

UDC 664.3:547

Досліджено поверхнево-активні властивості амідомідазолінів та їх солей. Мідазоліни отримано амидуванням лляної олії діетилентриаміном. В дослідженні використано оцтову та алкілсірчану соли алкілімідазолінів. Оцінено емульгуючу дію, здатність знижувати поверхневий натяг на межі розподілу фаз та антикорозійну дію. Кращу здатність утворювати емульсії показала оцтова сіль, а кращу антикорозійну дію алкіл сірчана сіль імідазоліну

Ключові слова: поверхнево-активні імідазоліни, захисний ефект, емульсія, поверхневий натяг, поверхнева активність

Исследовано поверхностно-активные свойства амидоимидазолинов и их солей. Имидазолины получены амидированием льняного масла диэтилентриамином. В исследовании использовались уксусная и алкилсерная соли алкилимидазолинов. Было оценено эмульгирующее действие, способность снижать поверхностное натяжение на границе раздела фаз и антикоррозионное действие. Лучшую способность образовывать эмульсии показала уксусная соль, а лучшее антикоррозионное действие – алкилсерная соль имидазолина

Ключевые слова: поверхностно-активные имидазолины, защитный эффект, эмульсия, поверхностное натяжение, поверхностная активность

INVESTIGATIONS OF SEVERAL SURFACE-ACTIVE PROPERTIES OF ALKYLIMIDAZOLINE SALTS

A. Melnik
Professor*

S. Malik
Postgraduate student*
e-mail: malik_sg@ukr.net

S. Kramarev
Scientist*

T. Matvieieva
PhD**

V. Papchenko
PhD**

*Department of technology of fats and fermentation products
National Technical University
“Kharkiv Polytechnic Institute”

Frunze st., 21, Kharkiv, Ukraine, 61019

**Ukrainian Research Institute of Oils and Fats
Dziuby st., 2A, Kharkiv, Ukraine, 61019

1. Introduction

Alkylimadazolines are well-known surface active substances. They found their application in different fields of industry such as production of household chemicals, perfumery production, oil and gas production/extraction, building industry etc [1, 2]. Because of their properties to react with acids they can easily absorb on the different positive charged surfaces, such as glass, fibers, metals, rocks. There are a lot of types of imidazolines which differ by their structure, alkyl and type of substitute near nitrogen atom.

In some application it is necessary to use nonneutralized form but in another cases neutralized imadazolines utilizes as well. There is a big difference in surface active properties of neutralized (imidazoline salts) and unneutralizes imadazolines. It is well known that fatty alkylimidazolines isn't soluble in water but only disperse in it. In the same time imidazoline salts not only have a good solubility in water but also have perfect foaming and emulsifying properties and in that form can be used as components of mild shampoos.

Unneutralized imidazoline are stable during storage in dry and cool place but in a little presence of water or alkaline they can rapidly hydrolyze with amidoamines formation [3]. In acidic media imadazolines are much more stable and can be stored long time even in form of water solutions. A lot of chemicals formulations with imadazoline in their composition are water solution. In this case it is required to use

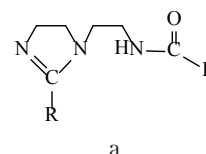
imidazoline salts due to their stability against hydrolysis. But in the form of salts imidazolines have other properties than unneutralized.

2. Statement of research problem

There is a lot of data about surface active properties of unneutralized imidazolines as well as properties of betaine SAS which made from imidazoline. Despite this the data about properties of imidazoline salts almost absent. Due to this the aim of the investigations was determination of such surface active properties as Ability to prevent corrosion, interfacial tension and emulsifying ability of different imidazoline salts.

3. Materials and methods

Amidoimidazolines of general formula (a) were used as unneutralized imidazoline.



It was synthesized by the reaction of linseed oil with diethylenetriamine under determined optimal conditions [4]. This product contains 67 % of imidazoline of formula (a). Obtained imidazoline was neutralized stoichiometric by amine value by acetic and alkylbenzenesulfuric acid to obtain imidazoline salts. Anticorrosive ability was estimated by standard method according to GOST 9.908 and method of maximum bubble pressure for interfacial tension determination as well. Determination of emulsifying ability was conducted with standard "bottle test".

4. Results and discussion

4.1 Corrosion rate and defensive effect

Because of imidazolines are widely used as components of corrosion inhibitors [5,6] in the first stage of investigations anticorrosive ability have been estimated. It has been measured for imidazoline and its salts as well as for reaction masses which have been took away during synthesis process of imidazoline.

Obtained results are shown on Fig. 1.

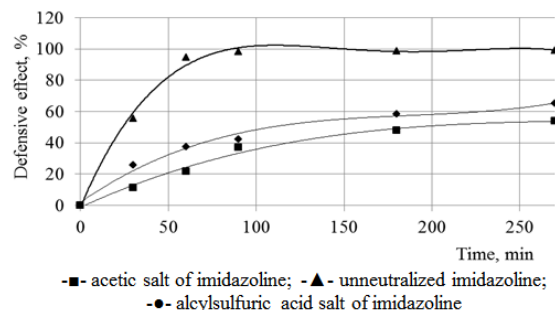


Fig 1. Dependence of defensive effect from time of imidazoline obtaining reaction and type of acid which took for neutralization

As we see on Fig.1 defensive effect of imidazoline and its salts increases with increasing of reaction time. Defensive effect of imidazoline which was neutralized with alkylsulfuric acid have a maximum value. After 60 minutes of reaction it was almost 95 % while defensive effect of unneutralized imidazoline and acetic salt of it were 37% and 22% respectively. Maximum defensive effect was more than 99% and it was reached after 270 minutes of synthesis process of imidazoline. The reason of it is that in this case maximum concentration of imidazolines in reaction masses is observed. Difference between alkylsulfuric and acetic salt happened due to their solubility in water. Acetic salt have an excellent water solubility so being adsorbed on metal surface can easily washed from here by water. Alkylsulfuric salts could be solved only in alcohol or hydrocarbons and caught not in water. Because of this being adsorbed on metal surface such salts prevent contact with aqueous media and as a result corrosion rate rapidly decreases. On Fig. 2 presented data about corrosion rate of investigated imidazolines and its salts.

As we can see corrosion rate decreases with raise of reaction time as in case unneutralized imidazoline and its salts as well. This effect caught easily been explained by that fact that in first period of imidazoline obtaining reaction there is a rapidly increasing of imidazoline content in reaction masses [4, 7].

Have been determined (Fig. 2), that minimum corrosion rate was in presence of alkylsulfuric salt of imidazoline. Corrosion rate in this case was only 0.076-0.032 mm/year after 90 minutes if synthesis. In the same time corrosion rate in the presence of acetic salt of imidazoline have been 1.8-3.0 mm/year which is 10-15 times more than alkylsulfuric acid salt. Moreover corrosion rate of unneutralized imidazoline was at the same level as acetic salt.

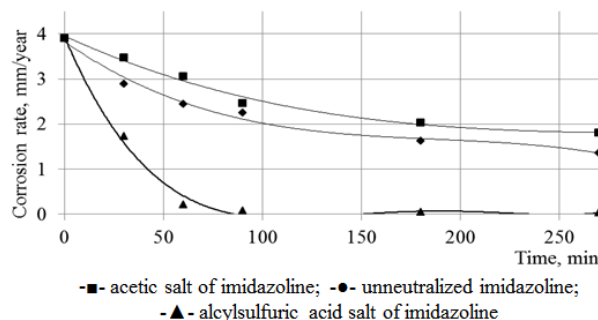


Fig. 2. Dependence of corrosion rate from time of imidazoline obtaining reaction and type of acid which took for neutralization

Corrosion rate in the media with presence of alkylsulfuric salt of imidazoline is less than 0.1 mm/year and it means that such compounds caught be used as highly effective corrosion inhibitors in aqueous media.

4.2 Interfacial tension of imidazolines and its salts.

Have been determined that imidazolines and its salts have an ability to adsorbs on solid surfaces of metals but the another important characteristic of surface-active substance (SAS) is ability to adsorbs on the interfacial border. Being adsorbed on phase boundary SAS usually promote decreasing of interfacial tension and as a result increase emulsifying ability. On Fig. 3 shown dependence of interfacial tension on border water/kerosene in the presence of imidazoline and its salt in different concentrations.

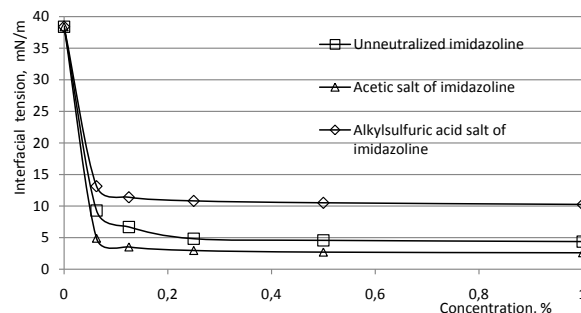


Fig. 3. Dependence of interfacial tension of imidazolines and its salts from its concentration

As shown on Fig. 3 interfacial tension decreased with increasing of SAS concentration. Minimum interfacial tension show acetic salt of imidazoline (2.6 mN/m) and maximum – alkylsulfuric salt of imidazoline (10.2 mN/m). The other characteristics of investigated SAS have been determined on the base of interfacial tension isotherms. The obtained results are in table 1.

Table 1
Interfacial tension, maximum adsorption, length and area of SAS molecule of imidazoline and its salts

Product	σ , mN/m	Γ_{\max} g-moll/ m ²	S, m ²	L, m
Unneutralized imidazoline	4,4	0,004736	3,63E-22	2,3E-28
Acetic salt of imidazoline	2,6	0,004027	4,21E-22	1,04E-28
Alkylsulfuric acid salt of imidazoline	10,2	0,002124	8,02E-22	1,98E-28

As shown in tabl. 1, maximum adsorption increases in row alkylsulfuric salt-acetic salt- unneutralized imidazoline. The value of maximum adsorption is in the same level as salts hydroxyethyl imidazoline salts [8] The area which occupy one molecule of SAS increases in row unneutralized imidazoline-acetic salt-alkylsulfuric salt. Obtained data caught be explained larger molecular mass and greater size of alkylsulfuric salt of imidazoline compare to unneutralized imidazoline. The area of unneutralized imidazoline and its acetic salt is in the same level because of low molecular weight and small size of acetic acid which form salt. This confirms results about defensive effect where best result have been shown by alkylsulfuric acid salt. Larger molecule of imidazoline salt provide better defense of metal surface.

4.3 Ability to form emulsion

It is well known that decreasing of interfacial tension leads to increasing the ability to emulsion formation [9, 10]. To investigate influence of imidazoline and its salts addition on emulsions formation standard “bottle” test have been conducted. The obtained results are shown on Fig. 4, 5.

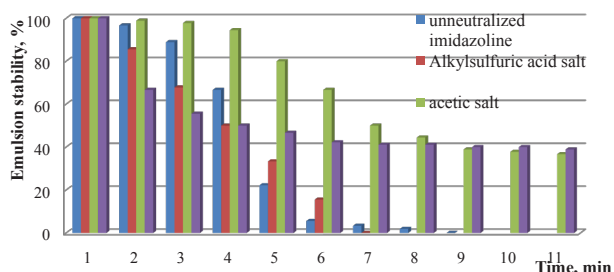


Fig. 4. Emulsion stability with addition of different imidazoline and its salts compare to sodium oleate. SAS concentration – 1 % wt

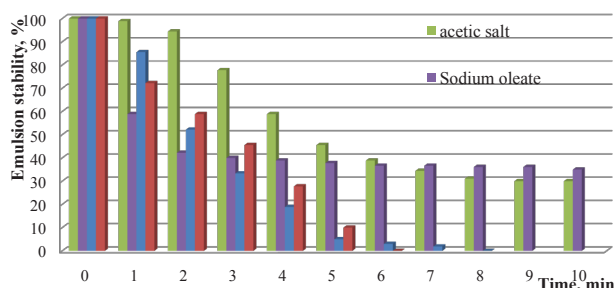


Fig. 5. Emulsion stability with addition of different imidazoline and its salts compare to sodium oleate. SAS concentration – 0.5 % wt

Have been determined (Fig. 1, 2) that best emulsifying ability have acetic salt of imidazoline. At the end of investigations there is 30% of undestroyed emulsion is left. Emulsion which was formed with unneutralized imidazoline was fully destroyed after 9 minutes of investigations and 6 minutes is required for destroying of emulsion formed by alkylsulfuric salt of imidazoline. Despite the best emulsion stability of acetic salt of imidazoline in this investigation it is still twice worse than emulsion stability which could be reached with use of hydroxyethyl imidazoline salts [8]

It should be noticed that sodium oleate and acetic salt form emulsion “oil in water” while unneutralized imidazoline and alkylsulfuric salt of imidazoline form emulsion “water in oil”. This happens due to the difference in HLB (hydrophilic-lipophilic balance) value of imidazoline and its salts. Calculated HLB of unneutralized imidazoline is 6,8 for alkylsulfuric salt – 4,1 and for acetic salt - 8,2. Obtained results are consistent with well known data that compounds with HLB from 0 to 8 promote “water in oil” emulsion formation while compounds with HLB from 8 to 13 promote “oil in water” emulsion formation [11].

5. Conclusions

On the base of conducted investigations the follow conclusions could be done:

1. The surface active properties of imidazoline depends not only from structure of imidazoline but also from type of acid which was took for neutralization;
2. The protective effect of imidazoline salts against corrosion increasing in row acetic salt- inneutralized imidazoline-alkylsulfuric salt of imidazoline
3. Corrosion rate in the presence on alkylsulfuric salt of imidazoline is less than 0.1 mm/year and on base of this index it could be used in compositions of corrosion inhibitors as main component.
4. Interfacial tension of acetic salt of imidazoline is 2.5 mN/m and by this value is at the level of many effective cationic surface active substances.
5. The highest among investigated interfacial tension of alkylsulfuric salt of imidazoline leads to low ability to form emulsion
6. The type of emulsion depends also from acid which took for neutralization

References

1. Divya Bajpai. Fatty imidazolines: Chemistry, Synthesis, Properties and Their industrial applications [Текст] / Bajpai Divya, V. K. Tyagi – Journal of oleo science. – 2008. – №. 7.
2. Tyagi, R. Imidazoline and its derivatives: an overview [Текст] / R. Tyagi, V. K. Tyagi, S. K. Pandey – Journal of oleo science. – 2007. - №. 56, P. 211-222.
3. Hydrolysis of 2-Substituted and 1,2-Disubstituted Imidazolines [Текст] / V. V. Lisitskii, Z. A. Akhmetchenko, I. E. Alekhina, Murinov Yu. I. - Russian Journal of Applied Chemistry. – 2007. – Vol. 80, № 5
4. Мельник, А. П. Дослідження одержання кисень- і азотовмісних похідних жирних кислот амідуванням лляної олії [Текст] / А.П. Мельник С.Г. Малік. – Вісник НТУ «ХП». – 2013 – № 38.

- Shaker, N. O. Adsorption and inhibitive properties of fatty imidazoline surfactants on mild steel [Текст] / N. O. Shaker, E. E. Badr, E. M. Kandeel. – Pelagia Research Library. Der Chemica Sinica. – 2011. – 2 (4): p. 26-35.
- Theoretical and experimental studies of structure and inhibition of imidazoline derivatives [Текст] / D.Wang, S. Li, Y. Ying, M. Wang, H. Xiao, Z. Chen – Corros. Sci. – 1999. – Vol. 41.
- Мельник, А. П. Дослідження утворення алкілімідазолінів з ріпакової олії [Текст] / А. П. Мельник, С. О. Крамарев, В. А. Руднев – Вісник НТУ «ХПІ». – 2010. - № 44. – С.87-92.
- Крамарев, С. О. Технологія одержання поверхнево-активних діацилгліцеринів та алкілімідазолінів амідуванням ріпакової олії [Текст]: автореф. дис. .. канд. техн. наук: спец. 05.18.06 “Технологія жирів, ефірних масел і парфумерно-косметичних продуктів” / С. О. Крамарев. – Харків, 2013. – 21 с.
- Mittal K. L. Micellization, solubilization, and microemulsions [Текст] / K. L. Mittal // American Chemical Society. – 1977 – 945 p.
- U.S. Pat. № 4464288. Emulsifier system / L.H. Sanders – 1984.
- Жогло, Ф.А. Жирсахара. Получение, свойства, применение [Текст] / Ф. А. Жогло // М. – Медицина. – 1975.

Досліджено процес суспензійної коолігомеризації ненасичених вуглеводнів фракції C₉ рідких продуктів піролізу в присутності органічних пероксидів. Встановлено залежність фізико-хімічних характеристик коолігомеру від природи ініціатора, зміну ненасиченості олігомеризату в ході процесу, вибрано стабілізатор суспензії, запропоновано ряд осаджувачів для стадії виділення коолігомеру

Ключові слова: суспензійна коолігомеризація, вуглеводнева фракція, ініціатор, коолігомер

Исследован процесс суспензионной коолигомеризации непредельных углеводородов фракции C₉ жидких продуктов пиролиза в присутствии органических пероксидов. Установлена зависимость физико-химических характеристик соолигомеров от природы инициатора, изменение ненасыщенности олигомеризата в ходе процесса, выбран стабилизатор суспензии, предложен ряд осадителей для стадии выделения соолигомеров

Ключевые слова: суспензионная коолигомеризация, углеводородная фракция, инициатор, коолигомер

УДК 678.747

ДОСЛІДЖЕННЯ СУСПЕНЗІЙНОЇ КООЛІГОМЕРИЗАЦІЇ НЕНАСИЧЕНИХ ВУГЛЕВОДНІВ ФРАКЦІЇ C₉, ІНІЦІЙОВАНА ОРГАНІЧНИМИ ПЕРОКСИДАМИ

О. М. Орбчук
Аспірант*

E-mail: or_oksana@ukr.net

У. В. Фуч
Аспірант*

E-mail: ylankafy4@mail.ru

Р. О. Субтельний
Кандидат технічних наук, доцент*

E-mail: subtelnyu@gmail.com

Б. О. Дзіняк
Кандидат технічних наук, доцент*

E-mail: dzinyak@lp.edu.ua

*Кафедра технології органічних продуктів
Національний університет

«Львівська політехніка»

вул. С. Бандери, 12, м. Львів, Україна, 79013

1. Вступ

Розвиток хімічної промисловості та розширення областей застосування декоративних і захисних матеріалів ставить перед лакофарбовою галуззю безліч різноманітних технічних завдань. До них відносяться не тільки покращення якості до світових стандартів,

але і зниження собівартості виробленої продукції. Одну з головних ролей в цьому відіграє модифікація лакофарбових матеріалів коолігомерами, які одержують з побічних продуктів процесів нафтопереробки. Враховуючи наявність сировини – побічних продуктів піролізу етиленових установок та широкої сфери застосування коолігомерів, їх виробництво є актуальним.