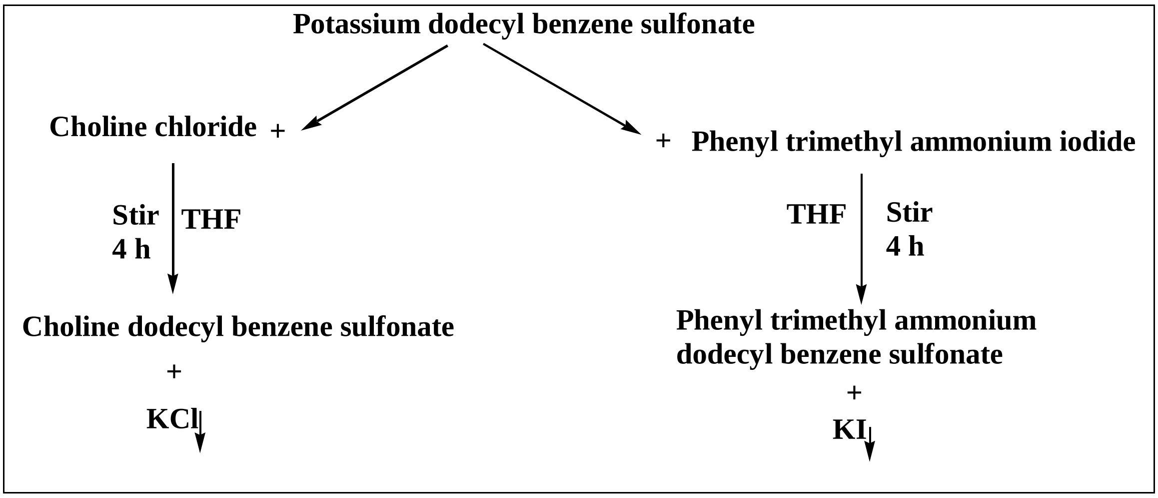
Abstract

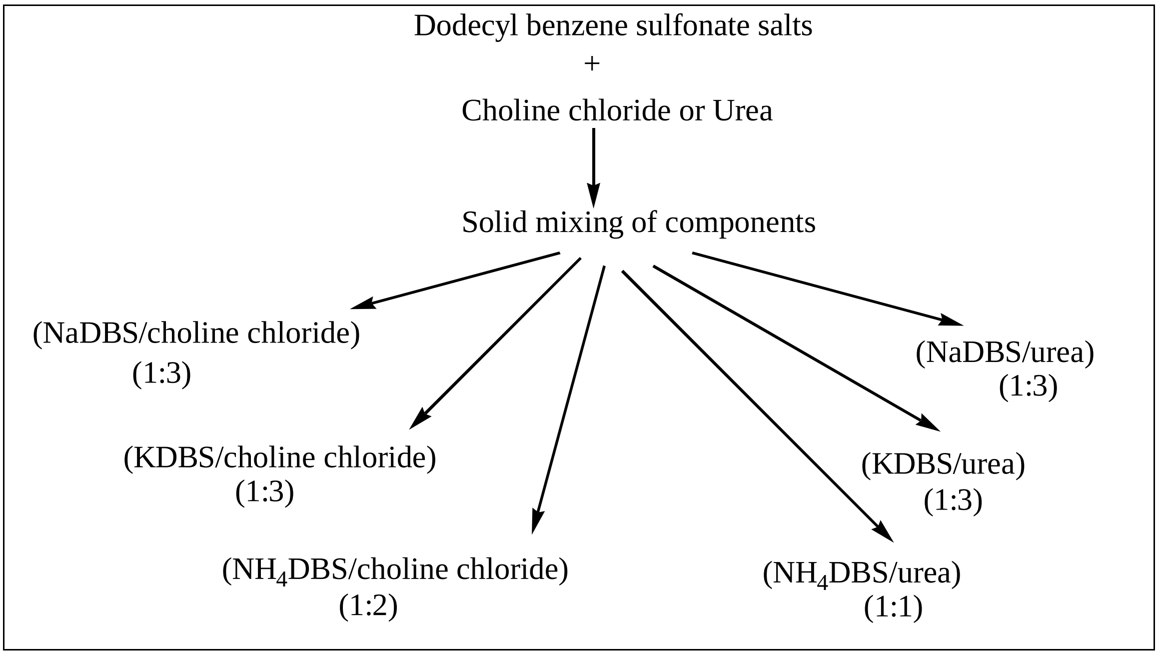
The work presented in this thesis includes the preparation and characterization of choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate, which were prepared and showed almost room temperature molten salts (ionic liquids) of 118 ^{o}C and 91.9 ^{o}C respectively, as shown in scheme (1):

Scheme (1)



Other molten salts (ionic liquids) based on mixing sodium, potassium, ammonium dodecyl benzene sulfonate, benzoic acid and salicylic acid with choline chloride showed a larger melting point depression than from of initial components, as shown in scheme (2) and (3):

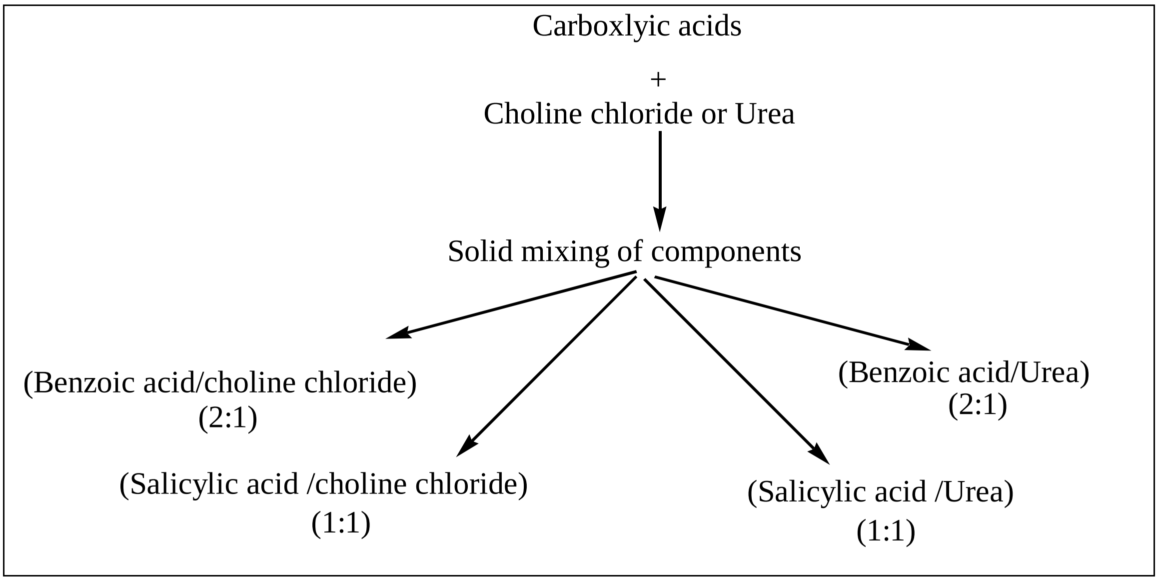
Scheme (2)



(Ammonium dodecyl benzene sulfonate /choline chloride) mixture has a deep eutectic point of 15 ^{o}C, while the two mixtures (benzoic acid / choline chloride) and (salicylic acid / choline chloride) gave a similar eutectic point of 60 ^{o}C, which were correspond with the room temperature molten salt (ionic liquids) definition, which is melt below the 100 ^{o}C. However, (sodium dodecyl benzene sulfonate /choline chloride) mixture and (potassium dodecyl benzene sulfonate /choline chloride) mixture afforded higher eutectic temperature than the room temperature molten salts.

Another set of mixtures that based on mixing the same previous compounds, but with urea instead of choline chloride. These mixtures showed with (NaDBS,KDBS and NH_4DBS) compounds lower eutectic points than with choline chloride of 105 ^{o}C, 100 ^{o}C, and 10 ^{o}C respectively. While with benzoic acid and salicylic acid afforded a little higher temperature of 75 ^{o}C and 77 ^{o}C respectively. Compositions of these mixtures attributed to the formation and interaction of hydrogen bonding or the formation of complex compounds of eutectic nature.

Scheme (3)



Chapter One

Introduction

Chapter

Two

Experimental

part

Chapter Three

Results & Discussion

Chapter Four

References

الأسم: عهد ديوان ساجت.

التحصيل الدراسي: ماجستير- علوم كيمياء.

سنة التخرج: بكالوريوس ٢٠٠٤

الجامعه:جامعة النهرين

المواليد: ١٩٨٣

العنوان: بغداد.

الايميل :لايوجد.

رقم الهاتف:لايوجد.

عنوان السكن: محله : ٣١٨ ، الزقاق:٩٠، الدار:١٥

تاريخ المناقشه : ٢٩-٥-٢٠٠٨

اسم المشرف: د.هادي محمد علي عبود.

عنوان الاطروحه: تحضير و تشخيص الأملاح المنصهرة (السوائل الأيونية) المستندة على مركبات السلفونيت.

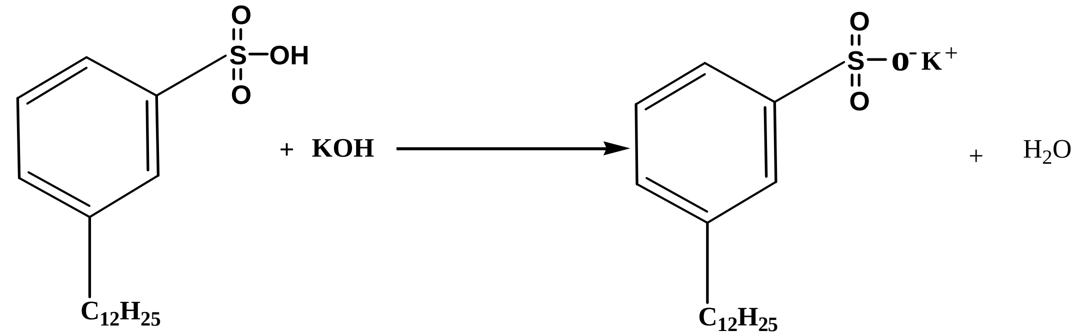
Chapter Three

Results and Discussion

3.1 Synthesis of dodecyl benzene sulfonate salts

3.1.1 Synthesis of potassium dodecyl benzene sulfonate [KDBS]

Potassium dodecyl benzene sulfonate are prepared via (acid –base) reaction by the neutralization (1mole:1mole) of dodecyl benzene sulfonic acid (98%) with (KOH) (40%) solution as outlined in section (2.5.1). The reaction might be described as state in scheme.(3-1).**(68)**

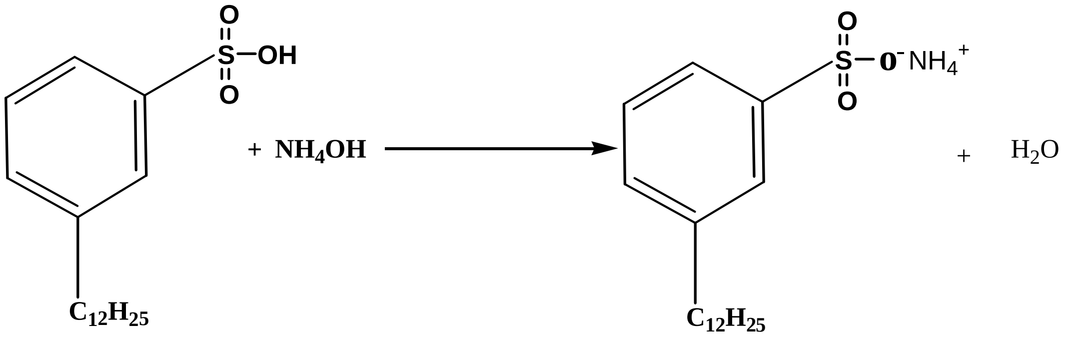


Scheme. (3-1): Reagents and conditions of reaction of dodecyl benzene sulfonic acid with KOH(40%) at room temperature.

The F.T.IR spectrum of the faint yellow KDBS as shown in figure (3-2) which showed the appearance of the characteristic absorption bands of ***v*** ($S(=O)_2$) at (1385, 1323) cm^{-1} for asymmetric vibration and (1192) cm^{-1} for symmetric vibration ; in addition the appearance of the characteristic absorption bands of ***v*** (S-O) of the sulfonate at (1045)cm^{-1} **(73,74)** . The appearance of the characteristic absorption bands in the region (3100) cm^{-1} due to stretching vibration of the ***v(C-H)*** aromatic, the appearance of the characteristic absorption band in the region (1638) cm^{-1} due to stretching vibration of the ***v(C=C)*** aromatic, the appearance of the characteristic absorption bands in the region (2893) cm^{-1} due to stretching vibration of the ***v(C-H)*** aliphatic. In addition to the previous characteristic bands of the aromatic ring, band at (880) cm^{-1} region of the spectrum indicates the Meta disubstituted on aromatic ring of KDBS.(**73**- 76)

3.1.2 Synthesis of ammonium dodecyl benzene sulfonate [NH_4DBS]

Ammonium Dodecyl benzene sulfonate are prepared via (acid –base) reaction by the neutralization (1mole:1mole) of dodecyl benzene sulfonic acid (98%) with (NH_4OH) (40%) solution as outlined in section (2.5.2). The reaction might be described as state in scheme.(3-2). **(68)**



dodecyl benzene sulfonic acid

ammonium dodecyl benzene sulfonate

NH_4DBS

Scheme. (3-2): Reagents and conditions of reaction of dodecyl benzene sulfonic acid with NH_4OH(50%) at room temperature.

The F.T.IR spectrum of NH_4DBS showed a similar bands a raised for the vibration of sulfonate group as shown be KDBS there bands appeared as characteristic absorption bands of ***v*** ($S(=O)_2$) at (1385, 1323) cm^{-1} for asymmetric vibration and (1192) cm^{-1} for symmetric vibration ; in addition the appearance of the characteristic absorption bands of

v (S-O) of the sulfonate at (1047) cm^{-1} **(73,74)** in additional bands which might be referred to the presence of NH_4 group appeared at the region (3383) cm^{-1} due to stretching vibration of the ***v(N-H)***.**(73, 75,76)** the appearance of the appearance of the characteristic absorption bands in the region (3050) cm^{-1} due to stretching vibration of the ***v(C-H)*** aromatic ; also the appearance of the characteristic absorption band in the region (1649) cm^{-1} due to stretching vibration of the ***v(C=C)*** aromatic; the appearance of the characteristic absorption bands in the region (2974) and (2926) cm^{-1} due to stretching vibration of the ***v(C-H)*** aliphatic. In addition to the previous characteristic bands of the aromatic ring, band at (881) cm^{-1} region of the spectrum indicates the Meta disubstituted on aromatic ring of NH_4DBS.(**73-** 76)

3.1.3 FTIR analysis of sodium dodecyl benzene sulfonate [NaDBS]

The FTIR analysis of the dried NaDBS was carried out to evaluate the vibrations of the variable groups that present in this compounds in an attempt to be compared with these obtained for the prepared KDBS and NH_4DBS.The FTIR spectrum in figure (3-1) of NaDBS showed that the characteristic absorption bands of ***v*** $(S(=O)_2)$ at (1383, 1329) cm^{-1} for asymmetric vibration and (1192) cm^{-1} for symmetric vibration; in addition the appearance of the characteristic absorption bands of ***v*** (S-O) of the sulfonate at (1047) cm^{-1} **(73,74)**. The appearance of the characteristic absorption bands in the region (3100) cm^{-1} due to stretching vibration of the ***v(C-H)*** aromatic. The appearance of the characteristic absorption bands in the region (2972) and (2925) cm^{-1} due to stretching vibration of the ***v(C-H)*** aliphatic. (**73-** 76) Therefore these results are in agreements with there obtained for KDBS and NH_4DBS.

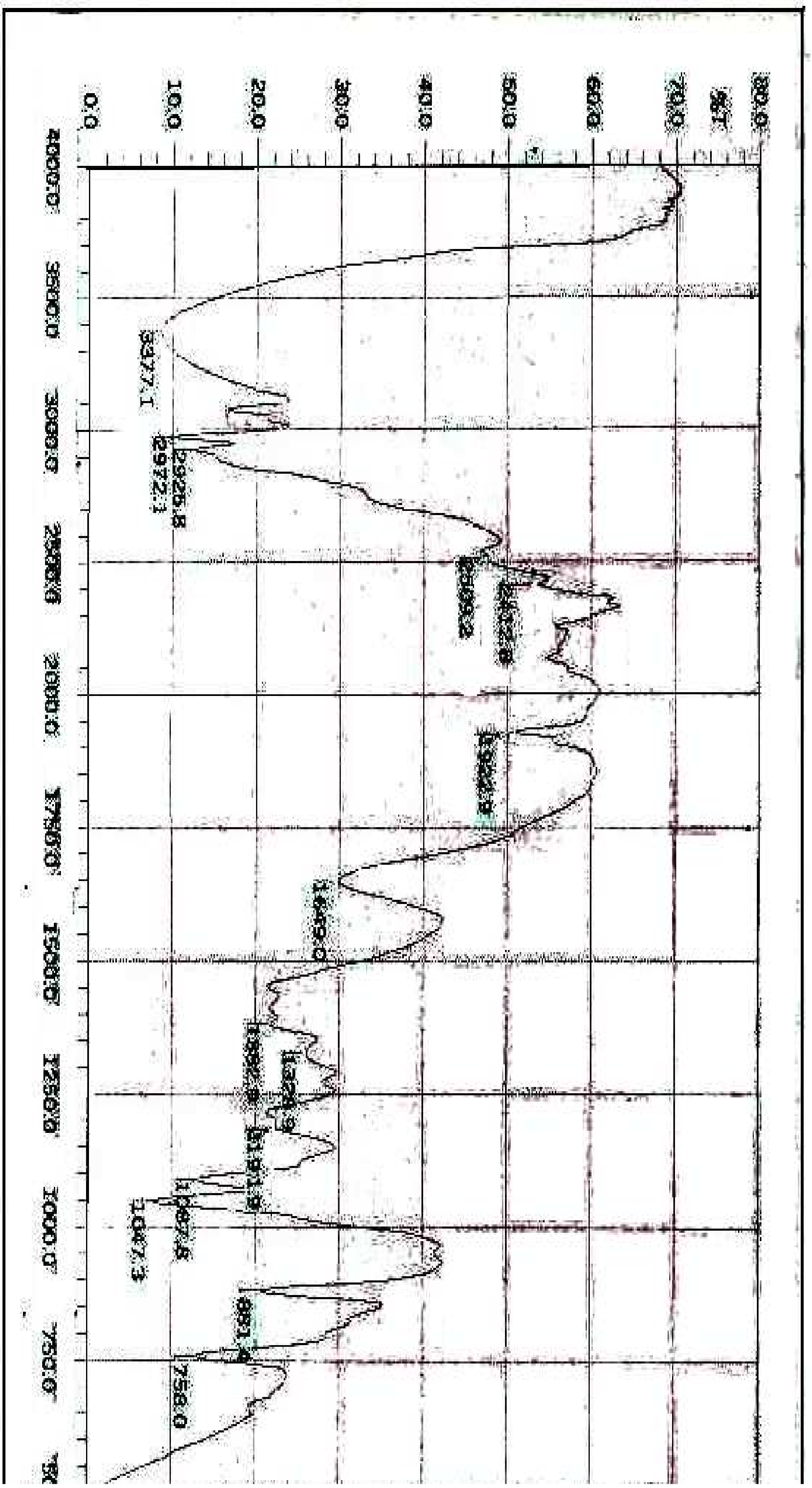


Figure (3-1): FTIR spectrum of Sodium dodecyl benzene sulfonate [NaDBS]

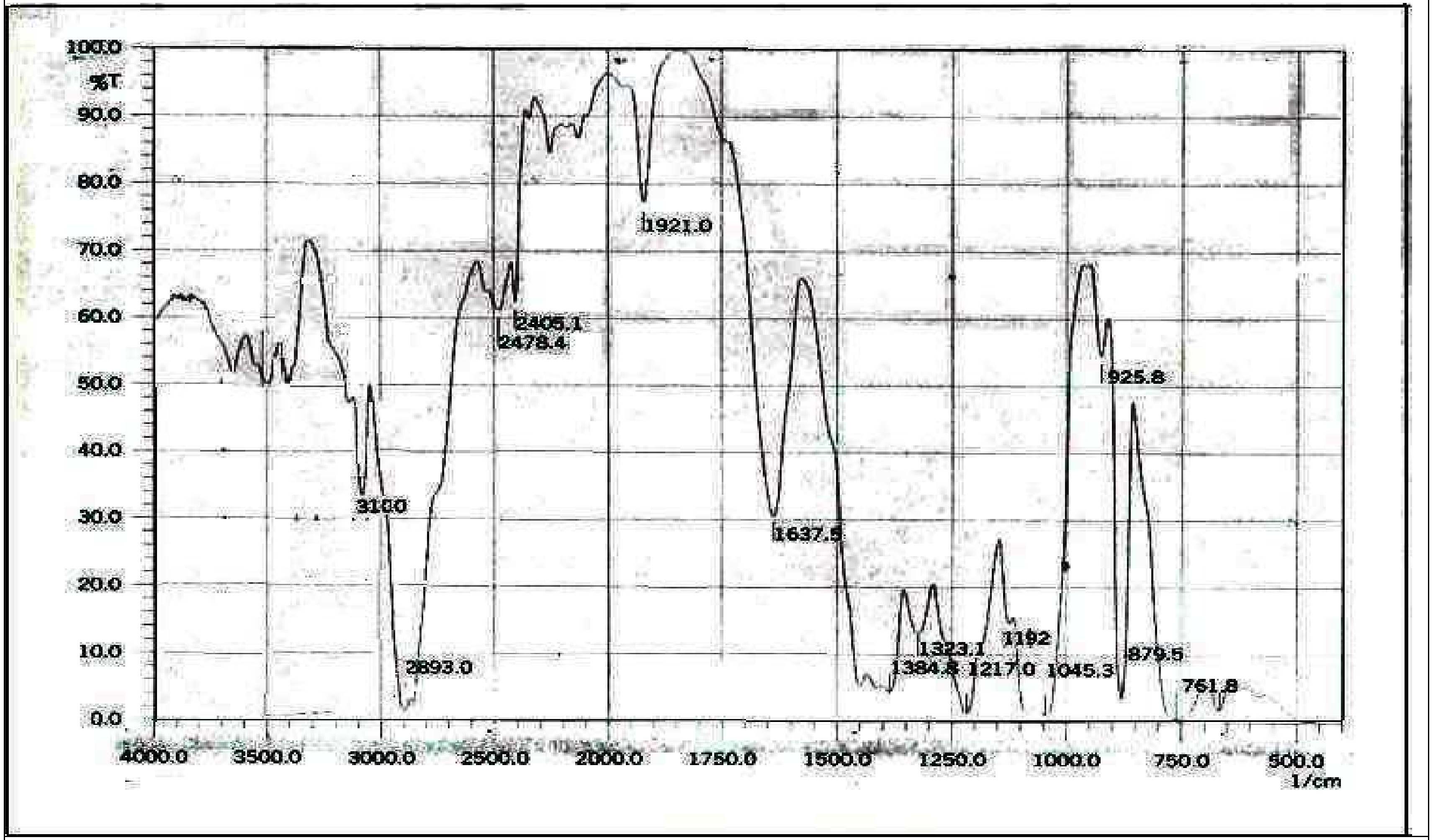


Figure (3-2): FTIR spectrum of potassium dodecyl benzene sulfonate [KDBS]

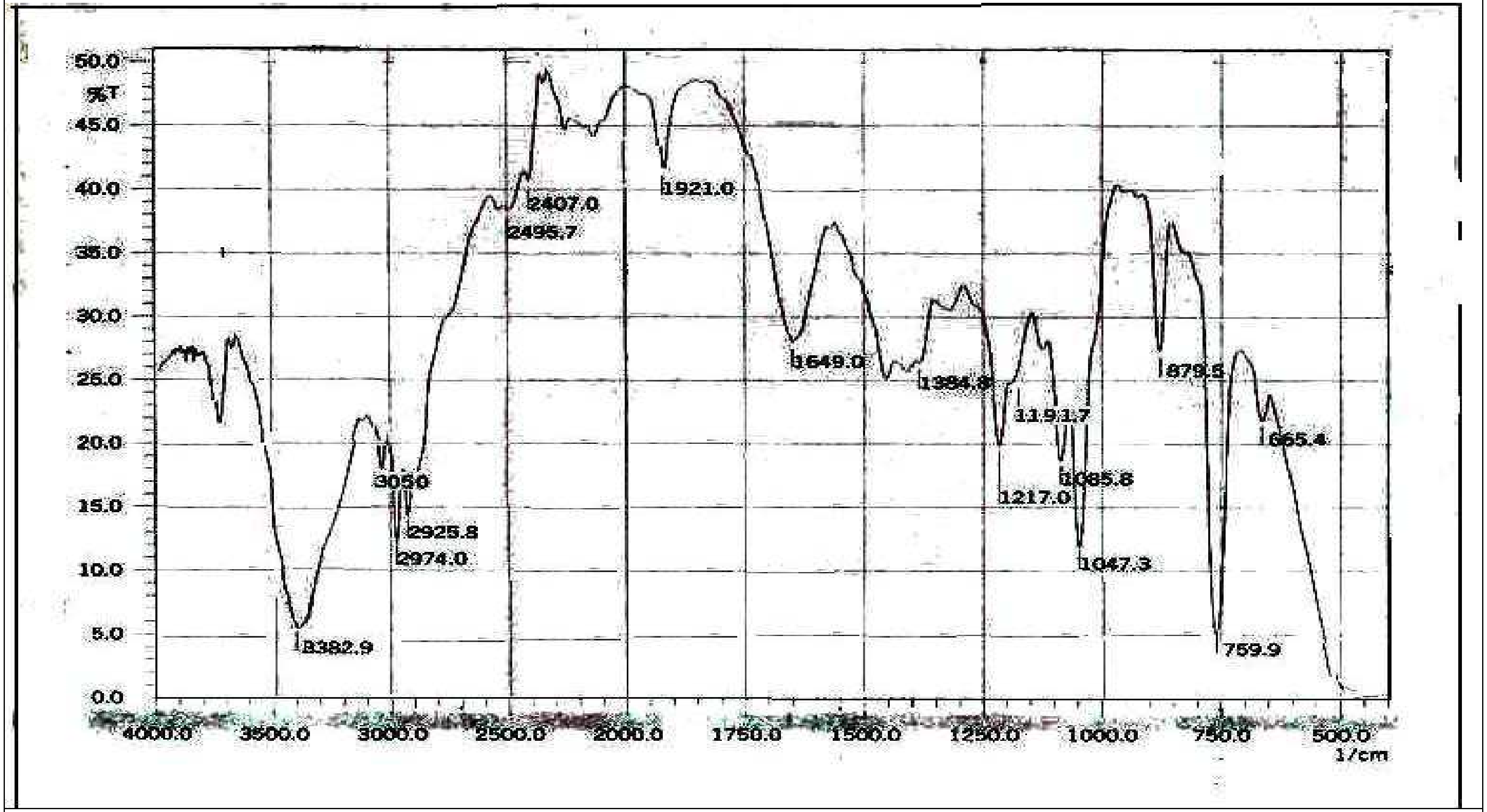


Figure (3-3): FTIR spectrum of ammonium dodecyl benzene sulfonate [NH_4DBS]

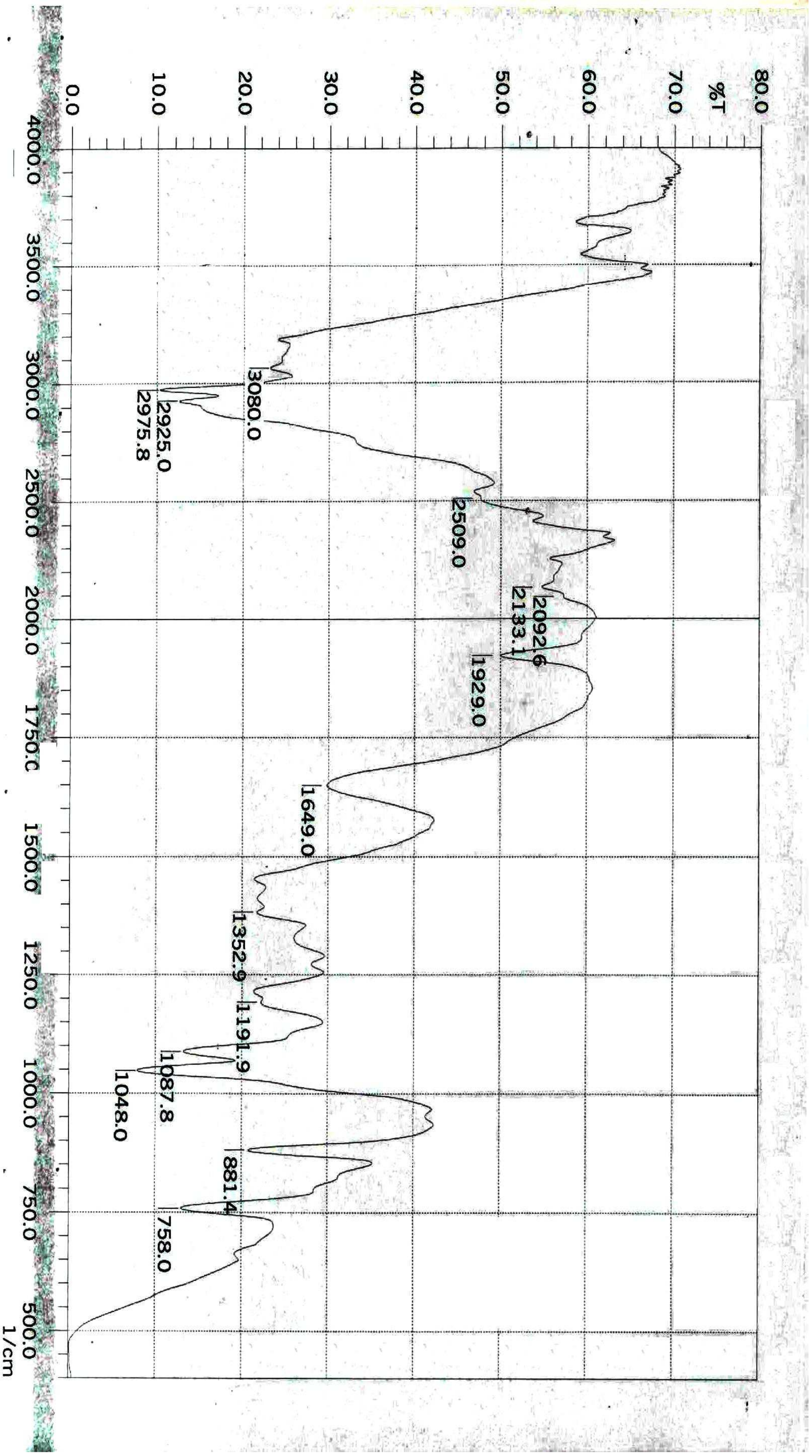


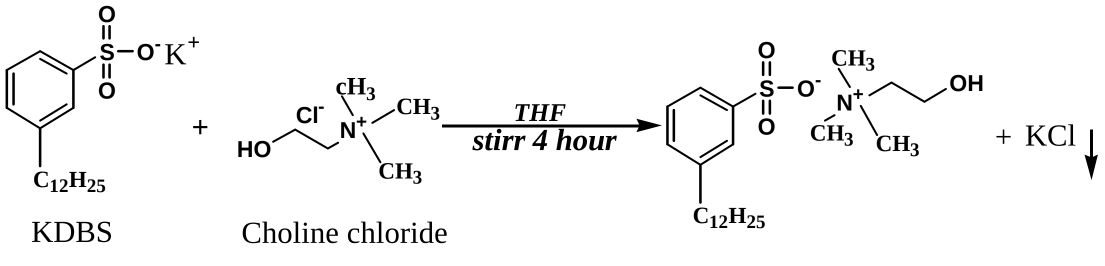
Figure (3-4): FTIR spectrum of dodecyl benzene sulfonic acid

3.2 Metathesis and Characterization of ionic liquids

Two solid ionic liquids containing; choline $[HOC_2H_4N(CH_3)_3]^+$ cation and phenyl trimethyl ammonium $[C_6H_5N(CH_3)_3]^+$ cation, with dodecyl benzene sulfonate $[Ph(C_{12}H_{25})SO_3]^-$ anion were synthesized via simple direct precipitation reactions in THF at room temperature . They were analyzed and characterized by the infrared spectroscopy. In addition, differential scanning calorimetry (DSC) was carried out to detect physical changes from room temperature up to 200 °C. Table (3-1) show melting points and suggested molecular weights and the color of their solid ionic liquids.

3.2.1 Metathesis of choline dodecyl benzene sulfonate

Choline dodecyl benzene sulfonate was prepared by reacting the solution of potassium dodecyl benzene sulfonate in THF with Choline chloride solution in THF also; with continuous stirring for (4) hours at room temperature. The melting point ,suggested molecular weight, color ,and the percentage of yield of product were outlined in table (3-1). .

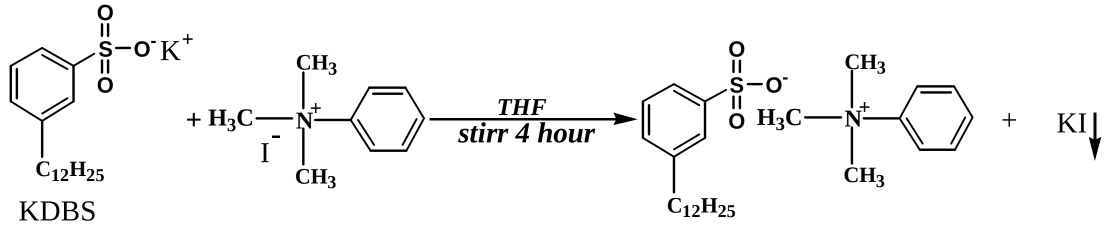


Scheme. (3-3): Reagents and conditions of reaction KDBS with choline chloride in THF, stir 4h at room temperature.

FTIR spectrum of the pale yellow solid material in Figure (3-5) showed the appearance of the characteristic absorption bands of ***v*** ($S(=O)_2$) at (1175) cm^{-1} for asymmetric vibration and at (1055) cm^{-1} for symmetric vibration; in addition appearance of the characteristic absorption band of ***v***(S-O) of the sulfonate at (1013) cm^{-1}.**(73,74)** This spectrum show the appearance of the characteristic absorption band (sharp peak) in the region (3415.7) cm^{-1} due to stretching vibration of the ***v (-OH)*** group; in addition appearance of the characteristic absorption band in the region (1215) cm^{-1} due to stretching vibration of the ***v(C-N)*** also, the appearance of the characteristic absorption band in the region (1126) cm^{-1} due to stretching vibration of the ***v(C-N).*****(73,72,77)** The appearance of the characteristic absorption bands in the region (3030) cm^{-1} due to stretching vibration of the ***v(C-H)*** aromatic ; the appearance of the characteristic absorption bands in the region (2928) and (2864) cm^{-1} due to stretching vibration of the ***v(C-H)*** aliphatic; also the appearance of the characteristic absorption bands in the regions (1412) and (1456) cm^{-1} due to the ***v(C-H)*** aliphatic; the appearance of the characteristic absorption band in the region (1634) due to stretching vibration of the ***v(C=C)*** aromatic. In addition to the previous characteristic bands of the aromatic ring, band at (880) cm^{-1} region of the spectrum indicate the Meta disubstituted on aromatic ring(73-76) .

3.2.2 Synthesis of phenyl trimethyl ammonium dodecyl benzene sulfonate

Phenyl trimethyl ammonium dodecyl benzene sulfonate was prepared by reacting a solution of potassium dodecyl benzene sulfonate in THF with phenyl trimethyl ammonium iodide solution in THF also; with continuous stirring for (4) hours at room temperature. The melting point ,suggested molecular weight ,color ,and the percentage of yield of product were outlined in table (3-1).



Scheme (3-4): Reagents and conditions of reaction KDBS with phenyl trimethyl ammonium iodide in THF,stir 4h at room temperature.

FTIR spectrum of the pale violet solid material in Figure (3-6) showed the appearance of the characteristic absorption bands of ***v*** $(S(=O)_2)$ at (1176) cm^{-1} for asymmetric vibration and at (1059) cm^{-1} for symmetric vibration; in addition appearance of the characteristic absorption band of ***v***(S-O) of the sulfonate at (1011) cm^{-1} .**(73,74)** This spectrum show the appearance of the characteristic absorption band in the region (1251) cm^{-1} due to stretching vibration of the ***v(C-N)*** (73,**77,72)**. The appearance of the characteristic absorption bands in the region (3040) cm^{-1} due to stretching vibration of the ***v(C-H)*** aromatic; also the appearance of the characteristic absorption bands in the regions (689) cm^{-1} and (673) cm^{-1} due to the ***v(C-H)*** aromatic; the appearance of the characteristic absorption bands in the region (2955) and (2924) and (2854) cm^{-1} due to stretching vibration of the ***v(C-H)*** aliphatic. **(72-74)** Also the appearance of the characteristic absorption bands in the regions (1408) and (1456) cm^{-1} due to the ***v(C-H)*** aliphatic; the appearance of the characteristic absorption band in the region (1601) cm^{-1} due to stretching vibration of the ***v(C=C)*** aromatic. **(73**-76)

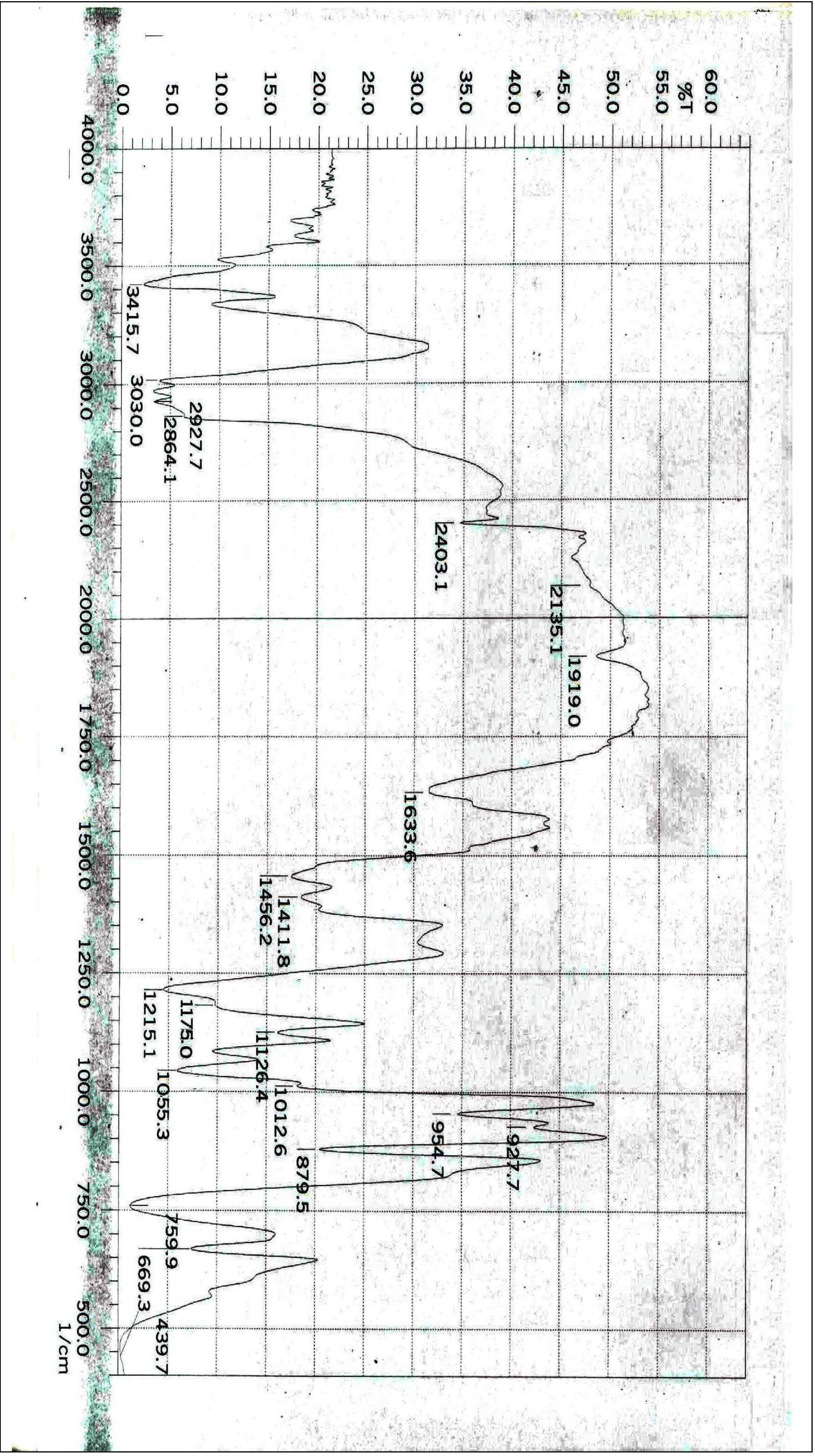


Figure (3-5): FTIR spectrum of choline dodecyl benzene sulfonate

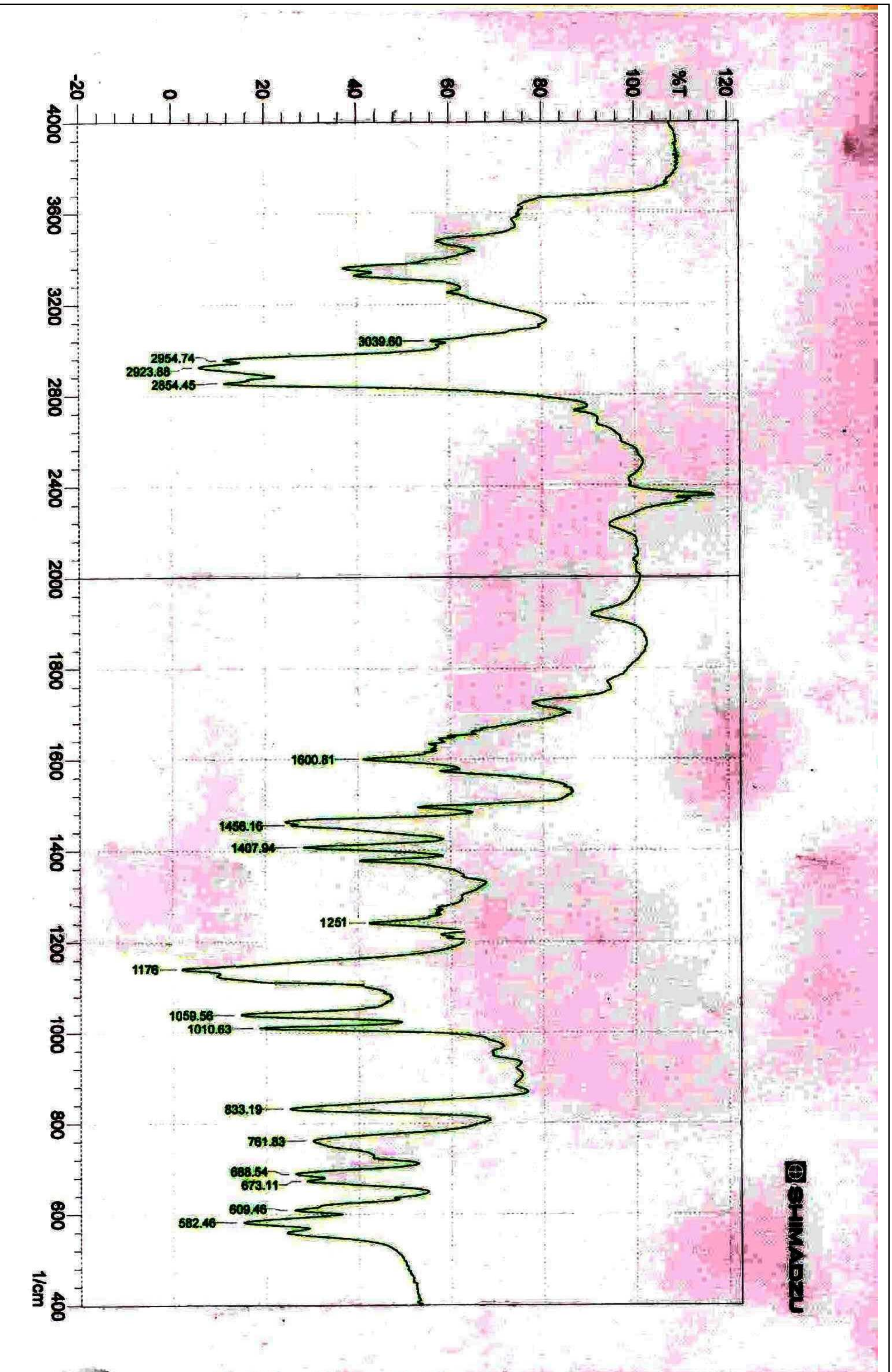


Figure (3-6): FTIR spectrum of phenyl trimethyl ammonium dodecyl benzene sulfonate [2a]

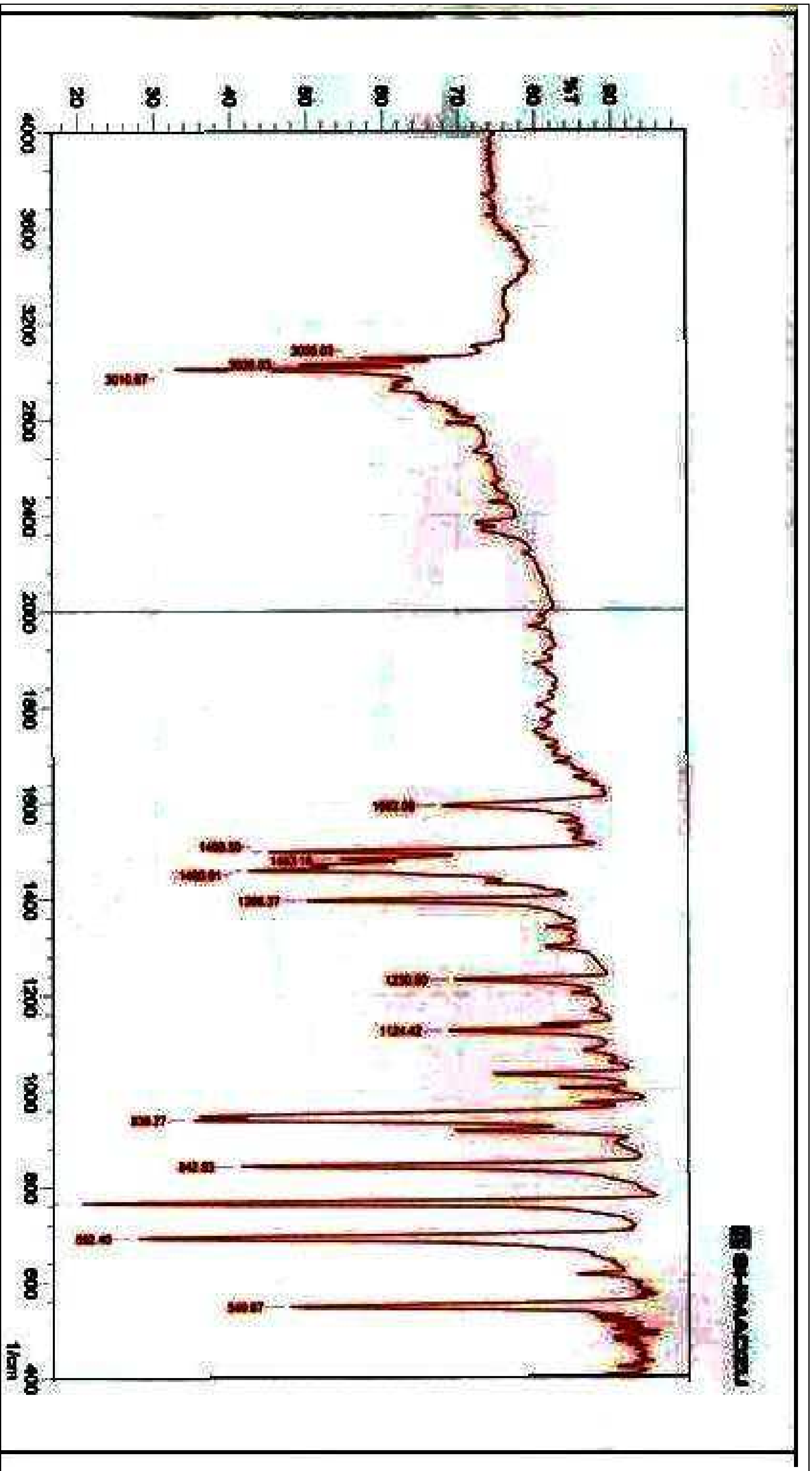


Figure (3-7): FTIR spectrum of phenyl trimethyl ammonium iodide

.

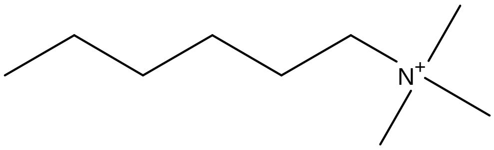
3.3 The effect of cation type on the melting point of ionic liquids

To design, syntheses and characterize new ionic liquids at desirable melting point temperature, it is known that the melting point of ionic liquids is governed by different factors, these factors are the interaction between the anionic and cationic species in the liquid, which are affected by ionic size, functionality, molecular mass, shape of both the cation and anion, hydrogen bonding, charge delocalization on either both cation/ and or anion. The symmetry of the cation is known to affect the melting point of ionic liquids.**(52, 79)**

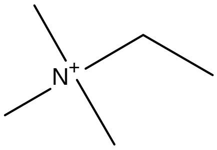
Table (3-1): Some physical properties of ionic liquids.

Molecular formula of ionic liquids	Yield (%)	T_m ^oC	M.WT g/mole	color
$[C_6H_5N(CH_3)_3]^+ [Ph(C_{12}H_{25})SO_3]^-$	40	91.9	461.00	Pale violet
$[HOC_2H_4N(CH_3)_3]^+ [Ph(C_{12}H_{25})SO_3]^-$	50	118.0	429.18	Pale yellow

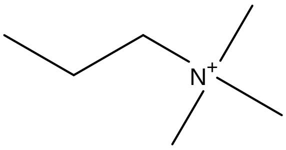
Table (3-1) show the melting points of choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate which are measured by differential scanning calorimetry (DSC) as shown in Fig. (3-8) and (3-9) respectively. As dodecyl benzene sulfonate anion is found in both ionic liquids, hence the effect of changing the cation size might be the major factor influencing the extend of melting point observed for both ionic liquids. It is found that when cation size was large the melting point becomes less than when the cation was relatively smaller. It might also indicated that the presence of phenyl group has large effect on the melting point than the aliphatic (HOC_2H_4) group attached to $-N(CH_3)_3$ group in both compounds. These finding are similar to recently reported where melting point of ionic liquid containing 1-methyl-3-octylimidazolium cation is lower than ionic liquid containing 1-methyl-3-butylimidazolium cation. **(13,34,52)** There is analogous manner when the ionic liquids containing 1-ethyl-3-ethylimidazolium cation and 1-methyl-3-methylimidazolium cation have melting points (14 °C , 22 °C) respectively **(31,52,71)** and Me_4N^+ gives a higher melting Point than Me_3N^+R (R=alkyl) up to a certain chain length; this is illustrated by the ethyltrimethylammonium, propyltrimethylammonium, and hexyltrimethylammonium as cations.**(80)**



Hexyl trimethyl ammonium



Ethyl trimethyl ammonium



Propyl trimethyl ammonium

Table (3-2): melting point, T_m of ionic liquids of the general formal $R_1R_2R_3R_4N^+Halide^-/2\ ZnCl_2$ (80) .

R1	R2	R3	R4	Halide ion	T_m / ^{0}C
Me	Me	Me	C_2H_5	Cl^-	53-55
Me	Me	Me	C_3H_7	Br^-	45-47
Me	Me	Me	C_6H_{13}	Br^-	41-43

The results for the long-chain quaternary ammonium cations could result from van der Waals interactions, which is similar to that recently reported ionic liquids based on metal halide/ substituted quaternary ammonium salt mixture.**(80)** Room temperature ionic liquids are organic salts composed entirely of ions and unlike the common inorganic salts, which melt at higher temperatures. These are liquids at ambient condition. For example when Na^+ in NaCl, which melt at 801 ^{0}C, is replaced by a bulky organic cation, say, 1-butyl-3-methylimidazolium cation, $[BMIm]^+$, the melting point of the resulting compounds, $[BMIm]^+Cl^-$, is lower to 65 ^{o}C. Further, when Cl^- is changed by a larger anion $[BF_4]^-$, the melting point is further decreased to -81^{o}C, thus making it an room temperature ionic liquids.**(81)** The yields of the products obtained in this work were 50% and 40% for choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate respectively as shown in table (3-1). The yield of synthesis solid ionic liquid that containing phenyl trimethyl ammonium cation was lower than yield of synthesis solid ionic liquid containing choline cation could be related to the rather slow to react by for what we believe are steric reasons, and reactions were essentially quantitative for shorter alkyl chain lengths, which is similar to the recently reported results of phosphonium ionic liquids.**(78)** Molten salts (ionic liquids) containing phenyl trimethyl ammonium cation showed pale violet color and while that showed containing choline cation are a pale yellow color. These differences in colors may be attributed to double bond conjugation; as conjugation of double bonds shifts the absorption maximum to longer wave lengths.**(77)** It was reported that each additional double bond in the conjugated pi-electron system shifts the absorption maximum to longer wave length.**(69)**

3.4 The Thermal Analysis of Ionic Liquids

One of the advantages of ionic liquid it's thermal robustness, resulting in a large thermal operating range, which in turn, enables excellent kinetic control for reaction proceeding in these liquids. Differential scanning calorimetry (DSC) figures (3-8) and (3-9) show the thermal analysis for choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate respectively. The scanning rate used was 2 °C/min; the weight of the sample was 10 mg; which was similar to that recently reported of the ionic liquids that based upon the dialkylimidazolium cations.**(77,80,82)** And organo-niobate molten salts (ionic liquids), **(55)** Generally, the temperature at which solid ionic liquids melt depends upon the potential energy between the ions. These solid ionic liquids can be considered as the difference in melting points between that solid ionic liquids choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate which were (118 °C, 91.9 °C) respectively. The concomitants change in melting point $\mathbf{T_m}$ will be related to the ionic lattice resulting from the formation of solid ionic liquids since: $\mathbf{E = - N_A e^2/4\pi\varepsilon_o r}$ (1)

Where:

E= **Latent heat of fusion**.

$\mathbf{N_A}$ = **Avogadro number** = 6.023×10^{23} mole $^{-1}$.

e = **Electron charge** = 1.602×10^{-19}.

$\boldsymbol{\varepsilon_o}$ = **Vacuum permittivity** = 8.854×10^{-12} F. m^{-1}.

r = **separation between the two ions**.**(80,82)**

1mW = 3.6×10^{6} J

Fig (3-13) show:

the **E** of choline dodecyl benzene sulfonate = – 1.2 mW = - 4320 kJ

Fig (3-14) show:

The **E** of phenyl trimethyl ammonium dodecyl benzene sulfonate

= – 0.42 mW = – 1512 kJ

The latent heat of fusion of choline dodecyl benzene sulfonate was higher than the latent heat of fusion of phenyl trimethyl ammonium dodecyl benzene sulfonate (**- 4320 kJ > -1512 kJ**).

So, those melting points of choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate were taken from the first heating curve; and the ionic liquids were stable to 200 °C, those results were correspond with when the crystal with the lowest melting point must be the one with the lowest lattice energy.**(86)** Since, the weight of phenyl trimethyl ammonium dodecyl benzene sulfonate was **10 mg** and the suggested molecular weight was 461g/mole.

That moles = weight of a sample / molecular weight of a sample. Moles = $10\times 10^{-3}/461 = 2.169\times 10^{-5}$ Mole

-1512 KJ $/2.169\times 10^{-5}$ Mole $= -6.970\times 10^{7}$ kJ/mole

From equation (1) we can determine the separation between the two ions (r), therefore $E = -N_Ae^2/4\pi\varepsilon_o r$

$$-6.970\times 10^{7} = -6.023\times 10^{23}\times (1.602\times 10^{-19})^2 / 4\times 3.14\times 8.854\times 10^{-12}\times r$$

$r = 1.992\times 10^{-12}$ m

Since, the weight of choline dodecyl benzene sulfonate was **10 mg** and the suggested molecular weight was 429.18 g/mole.

That moles = weight of a sample / molecular weight of a sample. Moles = $10\times 10^{-3}/429.18 = 2.33\times 10^{-5}$ Mole

-4320 kJ $/2.33\times 10^{-5}$ Mole $= -1.854\times 10^{8}$ kJ/mole

From equation (1) we can determine the separation between the two ions (r), therefore $E = -N_Ae^2/4\pi\varepsilon_o r$

$$-1.854\times 10^{8} = -6.023\times 10^{23}\times (1.602\times 10^{-19})^2 / 4\times 3.14\times 8.854\times 10^{-12}\times r$$

$r = 7.492\times 10^{-13}$ m

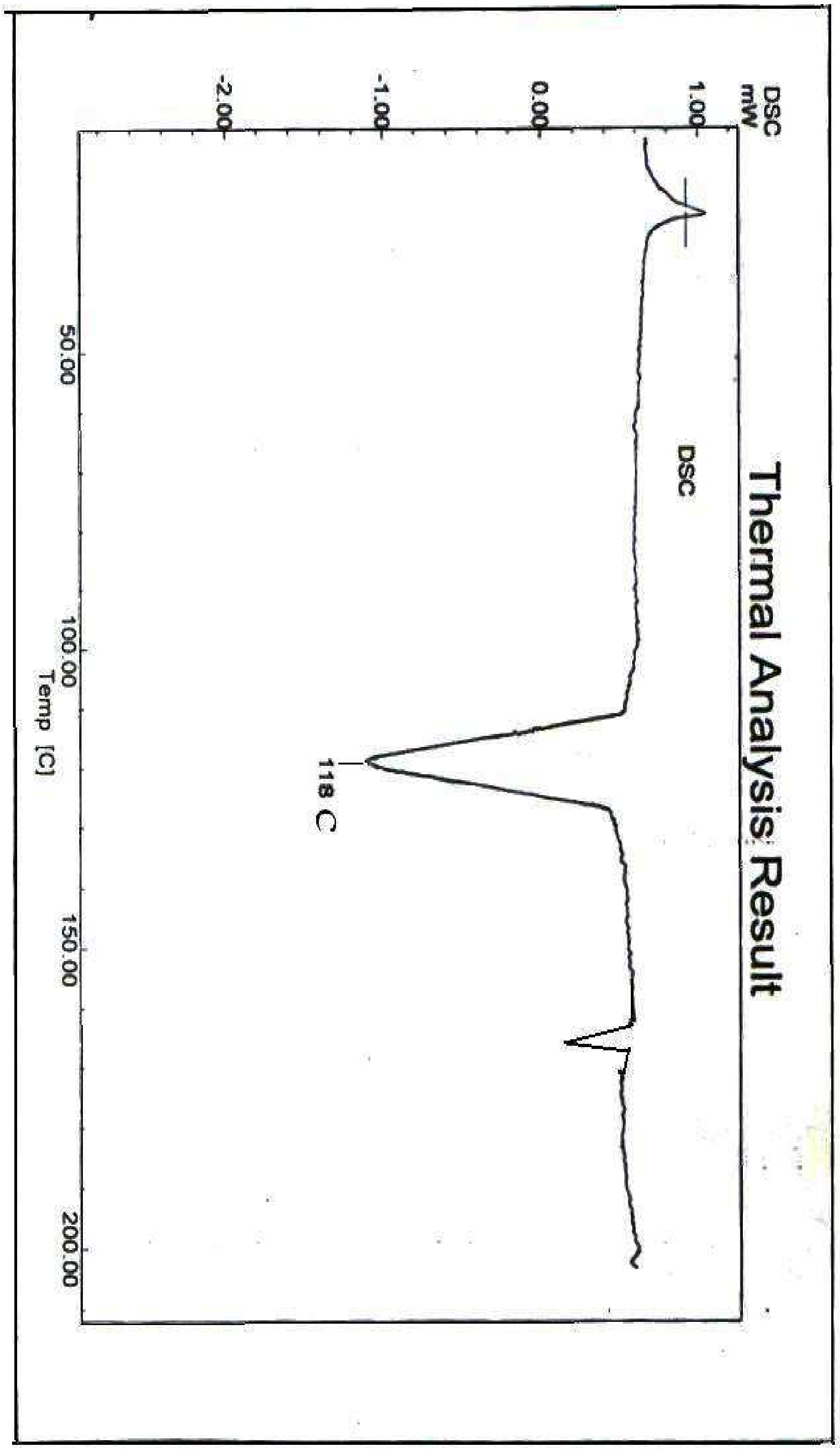


Figure (3-8): Thermogram of choline dodecyl benzene sulfonate

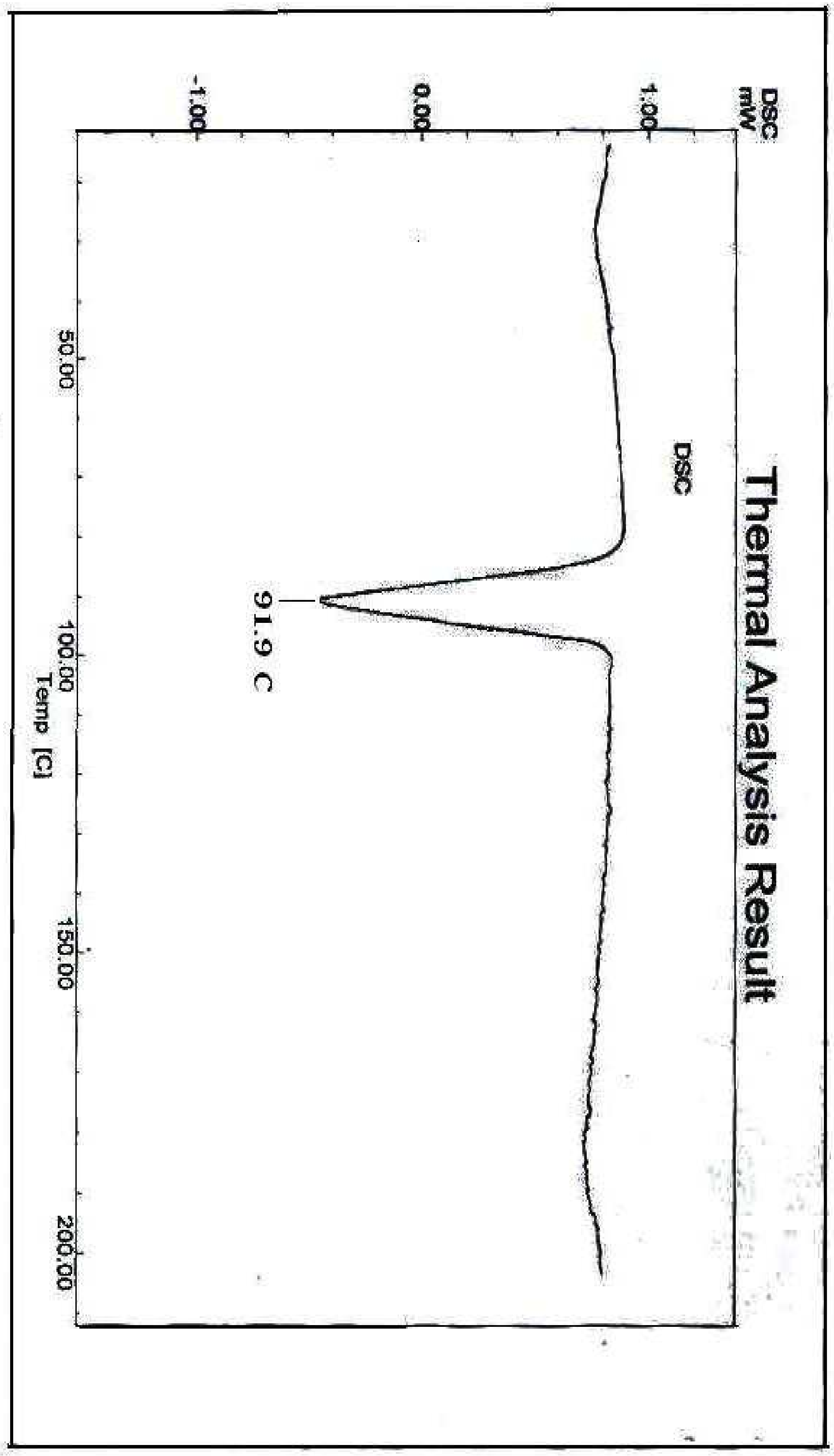


Figure (3-9): Thermogram of phenyl trimethyl ammonium dodecyl benzene sulfonate [2a]

3.5 Preparations of molten salts (ionic liquids) by mixing the solid components

3.5.1 Preparations of molten salts based upon choline chloride

Molten salts (ionic liquids) can be prepared by mixing their solid components and heating to elevated temperature until fluid achieved. The composition of the molten mixture were taken from 20 mole % to 80 mole % based on add choline chloride to DBS salts of sodium, potassium, ammonium, benzoic and salicylic acid. Those mixtures gave five molten salts showing variable melting points. Some of these molten salts may be classified as room temperature molten salt (ionic liquids) as they showed melting point below 100 °C, while the others gave melting points above 100 °C. This method is known to prepare the molten salts (ionic liquids) as also being used by present workers.**(55,80,83)**

3.5.1.1 Preparation of NaDBS /choline chloride mixtures

The phase behavior**:** preparation of NaDBS/choline chloride mixture having the mole composition as shown in table (3-3). The phase diagram is presented in Fig. (3-10). It is obvious that the addition of choline chloride had a significant affect on the melting point of pure NaDBS. The depression of the 300 °C melting points of NaDBS was gradually decreased with added choline chloride until the eutectic point of the mixture was reached at 135°C. The composition at this point was 75 mole % of choline chloride: 25 mole % NaDBS. Futher addition of choline chloride therefore showed an increase in the melting point of the mixture until the temperature of 302 °C was reached, which represents the melting point of pure choline chloride salt. As seen, the depression in melting point increased relatively latter until the mole % of choline chloride was

33%. After that a gradual decreasing of melting point was recorded until the melting point of the eutectic point was reached. Furthermore, this behavior was similar to the fast increase in melting point when the mole % of choline chloride was increased.

Table (3-3): Compositions and melting points of NaDBS/choline chloride mixtures.

Na DBS (mole %)	Choline chloride (mole %)	Moles of the components Na DBS : choline chloride	Melting point C
80	20	0.004:0.001	205
75	25	0.003:0.001	195
66	33	0.002:0.001	165
50	50	0.001:0.001	150
33	66	0.001:0.002	140
25	75	0.001:0.003	135
20	80	0.001:0.004	177

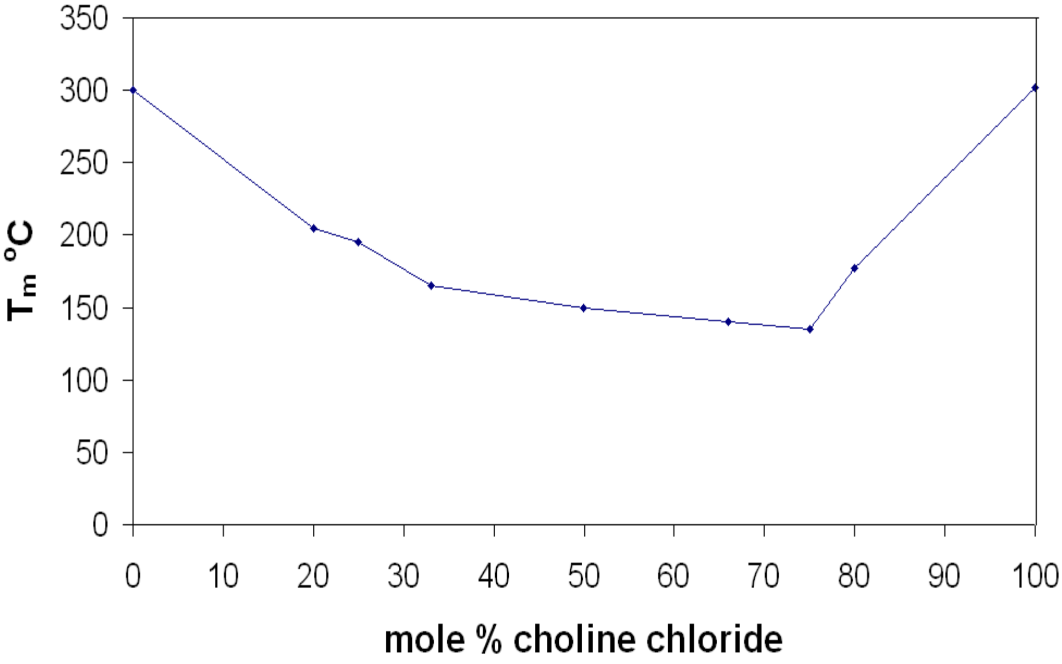


Fig (3- 10): Phase diagram of the melting points of NaDBS /choline chloride mixtures as a function of composition.

3.5.1.2 Preparation of KDBS / choline chloride mixtures

The phase behavior**:** preparation of KDBS / choline chloride mixture having the mole composition as shown in table (3-4). The phase diagram is presented in Fig. (3-11). It is clear that the addition of choline chloride had a significant affect on the melting point of pure KDBS. The depression of the 277 ^{o}C melting point of pure KDBS was gradually decreased with added choline chloride until the eutectic point of the mixture was reached at 125^{o}C. The composition at this point was 75 mole% of choline chloride **:** 25 mole% KDBS. The Further added choline chloride therefore showed an increase in the melting point of the mixture until the temperature of 302 ^{o}C was reached, which represents the melting point of pure choline chloride salt .As seen, the depression in melting point increased relatively latter until the mole % of choline chloride was 33%, where a gradual decreasing of melting point was recorded until the melting point of the eutectic point was reached. Furthermore, this behavior was similar to the fast increase in melting point when mole % of choline chloride was increased.

Table (3-4): Compositions and melting points of KDBS/choline chloride mixtures.

K DBS (mole %)	Choline chloride (mole %)	Moles of the components K DBS :choline chloride	Melting point ^{O}C
80	20	0.004:0.001	183
75	25	0.003:0.001	170
66	33	0.002:0.001	155
50	50	0.001:0.001	140
33	66	0.001:0.002	130
25	75	0.001:0.003	125
20	80	0.001:0.004	150

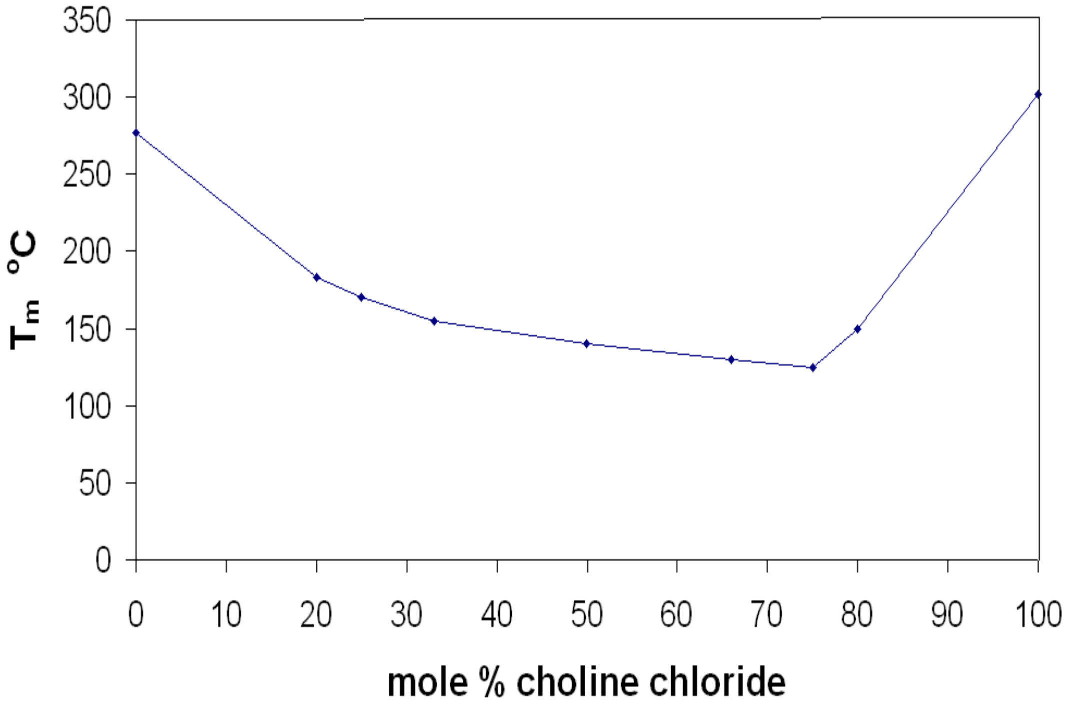


Fig (3- 11): Phase diagram of the melting points of K DBS / choline chloride mixtures as a function of composition.

3.5.1.3 Preparation of NH_4DBS /choline chloride mixtures

The phase behavior**:** preparation of NH_4DBS /choline chloride mixture having the mole composition as shown in table (3-5). The phase diagram is presented in Fig. (3-12). It is clear that the addition of choline chloride had a significant affect on the melting point of pure NH_4DBS, as it was increased from the -5 °C, which representing the melting point of pure NH_4DBS to 35 °C, at which the composition was 20 mole% of choline chloride and 80 mole% NH_4DBS. After this point the melting points were gradually decrease until it reached the eutectic point at 15°C, at which the composition was 66 mole% of choline chloride and 33 mole% NH_4DBS. Above the mole fraction of 66 mole % choline chloride the melting point increase gradually again until it reached 302 °C, which representing the melting point of pure choline chloride.

Table (3-5): Compositions and melting points of NH_4DBS /choline chloride mixtures.

NH_4 DBS (mole %)	Choline chloride (mole %)	Moles of the components NH_4 DBS :choline chloride	Melting point ^{O}C
80	20	0.004:0.001	35
75	25	0.003:0.001	30
66	33	0.002:0.001	25
50	50	0.001:0.001	20
33	66	0.001:0.002	15
25	75	0.001:0.003	25
20	80	0.001:0.004	40

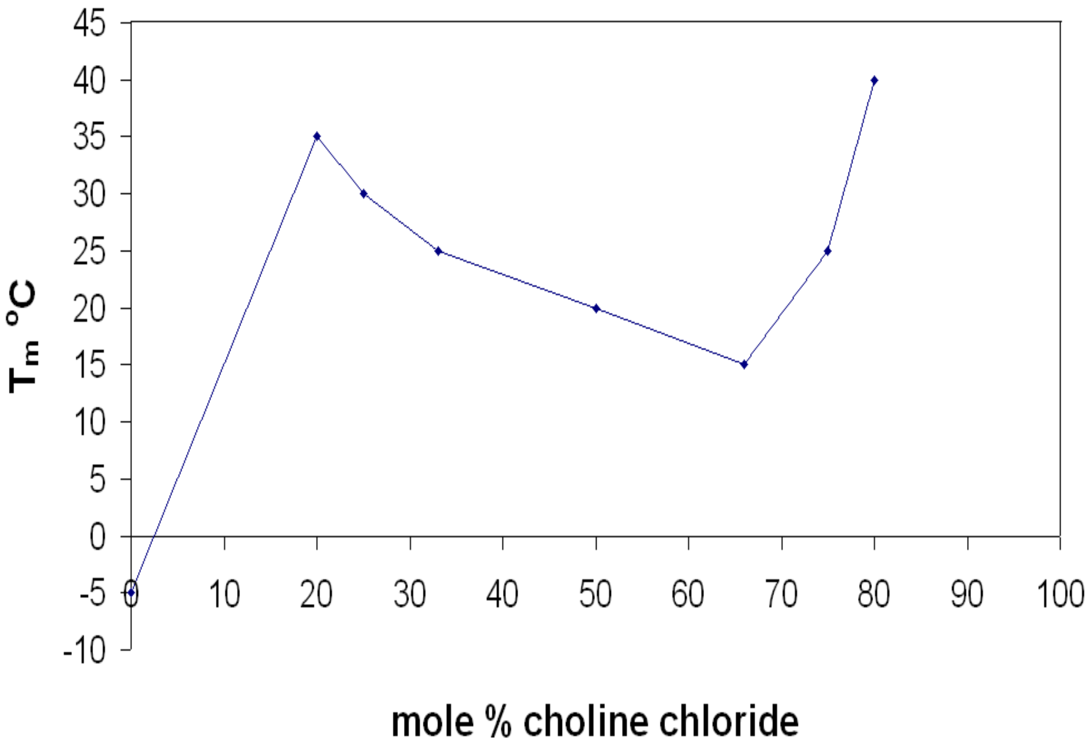


Fig. (3-12): Phase diagram of the melting points of (NH_4DBS /choline chloride) mixtures as a function of composition.

3.5.1.4 Preparation of Benzoic acid/choline chloride mixtures

The phase behavior**:** preparation of benzoic acid /choline chloride mixture having the mole composition as shown in table (3-6). The phase diagram is presented in Fig. (3-13). It is clear that the addition of choline chloride had a significant affect on the melting point of pure benzoic acid. As it was decreased from the 122 ^{o}C, which representing the melting point of pure benzoic acid to the 120 ^{o}C where that mole composition 20mole % of choline chloride and 80 mole % benzoic acid. Then the melting points sharply decrease until it reached the eutectic point at 60 ^{o}C, at which the composition was 33 mole % of choline chloride and 66 mole% benzoic acid. Above a mole fraction of 33mole % choline chloride the melting point increase gradually again until it reached 302 ^{o}C representing the melting point of pure choline chloride.

Table (3-6): Compositions and melting points of benzoic acid/choline chloride mixtures.

Benzoic acid (mole %)	Choline chloride (mole %)	Moles of the components benzoic acid :choline chloride	Melting point ^{O}C
80	20	0.004:0.001	120
75	25	0.003:0.001	100
66	33	0.002:0.001	60
50	50	0.001:0.001	65
33	66	0.001:0.002	85
25	75	0.001:0.003	95
20	80	0.001:0.004	105

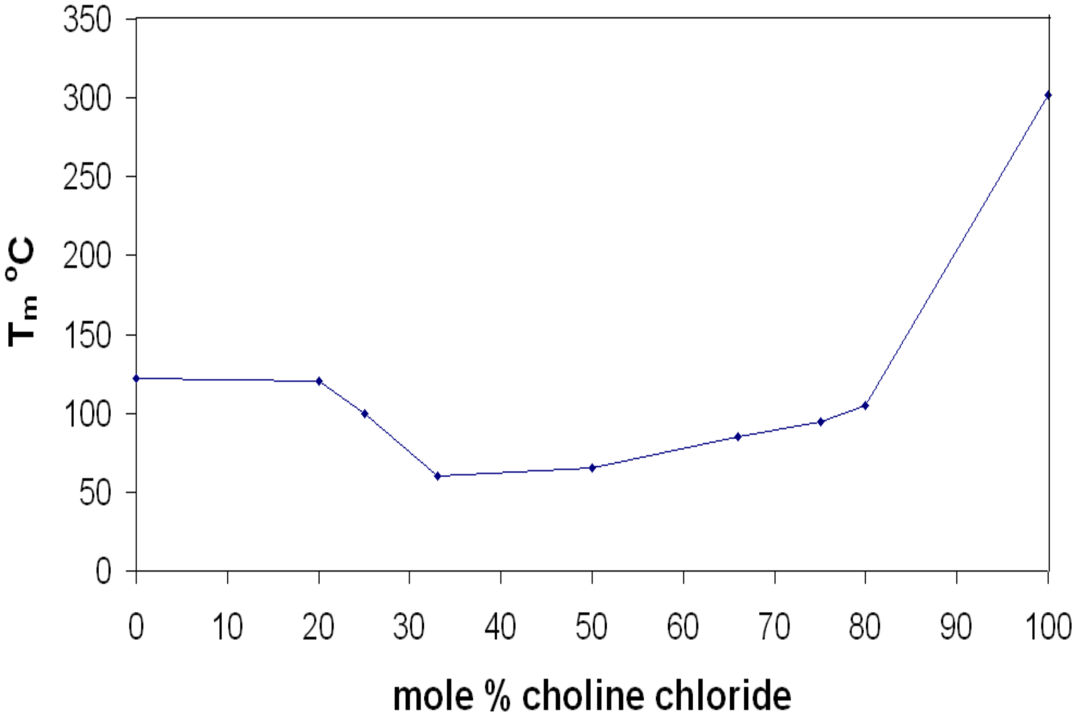


Fig. (3-13): phase diagram of the melting points of benzoic acid / choline chloride mixtures as a function of composition.

3.5.1.5 Preparation of Salicylic acid /choline chloride mixtures

The phase behavior**:** preparation of salicylic acid / choline chloride mixture having the mole composition as shown in table (3-7). The phase diagram is presented in Fig. (3-14). It is clear that the addition of choline chloride had a significant affect on the melting point of pure salicylic acid. The depression of the 160 °C melting point of pure salicylic acid was gradually decreased with added choline chloride until the eutectic point of the mixture was reached at 60°C. The composition at this point was 50 mole% of choline chloride **:** 50 mole% salicylic acid. The further added choline chloride therefore showed an increase in the melting point of the mixture until the temperature of 302 °C was reached, which represents the melting point of pure choline chloride salt. As seen, the depression in melting point increased relatively latter until the mole % of choline chloride was 20%, where a gradual decreasing of melting point was recorded until the melting point of the eutectic point was reached. Furthermore, this behavior was similar to the fast increase in melting point when mole % of choline chloride was increased.

Table (3-7): Compositions and melting points of salicylic acid/choline chloride mixtures.

Salicylic acid (mole %)	Choline chloride (mole %)	Moles of the components salicylic acid :choline chloride	Melting point ^{O}C
80	20	0.004:0.001	110
75	25	0.003:0.001	82
66	33	0.002:0.001	65
50	50	0.001:0.001	60
33	66	0.001:0.002	70
25	75	0.001:0.003	95
20	80	0.001:0.004	122

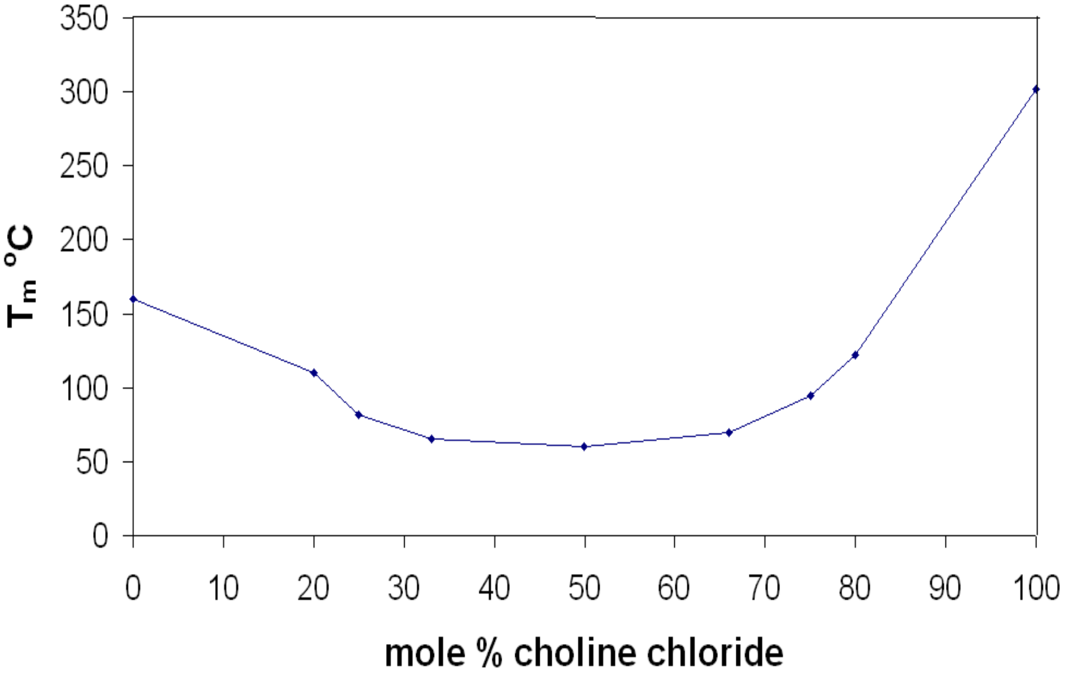


Fig. (3-14): Phase diagram of the melting points of salicylic acid / choline chloride mixtures as a function of composition.

3.5.1.6 Discussion

Table (3-9) illustrated the eutectic points and molar ratio of NaDBS / choline chloride mixture and KDBS /choline chloride mixture and NH_4DBS /choline chloride mixture. It is apparent that the eutectic points of NaDBS / choline chloride mixture and KDBS / choline chloride mixture were formed at molar ratio **1:3** but that eutectic point of NH_4DBS /choline chloride mixture was formed at molar ratio **1:2.** These results suggest a complex between the components or bridging of the NaDBS, KDBS and NH_4DBS between neighboring chloride ions. However, these findings are similar to the eutectics recently reported for carboxylic acids-choline chloride system **(83)**, choline chloride-urea system **(88)** , metal halid-Quatanary ammonium salts systems **(80)**, and organo-niobate molten salts (ionic liquids) **(55)** .

Table (3-8): Compositions and eutectic points of (component A /choline chloride) mixtures.

Component A	Melting point C^o	Eutectic point C^o	Molar ratio of Component A **:**choline chloride
NaDBS	**300**	**135**	**1:3**
KDBS	**277**	**125**	**1:3**
NH_4 DBS	**-5**	**15**	**1:2**
Benzoic acid	**122**	**60**	**2:1**
Salicylic acid	**160**	**60**	**1:1**

As seen Table (3-9) the eutectic points of NaDBS /choline chloride mixture and KDBS /choline chloride mixture and NH_4DBS / choline chloride mixture were 135 ^oC and 125 ^oC and 15 ^oC respectively, where are the pure constituents (choline chloride=302 ^oC and NaDBS =300 ^oC and KDBS =277 ^oC and NH_4DBS =-5 ^oC). There were general trend that eutectic points of NaDBS / choline chloride mixture and KDBS /choline chloride mixture and NH_4DBS /choline chloride mixture were governed by the cations size of ($NH_4^+ < K^+ < Na^+$). The ionic size of ammonium cation is bigger than that of potassium. And the cation size of sodium is the smallest one (NH_4^+= 1.48 A^o , K^+= 1.33 A^o, Na^+= 0.95 A^o). This observation is similar to behavior of the sodium chloride and potassium chloride and ammonium chloride as high temperature molten salts (ionic liquids), which have melting points of (801 ^{o}C , 770 ^{o}C, 338 ^{o}C) respectively.**(31,84)** Also decrease the lattice energy of a crystal for compounds which are predominantly ionic as well as increased ionic charges will result decrease melting point of the system.**(83,84)** As may be noticed, the addition of silver nitrate ($AgNO_3$) (0.1M) to mixtures of NaDBS/choline chloride and KDBS /choline chloride and NH_4DBS/choline chloride, remain unreactive for several weeks in the liquid. That result conclude that chloride ion was complexed by the sulfonate (NaDBS and KDBS and NH_4DBS), that analogous manner to the choline chloride - carboxylic acids system**(83)**, and urea - choline chloride system. **(88)**

Figure (3-13) and Figure (3-14) were Showed the phase diagrams for mixtures of benzoic acid /choline chloride and salicylic acid / choline chloride respectively as a function of composition, which is similar to the eutectics recently reported for carboxylic acids-choline chloride system **(83)**, choline chloride-urea system **(88)**, metal halid-Quatanary ammonium salts systems **(80)**, and organo-niobate molten salts (ionic liquids).**(55)** Table (3-9) is apparent that the eutectic point of benzoic acid / choline chloride was 60 ^{o}C. This point was formed at a composition of 33 mole % choline chloride suggesting a **2:1** complex between the benzoic acid and choline chloride or bridging of the acid between neighboring chloride ions. Also the eutectic point of salicylic acid /choline chloride was 60 °C. But this point was formed at a composition of 50 mole % choline chloride suggesting a **1:1** complex between salicylic acid with choline chloride, which is similar to the eutectic recently reported for the choline chloride-carboxylic acids system.**(83)** and choline chloride-urea system.**(88)** and metal halid-Quatanary ammonium salts systems **(80)**. The benzoic acid/choline chloride mixture and salicylic acid/choline chloride mixture and NH_4DBS /choline chloride mixture have eutectic points correspond with the definition of room temperature molten salt, which melt below 100 °C. Therefore, this can be considered as room temperature molten salt, which is similar to recently reported of carboxylic acids-choline chloride systems**(85, 83)**. And organo-niobate molten salts(ionic liquids).**(55)** The formation of the molten salts and the depression in melting points is the result of hydrogen bonding between benzoic acid and salicylic acid with chloride anion, which is reflected in the recently reported in the carboxylic acid-chloine chloride system.**(85,83)** Also, the difference in the molar ratio between the benzoic acid/ choline chloride mixture and salicylic acid /choline chloride mixture as outlined in table (3-9). This difference is likely attributed to the presence of the hydroxyl group as a functional group of salicylic acid beside to carboxylic group. These is analogous manner recently reported in the carboxylic acid-chloine chloride system.**(85,83)** The addition of sodium hydroxide (40%) to mixtures of (benzoic acid/choline chloride) and (salicylic acid /choline chloride), remain unreactive for several weeks in the liquid. That result conclude that chloride ion was complexed by the associated acid (benzoic acid and salicylic acid). If the acid did dissociate, then the choline salt and HCl would be formed and it is highly unlikely that the carboxylate salt of the choline cation would be liquid at ambient temperature. That is analogous manner to the choline chloride-carboxylic acids system**(83)**, and urea - choline chloride system **(88)**. There are general trend that molten salts that obtained from choline chloride with dodecyl benzene sulfonate salts and choline chloride with carboxylic acids were solids in the room temperature. That can be caused by the presence of aromatic ring, which is manner analogous to that recently reported molten salts based on choline chloride with different compounds that have aromatic ring. **(85)** Optimizing fluidity is of key important to the design of molten salts. It is shown that the fluid properties of these eutectic solvents are linked to the size of the mobile species and the availability of holes of appropriate dimensions to allow mobility. These eutectic mixtures are easy to prepare in pure state. All these systems, which were outlined in table (3-9), were constant and with three phases present, the phase rule tells us that there is no Degree of freedom at the eutectic point according to phase rule since:

Gibb's phase rule: $F=1+C-P$ (86, 87)

F = The number of degrees of freedom.

C = Number of components.

P = Number of phases.

$F=1+2-3=0$

Molten salts that containing sulfonate are have faint brown color and while carboxylic acids were colorless. These differences in colors may be attributed to double bond conjugation; as conjugation of double bonds shifts the absorption maximum to longer wave lengths.**(77)** It is reported that each additional double bond in the conjugated pi-electron system shifts the absorption maximum to longer wave length.**(69)**

3.5.2 Preparation of Molten salts based upon Urea

Molten salts (ionic liquids) can be prepared by mixing their solid components and heating to elevated temperature until fluid achieved. The composition of the molten mixture were taken from 20 mole % to 80 mole % based on add urea to DBS salts of sodium, potassium, ammonium, benzoic and salicylic acid. These mixtures gave five molten salts showing variable melting points. Some of these molten salts may be classified as room temperature molten salt as gave melting point below 100 °C. While the others gave melting points above 100 °C. This method is known to prepare the molten salts as also being used by present workers. **(55,80,83,88)**

3.5.2.1 Preparation of Na DBS /urea mixtures

The phase behavior**:** preparation of NaDBS/urea mixture having the mole composition as shown in table (3-9). The phase diagram is presented in Fig. (3-15). It is obvious that the addition of urea had a significant affect on the melting point of pure NaDBS. The depression of the 300 °C melting points of pure NaDBS was gradually decreased with added urea until the eutectic point of the mixture was reached at 105°C. The composition at this point was 75 mole % of urea **:** 25 mole % NaDBS. The further added urea therefore showed an increase in the melting point of the mixture until it reached 140 °C. The composition was 80 mole % urea and 20 mole % NaDBS. Increasing the added urea therefore showed an decrease in the melting point of the mixture until it reached 133°C, which represents the melting point of pure urea salt.

Table (3-9): Compositions and melting points of NaDBS/urea mixtures.

NaDBS (mole %)	Urea (mole %)	Moles of the components NaDBS :urea	Melting point ^{O}C
80	20	0.004:0.001	187
75	25	0.003:0.001	170
66	33	0.002:0.001	155
50	50	0.001:0.001	120
33	66	0.001:0.002	110
25	75	0.001:0.003	105
20	80	0.001:0.004	140

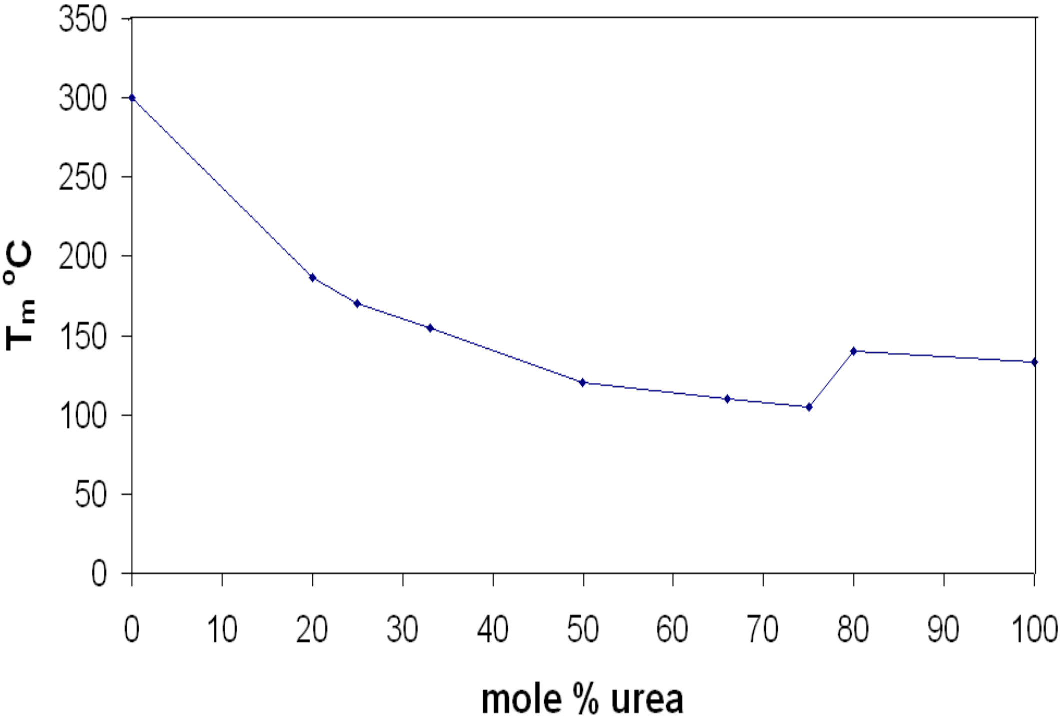


Fig. (3-15): Phase diagram of the melting points of NaDBS /urea mixtures as a function of composition.

3.5.2.2 Preparation of KDBS /urea mixtures

The phase behavior**:** preparation of KDBS / urea mixture having the mole composition as shown in table (3-10). The phase diagram is presented in Fig. (3-16). It is obvious that the addition of urea had a significant affect on the melting point of pure KDBS. The depression of the 277 °C melting point of pure KDBS was gradually decreased with added urea until the eutectic point of the mixture was reached at 100 °C.

The composition at this point was 75 mole % of choline chloride : 25 mole % KDBS. The further added urea therefore showed an increase in the melting point of the mixture until the temperature of 133°C, which represents the melting point of pure urea salt.

Table (3-10): Compositions and melting points of KDBS /urea mixtures.

KDBS (mole %)	Urea (mole %)	Moles of the components KDBS : urea	Melting point °C
80	20	0.004:0.001	180
75	25	0.003:0.001	160
66	33	0.002:0.001	145
50	50	0.001:0.001	115
33	66	0.001:0.002	105
25	75	0.001:0.003	100
20	80	0.001:0.004	130

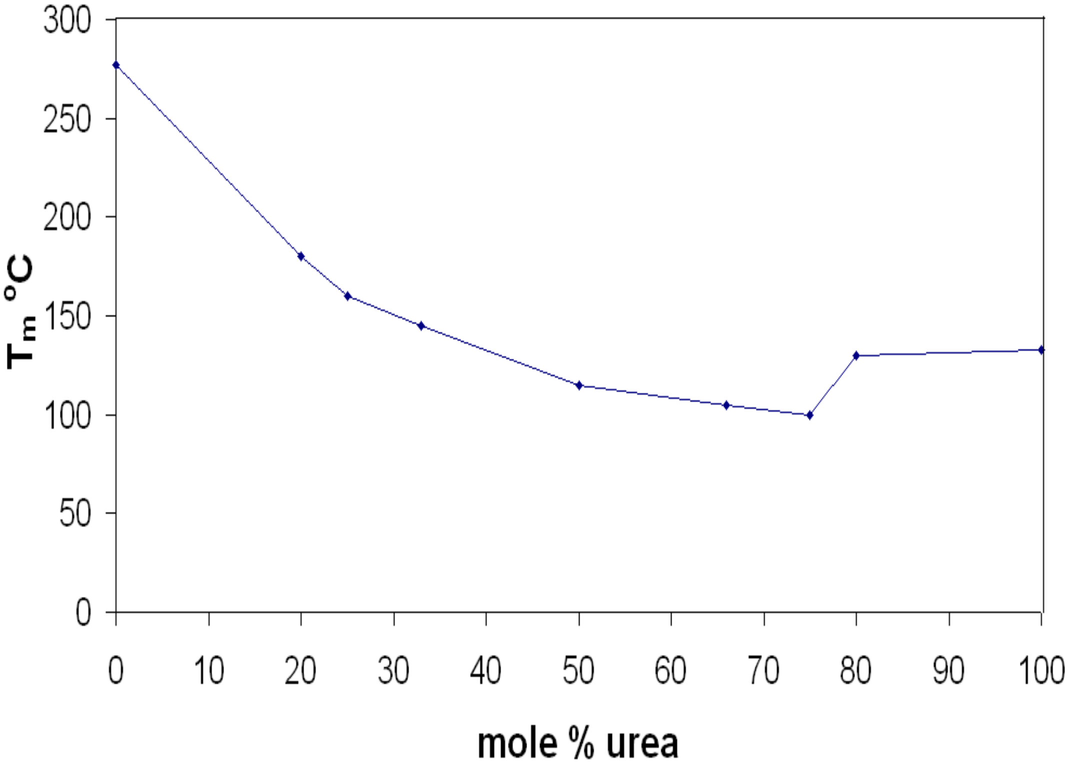


Fig. (3-16): Phase diagram of the melting points of KDBS /urea mixtures as a function of composition.

3.5.2.3 Preparation of NH_4DBS /urea mixtures

The phase behavior**:** preparation of NH_4DBS /urea mixture having the mole composition as shown in table (3-11). The phase diagram is presented in Fig. (3-17). It is obvious that the addition of urea had a significant affect on the melting point of pure NH_4DBS. As it was increased from the -5 ^oC, which representing the melting point of the pure NH_4DBS to 30 ^oC, at which the composition was 20 mole % urea and 80 mole % NH_4DBS. After this point the melting points decrease until it reached the eutectic point at 10^{o}C, at which the composition was 50 mole % of urea and 50 mole % NH_4DBS. Above the mole fraction of 50 mole % urea the melting point increase again until it reached 133 ^{o}C, which representing the melting point of pure urea salt. As seen, the depression in melting point increased relatively latter until the mole % of urea was 20 %, where a gradual decreasing of melting point was recorded until the melting point of the eutectic point was reached. Furthermore, this behavior was similar to the fast increase in melting point when mole % of urea was increased.

Table (3-11): Compositions and melting points of NH_4DBS /urea mixtures.

NH_4DBS (mole %)	Urea (mole %)	Moles of the components NH_4DBS :urea	Melting point ^{O}C
80	20	0.004:0.001	30
75	25	0.003:0.001	25
66	33	0.002:0.001	20
50	50	0.001:0.001	10
33	66	0.001:0.002	25
25	75	0.001:0.003	45
20	80	0.001:0.004	50

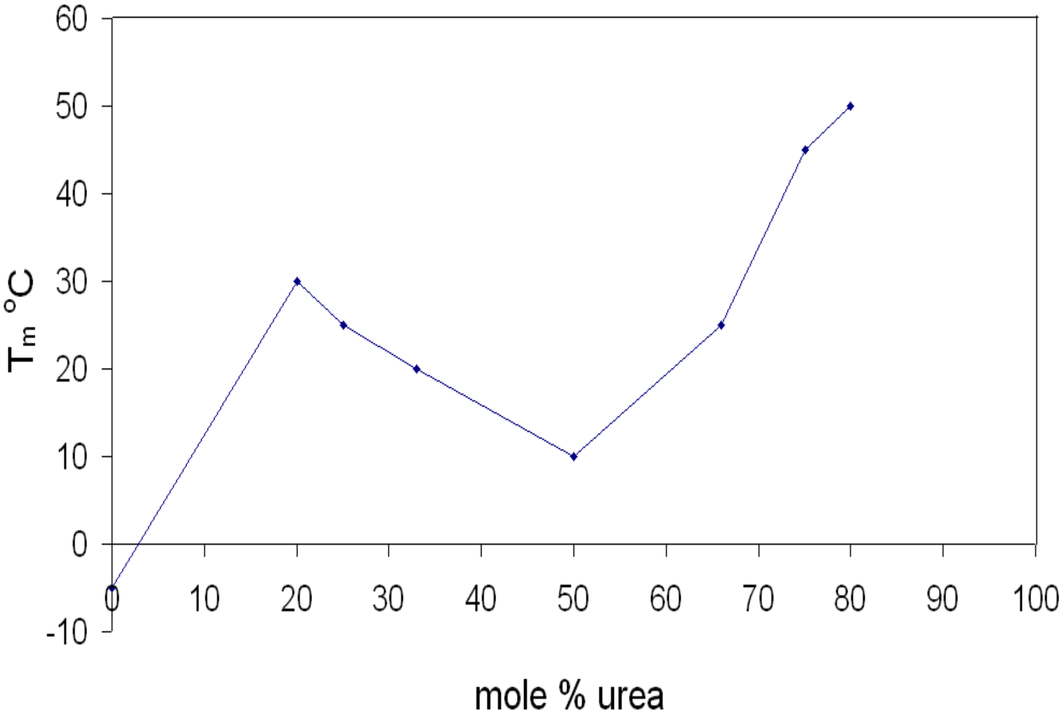


Fig. (3-17): Phase diagram of the melting points of NH_4DBS / urea mixtures as a function of composition.

3.5.2.4 Preparation of Benzoic acid/urea mixtures

The phase behavior**:** preparation of benzoic acid / urea mixture having the mole composition as shown in table (3-12). The phase diagram is presented in Fig. (3-18). It is obvious that the addition of urea had a significant effect on the melting point of pure benzoic acid. As it was decreased sharply from the 122 °C, which representing the melting point of the benzoic acid until it reached the eutectic point at 75 °C, at which the composition was 33 mole % of urea and 66 mole % of benzoic acid. Above the mole fraction of 33 mole % urea the melting point increase until 85 °C, at which the composition at this point was 66 mole % of urea and 33 mole % of benzoic acid. Above 85 °C the melting point increase gradually until it reached 133 °C, which representing the melting point of pure urea.

Table (3-12): Compositions and melting points of benzoic acid/urea mixtures.

Benzoic acid (mole %)	Urea (mole %)	Moles of the components benzoic acid : urea	Melting point ^{O}C
80	20	0.004:0.001	90
75	25	0.003:0.001	83
66	33	0.002:0.001	75
50	50	0.001:0.001	80
33	66	0.001:0.002	85
25	75	0.001:0.003	105
20	80	0.001:0.004	118

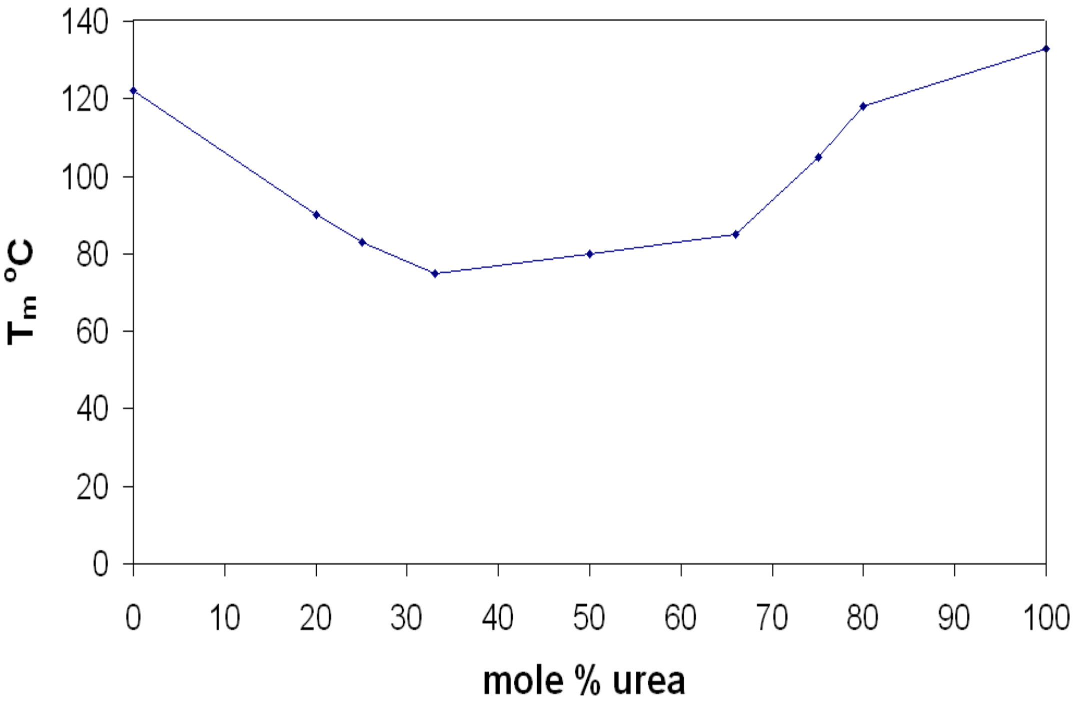


Fig. (3-18): Phase diagram of the melting points of benzoic acid / urea mixtures as a function of composition.

3.5.2.5 Preparation of salicylic acid /urea mixtures

The phase behavior**:** preparation of salicylic acid /urea mixture having the mole composition as shown in table (3-13). The phase diagram is presented in Fig. (3-19). It is obvious that the addition of urea had a significant effect on the melting point of pure salicylic acid. The depression of the 160 °C melting point of pure salicylic acid was gradually decreased with added urea until an eutectic point of the mixture was reached at 77°C, at which the composition was 66 mole % of urea **:** 33 mole % salicylic acid. The further added urea therefore showed an increase in the melting point of the mixture until the temperature of 133 °C, which represents the melting point of pure urea.

Table (3-13): Compositions and melting points of salicylic acid /urea mixtures.

Salicylic acid (mole %)	Urea (mole %)	Moles of the components salicylic acid :urea	Melting point °C
80	20	0.004:0.001	120
75	25	0.003:0.001	100
66	33	0.002:0.001	90
50	50	0.001:0.001	83
33	66	0.001:0.002	77
25	75	0.001:0.003	105
20	80	0.001:0.004	125

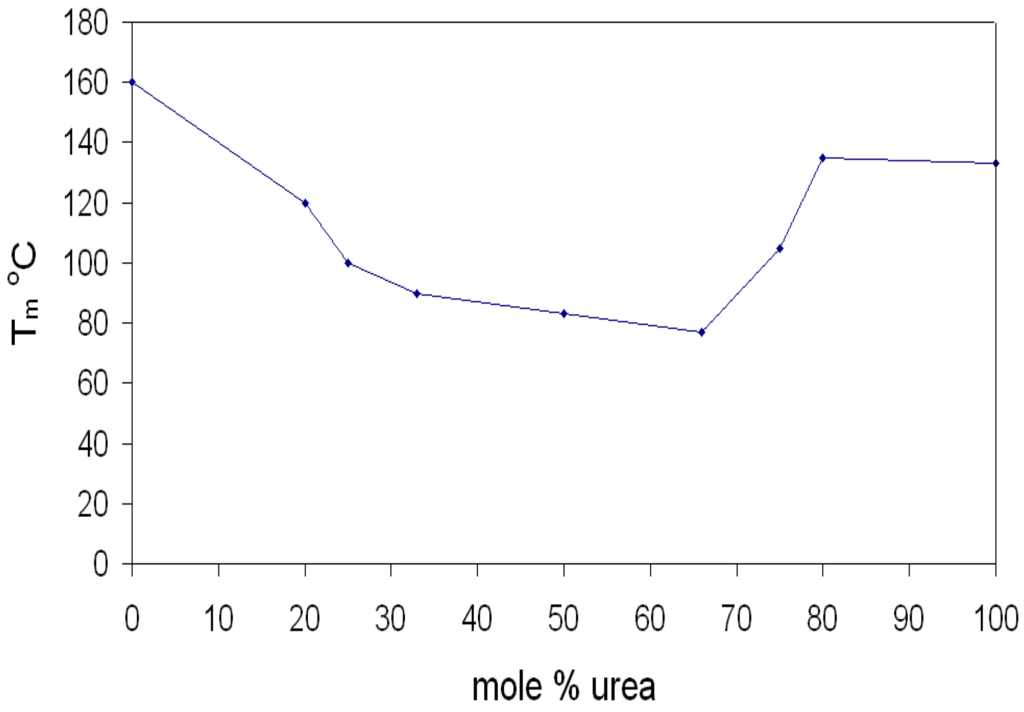


Fig (3-19): Phase diagram of the melting points of salicylic acid / urea mixtures as a function of composition.

3.5.2.6 Discussion

Table (3-14) illustrated the eutectic points and molar ratio of NaDBS / urea mixture and KDBS /urea mixture and NH_4DBS /urea mixture. It is apparent that the eutectic points of NaDBS / urea mixture and KDBS /urea mixture were formed at molar ratio **1:3** but that eutectic point of NH_4DBS /urea mixture was formed at molar ratio **1:**1. These results suggest a complex between the compontents. However, these findings are similar to the eutectics recently reported for carboxylic acids-choline chloride system **(83)**, choline chloride-urea system **(88)**, metal halid-Quatanary ammonium salts systems **(80)**, and Organo-niobate molten salts (ionic liquids).**(55)**

Table (3-14): compositions and eutectic points of component A /urea mixtures.

Component A	Melting point C°	Eutectic point C°	Molar ratio of Component A :urea
NaDBS	**300**	**105**	**1:3**
KDBS	**277**	**100**	**1:3**
NH_4DBS	**-5**	**10**	**1:1**
Benzoic acid	**122**	**75**	**2:1**
Salicylic acid	**160**	**77**	**1:1**

As seen Table (3-14) the eutectic points of NaDBS / urea mixture and KDBS / urea mixture and NH_4DBS / urea mixture were 105 ^oC and 100 ^oC and 10 ^oC respectively, where are the pure constituents (urea=133^oC and NaDBS =300 ^oC and KDBS =277 ^oC and NH_4DBS =-5 ^oC). There were general trend that eutectic points of NaDBS / urea mixture and KDBS / urea and NH_4DBS / urea mixture were governed by the cations size of ($NH_4^+ < K^+ < Na^+$). The ionic size of ammonium cation is bigger that of potassium. And sodium is the smallest one (NH_4^+= 1.48 A^o , K^+= 1.33 A^o, Na^+= 0.95 A^o). This observation is similar to behavior of the sodium chloride and potassium chloride and ammonium chloride as high temperature molten salts, which have melting points of (801 ^oC , 770 ^oC, 338 ^oC) respectively. **(31,84)** Also decrease the lattice energy of a crystal for compounds which are predominantly ionic as well as increased ionic charges will result decrease melting point of the system.**(83,84)**

Figure (3-18) and Figure (3-19) were Showed the phase diagrams for mixtures of benzoic acid / urea and salicylic acid / urea respectively as a function of composition, which is similar to the eutectic recently reported for carboxylic acids-choline chloride system (**83)**, choline chloride-urea system**(88)**, metal halid-Quatanary ammonium salts systems **(80)**,and organo - niobate molten salts (ionic liquids). **(55)** Table (3-14) is apparent that the eutectic point of benzoic acid / urea was 75 ^oC this point was formed at a composition of 66 mole % benzoic acid and 33 mole % urea suggesting a **2 : 1** complex between the benzoic acid and urea ; also that a eutectic point of salicylic acid / urea was 77 ^oC but this point was formed at a composition of 33 mole % salicylic acid and 66 mole % urea suggesting a **1 : 2** complex between salicylic acid with urea, which is similar to the eutectic recently reported for the choline chloride-carboxylic acids system.**(83)** choline chloride-urea system.**(88)** and metal halid-Quatanary ammonium salts systems**(80)**. The benzoic acid/urea mixture and salicylic acid /urea mixture and NH_4DBS /urea mixture have eutectic points correspond with the definition of room temperature molten salt, which melt below 100 ^oC. Therefore, this can be considered as room temperature molten salt, which is reflected in to recently reported of carboxylic acids-choline chloride systems.**(85,83)** The formation of the molten salts and the depression in melting points is the result of hydrogen bonding between benzoic acid and salicylic acid with urea molecule, which is reflected in the recently reported in the carboxylic acid-chloine chloride system.**(85,83)** Also, the difference in the molar ratio between the benzoic acid/urea mixture and salicylic acid / urea mixture as outlined in table (3-14). This different is likeyl attributed to the presence of the hydroxyl group as a functional group of salicylic acid beside to carboxylic group and the carbonyl group of the urea. These is analogous manner recently reported in the carboxylic acid-chloine chloride system.**(85,83)** Recently reported in the carboxylic acid - chloine chloride system.**(85,83)** And choline chloride-urea system.**(88)** The addition of sodium hydroxide (40%) to mixtures of benzoic acid / urea and salicylic acid / urea, remain unreactive for several weeks in the liquid. That results conclude that the urea molecule is complexed by the associated acid (benzoic acid and salicylic acid); that analogous manner to the choline chloride-carboxylic acids system**(83)**, and urea - choline chloride system reported previously**(88)**. There are general trend that molten salts that obtained from urea with dodecyl benzene sulfonate salts and urea with carboxylic acids were solids in the room temperature. That can be caused by the presence of aromatic ring caused this, which is similar to that recently reported molten salts based on choline chloride with different compounds that have aromatic ring. **(85)** All these systems, which were outlined in table (3-14), were constant and with three phases present, the phase rule tells us that there is a single Degree of freedom at the eutectic point according to phase rule since:

Gibb's phase rule: $F=1+C-P$ (86, 87)

F = the number of degrees of freedom.

C = number of components.

P = number of phases.

$\boldsymbol{F=1+2-3=0}$

Molten salts (ionic liquids) that containing sulfonate is having faint brown color and while carboxylic acids were colorless.

3.6 Conclusion

Preparation of the molten salts (ionic liquids) involved two methods, the first was metathesis of potassium dodecyl benzene sulfonate with choline chloride and phenyl trimethyl ammonium iodide in THF, which produced choline dodecyl benzene sulfonate and phenyl trimethyl ammonium dodecyl benzene sulfonate, and the effect of cation size was reflected on their melting point as they showed 118 ^{o}C and 91.9 ^{o}C respectively. The second method was the solid mixing of components with heating as included choline chloride was mixed with three dodecyl benzene sulfonate of sodium, potassium and ammonium when the effect of cations change in dodecyl benzene sulfonate were found to follow the order sodium, potassium, ammonium in decreasing the melting point as the mixtures as the mixtures were found to have 135 ^{o}C, 125 ^{o}C, 15 ^{o}C respectively. Choline chloride was mixed with salicylic acid and benzoic acid to elucidate the effect by possible hydrogen bond formation in the mixture on the melting point when they showed a similar eutectic point of 60 ^{o}C .for comparison, urea was also mixed with the same previous compounds and found to showed a melting points of 105 ^{o}C, 100 ^{o}C, 10 ^{o}C, 75 ^{o}C, and 77 ^{o}C respectively. The melting point/composition of the 10 previous ionic liquid mixtures were drawn to determine their nature and the eutectic points .While the two molten salts (ionic liquids) were identified by infrared measurements and differential scanning calorimetric determination indicated their melting points and found to be stable up to 200 ^{o}C.

3.7 Suggestions for Future work

The following suggestions can be postulated to ensure completion of the study in this work:

1. Investigating the hydrogen bonding formation with either choline chloride or sulfonate salts by solid formation of ionic liquids with other salts containing hydroxide or oxygen .
2. Extensive chemical identification of the products such as (NMR, CHN, X-ray).
3. Testing the resulted molten salts (ionic liquids) by (IR, DSC, T.G).

4. Determination of the physical properties of the Room temperature molten salts (Ionic liquids) such as (Density, Viscosity, and Conductivity).

Examining Committee's Certification

We, the Examining Committee, certify that we read this thesis and have examined the student (**Ahaad Diwan Sajet**) in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science, in Chemistry.

Chairman

Signature:

Name:

Date:

Member

Signature:

Name:

Date:

Member

Signature:

Name:

Date:

Supervisor

Signature:

Name:

Date:

Approved for the College of Graduate Studies

Signature:

Name**: Assist. Prof. Dr. LAITH ABDUL AZIZ Al-ANI**

Address: Dean of the College of Science Al-Nahrain University

Date:

Supervisor certification

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Science, and Al-Nahrain University as partial requirements for the **Degree of Master of Science in Chemistry.**

Signature:
Name: Dr. Hadi M.A. Abood
Date:

In view of the available recommendation, I forward this thesis for debate by the examining committee.

Signature:
Name: Assist. Prof. Dr. Salman A. Ahmed
Head of Chemistry Department
College of Science
Al-Nahrain University

Acknowledgement

Above all else, I want to express my great thanks to ALLAH for the uncountable gifts and for helping me to present this thesis.

The honor is mine to express my sincere thanks and gratitude to my supervisor Dr. hadi M . A. abood for his guidance and sustained efforts throughout this work.

I'm greatly indebted for the assistance given to me by Head and staff of Chemistry Department, College of Science, Al-Nahrain University.

I would like to express my deep thanks to my parents who has supported me during my study.

Finally, to those who helped in one way or on other, I would like to express my warmest gratitude.

Ahaad 2008

Chapter two

Experimental

2.1 Chemicals

The chemicals used in this work were listed in table (2-1).

Table (2-1): Specification of supplied chemicals.

Substance	**source**	**Purity (%)**
Absolute ethanol	Fluka	99.9
Ammonium hydroxide	BDH	98
Acetonitrile	BDH	99
Benzoic acid	BDH	99
Choline chloride	MERCH	99
Dodecyl benzene sulfonic acid	The general company for vegetable oils products. Iraq	98
Phenyl trimethyl ammonium iodide	BDH	99
Potassium hydroxide	BDH	99
Salicylic acid	Fluka	99
Sodium hydroxide	Fluka	98
Sodium Dodecyl benzene sulfonate	The general company for vegetable oils products. Iraq	98
Tetrahydrofurn	BDH	99
Urea	BDH	99

-

2.2 Instrumental

1. **Differential Scanning Calorimetry measurements**

The thermal analysis Figures (3-8) and (3-9) were recorded by ***SHIMADZU*** DSC-60 differential scanning calorimatry (DSC), Japan, 2004, with heat rate of 2 °C /min from room temperature , The weight of the sample was 10 mg. and the analysis was performed by ministry of sciences and technology. Iraq

2. **FTIR measurements**

The infrared spectra were recorded on a ***SHIMADZU*** 8300 Fourier Transform Infrared Spectrophotometer (F.T.IR), Japan, using the (KBr) disk in the wave number range (4000-400) cm^{-1}, was performed by Al-Nahrain University. Also another infrared spectra were recorded on a ***SHIMADZU*** 8400 Fourier Transform Infrared Spectrophotometer (FTIR) was performed by central organization of standardization and quality control.

3. **Melting points measurements**

Melting points of prepared compounds and the mixtures of molten salts were recorded using hot stage Gallen Kamp (England) type M.F.B. 600.01.

2.3 Chemical Analysis:

1. **Titration:** the concentration of dodecyl benzene sulfonic acid was determined by titrating of dodecyl benzene sulfonic acid with NaOH (1%) in presence of phenolphthalein as indicator, the concentration of acid was (98%).

2.4 Heating Technique

The following technique can be used for solid mixing of components to preparation of molten salts (ionic liquids) :

1. Hot plate. 2. Stand. 3. Clamp. 4. Thermometer 5. Beaker with oil
6. Beaker with mixture. 7. Glass rod.

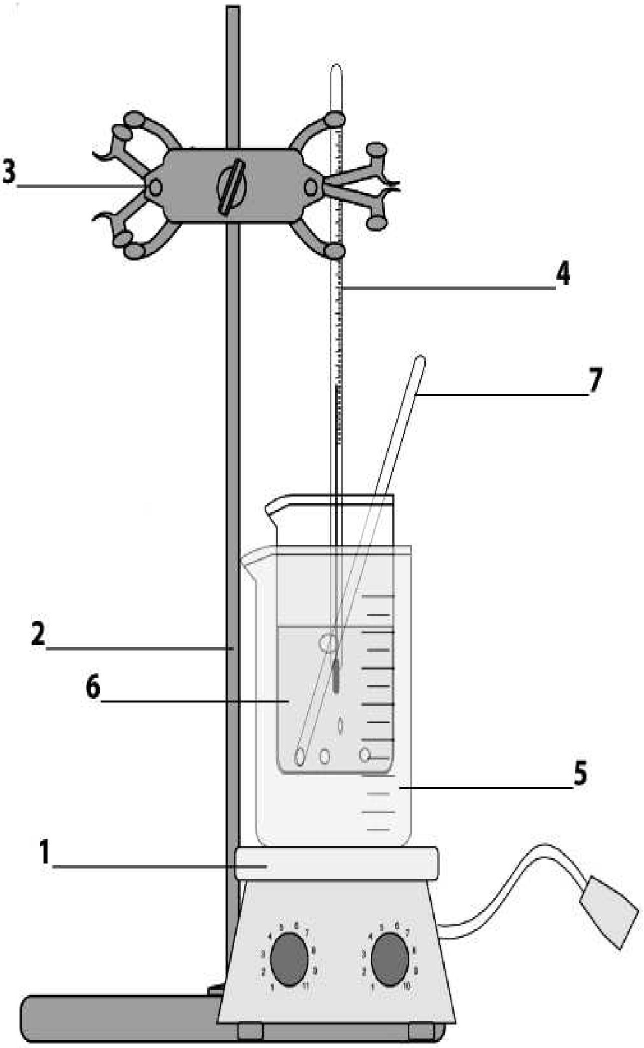
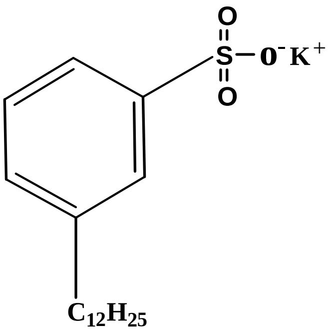


Fig. (2-1): Heating technique for solid mixing of components.

2.5 Synthesis of Dodecyl benzene sulfonate salts

2.5.1 Synthesis of Potassium dodecyl benzene sulfonate [KDBS]

Potassium Dodecyl benzene sulfonate [KDBS] are prepared by the neutralization (1mole:1mole) of dodecyl benzene sulfonic acid (98%) with potassium hydroxide (KOH) (40%) solution. Litmus paper was used to indicate the acid / base reaction. At pH=7 the reaction was completely taking place. To collect the solid residue vacuum filtration was used. The product was left in vacuum oven for (6 h) at 70 °C to ensure evaporate the moisture and the product were crushed and stored in a desicator to provide a dry storage conditions. Melting point= 277 °C, yield= 95%, The product have faint yellow color.

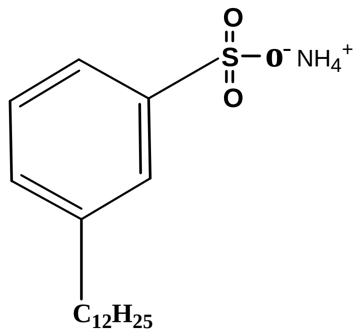


potassium dodecyl benzene sulfonate

[KDBS]

2.5.2 Synthesis of Ammonium dodecyl benzene sulfonate [NH_4DBS]

Ammonium Dodecyl benzene sulfonate [NH_4DBS] is prepared by the neutralization (1mole:1mole) of dodecyl benzene sulfonic acid (98%) with ammonium hydroxide (NH_4OH) (50%) solution. Litmus paper was used to indicate the acid / base reaction. At pH=7 the reaction was completely taking place. To collect the solid residue vacuum filtration was used. The product was left in vacuum oven for (6 h) at 70 °C to ensure evaporate the moisture and the product were stored in a desicator to provide a dry storage conditions. Melting point= -5 °C, yield= 98%, The product have faint yellow color.



ammoniumdodecyl benzene sulfonate
[NH_4DBS]

2.6 Preparation of Molten salts

There are two methods to prepare molten salts:

1) Metathesis of potassium dodecyl benzene sulfonate with choline chloride and phenyl trimethyl ammonium iodide in THF, which were described in the following sections.
2) Solid state mixing of components, which were described in the following sections.

2.6.1 Metathesis of Choline dodecyl benzene sulfonate

Two solutions of the reactants were prepared in THF solvents the first is of choline chloride of (0.003 mole, 0.418 g) was dissolved in 50 ml THF while another (0.003 mole, 1.092 g) of potassium dodecyl benzene sulfonate, also dissolved in another portion of 50 ml THF solvent, the first solution was added to the second solution at room temperature. When a continuous stirring was applied for 4 hours. During the course of stirring time a white precipitate was observed to form, the mixture was left to settle for 2 hours at (- 10 ^oC) in a freeze container, when this mixture left to reach room temperature, the solid white precipitate was separated by filtration. The weight of the precipitate (KCl) was (0.11 g), the precipitate was formed to contain chloride as confirmed by $AgNO_3$ test, the solvent was removed by rotary evaporation, the solid product, which was obtained after the evaporation, treated with acetonitrile solvent where the unreacted starting materials were dissolved and the product was precipitate with faint yellow color. The excess of acetonitrile solvent was evaporated from the product by heating in vacuum oven for 6 hours at 50 ^oC.

2.6.2 Metathesis of Phenyl trimethyl ammonium dodecyl benzene sulfonate

Two solutions of the reactants were prepared in THF solvents the first is of phenyl trimethyl ammonium iodide of (0.003 mole, 0.789 g) was dissolved in 50 ml THF while another (0.003 mole, 1.092 g) of potassium dodecyl benzene sulfonate, also dissolved in another portion of 50 ml THF solvent, the first solution was added to the second solution at room temperature. When a continuous stirring was applied for 4 hours. During the course of stirring time a pale yellowish white precipitate was observed to form, the mixture was left to settle for 2 hours at (- 10 ^oC) in a freeze container, when this mixture left to reach room temperature, the solid a pale yellowish white precipitate was separated by filtration, the weight of the precipitate (KI) was (0.19 g), the precipitate was formed to contain iodide as confirmed by $AgNO_3$ test. The solvent was removed by rotary evaporation, the solid product, which was obtained after the evaporation, treated with acetonitrile solvent where the unreacted starting materials were dissolved and the product was precipitate with pale violet color. The excess of acetonitrile solvent was evaporated from the product by heating in vacuum oven for 6 hours at 50 °C.

2.6.3 Preparation of Molten salts (Ionic liquids) by mixing the solid components.

In this method the proper weights of the components of the molten salt to be prepared dried, weighted and mixed together. The mixture then milled and put in a small beaker as Fig (2-1). the mixture then gradually heated with continuous stirring until it start to melt, when complete liquid phase is achieved, the mixture was heated top to 10 °C above that temperature, the liquid (melt) was left for a round 10 minute, when the heating was stopped and the melt kept to cool gradually and the melting points were taken as the temperature at which the first solid began to form. The solid state of the melts were crushed, and stored in a desicator to provide a dry storing condition.

2.6.3.1 Preparation of Molten mixtures of Dodecyl benzene sulfonate salts with Choline chloride

Dodecyl benzene sulfonate salts(DBS salts), which were used to prepare molten salts with choline chloride are sodium dodecyl benzene sulfonate [NaDBS] and potassium dodecyl benzene sulfonate [KDBS] and ammonium dodecyl benzene sulfonate [NH_4DBS]. A proper mixtures of (DBS salts / choline chloride) containing a molar ratio from 20 mole

% to 80 mole % choline chloride were prepared as described in (section 2.6.3). All prepared melt were very viscous liquids with faint brown color. he melting points of each composition were double checked by measuring them with Gallen kamp instruments which were found to be close to there observed visually.

2.6.3.2 Preparation of Molten salts of Benzoic acid/choline chloride mixtures

A proper mixture of (benzoic acid / choline chloride) containing a molar ratio from 20 mole % to 80 mole % choline chloride were prepared as described in (section 2.6.3). All prepared melt were of homogeneous colorless liquids . The melting points of each composition were double checked by measuring them with Gallen kamp instruments which were found to be close to there observed visually.

2.6.3.3 Preparation of Molten salts of Salicylic acid /choline chloride mixtures

A proper mixture of salicylic acid /choline chloride containing a molar ratio from 20 mole % to 80 mole % choline chloride were prepared as described in (section 2.6.3). All prepared melt were of homogeneous colorless liquids. The melting points of each composition were double checked by measuring them with Gallen kamp instruments which were found to be close to there observed visually.

2.6.3.4 Preparation of Molten mixture of Dodecyl benzene sulfonate salts with Urea

A proper mixtures of (DBS salts / urea) containing a molar ratio from 20 mole % to 80 mole % urea were prepared as described in (section 2.6.3). All prepared melt were very viscous liquids with faint brown color. The melting points of each composition were double checked by measuring them with Gallen kamp instruments which were found to be close to there observed visually.

2.6.3.5 Preparation of Molten salts of Benzoic acid/ urea mixtures

A proper mixture of benzoic acid /urea containing a molar ratio from 20 mole % to 80 mole % urea were prepared as described in (section 2.6.3). All prepared melt were of homogenous colorless liquids. The melting points of each composition were double checked by measuring them with Gallen kamp instruments which were found to be close to there observed visually.

2.6.3.6 Preparation of Molten salts of Salicylic acid/urea mixtures

A proper mixture of salicylic acid /urea containing a molar ratio from 20 mole % to 80 mole % urea were prepared as described in (section 2.6.3). All prepared melt were of homogenous colorless liquids.

Chapter one
Introduction

1.1 Historical Introduction

The early history of room temperature molten salts (ionic liquids) began in 1914 when the first room temperature molten salt was studied by Walden **(1)**. He reported the physical properties of ethyl ammonium nitrate; which has a melting point 12 °C and formed by the reaction of ethylamine with concentrated nitric acid. Hurly and Weir **(2)** have stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. In 1970 and 1980 Osteryoung et.al **(3, 4)** and Hussy et.al **(5, 6, 7)** carried out extensive studies on organic chloride - aluminum chloride ambient temperature ionic liquid and the first major review of room temperature ionic liquids as written by Hussey **(8)**. The ionic liquids based on Aluminum chloride ($AlCl_3$) can be regarded as the first generation of room temperature ionic liquids. The hygroscopic nature of $AlCl_3$ based ionic liquids has delayed the progress in their use. In many science applications they must be prepared and handled under inert gas atmosphere. Thus, the syntheses of air and water stable ionic liquids, which are considered as the second generation of ionic liquids attracted further interest in the use of ionic liquids in various fields. In 1992, Wilkes and Zaworotko reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium $[EMIM]^+$ cation with either tetrafluoroborate or hexaflourophosphate as anions for example $[EMIM]^+[BF_4]^-$, was prepared via metathesis of $[EMIM]^+I^-$ with $Ag[BF_4]$ in methanol.**(9)** Unlike the chloroaluminate ionic liquids, these ionic liquids could be prepared and safely stored outside of an inert atmosphere.(10) Generally, these ionic liquids are water insensitive, however, the exposure to moisture for a long time can cause some change in their physical and chemical properties. Beside the previous scientists who are pioneers in the field of ionic liquids, there are several scientists, e.g. welton, wasserscheid (11), MacFarlane(12), Endres (13), and others, who entered this field having a strong impact in introducing the ionic liquids in many applications. Rogers is one of the highly cited authors in the field of ionic liquids. They focused on the syntheses and characteristics of environmentally friendly ionic liquids as green solvents. They measured and published physicochemical properties for many ionic liquids with the aim of providing data to start evaluating the use of ionic liquids in a variety of processes. Also, they work on the development of new materials from cellulose utilizing ionic liquids.(13, 14)

Wasserscheid (11) is an active member of the ionic liquids community and focuses on the preparation and characterization of ionic liquids for use in the biphasic catalysis. For example, he could show that the use of hexaflorophosphate ionic liquids allow selective, biphasic oligomerization of ethylene to 1-olefins. Together with Welton; he edited a very important book entitled "ionic liquids in synthesis ", which presents the synthesis and physicochemical properties of ionic liquids as well as their use in catalysis ,polymerization, and organic and inorganic synthesis. (13)

MacFarlane has prepared a new air and water stable ionic liquids with the purpose of employing such ionic liquids as indicators for sensing and displaying an environmental parameter such as humidity.(12) This process was controlled by the color change of the ionic liquids where they are synthesized with either a colored cation or anion, so that the ionic liquids themselves are sensors. Also, he has published many papers on the use of ionic liquids in dectropolymerization and in the batteries. (13)

Ionic liquids are made by the quarternerization of the appropriate amine. This has been used to prepare a number of 1- alkyl -3-methylimidazolium trifluoromethanesulfonate salts. A methyl triflate is reacted with a stoichiometric amount of the 1-alkyl-imidazole in 1, 1, 1-trichloromethane. Since the methyl triflate is sensitive to moisture; the reaction must be carried out under anhydrous conditions**.** (10)

1.2 Molten salts (ionic liquids)

Molten salts (Ionic liquids) are salts that melt at ambient temperature . The term "molten salt" is self –descriptive; it is molten salts. Another common name is fused salts (15). The simplest example of a molten salt would be to take sodium chloride ("table salt") and heat it to a red heat (greater than 801 °C or 1474 F) where it would melt to a liquid. This liquid is stable, has a heat capacity similar to water (by volume) and flows much like water does (16,17).

Both sodium and chloride are notoriously reactive; sodium is one of the most electropositive substance (Element losing) and chlorine one of the most electronegative (Element gaining). These two opposite ions readily join to form stable sodium chloride via a strong ionic bond. The melting point of sodium chloride is 801 °C (1474 F); at which it becomes a liquid, and thus a" molten salt". (18)

Recently, interest in room-temperature molten salt has gone up due to their unique features and diverse applications. Room-temperature molten salts is mainly composed of cations and anions. Different combinations of cations and anions give rise to different room-temperature molten salt of the required properties. They are used as green substitutes for volatile organic solvents (19, 20) and also for industrial applications (21). Room-temperature molten salts (ionic liquids) have some unique properties such as high conductivity, negligible vapor pressure, nonflammable nature, wide electrochemical windows, wide liquidous temperature range (-96 °C to 300 °C) (22). These properties make them quite useful as alternative green solvents for syntheses and industrial applications.

With many chemical transformations taking place in solution, the role of solvent is vital. Although, in principle, any liquid could be employed as a solvent, polar organic solvents have been extensively used for both synthetic chemistry and extraction technologies and have largely superseded water, which was widely employed historically. However, the ever-increasing awareness of the detrimental health and environmental effects of organic solvents has given chemists the impetus to search for "Green Technologies".(23)

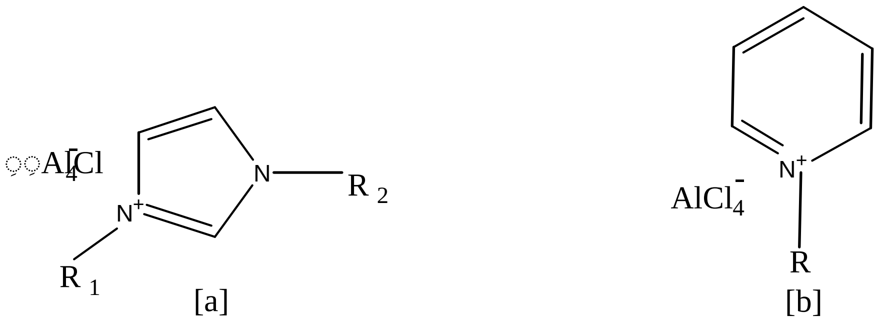
The obviously ideal situation for a chemical process, from an ecological point of view, involves no solvent.(24) Although many reactions can be performed without solvent, chemistry remains dominated by processes taking place in solution. Note that most of solvents have a significant solubility in the water phase, and therefore must be stripped from the water before it leaves the process, both for economic and environmental reasons. Moreover, if the solvent cannot be effectively recovered for recycle back to the system (reactor, extractor, etc) then the process will not be economically viable. (25)

Nowadays, there are several alternatives under investigation as solvents including the resurgence of water (26), perflouirnated hydrocarbons (27), and supercritical fluids, in particular CO_2 .(28)

Room temperature molten salts (ionic liquids) have been known since the beginning of this century (29), and are emerging as an attractive, alternative, green technology in both organic and organometallic chemistry. The synthesis and physical-chemical properties of molten salts, in particular halo-aluminates derivatives, have been extensively studied and a series of books on this subject is now available **(15)**, the use of ionic liquids as solvents for catalysis and organic synthesis has been recently reviewed.

Molten salts, or ionic liquids, can be described as liquid compounds that display ionic-covalent crystalline structures. This definition involves pure inorganic compounds (sodium chloride, m.p=801°C), organic compounds (tetra butyl phosphonium chloride, m.p=80 °C) or even eutectic mixtures of inorganic salts (such as lithium chloride/potassium chloride, m.p=352 °C) or organ mineral combinations (triethylammonium chloride/copper chloride, m.p=25 °C).

Organo-Choroaluminate ionic liquid, especially those resulting from the combination of N-alkylpyridinium chloride or 1, 3-dialkylimidazolium chloride and aluminum chloride scheme.(1-1), have a broad range of liquid phase down to -88 °C . **(14)**



Scheme (1-1): (a) 1, 3-dialkylimidazolium chloride and aluminum chloride and (b) N-alkylpyridinium chloride and aluminum chloride.

These liquids have been widely used in electrochemical technologies as solvents for highly charged complex ions, electronic absorption spectra, for organic synthesis and catalysis, including Ziegler-Natta reactions.**(30)**

Recently, room-temperature ionic liquids solvent have been extensively used in synthesis and also found application in analytical chemistry. **(31)**

Room-temperature molten salts (ionic liquids) are not always green, halides containing RTILS are very unstable to moisture and are hydrolyzed to produce harmful, corrosive volatile such as HF, POF_3, etc.**(32)**

The properties such as melting point, viscosity, density and hydrophobic can be varied by simple changes with the structure of the ions. For example, the melting point of 1-alkyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate is a function of the length of the 1-alkyl group, and form liquid crystalline phases for alkyl chain length over 12 carbon atoms.**(11)**

1.3 Importance of molten salt (ionic liquid)

Molten salt (Ionic liquid) are composed of only ions, they show very high ionic conductivity, non-volatility and non-flammability. The nonflammable liquids with high ionic conductivity are practical material for use in the electrochemistry. **(33)**

One of the interesting features of molten salt is their ability to conduct electricity. For example, solid sodium chloride (NaCl) does not conduct electricity; it is an insulator. If NaCl is placed into water, the mutual attraction both sodium and chloride have for water molecules cause their bonds to break. Dissolving and form ions (charged atoms or molecules) with in the water. These electrically charged ions can conduct electricity if there is a voltage potential (electric field). (33)

Electrochemistry basically needs two materials: electro conductive materials and ion conductive materials. Ionic liquid open the possibility of improving ion conductive materials.(13) The aqueous salt solution is one of the best electrolyte solutions for electrochemical studies. However, because water is volatile it's ions impossible to use this at wide temperature range or on a very small scale. Many other organic polar solvents have been used instead of water to prepare electrolyte solutions. They however, have more or less the same drawback, depending on the characteristics. The material known to be a nonvolatile ion conductor is the polymer electrolyte. There are some statements that the ionic liquids are thermally stable and never decompose. (14) This kind of statement has led a mistuned-standing that the ionic liquids indestructible. In fact the answer is no. However, while inorganic salts are entirely stable, the thermal stability of organic salts depends largely on their structure. Since most recently reported ionic liquids are organic compounds, their degradation begins at the weakest covalent bond. Nevertheless, molten salt are stable enough for ordinary to use at temperature of 200 ^{o}C to 300 ^{o}C. So it is not difficult to design noval molten salt (Ionic liquid) that can be decomposed at certain temperature or by certain trigger. It is also possible to design catalyst (or catalytic systems) that can decompose target ionic liquids. Some catalysts such as metal oxides or metal complexes have the potential to become excellent catalysts for the decomposition of certain molten salt under wild conditions. (18, 32)

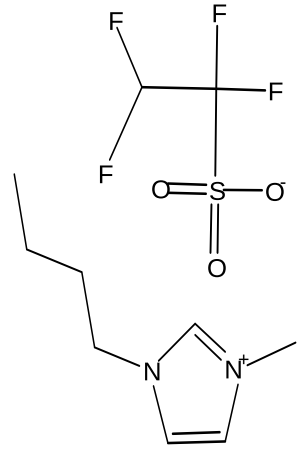
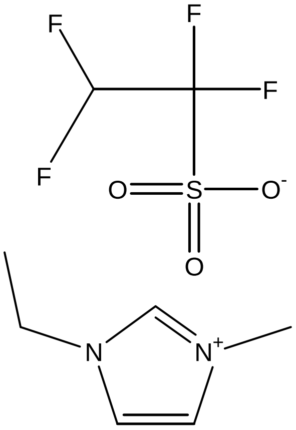
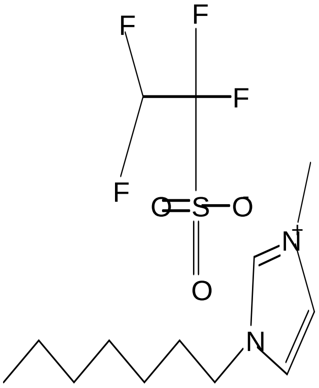
1.4 Types of Molten salts (Ionic liquids)

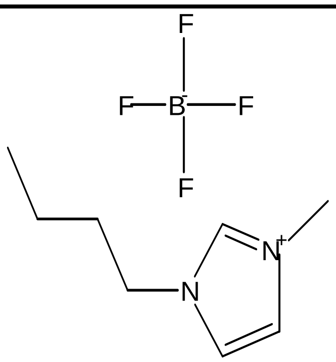
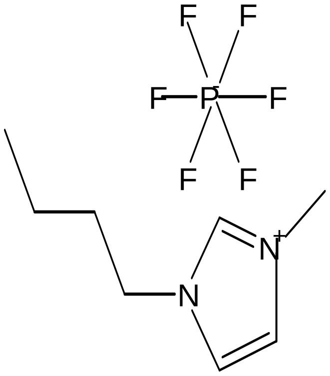
1.4.1 Room- temperature Ionic liquid (RTIL)

Room –temperature molten salt provide a new class of solvents where molecules are composed of ions. At normal temperature, ionic liquids have essentially zero vapor pressure and are thermally stable over a wide range of temperature, therefore, they are considered as environmentally friendly alternatives to classical organic solvents. **(34)** Most of the liquids with which we are familiar (e.g. water, ethanol, benzene …etc) are molecular. That is, regardless of whether they are polar or non-polar, they are basically constituted of molecules. However, since the early 1980 an exciting new class of room temperature ionic liquids has become available. These are the room-temperature ionic liquids which an unlike the molecular liquids, regardless of the degree of association, they are basically constituted of ions. This gives them the potential to behave very differently to conventional molecular liquids, when they are used as solvents. Ions are present in the liquid with an exactly equal number of positive and negative ions so that the whole liquid is electrically neutral. **(31)**

At present, most of the interest in room temperature molten salt is centered on the design of new solvents. While the development of "new solvents" has led the direction of possible applications for room temperature molten salt (ionic liquids), there is more potential for development for electrochemical applications. Table (1-1) shows some examples of RTIL and their structures and molecular weights.

Table (1-1): Some of RTIL with their structures and molecular weights.(32,33)

Chemical Name	Abbreviation	Structure	MW g/mole
1-butyl-3-methylimidazolium 1,12,2-tetraflouroethanesulfonate	**[BMIm][TFES]**		**284.18**
1-ethyl-3-methylimidazolium 1,12,2-tetraflouroethanesulfonate	**[EMIm][TFES]**		**292.25**
1-heptyl-3-methylimidazolium 1,12,2-tetraflouroethanesulfonate	**[HMIm][TFES]**		**362.38**

1-butyl-3-methylimidazoliumtetraflouro borate	**[BMIm][BF_4]**		**226.03**
1-butyl-3-methylimidazoliumhexaflouro phosphate	**[BMIm][PF_6]**		**284.18**

1.4.2 High -temperature molten salts (ionic liquids)

In the mid last century, there has been a rapid growth in research and development for five applications of high-temperature molten salt and liquid salts in nuclear system. In the 1950 s and 1960 s, the untied state investigated fluoride salts as coolants for aircraft nuclear propulsion and for breeder reactors. **(35)** While much technical progress was made, the programs were ultimately discontinued, molten and salt-cooled reactors are intrinsically high temperature machines because the melting points for salts that are useful in nuclear systems are between 350 °C and 500 °C. **(35)** The historic needs for high – temperature heat that could be provided with nuclear reactors was limited.**(35)** Renewed interest in molten and salt-cooled reactors has emerged because applications for high- temperature heat now exist:

1.Hydrogen production: There is a growing interest in hydrogen production systems that require high- temperature heat to convert water to hydrogen and oxygen. (35)

2. Brayton power cycles: In the ninth, brayton power cycles using nitrogen or helium have been developed to efficiently convert high-temperature heat to electricity, Historically, the traditional utility power conversion cycle, has been the steam cycle with temperature limited to – 550 ^{o}C a temperature too low to be efficiently coupled to salt-cooled reactors.(35)

3. Dry cooling: High – temperature reactors with high effiency and brayton cycles dramatically lower the cost of dry cooling and increase the number for nuclear-plant sitting.(35)

The currently popular molten salts (ionic liquids) that have quaternary heterocyclic cations (like alkylpyridinium or dialkylimidazolium) and inorganic anions have an ancestry traceable to traditional high temperature molten salts. The salts that were the transition between the truly high temperature molten salts (like cryolite or LiCl-KCl) and the present ionic liquids were the inorganic chloroaluminate. It is interesting to note that 30 years ago these salts were called "low temperature molten salts" everything is relative. The high temperature chloroaluminates are transition materials in history and in temperature. Sodium chloride _ aluminum chloride eutectic has a melting temperature of 107 ^{o}C very nearly meeting our present definition of room temperature which melt at a below 100 ^{O}C ionic liquid.(14)

They were molten salts at very high temperature, e.g. the melting points of sodium, potassium, aluminum and calcium chloride are respectively

801, 770, 190 and 782 ^{O}C, and most organic molecules are decomposed at these elevated temperatures.(31)

A comparatively high melting points of the pure alkali metal chlorides (LiCl= 613 ^{o}C; NaCl =801 ^{o}C; KCl= 776 ^{o}C; RbCl= 715 ^{o}C; CsCl= 646 ^{o}C) imposes sufficient experimental that many investigators have opted to use the much lower melting eutectic mixtures [LiCl/KCl (60/40 mole %) m.p. 450 ^{O}C; NaCl/KCl (50/50 mole %) 653 ^{O}C; LiCl/NaCl/KCl (43/33/24 mole %) 383^{O}C].(36)

The two eutectic with the conveniently low melting points have the drawback of containing lithium cations, which have a sufficiently small radius that considerable interaction occurs with anions this tendency and also the higher cost of lithium salts have induced other workers to prefer the sodium chloride – potassium chloride eutectic, particularly for reactions with potential industrial application. (37)

1.5 Characteristics of Room-temperature Molten salt (Ionic Liquid)

There are several preferable characterization of RTIL some of which are summarized:

1. Low melting point (treated as liquid at ambient temperature and has wide usable temperature range).(13,17,31,32,34)
2. Non-volatility (Thermal stability: non-flammability), hence they may be used in high vacuum systems and they eliminate many containment problems (13,17,31,32,34)
3. Composed by ion (high ion density; high ion conductivity). (13,17,38)
4. By combing different anions and cations, it is possible to generate a huge number of different ionic liquids, each with their own specific

properties, (various kinds of salts; designable; unlimited combination**).**$^{(31, 32, 34, 38)}$

5. They are good solvents for a wide range of both inorganic and organic material and unusual combinations of reagents can be brought into the same phase. $^{(31, 32, 34, 38)}$

6. They are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for two phase systems; this has been used to effect total catalyzed reactions hydrophobic ionic liquids can also be used as immiscible polar phase with water.$^{(31)}$

1.6 Physical Properties of Room-temperature Molten salt (Ionic Liquids)

A description of the physical properties of RTIL has been summarized and described now:

1. Melting point: As a class, ionic liquids have been defined to have melting points below 100 °C and most of them are liquid at room temperature. Both cations and anions contribute to the melting point of ionic liquid. The increase in anion size leads to a decrease in melting point.$^{(39)}$ For example, the melting point of 1-ethyl-3-imidazolium type ionic liquid with different anions such as $[BF_4]^-$ and $[Tf_2N]^-$ are 15°C $^{(40)}$ and – 3 °C $^{(10)}$, respectively. Cations size and the symmetry make an important impact on the melting points of ionic liquids. Large cations and increased asymmetric substitution results in a melting point reduction.$^{(13,(41-43))}$
2. Conductivity: Ionic liquids have reasonably good ionic conductivities compared with those of organic solvents/electrolyte systems (up to10 mS cm^{-1}).$^{(44)}$ At elevated temperature of e.g. 200 °C a conductivity of

0.1 mS cm^{-1} can be achieved for some systems. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolyte. Based on the fact that ionic liquids are composed solely of ions, it would be exerted that ionic liquids have high conductivities. This is not the case since the conductivity of any solution depends not only on the number of charge carrier but also their mobility. The large constituent ions of ionic liquids reduce the ion mobility which, in turn, leads to lower conductivities. Furthermore ion pair formation and /or ion aggregation lead to reduced conductivity. The conductivity of ionic liquid is inversely linked to their viscosity. Hence ionic liquids of higher viscosity exhibit lower conductivity. Increasing the temperature increase conductivity and lower viscosity. **(13,41,42)**

3. Viscosity: Generally, ionic liquids are more viscous than common molecular solvents and their viscosities are ranging from 10 mPas to about 500 mPas at room temperature. The viscosities of some popular air and water stable ionic liquid at room temperature are: 312 mPas $[BMIm]^+$ PF_6^- **(45)**; 154 mPas for $[BMIm]^+$ BF_4^- **(46)**; 52 mPas for $[BMIm]^+$ TF_2N^- **(10)**; 85 mPas for $[BMP]^+$ TF_2N^- **(12)**. The viscosity of ionic liquid is determined by Vander Waals forces and hydrogen bonding. Electrostatic forces may also play an important role. Alkyl chain lengthening in the cation lead to an increase in viscosity this is due to stronger Van der Waals forces between cations leading to increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has a pronounced effect on viscosity. The fluorinated anions such as BF_4^- and PF_6^- form viscous ionic liquid due to the formation of hydrogen bonding.**(47)** In general,

all ionic liquids show a significant decrease in viscosity as the temperature increases.(13,41,42)

4. Density: Ionic liquid in general are denser than water with values ranging 1 to 1.6 g/ml and their densities decrease with increase in the length of the alkyl chain in the cation.(48) For example, in ionic liquids composed of substituted imidazolium cation and $CF_3SO_3^-$ anions the density decrease from 1.39 g/ml for $[EMIm]^+$ to 1.33 g/ml for $[EEIm]^+$, to 1.29 g/ml for $[BMIm]^+$ and to 1.27 g/ml for $[BEIm]^+$, the densities of ionic liquid are also affected by the identity of anions. For example, the densities of 1-buty-3-methyl imidazolium type ionic liquids with different anions, such as BF_4^-, PF_6^-, and Tf_2N^- are 1.12g/ml, 1.21 g/ml, and 1.43 g/ml, respectively. The order of increasing density for ionic liquid composed of a single anions is: $[CH_3SO_3]^-=[BF_4]^-[CF_3CO_3]^-<[C_3F_7CO_2]^-<[(CF_3SO_2)_2N]^-$.(41,42,49)

5. Thermal stability: Ionic liquid can be thermally stable up to temperature of 450^{o}C. The thermal stability of ionic liquid is limited by the strength of their hetero atom-carbon and their heteroatom – hydrogen bonds; respectively.(39) Wilkes et al.(50) reported that the ionic liquid 1-ethyl-3-methyl imidazolium tetraflouroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-2-dimethyl-3-propyl imidazolium bis(trifluorosulfonyl)imide are stable up to temperature of 445 ^{o}C, 423 ^{o}C, and 457 ^{o}C, respectively. Our experiences show that such high temperatures are only tolerated by most liquids for a short time. Long time exposure to such high temperature inevitably leads to decomposition. Most of the ionic liquids have extremely low vapor pressures. This allows removing water by simple heating under vacuum. Water contents below 1 ppm are quite easy to achieve with most of the liquid. (13,33,41,42)

6. Large electrochemical window: The electrochemical widow is an important property and plays a key role in using ionic liquids in electrodepositing of metals and semiconductors. By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. **(38)** This value determines the electrochemical stability of solvents. As known, the electrodepositing of elements and compounds in water is limited by it's low electrochemical window of only about 1.2 V, on the contrary , ionic liquids have significantly larger electrochemical windows, e.g., 4.15V for $[BMIm]^+PF_6^-$ at a platinum electrode,**(51)** 4.10 V for $[BMIm]^+BF_6^-$ **(51)** and 5.5 V for $[BMP]^+Tf_2N^-$ at a glassy carbon electrode.**(12)** In general, the wide electrochemical windows of ionic liquids have opened the door to electrodeposited metals and semiconductors at room temperature which were formerly obtained only from high temperature molten salts. For example, Al, Mg, Si, Ge, and rare earth elements can be obtained from room temperature ionic liquids. The thermal stability of ionic liquids allows to electrodeposits Ta, Nb, V, Se and presumably many other ones at elevated temperature.**(17,32,33)**
7. Hygroscopic: The water content has an influence on the viscosity of the ionic liquid. Viscosity measurement indicates that ionic liquids become less viscous with increasing water content. Hydrolysis problems can also occur.**(32,33)**

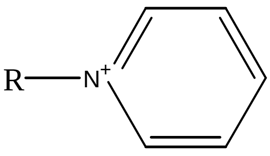
   Moisture sensitivity and the difficulty of separation of products containing heteroatom from the ionic liquid infect. In order to develop chemistry of ionic liquids, and increase the robustness of processes, water-stable ionic liquids have been found to be hydrophobic but yet readily dissolve many organic molecules.**(10,52)**

8. The color : The high quality ionic liquid have been reported to be colorless, even though they are not 100% pure. The color of less pure ionic liquid generally ranges from yellowish to orange. The formation of the color has been attributed to the use of raw materials with color or excessive heating during the synthesis of imidazolium salt. Number of precautions for synthesis of colorless ionic liquid has been described. A procedure for removal of color from impure ionic liquid using acidic alumina and activated charcoal has also been proposed.**(33,53)**

1.7 preparation of Molten salts (Ionic Liquids)

Room temperature molten salt (ionic liquids) recently have attract the attention of many workers due to their variable properties and scope of applications .

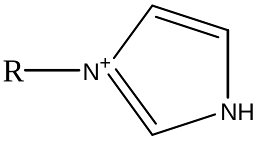
Invariably, these ionic liquids are either organic salts or mixtures consisting of at least one organic component. The most previously common salts in use are those with alkyl ammonium, alkylphosphonium, N-alkylpyridinium, and N, N-dialkylimidazolium cations.**(71)**



Methyl pyridinium

RPH_4^+

Alkyl phosphonium

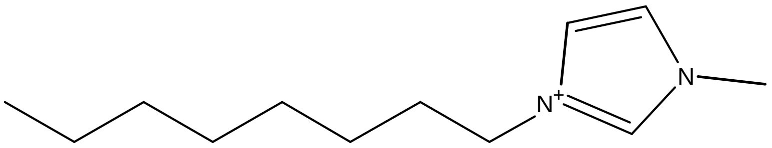


Methyl imidazolium

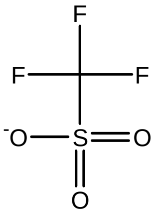
There are two basic methods for the preparation of molten salt (ionic liquids):

1. Metathesis of a halide salt with, for instance, a silver, group 1 metal or ammonium salt of the desired anion.**(32,54,55)**

   For example: $[OMIM]^{+}[TfO]^{-}$ ionic liquid was prepared via metathesis of 1-methyl-3-octylimidazoliumchloride $[OMIM]^{+}\,Cl^{-}$ with potassium trifluoromethylsulfonate $[TfO]^{-}\,K^{+}$ in acetonitrile.**(81)**



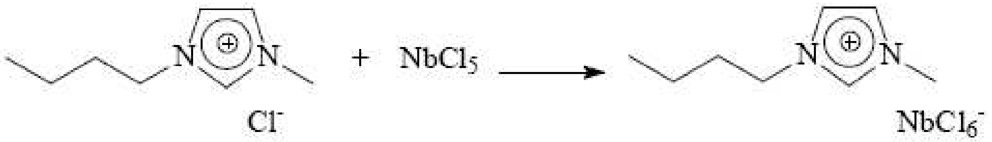
1-methyl-3-octylimidazolium cation



Trifluoro methyl sulfonate anion

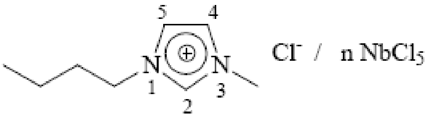
2. Acid-base neutralization reactions.**(54)**

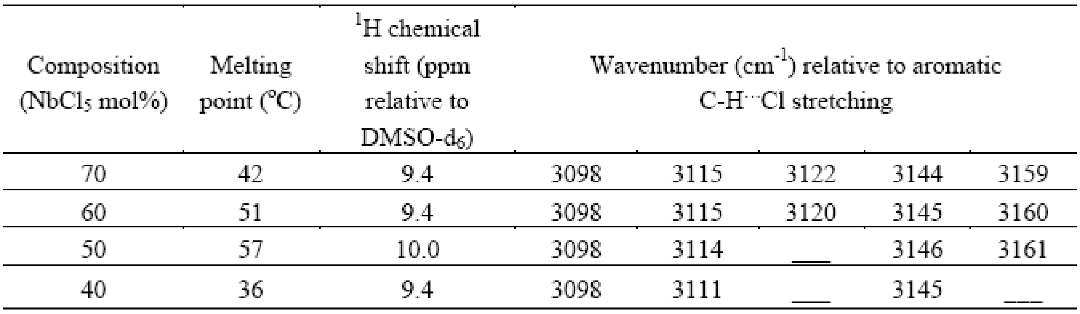
There are different types of molten salts (ionic liquids) prepared by this method, given for example: the association of 1-butyl-3-methyl imidazolium chloride and niobium pentachlioride, as shown in scheme. (1-2) for 50 % composition, yield pale brown solids at room temperature which became browned – red viscose ionic liquid when melted, probably affording an ionic species such as $NbCl_6^-$. Some spectroscopic and physical-chemical properties of these ionic mixtures depends upon their compositions, as can be seen in table (1-2). **(55)**



Scheme (1-2):1-butyl-3-methylimidazolium chloride and niobium pentachloride. (55)

Table (1-2): Some spectroscopic and physical-chemical properties of 1-butyl-3-methyl imidazolium chloride / niobium pentachloride ionic liquid. **(55)**





Composition ($NbCl_5$ mol%)	Melting point (°C)	^1H chemical shift (ppm relative to DMSO-d_6)	Wavenumber (cm^{-1}) relative to aromatic C-H···Cl stretching				
70	42	9.4	3098	3115	3122	3144	3159
60	51	9.4	3098	3115	3120	3145	3160
50	57	10.0	3098	3114	___	3146	3161
40	36	9.4	3098	3111	___	3145	___

1.8 Technological applications of Molten salt (Ionic Liquid)

There are several technological applications of Molten salts (ionic liquids) has been summarized:

1- Batteries.**(33)**

2- Fuel cells. **(33)**

3- Electrochemistry.**(33)**

4- Lubricants heat transfer. **(33)**

5- Solar energy conversion.**(33)**

6- Chemical oxidation\reduction baths.

7- Nuclear fuel rid waste. **(33,35)**

8-Industrial solvents. **(33)**

9-Making clean fuel. **(33)**

10-Enzymatic catalysis. **(33,54)**

11-Hydraulic fluids. **(33)**

12-Thermal fluids.**(16)**

1.9 Molten salts (Ionic liquids) as Novel media for various reactions

Most chemical reactions have been carried out in molecular solvents. For two millennia, most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. However, the new classes of emerged-ionic liquids solvents are often fluid at room temperature, and consist entirely of ionic species. They have many fascinating properties which make them of fundamental interest to all chemists. The thermodynamics and kinetics of reactions carried out in ionic liquids are different to those in conventional molecular solvents, and so the chemistry is different and unpredictable at our current state of knowledge. However, in addition to the scope for exciting new discoveries, ionic liquids have no measurable vapor pressure, and hence can emit no volatile organic compounds.**(52)**

Several organic reactions occur quite well in room temperature molten salts (ionic liquids).**(57,58)**, which are Hydrogenation.**(10,56)**, Hydroformylation.**(10)**, Diels-alder reaction.**(10,56,59)**, Suzuki coupling reaction.**(10)**, Zieglar-Natta reactions. **(30)**, and Heck reaction.**(10,56)**.

1.10 Green chemistry

Green chemistry is the use of chemistry for pollution prevention. More specifically, green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations. Instead, the new approach involves steps to decrease or eliminate the hazards in the system and eliminate the waste before it is produced.

Environmental issues need to be considered, before ionic liquid can be used routinely. Researchers need to find better ways to recycle ionic liquid. Many processes for cleaning up ionic liquids involve washing with water **(60)**. The link between molten salt (ionic liquids) and green chemistry is clearly related to the solvent properties of molten salt (ionic liquids) (low melting temperature, non-vapor pressure, non-flammability, thermal stability) **(14, 61)**, have excellent solvent power for organic and inorganic compounds, and are easily modified structurally to elicit desired physical properties. **(62, 63)**

Liquidus range is the span of temperature between the freezing point and boiling point of a liquid. The consequence for green chemistry is that ionic liquids are the ultimate non-volatile organic solvent. No molecular solvent (other than molten polymer) comes even close to the low volatility of ionic liquids**.** **(14)** Thus, the potential of ionic liquids to provide a nonvolatile solvent has become a practical target for reducing waste and hazards by eliminating traditional volatile organic solvents.

The recent interest surrounding ionic liquid, in regards to green chemistry and the associated development of new solvents and alternative technologies has largely been a result of their negligible vapor pressure which in habits evaporation into the air and allow simple recycle and reuse. The missing vapor pressure has very important advantages compared to other volatile organic chemicals. Therefore ionic liquid are not flammable and not explosive and a long range distribution via air can not be expected.

1.11 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique useful for measuring thermal and thermodynamic properties of materials such as, the specific heat, melting point and boiling point, glass transitions in amorphous /semi-crystalline materials, heats of fusion, reaction kinetics etc. the technique measure the temperature and the heat flow (in desired units, mW, W/g etc) corresponding to the thermal of materials, both as a function of time, or temperature.**(64,65)** differential scanning calorimetry (DSC) raises the temperature of a sample at a constant rate and measures the amount of energy required to make the temperature change. The resulting chart shows the amount of required energy temperature. The chart provides information on physical changes in the powder that take place at different temperatures and shows changes in the specific heat of the sample. Absorption of energy by the sample, e.g., an exothermic reaction such as melting or a glass transition T, results in negative slope on the chart. Energy given off by the sample, e.g. the exothermic reaction between the epoxy and the curing agent, results in a positive slope on the chart.**(66,67)**

1.12 Aim of the work

In view of the increasing interest in the recently growing field of new ionic solvents, which are liquids at room temperature, and in the light of their promising wide range of industrial applications, there is almost an academic interest in preparing more such type of solvents for an additional interest. Such interest may be arising from the existence of the consistent of ionic liquids mixtures. Due to production of them in large scale for other applications. These compounds required to be in a large cationic or anionic parts would result in a lower melting point i.e. having a large freezing point depression. One of such components is the dodecyl benzene sulfonate produced in a very large scale for the detergents industry. The second of widely used components is the urea as a fertilizers compound which is used with some other compounds for low temperature molten salts, practically with choline chloride. Therefore these compounds were used as major compounds and ions in preparing variable mixture in an attempt to prepare room temperature molten salts.

4.0 References

1. P.Walden, ***Bull, Acad, Imper, Sci***, 1914, **1**, 1800

2. F.H.Hurly and T.p.Weir, ***J. Electrochem. Soc***, 1951, **98**, 207.

3. H.L.chum, V.R.Kock, L.L.miller and R.A.Osteryoung, ***J. Am. Chem. Soc.***, 1975, **97**, 3264.

4. J.Robinson and R.A.Osteryoung, ***J. Am. Chem. Soc***. 1979, **101**, 323.

5. J.S.wilkes, J.A.Levisky, R, A, Wilson and C.L.Hussey, ***Inorg. Chem***., 1982, **21**, 1263.

6. T.B.Scheffler. C.L.Hussey, K.R.Seddon, C.M.Kear and P.D.Armitage, ***Inorg. Chem***., 1983,**22**,2099.

7. D.Appleby, C.L.Hussey, K.R.Seddon and ***J.E.Twp. Nature***, 1986,**323**,614.

8. C.L.Hussey, ***Adv. Molten Salt. Chem***.., 1983, **5**, 185.

9. J.S.Wilkes and M.J.Zaworotko, ***J.Chem. Soc.Chem. Com-mum***, 1992, **5,**965.

10. P.bonhŏtte, A. Dias, N.Papageoroiu, K.Kalyanasundraram and M.Grätzel, ***Inorg. Chem***.1996, **35**, 1168.

11. P. Wasserscheid and welton t (Eds) Ionic liquids in Synthesis (weinheim: wiley-vch). 2002

12. D.R.Macfarlan, P.Meakin, J.Sun, N Amini and M.for synth. ***J.Phys. Chem. B***, 1999, **103**, 4164.P.A.Z.

13. Frank endres, Sheriff Zien El Abedien,"air and water stable ionic liquids in physical chemistry" ***Phys. Chem. Chem. Phys***., 2006, **8**, 2101-2116.

14. John s.wilkes, "a short history of ionic liquids-from molten salt to Neoteric solvents" ***A review Green Chemistry***, 2002, **4**, 73-80.
15. C.l Hussy, In Advances in Molten Salts Chemistry; mamantov; c.eds; Elsevier; New York; 1983, 190-195.

16. Asako Narta, Wataru Shibayama and Hiroyuki Ohno, "Effect of structure on the thermal stability and conductivity of zwitter ionic liquids "***Aust.J.Chem***, 2006, **57**,139.

17. H.G.Macpherson," The molten salt adventure" ***Nuclear science and Engineering***, 1989, **90**, 374-380.

18. I.i.Albuabdoun, abstr, pap.-***Am.Chem.Soc***. (1989),**5,**198-98-pmse.

19. K .R .Seddon. 2003, ***Natl .Matter*** .2363.

20. J.Fuller and R.T. Carline, in molten salts, ed.P.C.Trulove H.C.Delong G.R.Stafford and S.Deki, PV 98-11, ***The Electrochemical Society Proceedings series Pennington, NJ***, 1998, **P**.227**..**

21. G .A. Baker ., Baker Sn, Pandy s and brightly fv, 2005**,** ***Analyst***, **130**, 800.
22. m .Freemantle 2003 ***Chem.Eng.News*** 819.

23. Volm, c.; Beckmann, o.; dabard, o.a.g. ***Angew.Chem***.1999, **111**,957.

24. Metzger, j.o.***Augew.Chem***, 1998, **110,** 3141; ***Angew .Chem .Chem .Int .Ed*** .1998, **37**; 2975.

25. Cusack; r.w.***Chem.Eng.Prog***.1996, **92**, 56.

26. (A) li, C.J.; Chan, t.h.organic reactions in aqueous media; wily; Chichester; 1997**.**
    (B) Aqueous phase organ metallic catalysis concepts and applications; cornels, Herrmann, w.a.; eds.; wily-vch; weinheim, 1996.

27. Suojiang Zhang, yuhuan Chen, rex x-f, ren, yanqiag zhang, jianmin zhang, and xiangping zhang," Solubility of CO2 in sulfonate ionic liquids at high pressure" ***J.Chem.Eng. Data***, 2005, **50**, 230-233.

28. Jessop, P.G.; IKariya, T, Noyori, R.***Chem.Rev***.1999, **99**,475.

29. Walden, p.bull.***Acad.Imper.Sci***. (st.petersburg) 1914, 405.c.a1914, **8**, 2291.
30. (A) Olivier, h. ***J. Mol. Catal, A-Chem***.1999, **146**,285.
    (b) Welton, T.***C hem.Rev***.1999, **99**, 2071.
    (c) Chauvin, Y.; Olivier, H .***Chemtech***, 1995, **25**, 26.

31. A.berthod, S. Carda-Broch, "Uses of Ionic liquids in analytical chemistry" ***J.A.C.S, Analytical Chemistry, 2002***.

32. Andrea mele, chieu D, Tran, and siliviaH, Depaoli lacerda," the structure of a room-temperature ionic liquid with and without trace amount of water: the role of C-H…O and C-H…O interactions in 1-n-butyl-3-methylimidazolium tetraflouroborate" ***Chem. Int. Ed***.2003, **42**, 4364-4366.

33. C.Hardacre, K .Seddon, J. McGrath," Room temperature ionic liquids" ***J.chem.Eng.Data***, 2004, **55**, 1390-1395.

34. Nicolas papaiconmou, Neal yakelis, Robert Bergman, and john m. Prausntiz, "synthesis and properties of seven ionic liquids containing 1-methyl-3-octylimidazolium or 1-butyl-4-methylpyridinium cations" ***J.chem.Eng.Data,*** 2006, **51**, 1389-1393.

35. W .Charles. Forsberg "Developments in molten salt and liquid-salt-Cooled reactors" ***American nuclear society annual meeting Pittsburgh, Pennsylvania***. 2004**.**

36. H.Bomb." the chemistry of molten salts "Benjamin, New York. 1967.

37. Debabrata seth, palash setue, anjan chakraborty and nilmonisarkar,"solvent relaxation of a room-temperature ionic liquid [bmim][PF_6] confined in a ternary microemulsion" ***J. Chem. Sci***. **119**, No. 2, ***2007***,PP. 105-111.

38. Inas m. alnashef, Matthew l. Leonard, Matthew c. kittle, Michael a. Matthews and john. W. weidner, "Electrochemical generation of superoxide in room-temperature ionic liquids" ***Electrochemical and Solid-State letters***, 2001, **4,** D16-D18.

39. P.wasserscheid and W.Keim, ***Anegw.Chem.Int.Ed***, 2000,**39**,3772.

40. J.Fuller, R.T.carlin and R.A.Osteryoung ***J.Electrochem.Soc***., 1997, **144**, 3881.

41. Chauvin y.; mussmann; l.; Olivier, h. ***Angew.Chem. Int.Ed***.1995, **34**, 2698

42. Suarez, p.a.z.; einloft, s.; dulius, j.e.l.; desouza, r.f.; DuPont, .***J.Chem. Phys***. 1998,**95**,1626.

43. J.D.Hlbery and R.D.Rogers, in ionic liquid in synthesis, Ed. P. Wassercheid and T.welton, Wily-VCH, Weincheim, 2003, pp.41-55.

44. B .Mark. shiflett, mark a. harmer, Christopher p.junk, and a. Yokosuka, "Solubility and Diffusivity of difluoromethane in Room-temperature Ionic Liquids" ***J.Chem.Eng. Data,*** 2006, **51**, 483-495.

45. S. Carda-broch, A.berthod and d.w.armstrong, ***Anal. Bio-Anal.Chem.*** 2003,**375**,191.

46. K.R.seddon, a. stark and m.j. Torres, ***Pure Appl.Chem***. 2000,**72**,2275. 12. D.R.MacFarlan, P.Meakin, J.Sun, N.Amini and M.For Synth .***J.Phys. Chem***. B, 1999, **103**, 4164.P.A.Z

47. P.A.Z.Suarez, S. Einloft, J.E.L.Dullius, R. F. De Souza and J.Dupont, ***J. Chem. Phys***., 1998, **95**, 1626.

48. K. N. marsh, J.A. boxall and R. lichtenthaler, fluid phase equilib**.** ***Pure Appl.chem,*** 2004, **219**, 93.

49. D .Chieu.Tran and Silvia H.De Paoli lacerde "determination of binding constants of cyclodextrins in room- temperature ionic liquids by near-infrared spectroscopy" ***J.A.C.S , Analytical Chemistry***.2002,**74**,5337-5341.

50. Wilkes, James D. Oxley, Tanya prozovor, and Kenneth S.Suslick"sonochemistry and sonoluminescence of room temperature ionic liquid" ***J. American Chemical society***.2003, **125**, 11138-11139.

51. U.Shroder , J.D. Wadhawan, R.G.Comton, F.Marken, P.A.Z. Suarez, C.S.Consorti, R.F. de Souza and J.Dupont, ***New J. Chem.***, 2000, **24**,1009.

52. Martyn J.Earle and Kenneth R. Seddon "ionic liquid. Green solvents for the future" ***Pure Appl. Chem***., 2000. **72**, No. 7, PP. 1391-1398,.

53. Prasun K.mandal, satyen saha, rana karmakar and anunay samanta, "salvation dynamics in room temperature ionic liquids: dynamic stokes shift studies of fluorescence of dipolar molecules" ***A review. Current Science***, 2006. . **90**, No. 3.

54. Thomas welton, "Room-temperature Ionic Liquids solvent for synthesis and catalysis" ***Chem, Rev***.1999, **99**, 2071-2083.

55. Valerio C.D.Soares, Melquizdeque B.Alves, Ernesto R.Souze, Ivana O.pinto, Joel C.Rubim, Carlos kleber,"Organo-Niobate ionic liquid :synthesis ,characterization and application as acid catalyst in pechmann reactions" ***International journal of Molecular Sciences***.2007,**8**,392-

56. Jairton DuPont, crestina S. consorti and john Spencer, "room temperature molten salts: neoteric "green" solvents for chemical reactions and processes" ***J. Braz..Chem.Soc***. 2000, ,**11**,No.4 ,337-344 ,.

57. Seddon, K.R., Ionic liquids: a Test of the future, ***Nature(Mater)***.2003**,** **2**,363-365.

58. Dupont, J., De Suza, R.F. and surez, p.a.z.," Ionic liquid (molten salt) phase Organ Metallic Catalysis" ***Chem, Rev***., 2002, **102**, 3667-3692.

59. (A) Olivier, h.***J.Mol.Catal.A-Cem***.1999.**146**, 285.
(b) Welton, t.***Chem Rev*** 1999,**99**,2071.
(c) Chauvin, y.; Olivier, h .***Chemtech***.1995, **25**

60. J.Joseph and U.V.Varadaraju, "Ionic liquid assisted synthesis and low temperature stabilization of alumina nanostructures"***J.Mater .Chem*** .**16**, 2006, 1315.

61.Huddleston.J.G.,visser,A.E.,Reichert.W.M.,willauer.H.D.,Broker,G.A. S.R.D.Characterization and Comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the Imidazolium cation. ***Green chem***.2001, **3**.156-164.

62. Hagiware, R.; Ito.Y." Room temperature Ionic liquids of alkyl imidazolium cations and fluoro anions". ***J.Fluorine Chem***., 2000, **105**, 221-227.

63. Wu, WI; Zhang, j., han.b, chem.j, liu, z., jiag, t., he, j., li., w, solubility of room-temperature ionic liquid in supercritical CO2 with and without organic compounds. ***Chem.Coummn***. 2003, 1412-1243.

64. Charles day, ***Physics Today***, p. 24-26(2003)**.**

65. K.f. kelton, G.H.Lee, A.K.Gangopadhyay, R.W.Hyers, T.J.Rathz, J.R.Rogers, M.B.Robinson, and D.S.Robinson, ***Physical Review letters***, 2003**, 19**, No.90.

66. William F.Smith and javad hashemi, "foundation of materials science and engineering", McGrawa Hill, P. 128(2006).

67. A.C.T. Tang, F.M.Sargent, ***Electronics letters***, 1991 . **27**, No.22, P.2018 – 2020.

68. Murray zanger, James McKee, "essentials of organic chemistry" the McGraw-Hill Companies 1997.

69. T.W.Graham Solomon "organic chemistry" john-widely and sons, Inc New York**,** 1999.P. 698.

70. W.T. AL-aubayee, M. Sc. Thesis College of sciences, Al-Nahrain University, Iraq (2004).

71. Hélène Valletta, Laurent ferron, Gerard coquerel, Frederic gullen, and jean-Christophe plaque vent," room temperature ionic liquids (RTIL) are convenient solvents for peptide synthesis"***ARKIOC*** 2006 (**IV**) 200-211

72. Buzzeo, M.C., evaus, r.g. and Compton, r.g., "non-haloaluminate room-temperature ionic liquids in electrochemistry "***-A review .Chem Phys Chem.***, 2004, **5,** 1106-1120. 398.

73. R. M. silverstein and x. webter "Spectrometric Identication of Organic Compounds" john-widely and sons, Inc New York, 1998**.**

74. B. Stuart, W. George , and P. McIntyre " Modern Infrared Spectroscopy " , John Weily and sons , New York ,(1996).

75. Nour Abed Al-razzak, M. Sc. Thesis College of sciences, Al-Nahrain University, Iraq (2007).

76. Mustafa S. Abed alla, M. Sc. Thesis College of sciences, AL-Nahrain University, Iraq (2007).

77. Mihkel Koel "physical and chemical properties of ionic liquids based on the dialkylimidazolium cations" ***Proc. Estonian Acad. Sci.Chem***. 2000, **49**, 3,145-155.

78. Christine j. barbaric, Andrew downward, Christine Kennedy, Allan j. Robertson and yuehui Zhou," Industrial preparation of phosphonium ionic liquids" ***The Royal Society of Chemistry***, 2003.

79. Greg drake, tom Hawkins, john Wilkes. "Structural effects on the physical properties of ionic liquids". ***Inorg.Chem*** (2006), **50**, 3600-3605.

80. Andrew p. Abbott, glen capper, David l, and Raymond rasheed," ionic liquids based upon metal halide/substituted quaternary ammonium salt mixtures" ***Inorg.Chem***. 2004, **43**, 3447-3452.

81. Muldon, m.j.; Gordon, C.M. and dunkin, i. r., Investigations of solvent-solute interactions in room temperature ionic liquids using solvatochromic dyes. ***J.Chem.Soc, Perkin Trans***., 2001, **2**,433-435.

82. W.E.Dasent "Inorganic Energetic", Bell and Bain Ltd, Glasgow, 1970.

83. Andrew p. Abbott, David Boothby, glen capper, David l. davides, and Raymond k. rasheed, "deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids" ***J.Am. Chem. Soc***.2004, **126**, 9142-9147.

84. James E. Huheey" Inorganic chemistry principles of structure and reactivity" Harper & Row, publishers, Inc, 1972.

85. Andrew P.Abbott, David Boothby, Glen Capper, David L.Davis and Raymond K. Rasheed "Ionic Liquids and their uses as solvents" 2000.

86. Jalal Mohammed saleh "Thermodynamics and it is application in Chemistry" (1992).

87. P.w. Atkins," Physical chemistry" W.H.Freeman &Co and Sunanas, Inc. 1999.205,206.

88. Andrew p. Abbott, glen capper, David l, Davies, Raymond k, rashed and vasuki tambyraja" Novel solvent properties of Choline chloride/Urea mixtures" ***Chem.Commun***, 2003, 70-71.

89. Rajender S. Varma and Vasudevan V. Namboodiri, "Solvent-free preparation of Ionic liquids using a household microwave oven" ***Pure Appl. Chem***., 2001 .**73**, No. 8, PP. 1309-1313.

90. Andrew P. Abbott, Glen Capper, David l, Davides,Katy.J.McKenzie, and Stephen U. Obi," Solubility of metal oxide in deep eutectic solvent based on choline chloride" ***J.Chem.Eng.Data.***2006, **51**, 1280-1282.

91. Andrew p. Abbott, glen capper, David l.davides, Raymond k. rasheed, and pragna shilkotra, "Selective extraction of metals from mixed oxide matrixes using Choline-based ionic liquids" ***Inorg. Chem***. 2005, **44**, 6497-6499.

92. Wasserscheid, P. Keim W. ***Angew.Chem.Int.ed*** 2000, **39**, 3772.

93. Gannon; T.J.; law, G., Watson; P.R.; Carmichael, A.J.; Seddon, R.R. Langmuir, 1999,**15**,8429.

94. Earle, M.J.; mccormac; P.B.; seddon, K.R.***Green Chem***...1999,**1**,23.

95. Rogers, R.D.and Seddon k.r., Ionic Liquids-solvents of the future? ***Science***, 2003 **302**,792-793.

96. Rodgers, R. and Seddon, K.R. (Eds)," ionic liquids, industrial applications for green chemistry", ***A.C.S. symposium series,*** 2002**, 818,** ***Washington DC***,.

97. Huddleston, J.G androgers, R.D., Room temperature ionic liquids as Noval media for clean liquid-liquid extraction.***Chem.Com-Mun***., 1998, **9**,1765-1766.

98. Van Rantwijk, f., Lau, R.M. and Sheldon R.A., biocatalyst transformations in ionic liquids, ***Trends Biotechnology***, 2003, **21**,131-138.

99.Armstrong, d.w., zhang, l.k., he, l and gross, m.l., ionic liquids as matrixes for matrix-assisted laser desorption/ionizationmass spectrometry.***Anal.Chem***., 2001,**73**,3679-3686.

100. Wang, p., zakeeruddin, s.m., moser, j.e.and gratzl.m, New ionic liquid electrolyte enhance the conversion efficiency of dye-sensitizes solar cell.***J.Phys.Chem .B.S***, 2005, **107**, 13280-13285.

الخلاصة

تضمنت الرسالة دراسة تحضير وتشخيص أملاح منصهرة (سوائل أيونية) تكون منصهرة في درجة حرارة الغرفة حيث تم تحضير كولين دودوسيل بنزين سلفونيت و فينل تراي ميثل أمونيوم دودوسيل بنزين سلفونيت وكانت درجة الانصهار لكل منهما هي ^{o}C (118, 91.9) على التوالي .تم تحضير أملاح منصهرة (سوائل أيونية) أخرى بواسطة خلط ، صوديوم دودوسيل بنزين سلفونيت ، بوتاسيوم دودوسيل بنزين سلفونيت، أمونيوم دودوسيل بنزين سلفونيت ، بنزويك أسد، ساليسالك أسد مع الكولين كلورايد وقد أظهرت عملية الخلط انخفاض كبير درجة الانصهار عن للمركبات الاصلية.الخليط المكون من(أمونيوم دودوسيل بنزين سلفونيت\ الكولين كلورايد) ينصهر عند $15\,^{o}C$ ، أيضا خليطي (بنزويك أسد\ الكولين كلورايد) و (ساليسالك أسد\ الكولين كلورايد) مع لهما درجة انصهار متشابهة مقدارها $60\,^{o}C$ ، وهذة الدرجة تنطبق مع تعريف ألاملاح المنصهرة (السوائل ألايونية) التي تنصهر في درجة حرارة أقل من $100\,^{o}C$، لذلك تعتبر أملاح منصهرة في درجة حرارة الغرفة. أظهرت الخلطات المكونة من (صوديوم دودوسيل بنزين سلفونيت\ الكولين كلورايد) و (بوتاسيوم دودوسيل بنزين سلفونيت \ الكولين كلورايد) درجات انصهار أعلى من $100\,^{o}C$. مجموعة أخرى من ألاملاح المنصهرة (السوائل الايونية) التي تم تحضيرها بواسطة خلط نفس المركبات السابقة لكن مع اليوريا بدلامن الكولين كلورايد هذة ألاملاح المنصهرة (السوائل الايونية) المكونة من مركبات السلفونيت لهما درجات انصهار أقل مما للاملاح المنصهرة المعتمدة على الكولين كلورايد التي تنصهر عند $105\,^{o}C$، $100\,^{o}C$، $10\,^{o}C$ على التوالي. بينما في حالة (بنزويك أسد\ اليوريا) و (ساليسالك أسد\ اليوريا) تنصهر بدرجات أعلى وكانت، $75\,^{o}C$، $77\,^{o}C$ على التوالي. ألاملاح المنصهرة (السوائل الايونية) تتكون نتيجة التداخل الذي يحصل بين مكونات الخليط وتكون تأصر هيدروحيني أو تكون معقد بين مكونات الخليط.

Republic of Iraq
Ministry of Higher Education
And Scientific Research
Al-Nahrain University
College of Science

Preparation and Characterization of Molten salts (Ionic Liquids) Based on Sulfonate Compounds

A Thesis
Submitted to the College of Science of Al-Nahrain University
as a partial Fulfillment of the requirements for the Degree of
Master of Science in Chemistry

By:
Ahaad Diwan Sajet Al-fatlawy
(B.Sc 2004)

Supervised by:
Dr. Hadi M.A. Abood

2008 May **1429 Jamad el Awwal**

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم

تحضير و تشخيص الأملاح المنصهرة (السوائل الأيونية) المستندة على مركبات السلفونيت

رسالة
مقدمة إلى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قِبَلْ
عهد ديوان ساجت الفتلاوي
بكالوريوس 2004(جامعة النهرين)

باشراف
الدكتور هادي محمد علي عبود

جمادى الأولى 1429　　**أيار ٢٠٠٨**

Contents

Chapter one: Introduction

Chapter two: Experimental part

Chapter three: Results and Discussion

List of Figures

List of Tables

List of Schemes

List of Abbreviations

Symbols	Full meaning used in this thesis
$[BMIm]^+[TFES]^-$	1-butyl-3-methylimidazolium 1,12,2-tetraflouroethanesulfonate
$[BMIm]^+ [BF_4]^-$	1-butyl-3-methylimidazoliumtetraflouroborate
$[BMIm]^+ [PF_6]^-$	1-butyl-3-methylimidazoliumhexaflourophosphate
C	Number of compounds
DBS salts	Dodecyl Benzene Sulfonate salts
DSC	Differential scanning calorimetry
DES	Deep eutectic solvent
$[EMIm]^+ [TFES]^-$	1-ethyl-3-methylimidazolium 1,12,2-tetraflouroethanesulfonate
e	Electron charge
E	Latent heat of fusion
ε_o	Vacuum permittivity
F	The number of degree of freedom
FTIR	Fourier transform infrared
$[HMIm]^+ [TFES]^-$	1-heptyl-3-methylimidazolium 1,12,2-tetraflouroethanesulfonate
IR	Infrared
J	Joules
KDBS	Potassium dodecyl benzene sulfonate
mW	Milli watt per hour
M.Wt	Molecular weight
NaDBS	Sodium dodecyl benzene sulfonate
NH_4DBS	Ammonium dodecyl benzene sulfonate
P	Number of phases
r	Separation between the two ions
RTIL	Room temperature ionic liquid
RTILS	Room temperature ionic liquid solvent
$[Tf_2N]^-$	Bis(trifluoromethylsulfonyl)-imide
T_m	Melting point
THF	Tetrahydrofuran
υ	Stretching

عنوان الاطروحة

Laplace Transform Method for Solving Ordinary Fractional Order Differential Equations with Constant Coefficients

حل المعادلات التفاضلية الإعتيادية ذات الرتب الكسرية والمعاملات الثابتة بإستخدام تحويل لابلاس

المشرف على الاطروحة: د. علاء الدين نوري احمد

اسم الطالبة: فرح انور فرجو

موعد المناقشة: ٢٠٠٧/١٢/٣١

عنوان السكن: م/ ٦١٥ ز/ ١٧ د/ ٦٥

رقم الهاتف: ٠٧٩٠١٢١٨٠١٩

البريد الالكتروني: farah_farjo@yahoo.com