

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) $[N_{8881}][Cl]$ 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 gas-liquid 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, cyclohexane/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 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 $[N_{8881}][Cl]$. 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 γ_{13}^{∞} 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 through 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, N-trimethyl-hydroxyethylammonium chloride, $[N_{1112}OH][Cl]$ 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 from the aqueous phase [18], [19]. The ammonium based ionic liquids: N-octyl-N-triethylammonium bis{(trifluoromethyl) sulfonyl} imide, $[N_{822}][NTf_2]$ [20] as well as (N-methyl-N-trioctylammonium bis{(trifluoromethyl) sulfonyl} imide, $[N_{1888}][NTf_2]$ [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{(trifluoromethyl) sulfonyl} imide, $[N_{111}2OH]$

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).

[NTf₂]) and revealed very high selectivity of (pyridine/heptane) [22].

This work reports γ_{13}^{∞} measurements for 33 solutes in the IL (methyltriocetylammmonium 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, cyclohexane/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 with the current investigated methyltriocetylammmonium 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
PURITY OF ORGANIC SOLUTES USED IN THIS WORK.

Compounds ^a	Supplier	Purity (mass fraction)	CAS No.	Analysis method
2,2-dimethylbutane	Sigma-Aldrich	≥ 0.99	75-83-2	GC
Pentane	Sigma-Aldrich	≥ 0.99	109-66-0	GC
Hexane	Sigma-Aldrich	≥ 0.99	110-54-3	GC
Heptane	Sigma-Aldrich	≥ 0.99	142-82-5	GC
n-Nonane	Sigma-Aldrich	≥ 0.99	111-84-2	GC
n-Decane	Sigma-Aldrich	≥ 0.99	124-18-5	GC
1-Pentene	Merck	≥ 0.99	109-67-1	GC
1-Hexene	Merck	≥ 0.99	592-41-6	GC
1-Heptene	Merck	≥ 0.99	592-76-7	GC
1-Nonene	Sigma-Aldrich	≥ 0.99	124-11-8	GC
1-Decene	Sigma-Aldrich	≥ 0.99	872-05-9	GC
Cyclohexene	Sigma-Aldrich	≥ 0.99	110-83-8	GC
Cyclohexane	Sigma-Aldrich	≥ 0.99	110-82-7	GC
Cyclooctane	Sigma-Aldrich	≥ 0.99	292-64-8	GC
1-Pentyne	Fluka	≥ 0.99	627-19-0	GC
1-Hexyne	Sigma-Aldrich	≥ 0.99	693-02-7	GC
1-Heptyne	Sigma-Aldrich	≥ 0.99	628-71-7	GC
Benzene	Sigma-Aldrich	≥ 0.99	71-43-2	GC
Toluene	Sigma-Aldrich	≥ 0.99	108-88-3	GC
Ethylbenzene	Sigma-Aldrich	≥ 0.998	100-41-4	GC
m-Xylene	Sigma-Aldrich	≥ 0.99	108-38-3	GC
p-Xylene	Sigma-Aldrich	≥ 0.99	106-42-3	GC
o-Xylene	Sigma-Aldrich	≥ 0.99	95-47-6	GC
Methanol	Sigma-Aldrich	≥ 0.999	67-56-1	HPLC
Ethanol	Sigma-Aldrich	≥ 0.998	64-17-5	GC
Propan-1-ol	Sigma-Aldrich	≥ 0.997	71-23-8	GC
Butan-1-ol	Sigma-Aldrich	≥ 0.998	71-36-3	GC
THF	Sigma-Aldrich	≥ 0.99	109-99-9	GC
Acetonitrile	Sigma-Aldrich	≥ 0.998	75-05-8	HPLC
Thiophene	Sigma-Aldrich	≥ 0.99	110-02-1	GC
(Acetone)	Sigma-Aldrich	≥ 0.999	67-64-1	HPLC
2-butanone	Sigma-Aldrich	≥ 0.99	78-93-3	GC
Water	Sigma-Aldrich	≥ 0.999	7732-18-5	HPLC
Methyltriocetylammmonium chloride	Sigma-Aldrich	≥ 0.97	5137-55-3	Karl-Fischer auto titrator

^a Names in parentheses are common names used in text.

Methyltriocetylammmonium chloride ionic liquid was supplied by Sigma Aldrich with a stated purity $\geq 97\%$. 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 $2.0 \text{ cm}^3\text{s}^{-1}$, 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 γ_{13}^{∞} 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, γ_{13}^{∞} , is a useful measure for the extraction process. The γ_{13}^{∞} 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]:

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

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_0 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 $P_0 J_2^3$; V_1^* represents molar volume of the solute; V_1^{∞} 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 γ_{13}^{∞} were discussed in literature [28]. The pressure drop is corrected with the use of (2):

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

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

$$V_N = (J_2^3)^{-1} (T_R - T_G) q_{ov}, \quad (3)$$

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 γ_{13}^{∞} utilizing GLC. However, the peaks obtained by GLC were symmetrical and γ_{13}^{∞} 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 γ_{13}^{∞} . In this present work, the ammonium ionic liquid [N₈₈₈₁] [Cl] displays low γ_{13}^{∞} data for all the solutes being examined. The relatively high γ_{13}^{∞} values were revealed by alkanes, as decane ($\gamma_{13}^{\infty} = 3.15$) at 343.15 K. The low γ_{13}^{∞} 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 (*N*-benzyl-*N*-dimethyl-*N*-tetradecylammonium cinnamate), low data of γ_{13}^{∞} 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 γ_{13}^{∞} values with a small

degree larger than one.

TABLE II
AVERAGE ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR THE SOLUTES IN THE IONIC LIQUID [N₈₈₈₁] [Cl] AT FOUR DIFFERENT TEMPERATURES: FOR THE STANDARD STATE OF SOLUTES HYPOTHETICAL LIQUID AT ZERO PRESSURE^a

Solute	Average γ_{13}^{∞} values			
	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

^a 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 γ_{13}^{∞} data at four different temperatures of the experimental work, and the results are shown in Table II. The γ_{13}^{∞} increases with an increase in solute alkyl chain in each class of the investigated solutes. From the γ_{13}^{∞} 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 carbon atoms. Alkenes, alkanes, cycloalkenes and cycloalkanes have high γ_{13}^{∞} 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 π -delocalized electrons contained in the structure of benzene. The benzene molecule has delocalized π -electrons which can strongly interact with the investigated IL via (n - π) which is stronger when compared to van der Waal's interactions. In the group of alcohols, low values of γ_{13}^{∞} 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 γ_{13}^{∞} .

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

Equation (4) can be written in:

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

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 [N₈₈₁] [Cl] AT THE REFERENCE TEMPERATURE $T_{\text{REF}} = 323.15$ K

Solute	$\Delta H_1^{E,\infty}$ (kJ · mol ⁻¹)	$\Delta G_1^{E,\infty}$ (kJ · mol ⁻¹)	$T_{\text{REF}} \Delta S_1^{E,\infty}$ (kJ · 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

^a 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⁻] anion of the ionic liquid, and also the polarisable π -electrons in thiophene as well as aromatic hydrocarbons. The positive values for acetonitrile ($\Delta H_1^{E,\infty} = 10.3$ kJ mol⁻¹), acetone ($\Delta H_1^{E,\infty} = 6.18$ kJ mol⁻¹) and 2-butanone ($\Delta H_1^{E,\infty} = 7.17$ kJ 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 [N₈₈₁] [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.

$$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \quad (6)$$

$$K_j^{\infty} = \frac{1}{\gamma_j^{\infty}} \quad (7)$$

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 [N₈₈₁] [Cl], the selectivity for the selected extraction difficulties ranges between ($S_{ij}^{\infty} = 1.09$ to 5.51) and the capacity ($K_j^{\infty} = 0.76$ to 3.02). In the IL *N*-benzyl-*N*-dimethyl-*N*-tetradecylammonium cinnamate for same separation difficulties, selectivity values range between ($S_{ij}^{\infty} = 1.23$ to 3.90) and capacity ($K_j^{\infty} = 0.28$ to 0.81) [29]. In [N₈₈₁]

[NTf₂]⁻ 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 ($K_j^{\infty} = 0.76$) in contrast to the other ILs, 1-benzyl-3-methylimidazolium dicyanamide, ($K_j^{\infty} = 0.03$) [31], for [N_{Bz} 1 1 14] [Cyn]⁻, ($K_j^{\infty} = 0.28$) [29] and for 1-benzyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl) imide, ($K_j^{\infty} = 0.11$) 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 ($K_j^{\infty} = 3.02$), 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 ($K_j^{\infty} = 2.52$) [32]. The published work for the ionic liquid [N-C₃OHmMOR] [NTf₂]⁻ showed high selectivity for the separation of heptane/thiophene ($S_{ij}^{\infty} = 118$) but lower capacity ($K_j^{\infty} = 0.53$) [33]. In ionic liquid trimethylhexylammonium bis((trifluoromethyl) sulfonyl) imide [34] and tetraoctylammonium bis((trifluoromethyl) 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}^{∞}) AND CAPACITIES (K_j^{∞}) AT INFINITE DILUTION FOR [N₈₈₈]⁺ [CL]⁻ FOR VARIOUS SEPARATION PROBLEMS AT $T = 323.15$ K

Separation mixtures	S_{ij}^{∞}	K_j^{∞}
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

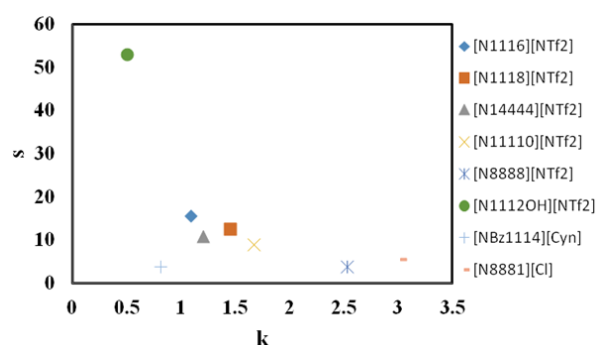


Fig. 1 Selectivity (s) plotted against capacity (k) for the other ammonium based ionic liquids with [NTf₂]⁻ and [Cyn]⁻ anions in the separation of (heptane/thiophene) problem [16], [29], [34], [35]

V. CONCLUSION

This work encompasses the evaluation of methyltriocetylammmonium 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 [N₈₈₈] [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 [N₈₈₈] [Cl] may be useful in heptane/thiophene extraction processes in liquid-liquid equilibria or extractive distillation.

ACKNOWLEDGMENTS

The authors would like to acknowledge the Durban University of Technology.

REFERENCES

- [1] W. Liu, Y. Ri, K. Ma, X. Xu, Z. Zhu, Y. Wang, Fluid Phase Equilib. 443 (2017) 44-49.
- [2] US6200366-Separation of alkenes and alkanes, USA Patent (2001), <http://www.google.com/patents/US6200366?utmsource=gb-gbplus-sharePatent>.
- [3] J. Pernak, M. Śmiglak, S.T. Griffin, W.L. Hough, T.B. Wilson, A. Pernak, J. Zabielska-Matejuk, A. Fojutowski, K. Kita, R.D. Rogers, Green Chem. 8 (2006) 798-806.
- [4] J. Bergh, C. Gucuyenar, E.A. Pidko, E.J.M. Hensen, J. Gascon, F. Kapteijn, Chem. Eur. J. 17 (2011) 8832-8840.
- [5] D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet, C. Chizallet, A.A. Quoineaud, G.D. Pirngruber, J. Am. Chem. Soc. 134 (2012) 8115-8126.
- [6] M. Azhin, T. Kaghazchi, M. Rahmani, Ind. Eng. Chem. 14 (2008) 622-638.
- [7] H. Bux, C. Chmelik, R. Krishna, J. Caro, J. Membr. Sci. 369 (2011) 284-289.
- [8] Z. Lei, W. Arlt, P. Wasserscheid, Fluid Phase Equilib. 241 (2006) 290-299.
- [9] J. Pernak, J. Feder-Kubis, Chem. Eur J. 11 (2005) 4441-4449.
- [10] P. Hapiot, C. Lagrost, Chem. Rev. 108 (2008) 2238-2264.
- [11] J. Pernak, J. Feder-Kubis, Chem. Eur J. 11 (2005) 4441-4449.
- [12] J. Cybulski, A. Wisniewska, A.K. Adamiak, Z. Dabrowski, T. Praczyk, A. Michalczyk, F. Walkiewicz, K. Materna, J. Pernak, Tetrahedron Lett. 52 (2011) 1325-1328.
- [13] M. Wlazlo, U. Domańska, Separ. Purif. Technol. 162 (2016) 162-170.
- [14] U. Domanska, M. Wlazlo, K. Paduszynski, Separ. Purif. Technol. (2017) 10.1016/j.seppur.2017.05.056.
- [15] B. Kabane, R. Chokkareddy, G. G. Redhi, J. Chem. Thermodyn. 137 (2019) 7-12.
- [16] U. Domańska, P. Papis, J. Szydlowski, J. Chem. Thermodyn. 77 (2014) 63-70.
- [17] W.E. Acree Jr, G.A. Baker, F. Mutelet, J-Ch Moise, J. Chem. Eng. Data 56 (2011) 3688-3697.
- [18] P. Okuniewska, U. Domanska, M. Wieckowski, J. Mierzejewska, Sep. Pur. Techn. 183 (2017) 11-20.
- [19] U. Domanska, P. Okuniewska, K. Paduszynski, M. Królikowska, M. Zawadzki, M. Wieckowski, J. Phys. Chem. B. 121 (2017) 7689-7698.
- [20] M. Wlazlo, U. Domańska, Separ. Purif. Technol. 162 (2016) 162-170.
- [21] U. Domanska, M. Wlazlo, K. Paduszynski, Separ. Purif. Technol. (2017) 10.1016/j.seppur.2017.05.056.
- [22] U. Domańska, P. Papis, J. Szydlowski, J. Chem. Thermodyn. 77 (2014) 63-70.
- [23] U. Domanska, A. Marciniak, J. Chem. Thermodyn. 40 (2008) 860-866.
- [24] T. M. Letcher, P. G. Whitehead, J. Chem. Thermodyn. 28 (1996) 843-849.

- [25] W. C. Moollan, M.Sc. Thesis, University of Natal, Durban. 1993.
- [26] D.H. Everett, Trans. Faraday Soc. 61 (1965) 1637-1645.
- [27] A.J.B. Cruickshank, B.W. Gainey, C.P. Hicks, T.M. Letcher, R.W. Moody, C.L. Young, Trans. Faraday Soc. 65 (1966) 1014-1031.
- [28] B.E. Poling, J.M. Prausnitz, Properties of Gases and Liquids (online), McGraw-Hill Publishing, 2001. Available from: <http://lib.myilibrary.com? ID=91317>
- [29] U. Domanska, A. Wisniewska, Z. Dabrowski, M. Karpinska, Fluid Phase Equilib. 460 (2018) 155-161.
- [30] N.V. Gwala, N. Deenadayalu, K. Tumba, D. Ramjugernath, J. Chem. Thermodyn. 42 (2009) 256-261.
- [31] M. Karpinska, M. Wlazlo, D. Ramjugernath, P. Naidoo, U. Domanska, RSC Adv 7 (2017) 7092-7107.
- [32] B. Kabane, G.G. Redhi, Fluid Phase Equilib. 493 (2019) 181-187.
- [33] M. Wlazlo, A. Marciniak, M. Zawadzki, B. Dudkiewicz, J. Chem. Thermodyn. 86 (2015) 154-161.
- [34] F. Mutelet, A. Revelli, J. Jaubert, L.M. Sprunger, W.E. Acree, G. A. Baker, J. Eng. Data 55 (2010) 234-242.
- [35] M. Wagner, O. Stanga, W. Scroer. Phys. Chem. Chem. Phys. 6 (2004) 4421-4431.