

King Fahd Univesity Of Petroleum & Minerals.
Chemistry Department

SUMMER TRAINING REPORT

CHEM 399

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For

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INTRODUCTION:

In 1933, shortly after Saudi Arabia was unified, the Government granted a concession to Standard Oil of California who recognized the potential of oil as a valuable export commodity and a source of revenue to begin building our nation. Standard Oil of California, the parent company of Chevron, was joined later by several other major oil companies and the venture became known as Aramco - the Arabian American Oil Company. In 1938, after five long years of exploration, oil was discovered in commercial volume when a well named **Dammam Number 7**, near today's headquarters in Dhahran, began to flow -- and ushered in a new era for Saudi Arabia. Things moved quickly, and in 1939 King 'Abd al-'Aziz visited Ras Tanura to inaugurate the first shipload of Saudi crude oil ever exported. The young Kingdom was now officially launched into the international petroleum industry.

I have been assigned to work in research and development center (R&DC). R&DC responsibilities are Conduct pioneering research, introduce new technology and provide specialized technical services that will enhance Company profitability and productivity in a cost-effective, timely and collaborative manner.

During the 8 weeks training I was working in research and development division(RDD).

Projects and assignments:

During summer training, I have been assigned for different major and minor work. The major assignment was ionic liquid project.

The minor assignments were:

- Stability of FCC gasoline.
- Determination of wax content of petroleum oils and asphalts.
- Competing area and solubility of some organic compounds using material studio software.

IONIC LIQUIDS PROJECT:

Ionic liquids are salt which have a melting point less than 100C.

They are accepted to be an organic cation and organic or inorganic anion.

From the late of 20th century, Ionic liquids received more Attention in researches because of its unique properties. Figure 1 shows the development in ionic liquids researches.

Ionic liquids have special properties that made them attractive for many researchers:

- Negligible vapour pressure.
- High ionic concentration and conductivity.
- Non-flammable.
- High thermal, chemical and electrochemical stability.
- Liquid over a wide temperature range.
- Dissolution of many organic and inorganic compounds.
- Variable miscibility with water and organic solvents.

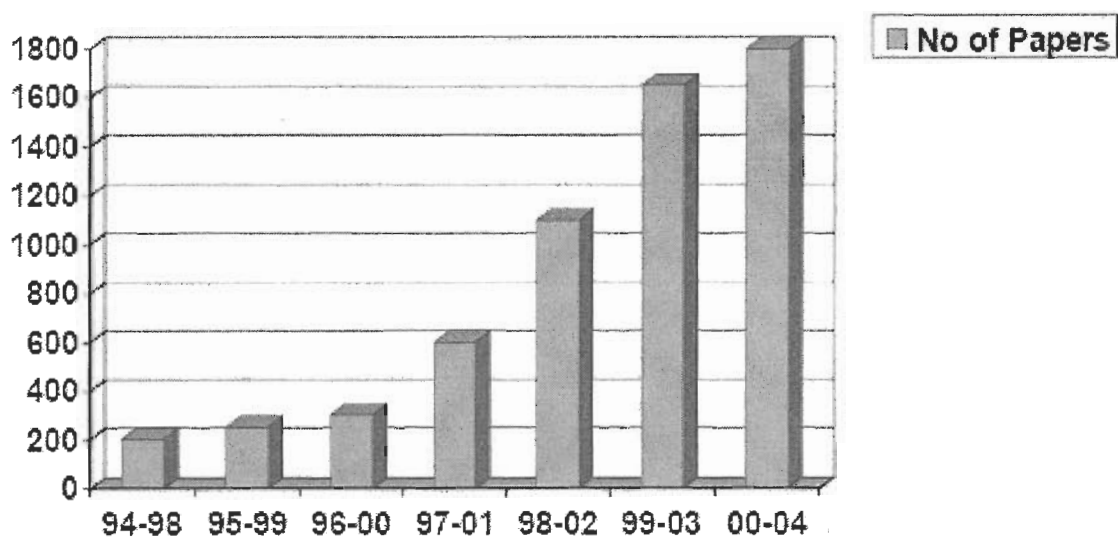


Figure 1. Development of ionic liquids research

Synthesis of ionic liquids:

Ionic liquids generally synthesized as follow:

For Imidazolium based Ionic Liquids

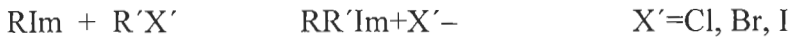
Reaction of N-alkylimidazole, RIm,

with alkyl salts (R'X) in appropriate organic solvents

(1) X⁻ is the anion of interest



(2) First step, alkylimidazolium halides are synthesized



(3) Anion exchange corresponding acids of their salts



The ionic liquid assignment:

The goal of this project was the synthesis of distillable room temperature ionic liquids and investigates the possibility of using them for different applications such as:

- Extraction of light oil fractions from the heavy refining cuts.
- Selective extraction of aromatics and paraffins.

Usually the separation of ionic liquids is a major problem associated with it.

Distillable ionic liquids are a new class that can be easily separated by distillation.

DIMCARB, dialkylammoniumcarbamate, was chosen for this study.

The general reaction for carbamate ionic liquids is:



The physical properties of carbamate ionic liquids ~~are~~ vary according to the alkyl group. Table 1 shows the influence of alkyl groups on the melting and dissociation temperature.

Table 1 Melting point and dissociation temperature of selected dialcarbs^{4,8}

R ₁	R ₂	Melting point/°C	Dissociation temperature/°C
Me	Me	30-45 ^a	60-61
Me	Et	-	62
Et	Et	17-33	62-63
Me	<i>n</i> -Pr	-	70-71
-(CH ₂) ₄	-	55-80	105

^a For the salt containing exactly 2 : 1 ratio of Me₂NH : CO₂.

Diethylamine carbamate ionic liquids have been synthesized as follow:

A 250 mL 3-necked round bottom flask was equipped with a water condenser and two gas purge tubes connected to CO₂ and diethylamine (DMA) gas cylinders and the entire setup placed into a ice bath. After cooling the reaction vessel to 0 C. 200 ml of diethylamine was added to the flask. CO₂ was bubbled into diethylamine solution in the vessel, at a slow rate. The ratio of reactants were Et₂NH : CO₂ in a 1.8 : 1.

The resulted solution was analyzed by mean of potentiostat to measure the conductivity of the solution.

Samples of water, diethylamine and ionic liquids were analyzed by potentiostat to measure there conductivity. The results is tabulated in table 2

Table 2 conductivity analysis

compound	currant (mA)
Diethyl amine	1.00E-09
Water with diethylamine	2.00E-06
diethylammoniumcarbamate with water	0.078
diethylammoniumcarbamate	2.00E-04

From table2, the conductivity of resulted diethylammoniumcarbamate is about 10⁵ times of the diethylamine.

By using density meter the density of ionic liquid and specific gravity have been determined:

Density of diethylammoniumcarbamate : 0.9640g/cm³ at 15C
S.P= 0.9650

NMR is a measure tool to investigate the purity of ionic liquids but it was not available during summer session.

Testing the ability of ionic liquids for light fractions extraction:

the prepared ionic liquid was mixed with different compounds and refining cuts to find their solubility in ionic liquids to find the possibility of use diethylcarbamate ionic liquids in extraction. Table 3 shows the experimental results.

Table 3. Separation of aromatics and aliphatics using 5ml ionic liquids

compound	phases
3 ml hexadecane	two phases
8ml dodecane	homogenous
8 ml Benzene	homogenous
8ml hexane	homogenous
8ml diesel	homogenous
8 ml light naphtha	homogenous
8ml full range naphtha	homogenous
8 ml kerosene	two phases
8 ml light naphtha and 0.5ml water	two phases
8ml full range naphtha and 0.5 ml water	two phases

The diethylcarbamate forms homogenous mixture with Benzene and paraffin up to C14 compounds. Diethylcarbamate is extremely soluble in water and it can be easily separated from the oil using small amount of water.

Phase diagram of diethylaminecarbamate and dodecane:

In order to find the solubility limits of dodecane in diethylaminecarbamate, an experiment to construct phase diagram for dodecane and diethylaminecarbamate system and the results were as follow:

diethylamine carbamate%	phases
98%	one phase
95%	one phase
90%	one phase
85%	one phase
80%	one phase
70%	two phases

Other ionic liquids :

Diphynelammoniumcarbamate was other ionic liquid that I had to synthesis. Same procedure for synthesis of dialkylammoniumcarbate was used but, it did not work. This can be a result of lower ability of denoting electrons of nitrogen atom due to withdrawing effect of aromatic ring.

THE MINOR ASSIGNMENTS:

DETERMINATION OF PARAFFIN WAX CONTENT OF PETROLEUM OILS AND ASPHALTA:

Paraffin wax content of crude oil and asphaltenes can be determined by extraction of wax and find the percentage of wax present in oil or asphaltenes as follow:

$$\text{wax}\% = \frac{\text{mass of wax}(g)}{\text{mass of sample}(g)} * 100$$

The extraction was performed based on ASTM D1500.

Procedure:

2.00 ± 0.25g of sample was added to clean and dry 250ml Erlenmeyer flask. The solution heated to dissolve the sample. 50 ml of hexane was added to the solution and carefully brought to boil on an electrical hot plate. 4 ml of concentrated sulfuric acid were added and the mixture vigorously to effect internal contact between acid and oil. The mixture was heated gently with continued swirling over the hot plate until and acid tar is formed .

The mixture allowed to settle for 2 hours. The clear asphalt free solution was carefully transferred to 250 ml separatory funnel. The acid tar formed will normally adhere to the sides of flask. The washed with 5ml of warmed hexane at 60C° for five times. The content of washed acid tar layer was transferred to the separatory funnel.

50 ml of warm water (about 40C) was added to the separatory funnel to wash the hexane layer and dilute the acid. The water layer was discarded and 15ml of 0.1M ammonium hydroxide solution was added to neutralize the remaining acid. Ammonium hydroxide layer was discarded. The solution was washed several times with 50 ml of warm water until no color change when several dopes of phenolphthalein were added.

The neutral hexane solution transferred to clean 125ml Erlenmeyer flask. The separatory funnel was washed three times with 5ml of hexane warmed at 60C and the resulted solution transferred to the 125ml Erlenmeyer flask. The flask was placed in water bath at 90C to evaporate the hexane.

20ml of methylene chloride warmed at 35C was added to the obtained sample from evaporation of hexane.

The filtration apparatus were cooled to -30C by placing it in a solution of methylene chloride and dry ice. The content of Erlenmeyer flask was poured to the glass filter.

The wax on filter was washed with 30ml of methylene chloride cooled to -30C.

The filtered wax was washed with hexane warmed to 60C to dissolve it.

When the wax was completely dissolved, the resulted solution was heated to 95C to evaporate the hexane. The flask was dried in oven at 105C for 15 minutes, allowed to cool in desiccator and then weight was recorded to nearest 0.1mg.

STABILITY OF MOTOR GASOLINE:

When gasoline is left for a certain period of time, gums and varnishes may build up and precipitate in the gasoline, causing "stale fuel." This will cause gums to build up in the cylinders and also the fuel lines, making it harder to start the engine. Gums and varnishes should be removed by a professional to extend engine life. Motor gasoline may be stored up to 60 days in an approved container. If it is to be stored for a longer period of time, a fuel stabilizer may be used. This will extend the life of the fuel to about 1-2 years, and keep it fresh for the next uses. Different testing methods can be used to determine the stability of gasoline and maximum storage period with significant change of its quality.

I have been introduced to two testing methods. They were:

- Gum content in fuels by get evaporation.
- Oxidation stability of gasoline (induction period method).

Gum content in fuels by get evaporation:

It has been proved that high content gum can cause induction-system deposits and sticking of intake valves.

In this method, a measured quantity of gasoline is evaporated under controlled temperature and flow of air or steam. The resulting residue is weighed and reported as milligrams per 100ml.

Oxidation stability of gasoline (induction period method):

The induction period used as an indication of the tendency of motor gasoline to form gum in storage. In this method, the sample is oxidized in pressure vessel(see Figure 1) initially filled at 15-25°C with oxygen pressure at 690 to 705KPa and heated at a temperature between 98- 102C. The pressure is recorded continuously until the break point is reached. The temperature of the vessel was 100C.

Break point: is the on pressure-time curve that is determined by a pressure drop exactly 14KPa within 15m minutes and succeeded by a drop of not less than 14KPa in 15 minutes.



Figure 1. Oxidation stability of gasoline pressure vessel

Conclusion:

During my summer training at research and development center, I have been exposed to different applications of chemistry in organic synthesis and analytical chemistry.

Synthesis of ionic liquids was an application of organic synthesis. Also analysis of ionic liquids performed using electrochemical technique (conductivity). Physical properties of ionic liquid such as density, solubility in other solvents and phase diagram have been done.

Other experience I have got was analysis and stability study of gasoline by using Oxidation stability of gasoline (induction period method) and Gum content in fuels by get evaporation methods. Also I have been introduced to different methods of crude oil characterization methods. They were cloud point, API, flash point, wax content determination, distillation and sulfur content determination.

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