ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы
«Жанармай, катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel,
catalysis and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

4 (453)

OCTOBER – DECEMBER 2022

PUBLISHED SINCE JANUARY 1947

PUBLISHED 4 TIMES A YEAR

ALMATY, NAS RK

Бас редактор:

ЖҰРЫНОВ Мұрат Жұрынұлы, химия ғылымдарының докторы, профессор, ҚР ҰҒА академигі, Қазақстан Республикасы Ұлттық ғылым академиясының президенті, АҚ «Д.В. Сокольский атындағы отын, катализ және электрохимия институтының» бас директоры (Алматы, Қазақстан) Н = 4

Редакция алқасы:

ӘДЕКЕНОВ Серғазы Мыңжасарұлы (бас редактордың орынбасары), химия ғылымдарының докторы, профессор, ҚР ҰҒА академигі, «Фитохимия» Халықаралық ғылыми-өндірістік холдингінің директоры (Қарағанды, Қазақстан) Н = 11

АГАБЕКОВ Владимир Енокович (бас редактордың орынбасары), химия ғылымдарының докторы, профессор, Беларусь ҰҒА академигі, Жаңа материалдар химиясы институтының құрметті директоры (Минск, Беларусь) Н = 13

СТРНАД Мирослав, профессор, Чехия ғылым академиясының Эксперименттік ботаника институтының зертхана меңгерушісі (Оломоуц, Чехия) Н = 66

БҮРКІТБАЕВ Мұхамбетқали, химия ғылымдарының докторы, профессор, ҚР ҰҒА академигі, әл-Фараби атындағы ҚазҰУ-дың бірінші проректоры (Алматы, Қазақстан) Н = 11

ХОХМАНН Джудит, Сегед университетінің Фармацевтика факультетінің Фармакогнозия кафедрасының меңгерушісі, Жаратылыстану ғылымдарының пәнаралық орталығының директоры (Сегед, Венгрия) Н = 38

РОСС Самир, PhD докторы, Миссисипи университетінің Өсімдік өнімдерін ғылыми зерттеу ұлттық орталығы, Фармация мектебінің профессоры (Оксфорд, АҚШ) Н = 35

ХУТОРЯНСКИЙ Виталий, философия докторы (PhD, фармацевт), Рединг университетінің профессоры (Рединг, Англия) Н = 40

ТЕЛТАЕВ Бағдат Бұрханбайұлы, техника ғылымдарының докторы, профессор, ҚР ҰҒА корреспондент-мүшесі, Қазақстан Республикасы Индустрия және инфрақұрылымдық даму министрлігі (Алматы, Қазақстан) Н = 13

ФАРУК Асана Дар, Хамдар аль-Маджида Шығыс медицина колледжінің профессоры, Хамдард университетінің Шығыс медицина факультеті (Карачи, Пәкістан) Н = 21

ФАЗЫЛОВ Серік Драхметұлы, химия ғылымдарының докторы, профессор, ҚР ҰҒА академигі, Органикалық синтез және көмір химиясы институты директорының ғылыми жұмыстар жөніндегі орынбасары (Қарағанды, Қазақстан) Н = 6

ЖОРОБЕКОВА Шарипа Жоробекқызы, химия ғылымдарының докторы, профессор, Қырғызстан ҰҒА академигі, ҚР ҰҒА Химия және химиялық технология институты (Бішкек, Қырғызстан) Н = 4

ХАЛИКОВ Джурабай Халикович, химия ғылымдарының докторы, профессор, Тәжікстан ҒА академигі, В.И. Никитин атындағы Химия институты (Душанбе, Тәжікстан) Н = 6

ФАРЗАЛИЕВ Вагиф Меджидоглы, химия ғылымдарының докторы, профессор, ҰҒА академигі (Баку, Әзірбайжан) Н = 13

ГАРЕЛИК Хемда, философия докторы (PhD, химия), Халықаралық таза және қолданбалы химия одағының Химия және қоршаған орта бөлімінің президенті (Лондон, Англия) Н = 15

«ҚР ҰҒА Хабарлары. Химия және технология сериясы»
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РҚБ (Алматы қ.).Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген **№ KZ66VPY00025419** мерзімдік басылым тіркеуіне қойылу туралы куәлік.
Тақырыптық бағыты: *органикалық химия, бейорганикалық химия, катализ, электрохимия және коррозия, фармацевтикалық химия және технологиялар.*
Мерзімділігі: жылына 4 рет.
Тиражы: 300 дана.
Редакцияның мекен-жайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., тел.: 272-13-19
http://chemistry-technology.kz/index.php/en/arhiv

© Қазақстан Республикасының Ұлттық ғылым академиясы, 2022

Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д.В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекен-жайы: «Аруна» ЖК, Алматы қ., Мұратбаев көш., 75.

Главный редактор:

ЖУРИНОВ Мурат Журинович, доктор химических наук, профессор, академик НАН РК, президент Национальной академии наук Республики Казахстан, генеральный директор АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского» (Алматы, Казахстан) Н = 4

Редакционная коллегия:

АДЕКЕНОВ Сергазы Мынжасарович (заместитель главного редактора), доктор химических наук, профессор, академик НАН РК, директор Международного научно-производственного холдинга «Фитохимия» (Караганда, Казахстан) Н = 11

АГАБЕКОВ В ладимир Енокович (заместитель главного редактора), доктор химических наук, профессор, академик НАН Беларуси, почетный директор Института химии новых материалов (Минск, Беларусь) Н = 13

СТРНАД Мирослав, профессор, заведующий лабораторией института Экспериментальной ботаники Чешской академии наук (Оломоуц, Чехия) Н = 66

БУРКИТБАЕВ Мухамбеткали, доктор химических наук, профессор, академик НАН РК, Первый проректор КазНУ имени аль-Фараби (Алматы, Казахстан) Н = 11

ХОХМАНН Джудит, заведующий кафедрой Фармакогнозии Фармацевтического факультета Университета Сегеда, директор Междисциплинарного центра естественных наук (Сегед, Венгрия) Н = 38

РОСС Самир, доктор PhD, профессор Школы Фармации национального центра научных исследований растительных продуктов Университета Миссисипи (Оксфорд, США) Н = 35

ХУТОРЯНСКИЙ Виталий, доктор философии (Ph.D, фармацевт), профессор Университета Рединга (Рединг, Англия) Н = 40

ТЕЛЬТАЕВ Багдат Бурханбайулы, доктор технических наук, профессор, член-корреспондент НАН РК, Министерство Индустрии и инфраструктурного развития Республики Казахстан (Алматы, Казахстан) Н = 13

ФАРУК Асана Дар, профессор колледжа Восточной медицины Хамдарда аль-Маджида, факультет Восточной медицины университета Хамдарда (Карачи, Пакистан) Н = 21

ФАЗЫЛОВ Серик Драхметович, доктор химических наук, профессор, академик НАН РК, заместитель директора по научной работе Института органического синтеза и углехимии (Караганда, Казахстан) Н = 6

ЖОРОБЕКОВА Шарипа Жоробековна, доктор химических наук, профессор, академик НАН Кыргызстана, Институт химии и химической технологии НАН КР (Бишкек, Кыргызстан) Н = 4

ХАЛИКОВ Джурабай Халикович, доктор химических наук, профессор, академик АН Таджикистана, Институт химии имени В.И. Никитина АН РТ (Душанбе, Таджикистан) Н = 6

ФАРЗАЛИЕВ Вагиф Меджид оглы, доктор химических наук, профессор, академик НАНА (Баку, Азербайджан) Н = 13

ГАРЕЛИК Хемда, доктор философии (Ph.D, химия), президент Отдела химии и окружающей среды Международного союза чистой и прикладной химии (Лондон, Англия) Н = 15

«Известия НАН РК. Серия химии и технологий».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан **№ KZ66VPY00025419,** выданное 29.07.2020 г.

Тематическая направленность: *органическая химия, неорганическая химия, катализ, электрохимия и коррозия, фармацевтическая химия и технологии.*

Периодичность: 4 раз в год.

Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, оф. 219, тел.: 272-13-19

http://chemistry-technology.kz/index.php/en/arhiv

© Национальная академия наук Республики Казахстан, 2022

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142, АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75.

Editor in chief:

ZHURINOV Murat Zhurinovich, doctor of chemistry, professor, academician of NAS RK, president of NAS RK, general director of JSC "Institute of fuel, catalysis and electrochemistry named after D.V. Sokolsky (Almaty, Kazakhstan) H = 4

Editorial board:

ADEKENOV Sergazy Mynzhasarovich (deputy editor-in-chief) doctor of chemical sciences, professor, academician of NAS RK, director of the international Scientific and production holding «Phytochemistry» (Karaganda, Kazakhstan) H = 11

AGABEKOV Vladimir Enokovich (deputy editor-in-chief), doctor of chemistry, professor, academician of NAS of Belarus, honorary director of the Institute of Chemistry of new materials (Minsk, Belarus) H = 13

STRNAD Miroslav, head of the laboratory of the institute of Experimental Botany of the Czech academy of sciences, professor (Olomouc, Czech Republic) H = 66

BURKITBAYEV Mukhambetkali, doctor of chemistry, professor, academician of NAS RK, first vice-rector of al-Farabi KazNU (Almaty, Kazakhstan) H = 11

HOHMANN Judith, head of the department of pharmacognosy, faculty of Pharmacy, university of Szeged, director of the interdisciplinary center for Life sciences (Szeged, ungary) H = 38

ROSS Samir, Ph.D, professor, school of Pharmacy, national center for scientific research of Herbal Products, University of Mississippi (Oxford, USA) H = 35

KHUTORYANSKY Vitaly, Ph.D, pharmacist, professor at the University of Reading (Reading, England) H = 40

TELTAYEV Bagdat Burkhanbayuly, doctor of technical sciences, professor, corresponding member of NAS RK, ministry of Industry and infrastructure development of the Republic of Kazakhstan (Almaty, Kazakhstan) H = 13

PHARUK Asana Dar, professor at Hamdard al-Majid college of Oriental medicine. faculty of Oriental medicine, Hamdard university (Karachi, Pakistan) H = 21

FAZYLOV Serik Drakhmetovich, doctor of chemistry, professor, academician of NAS RK, deputy director for institute of Organic synthesis and coal chemistry (Karaganda, Kazakhstan) H = 6

ZHOROBEKOVA Sharipa Zhorobekovna, doctor of chemistry, professor, academician of NAS of Kyrgyzstan, Institute of Chemistry and chemical technology of NAS KR (Bishkek, Kyrgyzstan) H = 4

KHALIKOV Jurabay Khalikovich, doctor of chemistry, professor, academician of the academy of sciences of tajikistan, institute of Chemistry named after V.I. Nikitin AS RT (Tajikistan) H = 6

FARZALIEV Vagif Medzhid ogly, doctor of chemistry, professor, academician of NAS of Azerbaijan (Azerbaijan) H = 13

GARELIK Hemda, PhD in chemistry, president of the department of Chemistry and Environment of the International Union of Pure and Applied Chemistry (London, England) H = 15

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Owner: RPA «National Academy of Sciences of the Republic of Kazakhstan» (Almaty).
The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan **No. KZ66VPY00025419,** issued 29.07.2020.
Thematic scope: *organic chemistry, inorganic chemistry, catalysis, electrochemistry and corrosion, pharmaceutical chemistry and technology.*
Periodicity: 4 times a year.
Circulation: 300 copies.
Editorial address: 28, Shevchenko str., of. 219, Almaty, 050010, tel. 272-13-19
http://chemistry-technology.kz/index.php/en/arhiv

© National Academy of Sciences of the Republic of Kazakhstan, 2022

Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: ST «Aruna», 75, Muratbayev str, Almaty.

NEWS
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC
OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
https://doi.org/10.32014/2518-1491.134
Volume 4, Number 453 (2022) 58-68

UDK 691.175.5/.8
SCSCTI 32.25.19

Zh. Kassenova*, S. Kozhabekov, A. Zhubanov, A. Galymzhan

Kazakh-British Technical University, Almaty, Kazakhstan.
E-mail: zhanar.kassenova@gmail.com

SYNTHESIS AND CHARACTERIZATION OF COMB-LIKE ALKYL FUMARATE – OCTADECEN-1 COPOLYMERS

Abstract. Handling oils and petroleum products with high content of paraffins and asphaltenes might cause problems especially when ambient temperature is lower than the pour point. Polymers with comb-like structures such as polyalkyl fumarates with long chain pending groups are considered to have pour point depressing properties. However, alkyl fumarates with long straight side groups are difficult to homopolymerize. Therefore, alkyl fumarates are usually undergo through copolymerization with other comonomers. The literature review revealed that the studies on the synthesis of the fumarate copolymers are limited. The current study focused on synthesis of alkyl fumarate copolymers with octadecen-1 through solution polymerization. Alkyl fumarates were obtained through esterification reaction between fumaric acid and fatty saturated alcohols. The structures of the synthesized alkyl fumarates and copolymers were confirmed using Fourier-transform infrared (FTIR) and Nuclear magnetic resonance (NMR) spectroscopy methods. The intrinsic viscosity of the copolymers was measured using capillary viscometer and the Huggins' method. The melting points of the products was also determined. The characterization of the synthesized alkyl fumarates and their copolymers with the α-olefin confirmed their expected structures and properties. The study helps to find optimal parameters to synthesize copolymers that have comb-like structure with long side groups and might be used as pour point depressants for heavy oils.

Key words: comb-like polymers, alkyl fumarate copolymers, solution polymerization, pour point depressants, wax inhibitors, intrinsic viscosity.

Ж. Касенова*, С. Кожабеков, Ә. Жубанов, А. Ғалымжан

Қазақстан-Британ техникалық университеті, Алматы, Қазақстан.
E-mail: zhanar.kassenova@gmail.com

АЛКИЛ ФУМАРАТТАР МЕН ОКТАДЕЦЕН-1-НІҢ СОПОЛИМЕРЛЕРІН СИНТЕЗДЕУ ЖӘНЕ ЗЕРТТЕУ

Аннотация. Құрамында парафиндері мен асфальтендері көп мұнай және мұнай өнімдерін тасымалдау кезінде мәселелер туындауы мүмкін, әсіресе қоршаған ортаның төмен температурасында бұл жағдайлар жиілеп кетеді. Осындай мәселеледі шешудің бір жолы – құю нүктесін төмендететін депрессорлық қоспа қолдану. Ұзын бүйірлік тізбектері бар полиалкил фумараттарға ұқсас тарақ тәрізді полимерлер депрессорлар ретінде қолдану мүмкіндігіне ие. Бірақ түзу ұзын бүйірлік тармақтары бар алкил фумараттардың гомополимеризация реакциясына түсуі қиынға соғады. Сондықтан көбінесе мұндай алкил фумараттарды басқа мономерлермен сополимерленуге ұшыратқызады. Әдебиеттерді шолу алкил фумаратты сополимерлердің синтезі саласындағы шектеулі зерттеулердің бар екенін көрсетті. Бұл мақала алкил фумаратты октадецен-1-мен ерітінді күйінде сополимерлеу реакциясына және алынатын өнімдердің қасиеттерін зерттеуге бағытталған. Алкил фумараттар фумар қышқылының майлы қаныққан біріншілік спирттермен этерификация реакциясы арқылы алынды. Синтезделген алкил фумараттар мен олардың сополимерлерінің құрылымдары инфрақызыл (ИҚ) Фурье спектроскопиясы және ядролық магниттік-резонанстық (ЯМР) спектроскопиясы арқылы расталды. Сополимерлердің меншікті тұтқырлығы капиллярлық вискозиметрмен өлшеніп, Хаггинс әдісімен график тұрғызу арқылы анықталды. Сонымен қатар, алынған өнімдердің балқу температуралары анықталды. Синтезделген алкил фумараттар мен олардың α-олефинмен сополимерлерін зерттеу күтілген құрылымдар мен қасиеттерді растады. Алынған сополимерлердің балқу температурасы мен меншікті тұтқырлығы арасындағы корреляция анықталды. Бұл жұмыс ауыр майлар мен жоғары құю температурасы бар мұнай өнімдері үшін депрессорлық қоспа ретінде пайдалануға болатын ұзын бүйірлік тізбектері бар тарақты сополимерлердің синтезінің оңтайлы параметрлерін анықтауға көмектеседі.

Түйін сөздер: тарақ тәрізді полимерлер, алкил фумараттың сополимерлері, ертіндідегі полимеризация, депрессорлық қоспа, парафиндер ингибиторлары, меншікті тұтқырлық.

Ж. Касенова*, С. Кожабеков, Ә. Жубанов, А. Ғалымжан

Казахстанско-Британский технический университет, Алматы, Казахстан.
E-mail: zhanar.kassenova@gmail.com

СИНТЕЗ И ИССЛЕДОВАНИЕ ГРЕБНЕОБРАЗНЫХ СОПОЛИМЕРОВ АЛКИЛ ФУМАРАТОВ С ОКТАДЕЦЕНОМ-1

Аннотация. Одна из частых проблем, возникающих при транспортировке нефти и нефтепродуктов при низких температурах окружающей среды, обусловлена выпадением кристаллов парафиновых углеводородов, которые, слипаясь в крупные частицы, создают пространственную структурную сетку в топливе. Применение депрессорных присадок позволяет снизить температуру застывания нефти. Полимеры с гребнеобразной структурой, как в случае с полиалкил фумаратами с длинными боковыми звеньями, имеют потенциал для применения их в качестве депрессорных присадок. Однако алкил фумараты с прямыми длинными ответвлениями сложно подвергаются гомополимеризации. Поэтому чаще всего такие алкил фумараты подвергают сополимеризации с другими мономерами. Литературный обзор показал ограниченные исследования в области синтеза сополимеров алкил фумаратов. Данное исследование направлено на синтез алкил фумаратов с октадецен-1-ом способом полимеризации в растворе. Алкил фумараты были получены реакцией этерификации фумаровой кислоты с жирными насыщенными первичными спиртами. Структуры синтезированных алкил фумаратов и их сополимеров были подтверждены с помощью инфра красной (ИК) Фурье спектроскопии и спектроскопией ядерно-магнитного резонанса (ЯМР). Характеристическая вязкость сополимеров была измерена капиллярным вискозиметром и определена методом Хаггинса. Кроме того, были измерены температуры плавления полученных продуктов. Исследование синтезированных алкил фумаратов и их сополимеров с α-олефином подтвердили ожидаемые структуры и свойства. Выявлена корреляция между температурами плавления и характеристическими вязкостями полученных сополимеров. Данная работа поможет при определении оптимальных параметров для синтеза сополимеров с гребнеобразной структурой с длинными боковыми звеньями, которые могут быть применены в качестве депрессорных присадок для тяжелых нефтей и нефтепродуктов с высокими температурами застывания.

Ключевые слова: гребнеобразные полимеры, сополимеры алкил фумарата, полимеризация в растворе, депрессорные присадки, ингибиторы парафиновых отложений, характеристическая вязкость.

Introduction. Due to depletion of light crude oils worldwide nowadays there is a tendency to produce and refine heavy oils with high content of paraffins and asphaltenes. During production, transportation, and storage of heavy oils, problems arise because of high viscosity and solid wax deposits that appear when operational temperature is below the pour point. Wax deposits usually consist of paraffins, asphaltenes and resins. They might lead to flow pressure drop and full or partial blockage of pipelines. The problem worsens especially during temporary shut downs when temperature and paraffins solubility decreases and gel forms. One of the methods to prevent wax deposits is to apply special chemical agents that decrease fluid viscosity and modify crystal growth. These chemicals are called pour point depressants (PPDs), flow improvers or wax inhibitors. They insert themselves inside crystal structures and change the growth dynamics, shapes, and surface properties. These agents modify crystal growth patterns by cocrystallization resulting in lowering pour point temperature and viscosity. Upon addition of the wax crystal modifiers to oil the crystals growth stops earlier and their surface shape becomes intrinsic. This shape in turn hinders intergrowth and interlock of crystals. However, there is no general universal form of a crystal modifier since its composition is specific to a crude oil type. Cocrystallization that helps widen operational temperature range occurs between normal alkanes in oil and long straight alkyl side chains of polymers used as flow improver (El-Dalatony et al., 2019:968).

In general, two types of copolymers have found application as chemical agents that improve flowability of crude oil. They are polymers with crystalline/amorphous diblock structure and comb-type polymers that are usually synthesised from esterified dicarboxylic unsaturated acids with another co-monomer. The latter type has significant advantage since they include both polar (carboxylic group) and non-polar parts (long alkyl groups). This would help to affect both compounds that contributes low flowing ability: paraffins being non-polar and asphaltenes that are considered polar (Jang et al., 2007:13174). Polymers with comb structure have long pending hydrocarbyl groups attached to the main chain. Thus, comb-like polymers have two types of structural units: the backbone and long side chains. They have intermediate positions between linear and branched structures. The comb-like polymers' physical and chemical properties differ from linear and branched structures (Plate et al., 1974:117).

Fumarates with long alkyl groups could be considered as an appropriate starting compound for synthesis of PPDs. Presence of double bond in dialkyl fumarates (DRFs) should give an ability to polymerize via radical polymerization mechanism where a double bond reform as a single bond. However, as literature review revealed DRFs with long alkyl groups do not homopolymerize very well. DRFs are considered to be 1,2-disubstituted ethylenes, and in the past it has been generally accepted that their homopolymerization tends to proceeds with difficulties due to steric hindrance of the substituents (Otsu et al., 1981:726). Further investigations revealed that DRFs do not homopolymerise in the absence of radical initiator even under high temperature. DRFs with alkyl groups of normal linear structure have low polymerisation reactivity and number of carbons does not affect it (Otsu et al., 1988:549). Effect of different alkyl groups on propagation and termination rate constants was studied. The results of the experiments correlated with the previous studies: the bulky di-tert-butyl substituents promote propagation reaction and suppress termination reaction (Matsumoto et al., 1996:296). Fortunately, fumarate is successfully copolymerize with electron-rich monomers like vinyl acetate (Borthakur et al., 1995:77), (Peng et al., 2002:66). Other studies focused on determining dependence between molecular weight of behenyl fumarate-vinyl acetate copolymer on pour point depressing performance (Borthakur et al., 1996:846). Copolymerizations of behenyl acrylate and behenyl fumarate in the presence of benzoyl peroxide in toluene (Sarmah et al., 2003:2722), vinyl acetate and behenyl fumarate by a bulk technique (Baruah et al., 2011:228) were reported. Prior studies in the area of fumarate copolymers were limited by number of comonomers and have not established dependence of their performance on the structure.

The objective of the research is to synthesize new type of copolymers of alkyl fumarates with the α-olefin through solution polymerization technique and to characterize the products that have potential to be used as pour point depressant for heavy oils.

Application of chemical agents as a method of mitigation the problem of solid wax deposits during heavy oils transportation is efficient as long as the appropriate structure of comb-like polymer is used. Thorough study of its synthesis and effect of reaction parameters on the product properties facilitates the process of selection of the most efficient pour point depressant.

Materials and Methods. The methods for synthesis of alkyl fumarates and their copolymers, and carried analysis are given below.

Esterification: Dihexadecyl fumarate (DHDF), Dioctadecyl fumarate (DODF), and dibehenyl fumarate (DBF) were synthesized through esterification reaction. The reaction took place between fumaric acid and primary fatty alcohols in the presence of p-toluenesulfonic acid at 120°C for 8 hours. The catalyst was applied in an amount of 1% of the reactants by weight. The molar ratio of fumaric acid and an alcohol was 1:2. The reagents were dissolved in toluene in a stream of dry nitrogen. Dean–Stark apparatus was connected to the reaction vessel to remove water that formed during esterification. The reaction took place until the calculated amount of water was released. The reaction solution was filtered in a hot state. Toluene was removed by vacuum distillation. The product was rinsed with ethyl alcohol and dried in vacuum at 40°C up to constant weight.

Copolymerization: The synthesized fumarates were copolymerized with octadecen-1 (ODC). The molar ratio of fumarate and ODC was 1:1. As an initiator of radical polymerization benzoyl peroxide was used in an amount of 2% of the reactants by weight. The monomers were dissolved in toluene. The concentration of the solution was 40% by weight. Copolymerization reactions were carried at 75-85°C and with a constant flow of nitrogen. The duration of the copolymerization was 15 hours. The copolymers were purified by the same way as the esterification products.

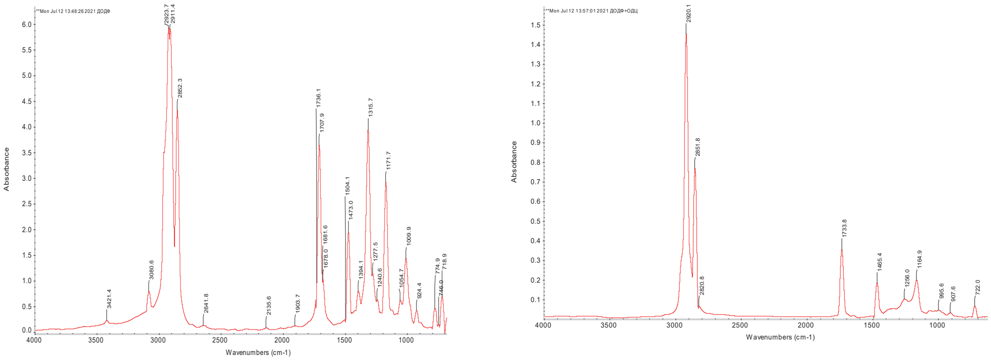
Instrumental methods: Melting points of the obtained alkyl fumarates were measured using OptiMelt - Automated Melting Point System (Stanford Research Systems, USA). The measurements were made with open capillaries.

Structural features and functional groups of the products were characterized by FTIR spectroscopy (Nicolet 5700) within a range of 4000-400 cm^{-1}. The samples were prepared by dissolving copolymers in xylene at a concentration of 20% by weight. In addition, ^{1}H and ^{13}C NMR spectra were obtained using a JNM-ECA Jeol 400 spectrometer operating at 399.78 and 100.53 MHz, respectively. The samples for the NMR analysis were dissolved in $CDCl_3$ and their chemical shifts δ were measured relative to the residual protons or carbon atoms in $CDCl_3$.

Intrinsic viscosity [η] of the synthesized copolymers were measured at 25°C with an Ubbelohde type viscometer and by the Huggins' plot method (Huggins, 1942:2718). Different concentrations of copolymers solutions in tetrahydrofuran were prepared (0.25; 0.50; 0.75; 1.0 % by weight). Relative viscosity is determined using flow times of pure solvent and the solutions. Specific and reduced viscosities are calculated after that. The plot was built indicating a relation between reduced viscosity and concentration of the solution. Intrinsic viscosity was determined by extrapolation of the curve to zero concentration.

Result and discussion. Characterization of the obtained products and data from the measurements are given and discussed below.

Characterization: The Fig 1 show FTIR spectra of DODF and DODF-ODC respectively.



a. b.

Figure 1. FTIR spectra of DODF (a) and DODF-ODC (b)

FTIR-spectra of obtained alkyl fumarates (Fig 1 a) have peaks at 3080 cm^{-1} of the C=C-H stretching vibrations and at 1681-1678 cm^{-1} of the isolated double bond C=C stretching vibrations. Weak intensity peaks at 1681-1678 cm^{-1} are specific to trans-disubstituted alkenes that corresponds to the structure of fumaric esters since fumaric acid is a trans-isomer of butenedioic acid. Absorption bands characteristic for C-H antisymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations at 2911 cm^{-1} and 2852 cm^{-1} are present in the spectra of the fumarates. The peaks at 1473 cm^{-1} corresponds to bending vibrations of C-H belonging to aliphatic groups. Characteristic vibrations at 1750-1700 cm^{-1} belongs to symmetric (ν_s) stretching vibrations of C=O in esters which is confirmed by presence of peaks at 1707 cm^{-1}. Absorption bands at 1315 cm^{-1} corresponds to vibrations of O=C–O.

Compared to the FTIR spectra of alkyl fumarate monomers, the FTIR spectra of the synthesized copolymers (Fig 1 b) do not contain stretching vibrations peaks of C=C-H and C=C double bonds at 3080 cm^{-1} and 1681-1678 cm^{-1} respectively. Meanwhile, stretching vibrations of C=O at 1707 cm^{-1} of fumarate monomer spectra shifted to the wavelength of 1733 cm^{-1} at copolymers spectra. The reason of the shift is that electron rich α-olefin comonomer has replenished electron deficiency of the alkyl fumarate. After copolymerization density of an electron cloud of former double carbon-carbon bond increased. As a result, inductive effect of C=O has lost its strength. The FTIR spectra of both alkyl fumarates and the copolymers has absorption bands at 722-718 cm^{-1} which corresponds to absorption region specific to fragments $(\text{-CH}_2)_n$, at n≥4. The resulting FTIR spectra reveals that all specific functional groups are present in a structure of alkyl fumarates and their copolymers. Absence of double bonds in the synthesized copolymers indicates that copolymerization reactions were conducted successfully.

Figs 2 and 3 represent ^{1}H and ^{13}C NMR spectra of DODF respectively.

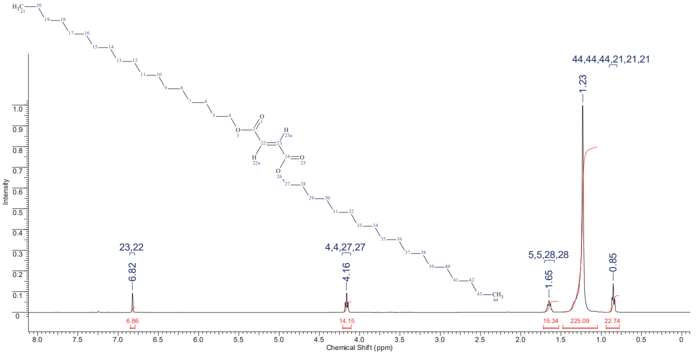


Figure 2. ^{1}H NMR spectrum of DODF

In the ^{1}H NMR spectrum of DODF (Fig 2) terminal methyl protons H-21, 21, 21, 44, 44, 44 are observed by multiplet signal at 0.84-0.87 ppm with integrated intensity of 6H. Unsaturated ethylene protons appeared as double proton H-22, 23 singlet at 6.82 ppm. Protons next to carboxylate groups were registered as four protons H-4, 4, 27, 27 multiplet at 4.15-4.18 ppm. Methylene protons H-5, 5, 28, 28 of dioctadecyl fragments resonated as four protons multiplet at 1.63-1.66 ppm. Other methylene protons of aliphatic parts were observed as intensive singlet at 1.23 ppm with integrated intensity of 60 H.

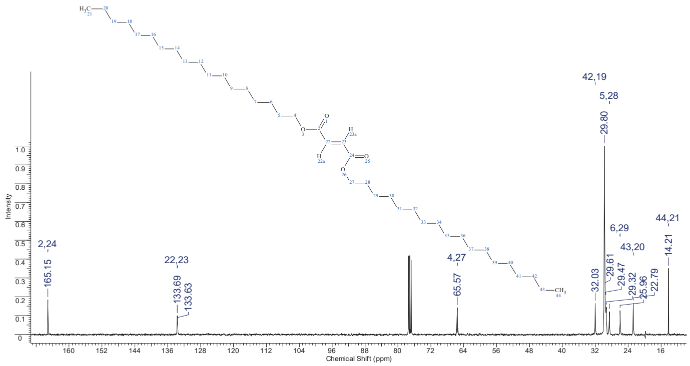


Figure 3. ^{13}C NMR spectrum of DODF

In the ^{13}C NMR spectrum of DODF (Fig 3) carbon atoms C-21, 44 of terminal methyl groups are observed at 14.21 ppm. Methylene carbon atoms of dodecyl fragment resonate at 65.57 (C-4, 27); 32.03 (C-19, 42); 28.50 (C-5, 28); 25.96 (C-6, 29); 23.79 (C-20, 43) ppm. Other methylene groups resonate at 29.47 and 29.80 ppm. Unsaturated carbon atoms C-22 and C-23 appeared at 133.69 ppm. Carbon atoms C-2, 24 of carboxyl groups resonated at 165.15 ppm.

Fig 4 shows ^{1}H NMR spectrum of DODF-ODC.

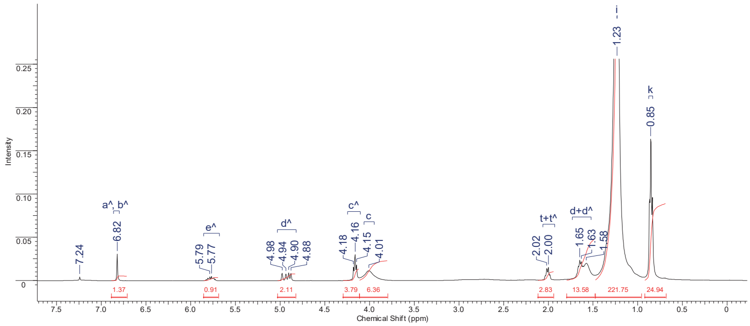


Figure 4. ^{1}H NMR spectrum of DODF-ODC

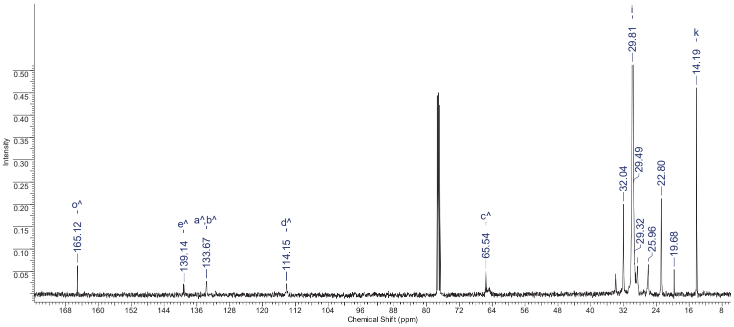


Figure 5. ^{13}C NMR spectrum of DODF-ODC

In the ^{1}H NMR spectrum of DODF-ODC copolymer (Fig 4) new bands have appeared that were not observed in the ^{1}H NMR spectrum of the alkyl fumarates. For instance, the bands at a region of 1.58-2.02 ppm are responsible for the presence of some methylene protons adjacent to long methylene chains. Also, the singlet with broad absorption band has appeared at 4.01 ppm that reveals proton next to carboxylate group. This proves that the double bond of the fumarate monomer opened up during copolymerization. Another newly appeared group of bands at the region of 4.88-4.98 and 5.77-5.79 ppm corresponds to terminal protons of the former double bond of octadecen-1. All the obtained spectra indicate that the synthesized alkyl fumarates and the copolymers have the appropriate structures.

The data related to other alkyl fumarates (DHDF and DBF) and copolymers (DHDF-ODC, DBF-ODC) are given in Table 1.

Table 1. Data of spectroscopic analysis of alkyl fumarates and their copolymers

	FTIR spectroscopy	^{1}H NMR spectroscopy
Dialkyl fumarate/ copolymer name	Wavenumber (cm^{-1}) of the absorption bands	Chemical shifts δ (ppm) of the absorption signals
DHDF	3080, 1679, 2926, 2904, 2853, 1472, 1393, 1711, 1314, 1167, 720	6.82, 4.15–4.18, 1.65, 1.23, 0.85
DBF	3079, 1681, 2924, 2906, 2850, 1472, 1395, 1709, 1316, 1169, 718	6.82, 4.15-4.17, 1.65, 1.23, 0.85
DHDF-ODC	2919, 2850, 1729, 1467, 1238, 1169, 923, 717	6.82, 5.79, 4.89–4.99, 4.15–4.19, 4.01, 2.01, 1.64–1.69, 1.58, 1.24, 0.88
DBF-ODC	2920, 2851, 2820, 1733, 1465, 1256, 1164, 995, 907, 722	6.82, 5.79, 4.89-4.98, 4.16, 4.00, 2.02-2.00, 1.57, 1.23, 0.85-0.84.

The synthesized fumarates and copolymers characteristics. The melting point and yield values for alkyl fumarates are given in Table 2.

Table 2. Synthesized alkyl fumarates and their measured melting points.

Alkyl fumarate	Melting point, °C	Yield, % wt.
Dihexadecyl fumarate (DHDF)	61,7-63,6	93
Dioctadecyl fumarate (DODF)	70.1-71.2	89
Dibehenyl fumarate (DBF)	76.8-80.8	83

The tendency of melting point to increase as molecular weight of the pending alkyl group increases is apparent. This corresponds to a general concept that melting points of linear homologous compounds rises as number of methylene groups are added. It could be explained by intermolecular forces that strengthens as more atoms are included in the structure (Chickos, 2001: 562).

The results of determined intrinsic viscosity [η] and measured melting point values of the copolymers are given in Table 3.

Table 3. Synthesized alkyl fumarate copolymers and their measured intrinsic viscosities

Copolymer	Intrinsic viscosity [η], dL/g	Melting point, °C	Yield, % wt.
DHDF-ODC	0.0277	56.3-59.3	66
DODF-ODC	0.0203	45.8-47.4	87
DBF-ODC	0.0308	57.9-59.5	84

All the curves of built Huggins' plot showed adequate linearity within a given concentration range. No abnormalities were observed, all curves have upward directions, indicating usual relationship between reduced viscosity and concentration of the polymers in solutions.

One of the aims of the study is to define parameters for the synthesis of high molecular weight alkyl fumarate copolymers. Intrinsic viscosity of a polymer in the solvent is one of the two ways along with molten viscosity to measure an average degree of polymerization. According to Mark-Houwink-Sakurada equation, intrinsic viscosity is directly proportional to molecular weight of a polymer. Moreover, viscosity is influenced by molecular weight distribution of a polymer. There is a direct relationship between intrinsic viscosity and a chain length (Sanches et al., 2005:690). It could be concluded that the higher intrinsic viscosity of a polymer, the higher molecular weight it has.

The results from Table 3 indicates that there is no apparent correlation between molecular weight of the alkyl group of fumarates and intrinsic viscosity of the respective copolymer. However, there is a correlation between melting point and intrinsic viscosity of the copolymers. It is well justifiable since intrinsic viscosity is directly proportional to a molecular weight of a polymer that affects important physical parameters such as transition temperatures and mechanical properties. In addition, a size of side groups pending from the main chain affects melting point of a polymer due to change in flexibility of the chain (Bunn, 1955:330).

Conclusion. The three copolymers of alkyl fumarates with octadecen-1 were synthesized by solution polymerization technique. The structures and specific functional groups were confirmed by FTIR and NMR spectroscopy methods. The results of the melting points and intrinsic viscosities measurements showed appropriate correlations. The study could be used to find optimal parameters for efficient copolymerization of alkyl fumarate copolymers. Generally, more study should be conducted to find optimal conditions for synthesis of alkyl fumarate copolymers since their comb-like structures make them appealing for application as pour point depressants.

Acknowledgements. *This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan under the theme "Synthesis and modification of copolymers based on vinyl monomers as pour point depressants for wax crude oils" (2020-2022) (Grant number AP08855445).*

Information about authors:

Kassenova Zhanar Sagatbekovna – PhD student, Kazakh-British Technical University, zhanar.kassenova@gmail.com, https://orcid.org/0000-0001-9123-0730;

Kozhabekov Serik Samsalykovich – Candidate of Chemical Sciences, Professor, Kazakh-British Technical University, skozhabekov.49@mail.ru, https://orcid.org/0000-0002-7689-9089;

Zhubanov Amin Abdirasululy – Kazakh-British Technical University, PhD student, amin.zhuban@gmail.com, https://orcid.org/0000-0003-1194-8094;

Galymzhan Aknur Zeiinkyzy – Master of Chemical Engineering, Kazakh-British Technical University, aknurzg@gmail.com, https://orcid.org/0000-0002-3080-7206.

REFERENCES:

Baruah S.D., Sarmah D., Laskar N.C. (2011). Copolymers of bulky fumarate: synthesis and their properties. J. Polym. Res., 18: 225–233. https://doi.org/10.1007/s10965-010-9410-8 (in Eng.).

Borthakur A., Laskar N.C., Mazumdar R.K., Rao K.V., Subrahmanyam B. (1995). Synthesis and evaluation of alkyl fumarate-vinyl acetate copolymers in combination with alkyl acrylates as flow improvers for Borholla crude oil, J. Chem. Tech. Biotechnol., 62: 75-80. https://doi.org/10.1002/jctb.280620112 (in Eng.).

Borthakur A., Chanda D., Choudhury S.R.D., Rao K.V., Subrahmanyam B. (1996). Alkyl fumarate-vinyl acetate copolymer as flow improver for high waxy Indian crude oils, Energy & Fuels, 10: 844-848. https://doi.org/10.1021/ef950237u (in Eng.).

Bunn C.W. (1955). The melting points of chain polymers, J. Polym. Sci., 16: 323–343. https://doi.org/10.1002/pol.1955.120168222 (in Eng.).

Chickos J.S., Nichols G. (2001). Simple relationships for the estimation of melting temperatures of homologous series, J. Chem. Eng., 46:562-573. https://doi.org/10.1021/je0002235 (in Eng.).

El-Dalatony M.M., Jeon B., Salama E., Eraky M., Kim W., Wang J., Ahn T. (2019). Occurrence and characterization of paraffin wax formed in developing wells and pipelines, Energies, 12: 967-989. https://doi.org/10.3390/en12060967 (in Eng.).

Huggins M.L. (1942). The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. J. Am. Chem. Soc., 64: 2716-2718. https://doi.org/10.1021/ja01263a056 (in Eng.).

Jang Y.H., Blanco M., Creek J., Tang Y., Goddard W.A. (2007). Wax Inhibition by comb-like polymers: support of the incorporation-perturbation mechanism from molecular dynamics simulations, J. Phys. Chem. B, 111: 13173-13179. https://doi.org/10.1021/jp072792q (in Eng.).

Matsumoto A., Sano Y., Yoshioka M., Otsu T. (1996). Kinetic study of radical polymerization of dialkyl fumarates using electron spin resonance spectroscopy. J. Polymer. Sci. A: Polymer. Chem., 34: 291-299. https://doi.org/10.1002/(SICI)1099-0518(19960130)34:2<291::AID-POLA15>3.0.CO;2-L (in Eng.).

Otsu T., Yasuhara T., Matsumoto A. (1988). Synthesis, characterization, and application of poly [substituted methylene]s, J. Macromol. Sci. Chem., A, 25: 537-554. https://doi.org/10.1080/00222338808053383 (in Eng.).

Otsu T., Ito O., Toyoda N., Mori S. (1981) Polymers from 1,2-disubstituted ethylenic monomers, 2a) homopolymers from dialkyl fumarates by radical initiator, Makromol. Chem., Rapid Commun., 2: 725 – 728. https://doi.org/10.1002/marc.1981.030021204 (in Eng.).

Peng H-Y., Yang Y-S., Qi G-R. (2002). N-dioctadecyl fumarate–vinyl acetate copolymer: synthesis, characterization and application as flow improver for oils, Pet. Sci. Technol., 20: 65-75. https://doi.org/10.1081/LFT-120002087 (in Eng.).

Plate N.A., Shibaev V.P. (1974). Comb-like polymers. Structure and properties, J. Polymer Sci.: Macromolecular Reviews, 8: 117-253. https://doi.org/10.1002/pol.1974.230080103 (in Eng.).

Sanches N., Dias M., Pacheco E. (2005). Comparative techniques for molecular weight evaluation of poly (ethylene terephthalate) (PET), Polym. Test, 24: 688–693. https://doi.org/10.1016/j.polymertesting.2005.05.006 (in Eng.).

Sarmah D., Baruah S.D. (2003). Synthesis, characterization, and thermal properties of copolymers of behenyl acrylate and behenyl fumarate, J. Applied Polymer Sci., 90: 2721–2726. https://doi.org/10.1002/app.12927 (in Eng.).

МАЗМҰНЫ

СОДЕРЖАНИЕ

CONTENTS

Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan

For information on Ethics in publishing and Ethical guidelines for journal publication see http://www.elsevier.com/publishingethics and http://www.elsevier.com/journal-authors/ethics.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see http://www.elsevier.com/postingpolicy), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service http://www.elsevier.com/editors/plagdetect.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации в журнале смотреть на сайтах:

www:nauka-nanrk.kz
http://chemistry-technology.kz/index.php/en/arhiv
ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Директор отдела издания научных журналов НАН РК *А. Ботанқызы*
Заместитель директор отдела издания научных журналов НАН РК *Р. Жәлиқызы*
Редакторы: *М.С. Ахметова, Д.С. Аленов*
Верстка на компьютере *Г.Д. Жадырановой*

Подписано в печать 05.12.2022.
Формат 60x88$^{1}/_{8}$. Бумага офсетная. Печать – ризограф.
9,0 п.л. Тираж 300. Заказ 4.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-19