# Methyltrioctylammonium Chloride as a Separation Solvent for Binary Mixtures: Evaluation Based on Experimental Activity Coefficients

B. Kabane, G. G. Redhi

Abstract—An ammonium based ionic liquid (methyltrioctylammonium chloride) [N8881] [Cl] was investigated as an extraction potential solvent for volatile organic solvents (in this regard, solutes), which includes alkenes, alkanes, ketones, alkynes, aromatic hydrocarbons, tetrahydrofuran (THF), alcohols, thiophene, water and acetonitrile based on the experimental activity coefficients at infinite THF measurements were conducted by the use of gasliquid chromatography at four different temperatures (313.15 to 343.15) K. Experimental data of activity coefficients obtained across the examined temperatures were used in order to calculate the physicochemical properties at infinite dilution such as partial molar excess enthalpy, Gibbs free energy and entropy term. Capacity and selectivity data for selected petrochemical extraction problems (heptane/thiophene, heptane/benzene, cyclohaxane/cyclohexene, hexane/toluene, hexane/hexene) were computed from activity coefficients data and compared to the literature values with other ionic liquids. Evaluation of activity coefficients at infinite dilution expands the knowledge and provides a good understanding related to the interactions between the ionic liquid and the investigated compounds.

*Keywords*—Separation, activity coefficients, ionic liquid, methyltrioctylammonium chloride, capacity.

#### I. INTRODUCTION

THIS work involves the determination of activity L coefficients at infinite dilution with the use of gas-liquid chromatography (GLC) at different temperatures with various organic solvents, including water in the ammonium based ionic liquid [N<sub>8 8 8 1</sub>] [Cl]. These physicochemical properties are useful and essential as they provide a clear knowledge regarding the interactions between the solvent (in this regard, ionic liquid) and solutes. In the petrochemical and chemical industries, many of the extraction processes are high energy consuming, while some utilize solvents which raise concerns regarding the environment and safety issues. In addition, separation comprising azeotropic systems of alcohols and alkanes, into their pure components are important for the consideration of reuse. The use of ordinary distillation process is way too difficult to separate the azeotropic mixtures, and not economically favourable than the currently used techniques in the extractive distillation [1]. The possibility to separate the specific extraction difficulties can be revealed by the continuous measurements of  $\gamma_{13}^{\infty}$  in various ionic liquid systems, due to the fact that these systematic measurements reveal useful information with regards to their structural influence, and also provide their appealing thermodynamic and physicochemical properties. This work expands the knowledge of the hydrophobic ionic liquid (IL) with long alkyl chains (methyltrioctylammonium chloride). The stability and efficiency of ionic liquids in extraction processes is promising, however ionic liquids also face setbacks due to their excessive viscosity and high cost. Efficient separation of alkenes from alkanes is a known industrial setback [2].

In the petrochemical industry, olefins such as butadienes, propylenes or ethylene are the most produced compounds. They are formed from hydrocarbon feedstock though cracking processes [3]. Extraction of olefins from hydrocarbons is the final stage in this process, which is traditionally achieved with distillation. The process of purification becomes expensive and energy intensive, because of the similar boiling points of alkanes and alkenes. New separation techniques based on adsorption-desorption systems [4], [5], on membrane extraction [6], [7] were suggested to overcome these separation setbacks. The first study in investigating the separation of (alkanes/alkenes) comprising ionic liquids dealt with the extraction encountered in separation industries (hexane/hexene) [8].

Ammonium based ionic liquids are popular for the food and pharmaceutical technology industries [9]. Ammonium based ionic liquids are stable compounds towards moisture and air which are considered to be antifungal, antibacterial and electrostatic agents [10], [11]. Choline chloride, N, N, Ntrimethyl-hydroxyethylammonium chloride, [N1112 OH] [Cl] salt is the most often used ammonium based ionic liquid. This type of liquid is biodegradable and non-toxic since it naturally occurs in several biological functions [12]. The ammonium and phosphonium based ionic liquids were utilized in (water/butanol) extraction [13]-[15], and in (hexane/benzene, cyclohexane/cyclohexene and hexane/hexene) [16], [17] or in the separation of 2-phenylethanol form the aqueous phase [18], [19]. The ammonium based ionic liquids: N-octyl-Ntriethylammonium bis{(trifluoromethyl) sulfonyl} imide,  $[N_{8,2}]$ 2 2] [NTf<sub>2</sub>] [20] as well as (N-methyl-N-trioctylammonium bis{(trifluoromethyl) sulfonyl} imide, [N1 8 8 8] [NTf2] [21] have been investigated in ternary systems for (butanol/water) separation. The average selectivity for the extraction of sulphur compounds or aromatic hydrocarbons from the aliphatic hydrocarbons has been presented by the ionic liquid choline bis{(triflouromethyl) sulfonyl} imide, [N<sub>111 2</sub>OH]

B. Kabane and G.G. Redhi\* are with the Physical Chemistry Laboratories, Department of Chemistry, Durban University of Technology, Durban-4000, South Africa (\*Corresponding author: phone: 0313732936; fax: +27 866740243; e-mail: redhigg@dut.ac).

[NTf<sub>2</sub>] and revealed very high selectivity of (pyridine/heptane) [22].

This work reports  $\gamma_{13}^{\infty}$  measurements for 33 solutes in the IL (methyltrioctylammonium chloride) utilizing g.l.c. at different temperatures, 313.15 to 343.15 K. Capacity and selectivity were calculated to examine the extraction potential for various separation problems viz; (hexane/hexane, heptane/benzene, hexane/toluene, cyclohaxane/cyclohexene and heptane/ thiophene). The types of interactions among the IL and solutes under investigation will be assessed based on physicochemical properties at infinite dilution. The consideration of the similarities current with the investigated methyltrioctylammonium chloride and other ILs in the literature, which is appealing in various separation processes will be taken to consideration.

# II. EXPERIMENTAL

A. Materials						
TABLE I						
Compounds <sup>a</sup>	Supplier	Purity (mass fraction)	CAS No.	Analysis method		
2,2-dimethylbutane	Sigma-Aldrich	≥ 0.99	75-83-2	GC		
Pentane	Sigma-Aldrich	$\geq 0.99$	109-66-0	GC		
Hexane	Sigma-Aldrich	$\geq 0.99$	110-54-3	GC		
Heptane	Sigma-Aldrich	$\geq 0.99$	142-82-5	GC		
n-Nonane	Sigma-Aldrich	$\geq 0.99$	111-84-2	GC		
n-Decane	Sigma-Aldrich	$\geq 0.99$	124-18-5	GC		
1-Pentene	Merck	$\geq 0.99$	109-67-1	GC		
1-Hexene	Merck	$\geq 0.99$	592-41-6	GC		
1-Heptene	Merck	$\geq 0.99$	592-76-7	GC		
1-Nonene	Sigma-Aldrich	$\geq 0.99$	124-11-8	GC		
1-Decene	Sigma-Aldrich	$\geq 0.99$	872-05-9	GC		
Cyclohexene	Sigma-Aldrich	$\geq 0.99$	110-83-8	GC		
Cyclohexane	Sigma-Aldrich	$\geq 0.99$	110-82-7	GC		
Cyclooctane	Sigma-Aldrich	$\geq 0.99$	292-64-8	GC		
1-Pentyne	Fluka	$\geq 0.99$	627-19-0	GC		
1-Hexyne	Sigma-Aldrich	$\geq 0.99$	693-02-7	GC		
1-Heptyne	Sigma-Aldrich	$\geq 0.99$	628-71-7	GC		
Benzene	Sigma-Aldrich	$\geq 0.99$	71-43-2	GC		
Toluene	Sigma-Aldrich	$\geq 0.99$	108-88-3	GC		
Ethylbenzene	Sigma-Aldrich	$\geq 0.998$	100-41-4	GC		
m-Xylene	Sigma-Aldrich	$\geq 0.99$	108-38-3	GC		
p-Xylene	Sigma-Aldrich	$\geq 0.99$	106-42-3	GC		
o-Xylene	Sigma-Aldrich	$\geq 0.99$	95-47-6	GC		
Methanol	Sigma-Aldrich	$\geq 0.999$	67-56-1	HPLC		
Ethanol	Sigma-Aldrich	$\geq 0.998$	64-17-5	GC		
Propan-1-ol	Sigma-Aldrich	$\geq 0.997$	71-23-8	GC		
Butan-1-ol	Sigma-Aldrich	$\geq 0.998$	71-36-3	GC		
THF	Sigma-Aldrich	$\geq 0.99$	109-99-9	GC		
Acetonitrile	Sigma-Aldrich	$\geq 0.998$	75-05-8	HPLC		
Thiophene	Sigma-Aldrich	$\geq 0.99$	110-02-1	GC		
(Acetone)	Sigma-Aldrich	$\geq 0.999$	67-64-1	HPLC		
2-butanone	Sigma-Aldrich	$\geq 0.99$	78-93-3	GC		
Water		> 0 990		HPLC		
Methyltrioctylammonium	Sigma-Aldrich	$\geq 0.97$	7732-18-5	Karl-		
chloride	Sigma-Aldrich		515/-55-3	Fischer auto titrator		
<sup>a</sup> Names in parentheses are common names used in text.						

Methyltrioctylammonium chloride ionic liquid was supplied by Sigma Aldrich with a stated purity  $\ge 97$  %. Low pressure of  $5 \cdot 10^{-3}$  Pa at temperature T = 343 K for a period of 7 hours was applied to additionally purify the ionic liquid. Karl-Fischer auto titrator was then utilized to determine the content of water of the ionic liquid before proceeding to the experimental work. The ionic liquid water content reported by mass fraction was found to be  $350 \cdot 10^{-6}$ . The purity of the solutes as per the supplier was better than 98 % and is listed in Table I. There was no need to further purify the solutes as the g.l.c. procedure removes any unwanted material on the column. Chromosorb was purified with the same method applied to purify the ionic liquid.

# **B.** Experimental Procedure

For the experiment, a gas chromatography that is equipped with a thermal conductivity detector was utilized. The software for processing and collecting data for the experiment was total chrom workstation. The flow rate of helium as a carrier gas was obtained with the use of a soap bubble flow meter located at the detector's outlet. The packing procedure and column preparation utilized in this present work has been stated earlier [23]-[25]. The stainless-steel column used had an inner diameter of 4 mm and was 1 m long. The column was cleaned with hot soapy water and acetone and it was then rinsed with the use of distilled water. In preparation of the column, a definite weighed portion of chromosorb was added in the IL followed by dichloromethane to ensure a uniform spread of the IL. Dichloromethane was the evaporated by the application of rotary evaporator.

The mass used for the ionic liquid and solid support material, respectively, was weighed utilizing an analytical balance with a precision of 0.0001 g. The packing of a column by mass percent of IL as the solvent varied within the range (26-32), which is sufficient to reduce any unwanted adsorption onto the packed column. The columns were conditioned by passing helium gas at a flow rate of 2.0 cm<sup>3</sup>s<sup>-1</sup>, and a temperature of 360 K for a period of about 8 h. The pressure drop was determined by a pressure transducer in the g.l.c with an uncertainty of about 0.1 hPa. The atmospheric pressure was determined utilizing a digital barometer with an uncertainty of 0.1 hPa. Sample solute packaging between 0.2-0.3 µl was injected manually to adequately ensure the state of infinite dilution of the solute on the packed column. The determination of activity coefficients were carried at varying temperatures, i.e. T = 313.15 to 343.15 K. The temperature of the packed column was kept constant between the ranges 313.15-343.15 K of the experimental work, with an estimated error of 0.02 K. Reproducibility of the results was verified by replicating the sample injection 3 times at each investigated temperature. The approximate overall error in  $\gamma_{13}^{\infty}$  was within 5%, with the feasible errors in measuring the retention time, vapour pressure, and also the column packing taken into account.

# III. EQUATIONS FOR CALCULATING LIMITING ACTIVITY COEFFICIENTS

Activity coefficients at infinite dilution,  $\gamma_{13}^{\infty}$ , is a useful measure for the extraction process. The  $\gamma_{13}^{\infty}$  for 33 volatile organic solvents partitioning between helium and ionic liquid as a solvent are computed through the determination of solute retention time based on [26], [27]:

$$\ln \gamma_{13}^{\infty} = \ln \left( \frac{n_3 RT}{V_N P_1^*} \right) - \frac{P_1^* (B_{11} - V_1^*)}{RT} + \frac{P_0 J_2^3 (2B_{12} - V_1^{\infty})}{RT}$$
(1)

where *R* is the gas constant; saturated vapour pressure of the solute at temperature *T* is denoted by  $P_1^*$ ;  $n_3$  represents number of moles of ionic liquid packing in the column; *T* is the temperature of the column;  $P_o$  is the outlet pressure;  $V_N$  denotes net retention volume of the solute; the second virial coefficient of pure solute is denoted by  $B_{11}$ ; the mean column pressure by  $P_0J_2^3$ ;  $V_1^*$  represents molar volume of the solute;  $V_1^\infty$  denotes partial molar volume of solutes at infinite dilution in the solvent (in this case, IL) and  $B_{12}$  the mixed second virial coefficient of helium as well as solute.

The values of  $B_{12}$  and physicochemical properties utilized in determining  $\gamma_{13}^{\infty}$  were discussed in literature [28]. The pressure drop is corrected with the use of (2):

$$J_2^3 = \frac{2}{3} \frac{\left(\frac{P_i}{P_0}\right)^3 - 1}{\left(\frac{P_i}{P_0}\right)^2 - 1}$$
(2)

The net retention volume  $(V_N)$  is determined by using (3):

$$V_{\rm N} = (J_2^3)^{-1} (T_{\rm R} - T_{\rm G}) q_{\rm ov}, \qquad (3)$$

#### IV. RESULTS AND DISCUSSION

# A. Physicochemical Properties and Limiting Activity Coefficients

The possibility of adsorption of solutes on to the solid support always raises some doubts about the measurements of  $\gamma_{13}^{\infty}$  utilizing GLC. However, the peaks obtained by GLC were symmetrical and  $\gamma_{13}^{\infty}$  were free of helium gas flow, showing that no notably adsorption took place. This indicates the sufficient amount of solvent on the column loading. The existing interactions at vapour phase between solvent and solutes at infinite dilution can be described by the values of  $\gamma_{13}^{\infty}$ . In this present work, the ammonium ionic liquid [N<sub>8 8 8 1</sub>] [Cl] displays low  $\gamma_{13}^{\infty}$  data for all the solutes being examined. The relatively high  $\gamma_{13}^{\infty}$  values were revealed by alkanes, as decane ( $\gamma_{13}^{\infty} = 3.15$ ) at 343.15 K. The low  $\gamma_{13}^{\infty}$  data presented by the investigated ionic liquid are an obvious increase in measured retention time between the solutes and ionic liquid under investigation. In recently published ionic liquid (Nbenzyl-N-dimethyl-N-tetradecylammonium cinnamate), low data of  $\gamma_{13}^{\infty}$  were presented to give an example of alcohols and aromatic hydrocarbons: butan-1-ol ( $\gamma_{13}^{\infty} = 0.173$ ) and benzene  $(\gamma_{13}^{\infty} = 1.55)$  at 338.15 K [29]. The other solutes including ketones, alkanes and alkenes revealed  $\gamma_{13}^{\infty}$  values with a small degree larger than one.

AVERAGE ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR THE SOLUTES IN THE IONIC LIQUID $[N_{8881}]$ [CL] AT FOUR DIFFERENT TEMPERATURES: FOR						
THE STANDARD STATE OF SOLUTES HYPOTHETICAL LIQUID AT ZERO PRESSURE <sup>A</sup>						
	Average $\gamma_{12}^{\infty}$ values					
Solute	T = 313.15 K	T = 323.15 K	T = 333.15  K	T = 343.15 K		
2,2- dimethylbutane	1.45	1.54	1.60	1.71		
Pentane	1.28	1.36	1.48	1.57		
Hexane	1.50	1.58	1.68	1.82		
Heptane	1.69	1.83	1.96	2.08		
n-Nonane	2.12	2.34	2.55	2.75		
n-Decane	2.38	2.62	2.88	3.15		
1-Pentene	1.08	1.15	1.23	1.34		
1-Hexene	1.25	1.31	1.40	1.50		
1-Heptene	1.44	1.53	1.63	1.73		
1-Nonene	1.81	1.93	2.09	2.28		
1-Decene	2.01	2.16	2.34	2.51		
Cyclohexene	0.931	0.996	1.07	1.16		
Cyclohexane	1.00	1.09	1.21	1.31		
Cyclooctane	1.14	1.23	1.33	1.42		
1-Pentyne	0.366	0.426	0.496	0.579		
1-Hexyne	0.397	0.452	0.534	0.619		
1-Heptyne	0.427	0.492	0.569	0.664		
Benzene	0.439	0.476	0.526	0.584		
Toluene	0.567	0.608	0.657	0.710		
Ethylbenzene	0.667	0.737	0.810	0.878		
m-Xylene	0.744	0.819	0.882	0.962		
p-Xylene	0.727	0.784	0.852	0.932		
o-Xylene	0.654	0.715	0.776	0.853		
Methanol	0.301	0.327	0.352	0.378		
Ethanol	0.423	0.438	0.461	0.481		
Propan-1-ol	0.533	0.558	0.597	0.637		
Butan-1-ol	0.687	0.714	0.753	0.790		
THF	0.587	0.632	0.675	0.713		
Acetonitrile	1.24	1.081	0.984	0.897		
Thiophene	0.310	0.332	0.373	0.420		
Acetone	0.791	0.764	0.746	0.731		
2-butanone	0.853	0.810	0.782	0.760		
Water	0.269	0.303	0.334	0.371		

TABLE II

<sup>a</sup> Standard uncertainties u are  $u(\gamma_{13}^{\infty}) = 5$  %, u(T) = 0.02 K.

A column packing of 0.3001 by mass fraction of the ionic liquid was used to obtain the average  $\gamma_{13}^{\infty}$  data at four different temperatures of the experimental work, and the results are shown in Table II. The  $\gamma_{13}^{\infty}$  increases with an increase in solute alkyl chain in each class of the investigated solutes. From the  $\gamma_{13}^{\infty}$  data, it is evident that the cyclic structures of alkanes show increased interactions as compared to linear alkanes with same number of carbon atoms. The observed effect is due to the stronger attractive interactions between the cyclic structures and the ammonium chains. The presence of double bond in alkenes caused increased interactions with the polar ammonium IL as compared to alkanes with same number of Alkenes, alkanes, cycloalkenes carbon atoms. and cycloalkanes have high  $\gamma_{13}^{\infty}$  in contrast to aromatic hydrocarbons except for alkynes, and this results from the strong attractive interactions between the investigated polar

ammonium ionic liquid and the six  $\pi$ -delocalized electrons contained in the structure of benzene. The benzene molecule has delocalized  $\pi$ -electrons which can strongly interact with the investigated IL via  $(n-\pi)$  which is stronger when compared to van der Waal's interactions. In the group of alcohols, low values of  $\gamma_{13}^{\infty}$  were observed implying an increased interactions with the IL under investigation. The strong interactions of alcohols with the ionic liquid result from the hydrogen bonding.

The following physicochemical properties at infinite dilution ( $\Delta H_1^{E^{\infty}}$ ,  $\Delta S_1^{E,\infty}$  and  $\Delta G_1^{E,\infty}$ ) are connected to  $\gamma_{13}^{\infty}$ .

$$\Delta G_1^{\mathrm{E},\infty} = RT \ln(\gamma_{13}^{\infty}) = \Delta H_1^{\mathrm{E},\infty} - T \Delta S_1^{\mathrm{E},\infty}$$
(4)

Equation (4) can be written in:

$$\ln(\gamma_{13}^{\infty}) = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R}$$
(5)

TABLE III

LIMITING PARTIAL MOLAR ENTHALPIES  $\Delta H_1^{E,\infty}$ , GIBBS ENERGIES  $\Delta G_1^{E,\infty}$  and ENTROPIES  $T_{\text{REF}} \Delta S_1^{E,\infty}$  for Solutes in the Investigated Ionic Liquid [N<sub>88</sub> s<sub>1</sub>] [CL] at the Reference Temperature  $T_{\text{REF}} = 323.15 \text{ K}$ 

Solute	$\Delta H_1^{\mathrm{E},\infty}$ (kJ ·	$\Delta G_1^{E,\infty}$ (kJ ·	$T_{\rm ref} \Delta S_1^{\rm E,\infty}$ (k
	$mol^{-1}$ )	$mol^{-1}$ )	$J \cdot mol^{-1}$
2,2-dimethylbutane	-4.73	1.16	-5.88
Pentane	-6.27	0.825	-7.09
Hexane	-5.57	1.23	-6.80
Heptane	-6.15	1.62	-7.77
n-Nonane	-7.72	2.28	-10.0
n-Decane	-8.34	2.58	-10.9
1-Pentene	-6.29	0.369	-6.66
1-Hexene	-5.48	0.734	-6.21
1-Heptene	-5.44	1.15	-6.59
1-Nonene	-6.84	1.77	-8.61
1-Decene	-6.65	2.07	-8.72
Cyclohexene	-6.37	-0.011	-6.36
Cyclohexane	-8.07	0.228	-8.29
Cyclooctane	-6.49	0.560	-7.05
1-Pentyne	-13.6	-2.29	-11.3
1-Hexyne	-13.4	-2.13	-11.3
1-Heptyne	-13.1	-1.91	-11.2
Benzene	-8.54	-1.99	-6.55
Toluene	-6.72	-1.34	-5.38
Ethylbenzene	-8.20	-0.818	-7.38
m-Xylene	-7.42	-0.537	-6.88
p-Xylene	-7.57	-0.652	-6.92
o-Xylene	-7.85	-0.900	-6.95
Methanol	-6.76	-3.00	-3.76
Ethanol	-3.92	-2.216	-1.70
Propan-1-ol	-5.39	-1.57	-3.82
Butan-1-ol	-4.21	-0.907	-3.30
THF	-5.79	-1.232	-4.56
Acetonitrile	9.66	0.210	9.45
Thiophene	-9.14	-2.97	-6.17
Acetone	2.34	-0.723	3.06
2-butanone	3.42	-0.566	3.98
Water	-9.56	-3.21	-6.35

<sup>a</sup> Standard uncertainties u are  $u(\gamma_{13}^{\infty}) = 5$  %, u(T) = 0.02 K.

The entropic and enthalpic contribution by linear regression of the obtained data was determined with the use of (5). The calculated data are shown in Table III. The computed values for partial excess molar entropies at reference temperature 323.15 K are small and some are positive and negative for various solutes. Ketones and acetonitrile are positive. The negative entropy values imply that a distinct solute molecule easily arranges itself in the investigated IL structure. The breaking of hydrogen bond is specified by the positive entropy values (ketones and acetonitrile). This occurs through their dissolution process in the studied ammonium based IL. The obtained negative values for  $\Delta H_1^{E,\infty}$ , except for ketones and acetonitrile suggest that the types molecular interactions occurring between the solvent and solute result from the solute-solvent pairs. This results from the interactions between the double bonds in alkenes and lone pair of electrons on [Cl<sup>-</sup>] anion of the ionic liquid, and also the polarisable  $\pi$ -electrons in thiophene as well as aromatic hydrocarbons. The positive values for acetonitrile ( $\Delta H_1^{E,\infty} = 10.3 \text{ kJ mol}^{-1}$ ), acetone  $(\Delta H_1^{E,\infty} = 6.18 \text{ kJ mol}^{-1})$  and 2-butanone  $(\Delta H_1^{E,\infty} = 7.17 \text{ kJ} \text{ mol}^{-1})$  are discussed as strong energetic interactions occurring between the particles of ionic liquid and the solutes. This suggests that the exothermic dissolution results from the hydrogen bonds among the IL and solute. Negative values for the calculated  $\Delta G_1^{E,\infty}$  were observed with the exception of alkenes and alkanes. This is described as negative deviation from the Raoult's law.

# B. Analysis of the Separation Potential

The separation potential and suitability of the investigated ionic liquid  $[N_{8\ 8\ 1}]$  [Cl] for possible use in separation technology was determined based on the selectivity and capacity values, and these parameters form part of the importance of this work. Equations (6) and (7) were utilized to compute selectivity and capacity values at infinite dilution for the chosen petrochemical extraction difficulties at 323.15 K.

$$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \tag{6}$$

$$\mathbf{K}_{j}^{\infty} = \frac{1}{\gamma_{j}^{\infty}} \tag{7}$$

From (6) and (7), *i* represents heptane, cyclohexane or hexane, and j denotes thiophene, benzene, toluene, cyclohexene or hexene. The capacity and selectivity values for the chosen separation problems at 323.15 K (hexane/toluene, hexane/hexene, heptane/thiophene, cyclohexane/cyclohexene as well as heptane/benzene) are listed in Table IV, and in contrast with the literature for the (heptane/thiophene) separation problems in Fig. 1. For the investigated ammonium ionic liquid [N<sub>8 8 8 1</sub>] [Cl], the selectivity for the selected extraction difficulties ranges between ( $S_{ij}^{\infty} = 1.09$  to 5.51) and the capacity ( $K_i^{\infty} = 0.76$  to 3.02). In the IL N-benzyl-Ndimethyl-N-tetradecylammonium cinnamate for same separation difficulties, selectivity values range between ( $S_{ij}^{\infty}$  = 1.23 to 3.90) and capacity ( $K_i^{\infty} = 0.28$  to 0.81) [29]. In [N<sub>8881</sub>]

[NTf<sub>2</sub>] published earlier [30], the selectivity for some of the petrochemical difficulties: (hexane/hexene,  $S_{ij}^{\infty} = 1.30$ ), (heptane/benzene,  $S_{ij}^{\infty} = 4.00$ ) at temperature, T = 323.15 K [30]. For hexane/hexene, the investigated ionic liquid presents larger capacity value ( $K_i^{\infty} = 0.76$ ) in contrast to the other ILs, 1-benzyl-3methylimidazolium dicynamide, ( $K_i^{\infty} = 0.03$ ) [31], for  $[N_{Bz \ 1 \ 1 \ 14}]$  [Cyn],  $(K_j^{\infty} = 0.28)$  [29] and for 1-benzyl-3methylimidazolium bis{(triflouromethyl) sulfonyl} imide,  $(K_i^{\infty} = 0.11)$  at temperature, T = 328.15 K. The presented ionic liquid offers possible industrial application in the separation of heptane/thiophene where it reveals selectivity of  $(S_{ij}^{\infty} = 5.51)$ and large capacity ( $K_i^{\infty} = 3.02$ ), as compared to the ionic liquid that present selectivity of  $(S_{ij}^{\infty} = 3.90)$  and capacity  $(K_j^{\infty})$ = 0.81) [29], and also the recent published ionic liquid (trihexyltetradecylphosphonium dicyanamide) with  $(S_{ij}^{\infty} =$ 3.72) and capacity ( $K_i^{\infty} = 2.52$ ) [32]. The published work for the ionic liquid [N-C<sub>3</sub>OHmMOR] [NTf<sub>2</sub>] showed high selectivity for the separation of heptane/thiophene ( $S_{ij}^{\infty} = 118$ ) but lower capacity ( $K_i^{\infty} = 0.53$ ) [33]. In ionic liquid trimethylhexylammonium bis{(triflouromethyl) sulfonyl} imide [34] and tetraoctylammonium bis{(triflouromethyl) sulfonyl} imide [35], the selectivity and capacity values for heptane/thiophene were ( $S_{ij}^{\infty} = 15.6$ ) with lower capacity ( $K_j^{\infty}$ = 1.09) and  $(S_{ij}^{\infty} = 3.81)$  and capacity  $(K_j^{\infty} = 2.53)$ , respectively.

TABLE IX

SELECTIVITIES  $(S_{ij}^{\infty})$  AND CAPACITIES  $(K_j^{\infty})$  AT INFINITE DILUTION FOR  $[N_{888}]$ 

1 [CE] FOR VARIOUS SELARATION I ROBLEMS AT $1 = 525.15$ K					
Separation mixtures	$S_{ij}^{\infty}$	$K_j^{\infty}$			
Heptane/benzene	4.27	2.81			
Heptane/thiophene	5.51	3.02			
Hexane/toluene	2.60	1.62			
Hexane/hexene	1.20	0.76			
Cyclohexane/cyclohexene	1.09	1.00			





#### V. CONCLUSION

This work encompasses the evaluation of methyltrioctylammonium chloride as an extraction agent for volatile organic solvents (herewith referred as solutes). The data were obtained at four different temperatures, i.e. (313.15 to 343.15) K with the use of g.l.c. The physicochemical properties including ( $\Delta H_1^{E\infty}$ ,  $\Delta S_1^{E,\infty}$  and  $\Delta G_1^{E,\infty}$ ) at infinite dilution are computed and interpreted in regards of intermolecular interactions occurring within the solutes and ionic liquid. The data acquired here for [N<sub>8 8 8 1</sub>] [Cl] may be functional in some of the selected extraction difficulties. Comparison of the data obtained in this work is made with other ionic liquids in the literature. Relatively low selectivity values infer that the IL studied in this work is of little usage for extraction processes, yet, the comparatively high capacity revealed by the IL in comparison to other IL literature is useful. The ionic liquid [N<sub>8 8 8 1</sub>] [Cl] may be useful in heptane/ thiophene extraction processes in liquid-liquid equilibria or extractive distillation.

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