{H}_7)_4\text{NBr} \approx (\text{C}_2\text{H}_5)_4\text{NBr} \approx (\text{CH}_3)_4\text{NBr}$ > $(\text{CH}_3)_4\text{NI}$, respectively, in the monomer and micellar regions. The ions with more hydration ability are less effective in

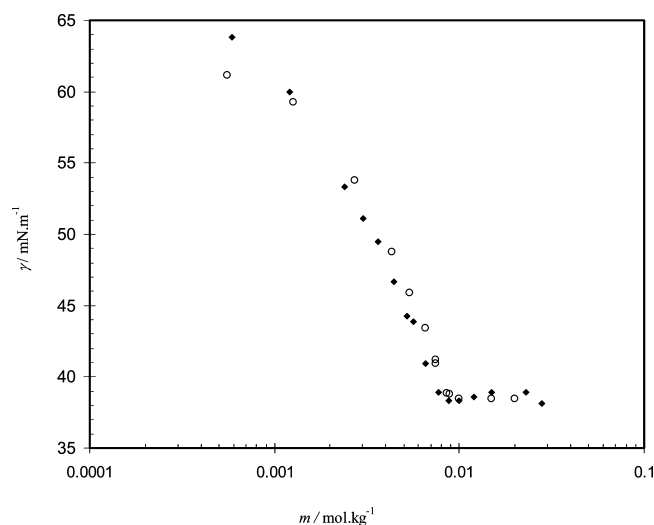


Figure 2. Surface tension as a function of m (log scale) for $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions before and after purification at 298.15 K: \circ , after purification; \blacklozenge , before purification.

neutralizing the charges of the micelle surface. The polarizabilities of Cl^- , Br^- , and I^- are 4.0 \AA^3 , 4.53 \AA^3 , and 6.90 \AA^3 , respectively.²⁵ The strongly polarized halide anions (like Br^- or I^-) seem to be more “surface active” than the weakly polarized ion (Cl^-). Generally, the ions with a high polarizability due to strong interaction with the electric field at the interface would enhance the binding of anions at the aggregate, and then the electrostatic repulsion between charged headgroups in the surface layer decreases, and therefore surface activity of the investigated anions follows the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. For $m < \text{cmc}$ concentration region in which the surface layer of the solution has not been saturated by the SAIL yet, at a same SAIL concentration the surface tension of the solution is more decreased in the presence of added electrolytes, and then the ability of the added electrolytes in the reduction of surface tension follows the order $(\text{CH}_3)_4\text{NI} > (\text{CH}_3)_4\text{NBr} > (\text{CH}_3)_4\text{NCl}$ > pure water. However, at $m > \text{cmc}$ concentration region in which the surface layer of the solution has been saturated by the SAIL, the values of the experimental surface

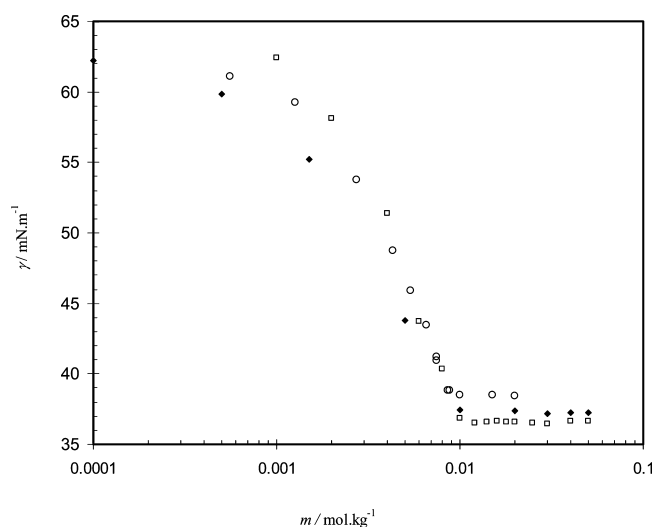


Figure 3. Comparison of the experimental surface tension data as a function of m (log scale) for $[\text{C}_{12}\text{mim}][\text{Br}]$ aqueous solutions measured in this work with those taken from the literature at 298.15 K: \circ , this work; \blacklozenge , ref 26; \square , ref 25.

tension follow the order pure water $\approx (\text{CH}_3)_4\text{NCl} > (\text{CH}_3)_4\text{NBr} > (\text{CH}_3)_4\text{NI}$.

The cmc values determined from the intersection of two straight lines plotting the surface tension values versus $\log m$ are listed in Tables 3 and 4. As can be seen, the cmc values of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solutions decrease drastically upon the addition of electrolytes, and therefore all the investigated electrolytes have salting-out effects on the aggregation of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solutions. The results show that the salting-out-inducing anions are predominately responsible for the observed effect, while the cations have a smaller effect on the salting-out strength. The ability of the tetraalkylammonium halides to promote the aggregation of $[\text{C}_{12}\text{mim}][\text{Br}]$ was found to decrease in the order: $(\text{CH}_3)_4\text{NI} \gg (\text{C}_4\text{H}_9)_4\text{NBr} >$

$(\text{C}_3\text{H}_7)_4\text{NBr} > (\text{C}_2\text{H}_5)_4\text{NBr} > (\text{CH}_3)_4\text{NBr} \gg (\text{CH}_3)_4\text{NCl}$. $[\text{C}_{12}\text{mim}][\text{Br}]$ is a cationic surfactant and therefore the electrostatic binding of the anions of the added electrolytes with the cationic headgroups of $[\text{C}_{12}\text{mim}][\text{Br}]$ leads to the reducing the electrostatic repulsion among the $[\text{C}_{12}\text{mim}][\text{Br}]$ headgroups and then lowering its cmc value. The larger sized hydrophobic counterions are weakly hydrated and highly polarizable and can bind more efficiently at the surface of the aggregates and decrease the electrostatic repulsion between the head groups of the surfactant, thus increasing the tendency of the surfactant aggregation and then lowering its cmc value. Furthermore, the reduction in the cmc values can also be correlated to the hydrophobic chain length of the added electrolytes. The increased ionic size from $(\text{CH}_3)_4\text{N}^+$ to $(\text{C}_4\text{H}_9)_4\text{N}^+$ enhances the hydrophobic interactions between the hydrophobic portion of $(\text{C}_n\text{H}_{n+1})_4\text{N}^+$ cations and hydrophobic chains of $[\text{C}_{12}\text{mim}]\text{Br}$ at the micelle surface, which is consequence of overcoming steric hindrance. On the other hand, incorporation of the hydrophobic portion of $(\text{C}_n\text{H}_{n+1})_4\text{N}^+$ cations into the micelles leads to the reduction of the repulsive interactions between the ionic head groups, lowering the cmc values and enhancing the micellization of the surfactant. The obtained results show that the effect of the concentration of electrolyte on the cmc can be described by the following equation:²⁷

$$\log \text{cmc} = a - k_s m_s \quad (1)$$

where, m_s is molality of the added salt, a and k_s are adjusted parameters. The k_s parameter can be correlated with the salting constant (similar to the empirical equation of salt effect²⁷). A positive (or negative) value of k_s indicates a salting-out (or salting-in) effect on the SAIL aggregation behavior. The obtained k_s values for different investigated salts, given in Tables 3 and 4, are positive and they decrease in the order: $(\text{CH}_3)_4\text{NI} \gg (\text{C}_4\text{H}_9)_4\text{NBr} > (\text{C}_3\text{H}_7)_4\text{NBr} > (\text{C}_2\text{H}_5)_4\text{NBr} > (\text{CH}_3)_4\text{NBr} \gg (\text{CH}_3)_4\text{NCl}$. As can be seen, in comparison to the salts additives, temperature has a very slight effect on the

Table 3. Surface and Micellar Properties of $[\text{C}_{12}\text{mim}][\text{Br}]$ Aqueous Solutions in the Absence and Presence of Various Electrolytes at 298.15 K and Atmospheric Pressure

	m_s mol·kg ⁻¹	cmc mmol·kg ⁻¹	Γ_{\max} μmol/m ²	A_{\min} nm ²	pC ₂₀	Π_{cmc} mN·m ⁻¹	k_s kg·mol ⁻¹	γ_{cmc} mN·m ⁻¹
no salt	0.000	8.73	3.1	0.54	2.5	33.9		38.7
$(\text{CH}_3)_4\text{NBr}$	0.010	6.15	1.3	1.30	3.3	35.8	10.66	36.5
	0.020	5.54	1.2	1.35	3.3	34.9		36.6
	0.035	3.54	0.8	2.03	3.8	32.6		36.4
	0.010	5.65	2.7	0.62	2.8	36.9	10.84	35.4
$(\text{C}_2\text{H}_5)_4\text{NBr}$	0.020	4.79	2.6	0.64	2.8	35.0		35.2
	0.035	3.50	2.5	0.66	2.8	31.1		34.1
	0.010	5.24	3.1	0.53	2.7	35.2	11.25	36.2
$(\text{C}_3\text{H}_7)_4\text{NBr}$	0.020	4.62	2.2	0.76	2.9	35.1		35.8
	0.035	3.32	1.9	0.86	3.0	31.9		33.9
	0.010	4.93	4.8	0.35	2.6	34.5	12.75	35.7
$(\text{C}_4\text{H}_9)_4\text{NBr}$	0.020	4.57	3.8	0.44	2.6	32.6		35.8
	0.035	2.88	1.7	0.99	3.0	29.4		35.5
	0.010	7.21	2.9	0.58	2.6	33.5	4.62	38.8
$(\text{CH}_3)_4\text{NCl}$	0.020	6.18	1.9	0.86	2.8	33.4		38.9
	0.035	6.00	1.9	0.87	2.9	35.4		36.8
	0.010	2.33	0.7	2.30	5.3	41.8	20.35	30.5
$(\text{CH}_3)_4\text{NI}$	0.020	1.77	0.6	2.68	5.8	41.6		30.6
	0.035	1.45	0.4	4.19	7.3	40.3		29.7

Table 4. Surface and Micellar Properties of [C₁₂mim][Br] Aqueous Solutions in the Absence and Presence of Various Electrolytes at 308.15 K and Atmospheric Pressure

	m_s mol·kg ⁻¹	cmc mmol·kg ⁻¹	Γ_{\max} μmol/m ²	A_{\min} nm ²	pC ₂₀	Π_{cmc} mN·m ⁻¹	k_s kg·mol ⁻¹	γ_{cmc} mN·m ⁻¹
no salt	0.000	8.577	2.893	0.574	2.475	33.942		38.069
(CH ₃) ₄ NBr	0.010	6.169	1.039	1.598	3.518	35.505	10.63	36.055
	0.020	5.539	0.996	1.667	3.539	35.064		36.137
	0.035	3.504	0.859	1.933	3.753	32.729		35.651
	0.010	5.630	2.121	0.783	2.923	36.304		34.836
(C ₂ H ₅) ₄ NBr	0.020	4.769	1.969	0.843	3.007	35.395	10.69	34.585
	0.035	3.483	1.701	0.976	3.010	30.725		33.885
	0.010	5.153	3.012	0.551	2.724	35.009		36.067
	0.020	4.427	2.614	0.635	2.817	33.83		35.172
(C ₃ H ₇) ₄ NBr	0.035	3.167	2.249	0.738	2.906	30.448	11.67	33.542
	0.010	4.878	4.671	0.355	2.588	34.743		35.253
	0.020	4.579	2.587	0.642	2.755	32.269		35.852
	0.035	2.878	1.521	1.092	3.063	29.059		34.831
(CH ₃) ₄ NCl	0.010	6.929	1.508	1.101	2.958	33.731	4.85	38.031
	0.020	6.131	1.964	0.845	2.808	33.355		38.395
	0.035	5.736	1.763	0.942	2.977	34.799		36.045
	0.010	2.362	0.534	3.11	6.085	41.085		30.215
(CH ₃) ₄ NI	0.020	1.792	0.469	3.541	6.674	41.031	18.91	30.159
	0.035	1.615	0.336	4.942	7.704	38.848		29.152

aggregation and surface behavior of [C₁₂mim][Br] in aqueous solutions.

Tables 3 and 4 also show that for [C₁₂mim][Br] aqueous solutions, the γ_{cmc} (surface tension at cmc) values decrease upon addition of the electrolytes. Actually, γ_{cmc} is the measure of efficiency of the surfactant to populate at the air–liquid interface. The obtained values of γ_{cmc} for the anions of the added electrolytes decrease in the order: Cl⁻ > Br⁻ > I⁻. As mentioned above, the larger sized anions lead to a tighter arrangement of surfactant molecules at the air/liquid interface by decreasing the electrostatic repulsion between the head groups of the surfactant, thus lowering the γ_{cmc} value. In Table 5, the obtained micellization parameters in this work have been compared to those taken from the literature. As can be seen, there is a good agreement between our data and those taken from the literature.

Table 5. Comparison of Literature Data for Micellization of [C₁₂mim][Br] in Water at 298.15 K and Atmospheric Pressure with Data of This Study

cmc mmol·kg ⁻¹	γ_{cmc} mN·m ⁻¹	Π_{cmc} mN·m ⁻¹	pC ₂₀	Γ_{\max} μmol·m ⁻²	A_{\min} nm ²
This Study					
8.728	38.677	33.938	2.454	3.095	0.537
Literature					
(10.9 ^a , 8.5 ^b) ⁹	(39.4) ⁹ (37.4) ²⁵ (36.8) ²⁶	(33.6) ⁹	(2.67) ⁹ (2.38) ²⁶	(1.9) ⁹ (3.03) ²⁶	(0.86) ⁹ (0.55) ²⁶
(9.0 ^b , 12.0 ^c , 10.0 ^d) ³⁰					
(9.0 ^b , 12.0 ^c) ³¹ (4.3 ^a) ³²					
(4.0 ^a) ³³					
(9.68 ^b) ²⁵ (10.6 ^a) ²⁶					

^aFrom the surface tension. ^bFrom the electrical conductivity. ^cFrom the fluorescence. ^dFrom the volumetric.

The maximum surface excess concentration (saturation adsorption), Γ_{\max} , and minimum area occupied by a single IL molecule at the air/solution interface, A_{\min} , (which reflects the packing density of surfactant molecules at the interface) were obtained by applying the Gibbs adsorption isotherm to the tensiometric profiles in the concentration range below and close to the cmc.²⁸

$$\Gamma_{\max} = -\frac{1}{iRT} \left(\frac{\partial \gamma}{\partial \ln m} \right)_{T,P} \quad (2)$$

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \quad (3)$$

where γ is the surface tension in mN·m⁻¹, R is the gas constant (8.314 J·mol⁻¹·K⁻¹), N_A is Avogadro's number, T is the absolute temperature, m is the surfactant molality, and $((\partial \gamma / \partial \ln m))_{T,P}$ is the slope of the linear fit of the data before the cmc in the surface tension plots. The parameter i represents the number of components constituting the surfactant which are adsorbed at the interface²⁹ which was taken as equal to 2. As presented in Tables 3 and 4, the Γ_{\max} values of [C₁₂mim][Br] in the presence of the investigated organic electrolytes are lower than that in the salt-free system and decrease by increasing electrolyte concentrations. From eq 3 we can see that the higher the adsorption is, the smaller is the effective area of surfactant molecule at the surface and then A_{\min} followed the reverse trend to that of Γ_{\max} . The abilities of the anions and cations of the investigated electrolytes to decrease the Γ_{\max} values were found to decrease in the order: I⁻ > Br⁻ > Cl⁻ and (CH₃)₄N⁺ > (C₂H₅)₄N⁺ > (C₃H₇)₄N⁺ > (C₄H₉)₄N⁺, respectively. These results reflect that the packing of [C₁₂mim]Br molecules at the interface decreases in the presence electrolytes.

From the surface tension plots, two additional parameters can be obtained, that is, the adsorption efficiency, pC₂₀, and the effectiveness of surface tension reduction, Π_{cmc} . These parameters are defined as²⁸

$$pC_{20} = -\log C_{20} \quad (4)$$

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (5)$$

where C_{20} is the surfactant concentration at which the surface tension of pure solvent is reduced by $20 \text{ mN}\cdot\text{m}^{-1}$, γ_0 and γ_{cmc} are the surface tensions of pure solvent and the solution at cmc, respectively; pC_{20} is the minimum concentration needed to lead to a saturation of the surface adsorption. Thus, pC_{20} can be a measure of the efficiency of the adsorption of surfactant molecules at the air–liquid interface. The larger value of pC_{20} is, the higher is the adsorption efficiency of the surfactant. On the other hand, the parameter Π_{cmc} indicates the maximum reduction of surface tension caused by the dissolution of surfactant molecules; hence, it becomes a measure for the effectiveness of the surfactant to lower the surface tension of the solvent,²⁸ and the greater the Π_{cmc} value is, the higher is the effectiveness of the surfactant. The values of these two parameters are also listed in Tables 3 and 4. The values of pC_{20} and Π_{cmc} were found to be lower in water as compared to that in aqueous electrolyte solutions and followed the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$ and $(\text{CH}_3)_4\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > (\text{C}_3\text{H}_7)_4\text{N}^+ > (\text{C}_4\text{H}_9)_4\text{N}^+$, which indicates that the surface activity of $[\text{C}_{12}\text{mim}][\text{Br}]$ in the presence of electrolytes is somewhat superior to that in pure water. The larger anions tend to lose their hydration sheath easily as a result of their larger polarizability and cavitation force and then are adsorbed to the surface.

4. CONCLUSION

The micellization and surface activity of the SAIL, $[\text{C}_{12}\text{mim}][\text{Br}]$, were investigated in aqueous solutions of organic electrolytes $(\text{CH}_3)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, $(\text{C}_3\text{H}_7)_4\text{NBr}$, $(\text{C}_4\text{H}_9)_4\text{NBr}$, $(\text{CH}_3)_4\text{NCl}$, and $(\text{CH}_3)_4\text{NI}$ by means of surface tension measurements at 298.15 K and 308.15 K. It was found that, in comparison to the anions additives, temperature and cations have very slight effects on the aggregation and surface behavior of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solutions. All the investigated tetraalkylammonium halides have salting-out effects on the aggregation of $[\text{C}_{12}\text{mim}][\text{Br}]$ in aqueous solutions and their abilities to promote the aggregation of $[\text{C}_{12}\text{mim}][\text{Br}]$ decrease in the order $(\text{CH}_3)_4\text{NI} \gg (\text{C}_4\text{H}_9)_4\text{NBr} > (\text{C}_3\text{H}_7)_4\text{NBr} > (\text{C}_2\text{H}_5)_4\text{NBr} > (\text{CH}_3)_4\text{NBr} \gg (\text{CH}_3)_4\text{NCl}$. At $m < \text{cmc}$ and $m > \text{cmc}$ concentration regions, the values of the experimental surface tension follow the order pure water $> (\text{CH}_3)_4\text{NCl} > (\text{CH}_3)_4\text{NBr} > (\text{CH}_3)_4\text{NI}$ and pure water $\approx (\text{CH}_3)_4\text{NCl} > (\text{CH}_3)_4\text{NBr} > (\text{CH}_3)_4\text{NI}$, respectively. The abilities of the anions of the investigated electrolytes to decrease the cmc, Γ_{max} and γ_{cmc} and increase pC_{20} , Π_{cmc} and A_{min} values were found to decrease in the order: $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

In conclusion, we can regulate the aggregation behavior of SAILs by selecting the right salt at a suitable concentration not only for their fundamental interest but also for particular applications in many fields.

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Notes

The authors declare no competing financial interest.

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