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Evaluation of the Performance of Trigeminal Tricationic Ionic Liquids for Separation Problems

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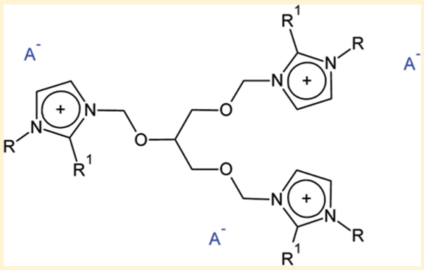
ABSTRACT: For the first time, the performance of six new trigeminal tricationic ionic liquids (TTILs) was evaluated for different separation problems. The different selectivity and capacity values obtained on these TTILs show that the choice of the anion, the cation, and the functionalized chain plays an important role on the efficiency of the separation process. It was found that two TTILs have the highest selectivity and capacity observed up to now for numerous separation problems such as the separation of aromatics (or alcohols or thiophene) from aliphatic hydrocarbons. The solvation characteristics of this class of ionic liquids were also evaluated using linear solvation energy relationships (LSERs). Results indicate that TTILs and monocationic ionic liquids have similar solvation properties.



■ INTRODUCTION

New strategies are necessary for efficient and clean separation processes in the biotechnology and chemical industries. The new technology will have to reduce the amount of organic solvent needed for these separation processes, leading lower to volatile organic compound (VOC) emissions. Since more than thirty million tons of VOCs are released annually, even a 10 % reduction in these levels would have a significant impact on air quality. Among the new advances, ionic liquids (ILs) are being widely promoted as probable substitutes for traditional industrial solvents such as VOCs in a host of processes.

Overall, as a class of solvent, ILs frequently combine the attractive features of excellent chemical stability, high thermal stability, and exceedingly low vapor pressure in a single solvent. ILs are commonly comprised of an asymmetric, bulky organic cation paired with a weakly coordinating anion that may be organic or inorganic in nature. The properties of the anion and functionality presented at the cationic or anionic site offer a means to alter the specific attributes of the solvent proper, giving rise to the notion of tuning, often in a stepwise fashion, the key solvent features for the task at hand. Nowadays, it is widely accepted that ILs are among the most intriguing and diverse alternative media available not only for conventional solvent-driven chemical processes like synthesis and (bio)-catalysis, but also next-generation electrolytes, lubricants, and modifiers of mobile and stationary phases within the separation sciences.[1−3] Numerous works have shown that a large number of ILs exhibit selectivities and capacities better than the solvents typically employed to solve industrial separation problems.[4−10] For instance, IL-assisted extractive distillation or liquid−liquid extraction forms a powerful approach in the separation of ethanol−water mixtures[11] and thiophene from aliphatic hydrocarbons.[12] Marciniak analyzed the influence of the cation and anion structures of the IL but also the effect of the temperature on the selectivity and the capacity for aliphatics/aromatics and *n*-hexane/hex-1-ene separation problems.[13] The author showed that the highest values of selectivity is observed with ILs containing small alkyl chains, for example, based on following cations: [MMIM]$^+$, [EMIM]$^+$, [EPY]$^+$, and [Et$_3$S]$^+$ coupled to a thiocyanate group in the structure. Unfortunately, when the dialkylimidazolium-based ILs reveals high values of the selectivity, the capacity always takes low values.

Multifunctional ILs (especially dicationic and tricationic ILs) present a greater range of physical properties than most traditional monocationic ILs.[14,15]

Recently, it was found that thermal stabilities of tricationic ILs with the [N(Tf)$_2$] counteranion range from (355 to 430) °C which is higher than monocationic ILs and similar to dicationic ILs. The presence of oxygen atoms in the molecule decreased its thermal stability. The high capacitance values obtained at higher temperatures with an operating voltage of approximately 3.5 V (similar to battery values) lead to possible applications for these novel trigeminal tricationic ionic liquids (TTILs) as high energy sources; hence, the application of such electrolytes for a special low-current load could be envisaged. Additionally, other applications such as electrodeposition, lithium ion batteries, and gas chromatographic stationary phases could be considered.[16]

The gas chromatography technique has been used to determine the physicochemical properties (partition coefficients, activity coefficients, selectivity) of numerous ILs.[17,18] Up to now, the performance of TTILs for separation problems has not been evaluated. This work presents a characterization of six TTILs composed of a polar alkyl chain grafted on the cation and of tetrafluoroborate [BF$_4$], dicyanamide [N(CN)$_2$], or bis(trifluoromethylsulfonyl)imide [N(Tf)$_2$] as the anion. Their molecular structures are given in Figure 1 and in Table 1.

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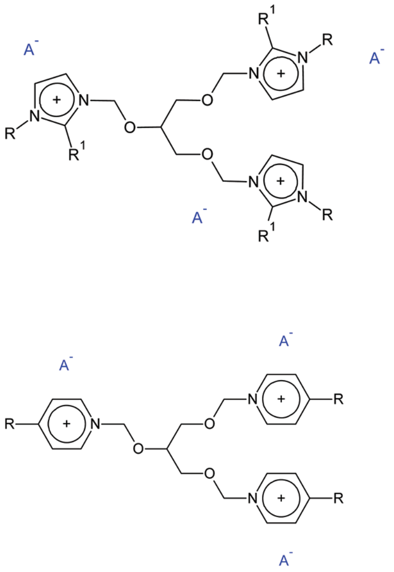

Figure 1. Chemical structure of the investigated ILs.

This choice was didacted by the low viscosity of the dicyanamide anion based ILs.[19] In previous work, high selectivities obtained with dicyanamide-based ILs indicate that such ILs should be used for the liquid−liquid extraction of numerous VOCs from aliphatic mixtures. Moreover, grafting a polar chain on the cation of dicyanamide-based ILs increases their potential spectacularly. Some $[N(Tf)_2]$-based ILs also generate a particular interest since the selectivity values obtained are equivalent to the classical solvent used in the industry.

Before being used as a solvent, one of the most important steps is to have a good knowledge of solute−solvent interactions. Crowhurst et al.[20] proposed characterizing the physicochemical properties of ILs using the Kamlet and Taft's approach.[21−24] Parameters such as hydrogen bond acidity, hydrogen bond basicity, and dipolarity/polarizability are determined using the UV−vis technique. A similar approach based on the gas chromatography technique was proposed to quantify various intermolecular solute−IL interactions. Among others, Abraham et al. have developed the linear solvation energy relationship model (LSER) allowing the correlation of thermodynamic properties of phase transfer processes.[25−28] The most recent representation of the LSER model is given by eq 1

$$\log \mathrm{SP} = c + eE + sS + aA + bB + lL \tag{1}$$

where SP is a solute property related with the free energy change such as the gas−liquid partition coefficient, specific retention volume, or adjusted retention time at a given temperature. The capital letters represent the solutes properties and the lower case letters the complementary properties of the ILs. The solute descriptors are the excess molar refraction E, dipolarity/polarizability S, hydrogen bond acidity and basicity, A and B, respectively, and the gas−liquid partition coefficient on n-hexadecane at 298 K, L. The coefficients c, e, s, a, b, and l are not simply fitting coefficients; they reflect complementary properties of the solvent phase.

The system constants are identified as the opposing contributions of cavity formation and dispersion interactions, l, the contribution from interactions with one-pair electrons, e, the contribution from dipole-type interactions, s, the contribution from the hydrogen-bond basicity of the stationary phase (because a basic phase will interact with an acid solute), a, and b the contribution from the hydrogen-bond acidity of the stationary phase. The system constants are determined by multiple linear regression analysis of experimental log SP(log K_L in this work) values for a group of solutes of a sufficient number and variety to establish the statistical and chemical validity of the model.

In this work, gas−liquid chromatography was used to quantify intermolecular solute−TTIL interactions and to predict their potential in various extraction and extractive distillation processes. Since trigonal tricationic ILs are a new class of ILs, it is necessary to characterize them based on their solvation properties and relative polarity compared to the classical monocationic ILs and other common organic solvents. The main objective is to evaluate if more complex multifunctional ILs (tricationic, trianionic, etc.) can be beneficial for separation process problems.

■ EXPERIMENTAL PROCEDURES

Materials and Reagents. *Synthesis of Tested ILs.* 1,2,3-Tri(chloromethoxy)propane was prepared by passing gaseous HCl through a mixture of formaldehyde and glycerol.[29] The product was distilled under reduced pressure. Trigeminal tricationic chlorides were prepared in a very good yields by the nucleophilic attack of 1-methyl-, 1-benzyl-, 1-octyl-2-methylimidazole, or 4-dimethylaminopyridine on 1,2,3-tri(chloromethoxy)-propane. The reaction was carried out for 1 h, and the product was purified by extraction with heptane in 343 K. The final products of trigeminal tricationic chlorides were hygroscopic compounds with the yield 87.9 % for 1-methyl-; 91.2 % for 1-benzyl-; and 93.4 % for 1-octyl-2-methylimidazolium and 93.2 % for the 4-dimethylaminopyridine derivative.

Imidazolium (**1a**−**e**) and 4-dimethylaminopyridinium (**2a**) ILs were prepared via metathesis reactions from corresponding trigeminal tricationic chlorides and appropriate sodium or lithium salts: $NaN(CN)_2$, $NaBF_4$, $LiN(CF_3SO_2)_2$.[30] The reaction was completed by heating (at 328 K) on a water bath with stirring (24 h). After removing solvent in vacuum, the product was once again dissolved in anhydrous acetone or dichloromethane to filter reduced NaCl and excess of used sodium or lithium salts.

Table 1. Structures of the TTILs Studied in This Work

salts	R	R′	A	yield/%	water mass %	Cl (ppm)	purity
1a	CH_3	H	$[N(Tf)_2]$	97.5	0.004	180	99.9
1b	CH_3	H	$[N(CN)_2]$	90.7	0.028	342	99.9
1c	C_8H_{17}	CH_3	$[N(Tf)_2]$	98.3	0.001	155	99.9
1d	C_8H_{17}	CH_3	$[BF_4]$	87.4	0.011	276	99.9
1e	$CH_2C_6H_5$	H	$[N(Tf)_2]$	96.9	0.002	128	99.9
2a	$N(CH_3)_2$		$[N(Tf)_2]$	98.0	0.006	107	99.9

All obtained ILs are air-stable under ambient conditions and may be handled under normal laboratory conditions. The purity of each ILs and their impurities, water mass fraction found by Karl Fischer method, and chloride content are given in Table 1.

In addition to the treatment mentioned above, each IL was further purified by subjecting the liquid to a very low pressure of about 5 Pa at 343 K for approximately 24 h. Next, packed columns were conditioned for a 12 h duration. Based upon our experience, we can safely assume that this procedure adequately removes any volatile chemicals and moisture from the IL and Chromosorb. Beyond this soft thermal treatment, no other attempts were made to analyze or specifically identify the impurities remaining within the ILs. Test solutes were purchased from Aldrich at a purity ≥ 99.5 % and were used without further purification because our gas−liquid chromatography technique efficiently separates any impurities on the column.

Apparatus and Experimental Procedure. Inverse chromatography experiments were carried out using a Varian CP-3800 gas chromatograph equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. The helium flow rate was adjusted to obtain adequate retention times. Methane was used to determine the column hold-up time. Exit gas flow rates were measured with a soap bubble flow meter. The temperature of the oven was determined with a Pt100 probe and controlled to within ± 0.1 K. A personal computer directly recorded detector signals, and the corresponding chromatograms were generated using Galaxie software.

Using a rotary evaporation preparatory technique, 1.0 m length columns were packed with a stationary phase consisting of (20 to 35) mass % of IL on Chromosorb WHP (60−80 mesh). After evaporation of chloroform in vacuo, the support was equilibrated at 333 K during 6 h. Before conducting measurements, each packed column was conditioned for 12 h at 363 K with a flow rate of 20 $\text{cm}^3\cdot\text{min}^{-1}$. The packing level was calculated from the masses of the packed and empty columns and was checked throughout experiments. The masses of the stationary phase were determined to a precision of ± 0.0003 g. A (1 to 5) μL volume of the headspace sample vapor was injected to satisfy infinite dilution conditions, and each experiment was repeated at least twice to confirm reproducibility. Retention times were generally rigorously reproducible to within (0.01 to 0.03) min. To verify stability under these experimental conditions, ruling out the elution of the stationary phase by the helium stream, measurements of retention time were repeated systematically each day for three selected typical solutes. No changes in the retention times were observed during this study.

■ THEORETICAL BASIS

Activity coefficients at infinite dilution for solute 1 in IL 2, $\gamma_{1,2}^{\infty}$, were calculated with the following expression:[31]

$$\ln \gamma_{1,2}^{\infty} = \ln\left(\frac{n_2 RT}{V_N P_1^0}\right) - P_1^0 \cdot \frac{B_{11} - V_1^0}{RT} + \frac{2B_{13} - V_1^{\infty}}{RT} \cdot JP_0 \tag{2}$$

where n_2 is the number of moles of stationary phase component within the column, R is the gas constant, T is the oven temperature, V_N is the net retention volume, B_{11} is the second virial coefficient of the solute in the gaseous state at temperature T, B_{13} is the mutual virial coefficient between solute 1 and the carrier gas (helium, denoted by "3"), and $P_1{}^0$ is the probe vapor pressure at temperature T. All thermodynamic properties of the pure solutes needed for these calculations were given in a previous work.[5]

The knowledge of the activity coefficient at infinite dilution as function of the temperature allows us to determine the excess Helmholtz energy and the excess entropy at infinite dilution, $\Delta \bar{H}_1^{E,\infty}$ and $\Delta \bar{S}_1^{E,\infty}$, respectively.

$$RT \ln \gamma_{1,2}^{\infty} = \Delta \bar{H}_1^{E,\infty} - T\Delta \bar{S}_1^{E,\infty} \tag{3}$$

Gas-to-IL partition coefficients, K_L, used in the LSER approach were calculated using the expression

$$K_L = \frac{RT}{\gamma_{1,2}^{\infty} P_1^0 V_{\text{solvent}}} \tag{4}$$

■ RESULTS AND DISCUSSION

Activity Coefficients at Infinite Dilution of Organic Compounds in ILs. The uncertainty of γ_i^{∞} values may be obtained from the law of propagation of errors. The following measured parameters exhibit uncertainties which must be taken into account in the error calculations with their corresponding standard deviations: the adjusted retention time t_R', ± 0.01 min; the flow rate of the carrier gas, ± 0.1 $\text{cm}^3\cdot\text{min}^{-1}$; mass of the stationary phase, ± 2 %; the inlet and outlet pressures, ± 0.002 bar; the temperature of the oven, ± 0.1 K. The main source of uncertainty in the calculation of the net retention volume is the determination of the mass of the stationary phase. The estimated uncertainty in determining the net retention volume V_N is about ± 2 %. Taking into account that thermodynamic parameters are also subject to an error, the resulting uncertainty in the γ_i^{∞} values is about ± 3 %.

For all ILs studied in this work, no interfacial adsorption was observed while the average relative standard deviation between data sets obtained from different packed columns was less than 2 %. Experimental activity coefficients at infinite dilution calculated using eq 2 are listed in Tables 2 to 7. Table 8 lists the limiting partial molar excess Gibbs energies $\Delta \bar{G}_1^{E,\infty}$ of selected solutes in three TTILs at a reference temperature 312.45 K together with their enthalpy $\Delta \bar{H}_1^{E,\infty}$ and entropy $\Delta \bar{S}_1^{E,\infty}$ contributions, as calculated from the temperature dependence of the limiting activity coefficient. The TTILs studied show similar behaviors to monodialkylimidazolium ILs. Activity coefficients at infinite dilution for most organic compounds decrease with an increase in temperature. Of the series of organic compounds studied, alkanes exhibit the lowest solubility in these seven TTILs. Large positive $\Delta \bar{G}_1^{E,\infty}$ values encountered for aliphatic hydrocarbons and corresponding to their low solubilities in TTILs are seen to be of the enthalpic and entropic origins. The partial molar excess Gibbs energy decreases with an increasing of the alkyl chain length grafted onto the imidazolium cation. In this case, an enhanced solubility of apolar compounds is obtained. For the $[\text{N(Tf}_2)]$ based TTIL (see **1a**), $\Delta \bar{G}_1^{E,\infty}$ value for dodecane is mainly due to a enthalpic contribution. Changing $[\text{N(Tf)}_2]$ by $[\text{N(CN)}_2]$ leads to an important increase of the entropic contribution (80 %). An important entropy contribution to $\Delta \bar{G}_1^{E,\infty}$ suggests that solute molecules arrange in the IL structure, following the highly orientational character of involved intermolecular forces. For compounds containing the same number of carbon atoms

Table 2. Experimental Activity Coefficients at Infinite Dilution γ_{12}^{∞} of 47 Organic Compounds in Tricationic 1a

	experimental γ_{12}^{∞} at T/K		
solute	312.45	322.45	332.45
hexane	17.70	17.91	14.46
3-methylpentane	12.01	15.25	11.96
heptane	30.45	30.13	25.19
2,2,4-trimethylpentane	30.78	28.46	26.78
octane	56.14	53.50	44.52
nonane	109.82	94.41	79.17
decane	155.49	134.55	111.47
undecane	240.21	205.49	171.99
dodecane	339.46	292.86	251.73
tridecane	495.19	430.58	370.55
methylcyclopentane	11.07	10.33	9.01
cyclohexane	11.74	10.63	9.10
methylcyclohexane	18.46	16.24	13.90
cycloheptane	27.04	33.95	41.94
benzene	0.86	0.83	0.82
toluene	1.39	1.35	1.33
ethylbenzene	2.37	2.31	2.25
m-xylene	2.39	2.31	2.25
p-xylene	2.36	2.31	2.25
o-xylene	2.04	1.98	1.94
1-hexene	9.18	9.06	7.37
1-hexyne	3.55	3.25	3.01
1-heptyne	5.83	5.33	5.02
2-butanone	0.31	0.30	0.28
2-pentanone	0.52	0.52	0.53
3-pentanone	0.51	0.51	0.52
1,4-dioxane	0.30	0.30	0.31
methanol	0.52	0.49	0.46
ethanol	0.86	0.79	0.72
1-propanol	1.26	1.13	1.01
2-propanol	1.17	1.04	0.94
2-methyl-1-propanol	1.71	1.54	1.36
1-butanol	1.87	1.67	1.46
trifluoroethanol	0.26	0.24	0.23
diethylether	1.80	1.70	1.52
diisopropyl ether	5.68	5.16	4.50
chloroforme	0.73	0.72	0.72
dichloromethane	0.42	0.44	0.45
tetrachloromethane	3.01	2.73	2.52
acetonitrile	0.21	0.20	0.21
nitromethane	0.23	0.23	0.23
1-nitropropane	0.44	0.43	0.42
triethylamine	2.10	2.01	2.70
pyridine	0.20	0.22	0.26
thiophene	0.68	0.67	0.66
formaldehyde	0.07	0.07	0.08
propionaldehyde	0.31	0.31	0.31

Table 3. Experimental Activity Coefficients at Infinite Dilution γ_{12}^{∞} of 47 Organic Compounds in Tricationic 1b

	experimental γ_{12}^{∞} at T/K		
solute	312.45	322.45	332.45
hexane	55.11	39.63	28.88
3-methylpentane	49.28	45.66	42.43
heptane	104.58	87.15	73.17
2,2,4-trimethylpentane	92.89	83.76	75.85
octane	141.82	121.27	104.36
nonane	211.22	187.11	166.57
decane	248.35	229.73	213.18
undecane	294.96	283.42	272.77
dodecane	334.89	323.77	313.44
tridecane	397.3	385.83	375.13
methylcyclopentane	63.94	35.29	19.95
cyclohexane	44.42	29.75	20.25
methylcyclohexane	74.24	51.37	36.08
cycloheptane	116.61	123.36	130.2
benzene	2.94	2.77	2.61
toluene	5.55	5.25	4.98
ethylbenzene	10.98	10.39	9.86
m-xylene	11.09	10.49	9.94
p-xylene	10.49	9.95	9.45
o-xylene	8.5	8.21	7.95
1-hexene	57.1	51.86	47.28
1-hexyne	13.98	12.36	10.99
1-heptyne	25.17	22.58	20.34
2-butanone	1.59	1.45	1.32
2-pentanone	3.27	3.16	3.06
3-pentanone	3.16	3.08	3.01
1,4-dioxane	0.94	0.95	0.96
methanol	0.3	0.30	0.3
ethanol	0.73	0.70	0.67
1-propanol	1.23	1.16	1.09
2-propanol	1.43	1.32	1.22
2-methyl-1-propanol	2.1	1.92	1.76
1-butanol	2.21	2.03	1.87
trifluoroethanol	0.14	0.15	0.15
diethylether	13.41	9.45	6.75
diisopropyl ether	33.48	25.80	20.1
chloroform	0.95	0.99	1.03
dichloromethane	0.61	0.64	0.68
tetrachloromethane	7.2	6.87	6.57
acetonitrile	0.52	0.52	0.52
nitromethane	1.26	0.75	0.45
1-nitropropane	1.45	1.46	1.46
pyridine	0.87	0.88	0.88
thiophene	1.5	1.48	1.46
formaldehyde	0.27	0.16	0.1
propionaldehyde	1.13	1.11	1.09

but originating from different solute families, it was observed that $\gamma_{\text{alcohol}} < \gamma_{\text{aromatic}} < \gamma_{\text{alkyne}} < \gamma_{\text{alkene}} < \gamma_{\text{alkane}}$. This overall trend is followed for all ILs, regardless of the cation or anion identity. The lowest solubility of apolar compounds is observed with TTILs **1b**. It is noteworthy that the presence of multiple bonds within the solute increases the solubility considerably. In the case of aromatic compounds such as benzene or thiophene, the $\Delta \overline{G}_1^{E,\infty}$ values are negative for TTILs **1a** and **1c** and positive for **1b**. The enthalpic contribution of the $\Delta \overline{G}_1^{E,\infty}$ values is of the same order than entropic contribution for TTILs **1a** and **1b**. Increasing the chain length grafted on the cation leads to a zero enthalpic contribution and an increase of entropic contribution. These observations are in good agreement with the NMR study, indicating that the solubility of thiophene or benzene in IL strongly depends on the structure of the IL.[33] For methanol, the similar evolution of $\Delta \overline{H}_1^{E,\infty}$ and $\Delta \overline{S}_1^{E,\infty}$ is observed by changing the $[\mathrm{N(Tf)_2}]$ anion by $[\mathrm{N(CN)_2}]$. In general, the infinite dilution activity coefficients of the alcohols are relatively small, with the solubility of alcohols and chloroalkanes being of the same order in TTILs than in dialkylimidazolium-based ILs. The introduction of dicyanamide anion in TTILs (**1b**)

Table 4. Experimental Activity Coefficients at Infinite Dilution γ_{12}^{∞} of 47 Organic Compounds in Tricationic 1c

	experimental γ_{12}^{∞} at T/K		
solute	312.55	322.45	332.45
hexane	2.56	2.44	2.14
3-methylpentane	2.32	2.28	1.95
heptane	3.45	3.37	3.04
2,2,4-trimethylpentane	3.51	3.41	3.15
octane	4.50	4.26	4.02
nonane	6.49	6.09	5.71
decane	7.69	7.20	6.79
undecane	10.05	9.41	8.77
dodecane		11.69	11.02
methylcyclopentane	1.74	1.68	1.54
cyclohexane	1.71	1.64	1.53
methylcyclohexane	2.17	2.08	1.94
cycloheptane	2.95	4.15	5.61
benzene	0.30	0.30	0.30
toluene	0.40	0.40	0.41
ethylbenzene	0.56	0.56	0.57
m-xylene	0.57	0.57	0.57
p-xylene	0.57	0.57	0.57
o-xylene	0.51	0.51	0.52
1-hexene	1.65	1.59	1.52
1-hexyne	0.81	0.79	0.77
1-heptyne	1.02	1.01	1.01
2-butanone	0.15	0.15	0.14
2-pentanone	0.20	0.21	0.21
3-pentanone	0.19	0.20	0.20
1,4-dioxane	0.19	0.20	0.20
methanol	0.35	0.34	0.30
ethanol	0.48	0.45	0.41
1-propanol	0.56	0.52	0.48
2-propanol	0.53	0.49	0.45
2-methyl-1-propanol	0.66	0.60	0.54
1-butanol	0.68	0.62	0.58
trifluoroethanol	0.18	0.09	0.08
diethylether	0.54	0.55	0.52
diisopropyl ether	1.10	1.09	1.09
chloroform	0.26	0.26	0.27
dichloromethane	0.19	0.20	0.20
tetrachloromethane	0.70	0.68	0.71
acetonitrile	0.17	0.16	0.17
nitromethane	0.21	0.20	0.20
1-nitropropane	0.24	0.23	0.23
triethylamine	1.43	1.38	1.23
pyridine		0.11	0.13
thiophene	0.27	0.27	0.27
formaldehyde	0.03	0.04	0.04
propionaldehyde	0.08	0.17	0.17
butyraldehyde	0.15	0.27	0.27

decreases considerably the solubility of alcohols. A similar behavior is observed when a methylbenzyl is grafted in the imidazolium of TTILs (**1e**). The hydroxyl group can potentially interact with either the anion and/or the cation of the IL. Interestingly, these classes of compound follow similar trends as the hydrocarbons. Branched-chain alcohols have a lower solubility compared to linear alcohols, and their activity coefficients increase with increasing chain length. Notably, ketones and aldehydes strongly interact with ILs and thus show even higher solubilities.

Table 5. Experimental Activity Coefficients at Infinite Dilution γ_{12}^{∞} of 44 Organic Compounds in Tricationic 1d

	experimental γ_{12}^{∞} at T/K		
solute	312.55	322.45	332.95
hexane	5.22	4.78	4.48
3-methylpentane	5.15	4.65	4.32
heptane	6.62	6.29	5.88
2,2,4-trimethylpentane	8.72	7.83	7.07
octane	8.31	8.06	7.58
nonane	11.63	11.24	10.61
decane	13.52	13.07	12.53
undecane	17.38	16.92	15.98
methylcyclopentane	3.52	3.23	3.00
cyclohexane	3.41	3.13	2.86
methylcyclohexane	4.22	3.87	3.70
cycloheptane	11.60	7.43	10.28
benzene	0.55	0.54	0.53
toluene	0.77	0.77	0.76
ethylbenzene	1.11	1.12	1.11
m-xylene	1.15	1.14	1.12
p-xylene	1.14	1.14	1.11
o-xylene	1.00	1.00	0.98
1-hexene	3.21	3.08	2.89
1-hexyne	1.15	1.15	1.13
1-heptyne	1.46	1.49	1.48
2-butanone	0.44	0.41	0.37
2-pentanone	0.62	0.62	0.61
3-pentanone	0.62	0.62	0.61
1,4-dioxane	0.42	0.42	0.41
methanol	0.41	0.38	0.34
ethanol	0.60	0.55	0.50
1-propanol	0.72	0.66	0.59
2-propanol	0.73	0.69	0.61
2-methyl-1-propanol	0.86	0.77	0.69
1-butanol	0.91	0.81	0.72
diethylether	1.41	1.38	1.32
diisopropyl ether	3.39	3.32	3.00
chloroform	0.26	0.27	0.28
dichloromethane	0.20	0.21	0.22
tetrachloromethane	1.08	1.07	1.05
acetonitrile	0.26	0.26	0.25
nitromethane	0.46	0.24	0.23
1-nitropropane	0.48	0.41	0.40
triethylamine	0.59	0.26	0.14
pyridine	0.40	0.32	0.25
thiophene	0.40	0.40	0.40
formaldehyde	0.08	0.08	0.09
propionaldehyde	0.37	0.37	0.36

Results indicated that the solubility of organic compounds in trigeminal tricationic imidazolium (1) based $[\mathrm{N(Tf)_2}]$ increases with an increase of the alkyl chain length. An increase of the solubility is also observed by changing the anion $[\mathrm{BF_4}]$ to $[\mathrm{N(Tf)_2}]$. The solubilities of organic compounds in TTILs **1e** and **2a** are of the same order. While both TTILs have the same anion, the structure of the cation is strongly different (benzylimidazolium for **1e** and 4-dimethylamino pyridinium for **2a**). This demonstrates that the influence of the combination of anion/cation and of the structure of the cation (R, R′) is important on the solubility of organic compounds in ILs.

Selectivity and Capacity at Infinite Dilution. Selectivities and capacities at infinite dilution, respectively, S_{12}^{∞} and k_1^{∞},

Table 6. Experimental Activity Coefficients at Infinite Dilution γ_{12}^{∞} of 44 Organic Compounds in Tricationic 1e

	experimental γ_{12}^{∞} at T/K		
solute	312.55	322.85	332.65
hexane	10.95	8.34	7.44
3-methylpentane	9.43	7.65	
heptane	15.12	12.89	10.98
2,2,4-trimethylpentane	17.66	14.36	11.93
octane	22.04	18.90	16.50
nonane	35.46	29.92	26.29
decane	47.34	39.88	35.11
undecane	69.08	57.32	50.41
methylcyclopentane	5.92	4.88	4.35
cyclohexane	5.68	4.72	4.22
methylcyclohexane	8.16	6.80	6.18
cycloheptane	9.89	13.00	16.04
benzene	0.54	0.51	0.52
toluene	0.82	0.75	0.77
ethylbenzene	1.19	1.14	1.15
m-xylene	1.26	1.20	1.19
p-xylene	1.25	1.17	1.19
o-xylene	1.09	1.01	1.04
1-hexene	5.20	4.34	3.98
1-hexyne	1.87	1.73	1.64
1-heptyne	2.65	2.50	2.39
2-butanone	0.18	0.17	0.16
2-pentanone	0.27	0.27	0.28
3-pentanone	0.25	0.26	0.27
1,4-dioxane	0.19	0.20	0.20
methanol	0.37	0.33	0.34
ethanol	0.59	0.53	0.49
1-propanol	0.76	0.68	0.63
2-propanol	0.73	0.65	0.60
2-methyl-1-propanol	1.01	0.88	0.80
1-butanol	3.61	2.85	2.42
diethylether	0.94	0.92	0.90
diisopropyl ether	2.72	2.46	2.42
chloroform	0.44	0.46	0.47
dichloromethane	0.28	0.29	0.31
tetrachloromethane	1.46	1.43	1.24
acetonitrile	0.16	0.16	0.16
nitromethane	0.20	0.19	0.19
1-nitropropane	0.14	0.18	0.19
triethylamine		0.11	0.15
pyridine	0.12	0.14	0.15
thiophene	0.42	0.41	0.42
formaldehyde		0.01	0.01
propionaldehyde		0.03	0.03

calculated from activity coefficients are reported in Table 9 for TTILs and other ILs for illustrative separation problems at 323.15 K: hexane/benzene, hexane/methanol, hexane/thiophene, and cyclohexane/thiophene:

$$S_{12}^{\infty} = \frac{\gamma_{1/\mathrm{RTIL}}^{\infty}}{\gamma_{2/\mathrm{RTIL}}^{\infty}} \tag{5}$$

$$k_1^{\infty} = \frac{1}{\gamma_{1/\mathrm{RTIL}}^{\infty}} \tag{6}$$

Table 7. Experimental Activity Coefficients at Infinite Dilution γ_{12}^{∞} of 47 Organic Compounds in Tricationic 2a

	experimental γ_{12}^{∞} at T/K		
solute	312.95	322.85	332.65
hexane	10.20	7.98	7.16
3-methylpentane	9.05	7.36	6.34
heptane	15.76	13.70	11.85
2,2,4-trimethylpentane	16.50	13.97	12.05
octane	23.57	20.22	18.04
nonane	38.75	33.28	29.44
decane	52.41	45.28	40.15
undecane	77.74	66.82	58.48
dodecane	108.53	93.91	83.11
tridecane	162.73	136.36	121.45
tetradecane	226.87	194.92	169.79
methylcyclopentane	5.89	5.07	4.55
cyclohexane	5.94	5.11	4.51
methylcyclohexane	8.08	6.98	6.30
cycloheptane	10.75	13.80	17.89
benzene	0.34	0.34	0.35
toluene	0.49	0.49	0.51
ethylbenzene	0.80	0.81	0.83
m-xylene	0.74	0.75	0.76
p-xylene	0.73	0.73	0.75
o-xylene	0.65	0.63	0.66
1-hexene	4.81	4.32	3.93
1-hexyne	1.57	1.50	1.46
1-heptyne	2.27	2.21	2.16
2-butanone	0.22	0.20	0.19
2-pentanone	0.33	0.33	0.34
3-pentanone	0.32	0.32	0.33
1,4-dioxane	0.21	0.21	0.22
methanol	0.37	0.34	0.34
ethanol	0.59	0.53	0.49
1-propanol	0.79	0.70	0.65
2-propanol	0.73	0.64	0.61
2-methyl-1-propanol	1.02	0.89	0.82
1-butanol	1.07	0.93	0.86
trifluoroethanol	0.17	0.16	0.16
diethylether	1.10	1.03	1.03
diisopropyl ether	3.02	2.87	2.74
chloroform	0.34	0.34	0.35
dichloromethane	0.24	0.25	0.26
tetrachloromethane	1.15	1.07	1.04
acetonitrile	0.16	0.16	0.16
nitromethane	0.18	0.18	0.18
1-nitropropane	0.29	0.28	0.29
pyridine	0.12	0.13	0.14
thiophene	0.28	0.28	0.29
formaldehyde	0.04	0.05	0.05
propionaldehyde	0.21	0.20	0.21

Concerning the separation of benzene from hexane, the selectivities obtained using TTILs are of the same order of magnitude as for classical solvents used in industry like sulfolane (30.5), dimethylsulfoxide (22.7), and *N*-methyl-2-pyrrolidinone (12.5). The selectivity and capacity of TTILs strongly decrease when the $[\mathrm{N(Tf)_2}]$ anion is changed by $[\mathrm{BF_4}]$. A better capacity may be obtained by a moderate lengthening in the alkyl chain grafted to the imidazolium cation. Indeed, longer alkyl chains usually increase the capacity, but with detriment to selectivity, as seen with $[\mathrm{N(Tf)_2}]$-based TTILs.

Both ILs **1a** and **2a** have the highest selectivity and capacity observed up to now for the separation problem of benzene

Table 8. Partial Molar Excess Gibbs Energies $\Delta\bar{G}_1^{E,\infty}$, Enthalpies, and Entropies of Organic Solutes in TTILs at a Reference Temperature T = 312.45 K

solute	$\Delta\bar{G}_1^{E,\infty}$	$\Delta\bar{H}_1^{E,\infty}$	$T\Delta\bar{S}_1^{E,\infty}$
	1a		
dodecane	15.14	12.92	−2.23
benzene	−0.39	2.05	2.45
methanol	−1.70	5.30	6.99
chloroform	−0.82	0.59	1.41
thiophene	−1.00	1.29	2.29
	1b		
dodecane	15.10	2.90	−12.24
benzene	2.80	5.22	2.34
methanol	−3.13	0.00	3.13
chloroform	−0.13	−3.47	−3.36
thiophene	1.05	1.18	0.11
	1c		
dodecane	6.52	4.75	−1.77
benzene	−3.13	0.00	3.13
methanol	−2.73	6.70	9.38
chloroform	−3.50	−1.65	1.87
thiophene	−3.40	0.00	3.40

from hexane. To our knowledge, it is the first time that ILs present a high selectivity and a high capacity. Dicyanamide-based TTILs behave similarly to dialkylimidazolium dicyanamide and appear to be a good choice for separating hexane/methanol, hexane/thiophene, and cyclohexane/thiophene mixtures. In general, TTILs studied in this work may be used for specific separation problems. The different selectivities (from 7 to 51) and capacities (from 0.14 to 3.3) obtained on these six TTILs show that the choice of the anion, the cation, and the functionalized chain used play an important role on the efficiency of the separation process. Recently, Meindersma et al.[42] found that the best ILs for the separation of aromatic and aliphatic hydrocarbons are [bmim]$C(CN)_3$, [3-mebupy]$N(CN)_2$, [3-mebupy]$C(CN)_3$, and [3-mebupy]$B(CN)_4$. The aromatic distribution coefficients of these ILs are about 1.5 to 1.9, and the aromatic/aliphatic selectivities are close to 25 to 30 at 303 K. The aromatic distribution coefficients on TTILs **1a**, **1e**, and **2a** at 323 K are higher than conventional ILs, and the aromatic/aliphatic selectivities obtained are of the same order than monocationic ILs.

Linear Solvation Energy Relationship (LSER) Characterization. The LSER model has been used to characterize interactions between solute molecules and the TTILs investigated in this work. Coefficients c, e, s, a, b, and l of TTILs presented in Table 10 were obtained by multiple linear regression of the logarithm of the gas−liquid partition coefficients log K_L of 44 solutes. LSER parameters of organic compounds used to the determination of LSER coefficients are taken from the literature.[25−28] Poole and Poole[32] found that the system constants of LSER model for the monocationic ILs fall into the range $e = -0.62$ to 0.86, s = 1.7 to 2.8, a = 2.1 to 7.3, b = 0 to 1.07, and l = 0.35 to 0.96. Compared with the scale of TTILs, we can see that both scales are similar indicating that the solvation properties for mono and tricationic ILs are classical and fit quite well into the scales developed for polar molecular solvents. The LSER treatment indicates that the most dominant interaction constants for TTILs are strong dipolarity (s), hydrogen bond basicity (a), and dispersion forces (l). The dispersion forces (l) are nearly constant for the TTILs studied. Increasing the alkyl chain length grafted on the cation increases the polarizability of ILs leading to stronger London dispersive forces. The hydrogen-bond acidity (b), the hydrogen-bond basicity (a), and dipolarity (s) terms seemed to vary for each IL.

The ($c + lL$) term gives information on the effect of cohesion of the ILs on solute transfer from the gas phase. In general, the

Table 9. Selectivities S_{12}^{∞} and Capacities k_1^{∞} at Infinite Dilution for Different Separation Problems at 323.15 K

ILs		$S_{12}^{\infty}/k_1^{\infty}$			
anion	cation	hexane/benzene	hexane/methanol	hexane/thiophene	cyclohexane/thiophene
	1a	21.58/1.93	36.55/2.04	26.73/1.47	15.86/1.47
	1b	51.45/0.33	516.27/3.33	103.25/0.67	−/0.67
	1c	8.13/3.33	7.17/2.94	9.03/3.7	6.07/3.7
	1d	8.85/1.85	12.57/2.63	11.95/2.5	7.825/2.5
	1e	16.35/1.96	25.27/3.03	20.34/2.44	11.51/2.44
	2a	23.47/2.84	23.47/2.94	28.5/3.57	18.25/3.57
[CH_3SO_3]	1-ethyl-3-methylimidazolium	48.1/0.23	826/4	110/0.53	51.9/0.53
[$N(Tf_2)$]	1,3-dimethoxyimidazolium	21.3/0.47	42.05/0.94	24.8/0.94	12.6/0.94
	1-(methylethylether)-3-methylimidazolium	15.5/0.85	17.4/0.93	18.1/1.0	10.9
	1-ethanol-3-methylimidazolium	20.6/0.47	49.1/1.12	24.7/0.56	14.2/0.56
	1-ethyl-3-methylimidazolium	37.5/1.43	19.5/1.20		
	1-(hexylmethylether)-3-methylimidazolium	9.1/1.23	6.8/0.91	10.0/1.35	6.4/1.35
	1,3-bis(hexylmethylether)imidazolium	4.9/1.67	3.2/1.06	5.3/1.75	3.7/1.75
	1-butyl-3-methylimidazolium	16.7/1.11			
	1-hexyl-3-methylimidazolium	9.5/1.29	6.1/0.82		
	trimethylhexylammonium	9.9/1.01	8.5/0.86	10.7/1.09	7.2/1.09
	4-methyl-*N*-butylpyridinium	18.8/1.43	21.2/0.83	10.6/1.56	6.1/1.56
	triethylsulphonium	21.6/0.91	17.8/0.77	25.5/1.05	14.3/1.05
	trihexyl(tetradecyl) phosphonium	2.7/2.56	1.1/1.02	2.6/2.5	1.95/2.5
[$N(CN)_2$]	1-cyanopropyl-3-methylimidaolium	56.0/0.22	432/1.69	105/0.41	41.3/0.41
	1-ethyl-3-methylimidazolium	43.4/0.39	255/2.27	69.6/0.63	28.8/0.63
[BF_4]	1-ethanol-3-methylimidazolium	−/0.10	−/0.98	−/0.17	136.1/0.17
[PF_6]	1-ethanol-3-methylimidazolium	−/0.17	−/0.77	−/0.23	59.7/0.23

Table 10. LSER Constants of TTILs Studied in This Work[a]

IL	T/K	c	e	s	a	b	l	R^2	F	SD
1a	312.45	−0.738 (0.058)	0.096 (0.072)	2.459 (0.067)	2.153 (0.097)	0.887 (0.072)	0.523 (0.014)	0.990	804	0.082
	322.45	−0.788 (0.048)	0.143 (0.060)	2.378 (0.056)	2.047 (0.08)	0.864 (0.06)	0.490 (0.012)	0.993	1098	0.068
	332.45	−0.729 (0.046)	0.132 (0.057)	2.293 (0.054)	1.923 (0.077)	0.736 (0.057)	0.446 (0.011)	0.992	1085	0.064
1b	312.45	−1.424 (0.112)		2.589 (0.095)	4.253 (0.187)	0.551 (0.125)	0.674 (0.028)	0.976	380	0.147
	322.45	−1.251 (0.099)		2.490 (0.093)	3.910 (0.170)	0.448 (0.136)	0.599 (0.024)	0.979	424	0.13
	332.45	−1.078 (0.101)		2.376 (0.096)	3.552 (0.174)	0.375 (0.140)	0.525 (0.025)	0.974	352	0.132
1c	312.55	−0.490 (0.066)		1.826 (0.051)	2.032 (0.101)	0.808 (0.083)	0.709 (0.018)	0.987	689	0.072
	322.45	−0.516 (0.063)		1.832 (0.053)	2.088 (0.102)	0.655 (0.084)	0.669 (0.016)	0.986	674	0.076
	332.45	−0.471 (0.056)		1.712 (0.050)	1.756 (0.109)	0.685 (0.081)	0.620 (0.015)	0.988	733	0.068
1d	312.55	−0.551 (0.089)		1.995 (0.049)	3.113 (0.105)	0.167 (0.075)	0.702 (0.016)	0.990	872	0.077
	322.45	−0.529 (0.067)		2.023 (0.056)	2.922 (0.118)	0.078 (0.085)	0.647 (0.018)	0.986	672	0.076
	332.95	−0.531 (0.064)		1.970 (0.053)	2.743 (0.112)	0.085 (0.080)	0.605 (0.0177)	0.987	665	0.072
1e	312.55	−0.825 (0.076)		2.464 (0.061)	2.297 (0.142)	0.869 (0.093)	0.623 (0.021)	0.990	874	0.083
	322.85	−0.759 (0.071)		2.324 (0.057)	2.116 (0.132)	0.806 (0.087)	0.575 (0.019)	0.990	885	0.078
	332.65	−0.733 (0.073)		2.234 (0.057)	1.965 (0.132)	0.736 (0.086)	0.535 (0.020)	0.990	778	0.076
2a	312.95	−0.705 (0.058)	0.362 (0.073)	2.368 (0.074)	2.261 (0.101)	0.707 (0.089)	0.592 (0.014)	0.990	786	0.081
	322.85	−0.660 (0.064)	0.366 (0.075)	2.251 (0.073)	2.103 (0.100)	0.667 (0.086)	0.546 (0.018)	0.990	746	0.079
	332.65	−0.645 (0.056)	0.359 (0.067)	2.158 (0.067)	1.963 (0.091)	0.606 (0.080)	0.509 (0.015)	0.991	789	0.079

[a] R^2 is the squared correlation coefficient, and F is the Fisher F-statistic; SD refers to the standard deviation.

ILs are cohesive solvents; they interact weakly via nonbonding and π-electrons (e system constant is zero) and are not much different to other polar nonionic liquids. The TTILs are roughly as dipolar/polarizable as classical solvents. The s system constant decreases slightly with temperature, but dipole-type interactions are still an important interaction at 332 K. The same behavior is observed for hydrogen-bond basicity and acidity with the a and b system constants decreasing with temperature. The hydrogen-bond basicity of the IL (a system constant) is considerably larger than values obtained for nonphases (0 to 2.1).[34] The hydrogen-bond basicity of ILs depends on the anion grafted on the cation. ILs can be slightly more hydrogen-bond basic than dimethyl sulfoxide and N-methylpyrrolidinone, and are weak to moderate hydrogen-bond acids, similar to the aliphatic alcohols.

Changing [N(Tf)$_2$] by the [BF$_4$] anion on TTILs decreases strongly the acidity (b term) and slightly the l term but also increases the basicity (a term). The results show that an increasing of the chain length grafted on the cation decreases the polarity, the acidity, and the basicity properties of the TTILs but increases the l term. We can observe that system constants of TTILs decrease with an increase of temperature. This indicates that the selectivity of the ILs toward mixtures is better at low temperatures. Similar behavior was observed by Li and Poole when studying the polar stationary phase poly(diethylene glycol succinate).[35] As proposed by Atapattu and Poole,[36] it is reasonable to assume that cavity formation is facilitated by increasing temperature. In this case, the interactions of TTIL−TTIL decrease, and therefore, the decrease in the l system constant results from weaker dispersion interactions between solutes and the TTIL. Although there is a significant decrease in the l system constant at higher temperatures, it remains an important contribution to the retention mechanism.

As expected, the high a value obtained with TTILs coupled with the dicyanamide anion indicated that this anion is a ligand having Lewis basic properties.[37−41] This is in distinct contrast to many of the anions, such as [PF$_6$], [BF$_4$], [TFSA], and [CF$_3$SO$_3$], typically present in ILs, which are characterized as being very weak Lewis bases.

LSER coefficients e, s, a, b, and l of TTILs may be used to have a better understanding of major interactions governing during the extraction processes. As an example, a linear correlation between the selectivity S_{12}^{∞} for the separation of the system {hexane/benzene} for TTILs and monocationic ILs and LSER coefficients of ILs may be obtained:

$$S_{12}^{\infty} = 10.1s + 3.30a + 25.5b - 40.41 \qquad (7)$$

Figure 2 presents the plot of the calculated selectivity versus the experimental selectivity. Equation 7 describes well the experimental data discussed in our previous work on monocationic ILs. First, it was demonstrated that good selectivity is obtained when the alkyl chain length grafted on the cation is short. Let us remind that an increase of the alkyl chain increases the dispersive force and then the l term in the LSER model. From eq 7, this leads to a decrease of the selectivity. Second, experimental data showed that alcohol or cyano-functionalized ILs have a higher selectivity than diakylimidazolium-based ILs. While these families of ILs have basic properties (important a term), eq 7 agrees well with this observation.

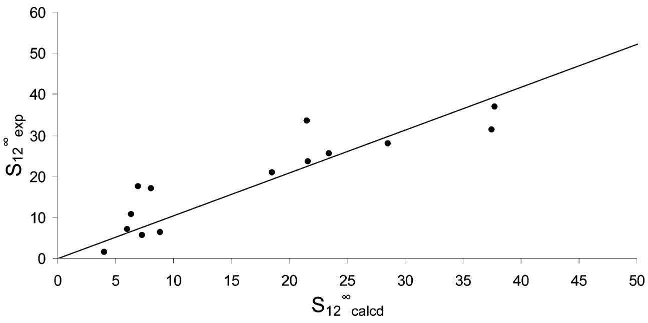

Figure 2. Calculated vs experimental selectivity at infinite dilution of 17 ILs for the system {hexane/benzene} at 313.15 K.

■ CONCLUDING REMARKS

In this work, the performance of six new trigeminal tricationic ILs was evaluated for different separation problems for the first time. The different selectivity and capacity values obtained on these six TTILs show that their structure has an important influence on the efficiency of the separation process. It was found that some TTILs have higher selectivity and capacity at infinite dilution than the generally used organic solvents such as NMP or sulfolane, as well as many other ILs in the separation of aromatic alcohols from aliphatic hydrocarbons. The selectivity and capacity of TTILs strongly depend on the anion. A good capacity is obtained by a moderate lengthening in the alkyl chain grafted to the imidazolium cation. Then, the LSER correlation shows that the solvation properties of tricationic ILs are similar to monocationic ILs.

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Notes

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