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SELECTIVITY OF FORMATION AND YIELD OF DICARBOXYLIC ACID MONO- AND DIESTERS UNDER STATIONARY CONDITIONS

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Abstract. The effect of temperature, catalyst type, alcohol and dicarboxylic acid structures, as well as reagents ratio on the selectivity of formation and yield of mono- and diesters has been determined under stationary conditions for adipic (AA) and succinic acids (SA) esterification by C_2–C_5 aliphatic alcohols. It has been proved by the theory and experiments that maximum selectivity of dicarboxylic acids (DCA) monoesters formation during their esterification by alcohols is achieved at the ratio between flow rate constants of monoester and DCA less than 0.1. The high yield of monoester (40–60 %) was found to be for only such reaction systems as SA–2-methylpropan-1-ol (catalysts H_2SO_4 and *p*-toluenesulfoacid) and SA–pentan-1-ol (catalyst *p*-toluenesulfoacid).

Keywords: selectivity, yield, monoether, dicarboxylic acid, C_2–C_5 alcohols.

1. Introduction

The aim of dicarboxylic acids (DCA) esterification by alcohols is providing maximum yield of diesters (DE) used as high-boiling solvents, plasticizers, lubricants, *etc*. At the same time the intermediate products of DCA and alcohol interaction – monoesters (ME) – are used as a raw material for the organic synthesis, reagents for electrochemical synthesis of high diesters, an additive to gasoline (0.1–0.3 %) that improves combustion process and decreases CO and NO_x content in exhausts, *etc*. [1, 2]. Monoesters of succinic and glutaric acids are obtained *via* interaction of their anhydrides with methanol or ethanol without catalysts. Another method of DCA monoesters obtaining is a partial saponification of corresponding DE by alkaline solutions in absolute alcohol at room temperature. In particular, the yield of malonic acid monoesters is 75–82 % (KOH hydrolysis), the yield of nonandicarboxylic acid monoesters is 60–64 % (Ba(OH)$_2$ hydrolysis) [3].

DCA monoesters are also obtained *via* the reaction between diester, alcohol and corresponding acid [2].

The aim of this work is to determine the effect of temperature, catalyst type, alcohol and dicarboxylic structures, as well as reagents ratio on the selectivity of formation and yield of mono- and diesters under stationary conditions for the reaction between DCA and C_2–C_5 alcohols and to evaluate the prospects of monoesters obtaining *via* this method.

2. Experimental

The regularities of adipic (AA) and succinic (SA) acids esterification by C_2–C_5 aliphatic alcohols were studied in a glass temperature-controlled reactor within 333–368 K under stationary conditions. One more condition was that the reaction temperature was lower than the boiling temperature of water and alcohol azeotropic mixture. The reactor was equipped with a back condenser and a mixer with water seal. The rotation speed was 500 rev/min. After definite time intervals the samples were withdrawn to determine the acid number of DCA esterification products and to analyze the formed DE by chromatography.

The beginning of the reaction was the moment of catalyst introduction into the mixture heated to the reaction temperature. The alcohol:DCA molar ratio was (16–24):1. Sulfate acid, *p*-toluenesulfoacid (TSA) and stanum(II) perfluorine(4-methyl-3,6-dioxaoctane)sulfonate (Sn(pfos)$_2$) were used as catalysts.

Under great excess of an alcohol the esterification reaction proceeds according to the scheme:

$$DCA \xrightarrow{k_{1,ef}} ME \xrightarrow{k_{2,ef}} DE$$
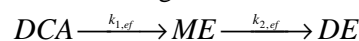
where $k_{1,ef}$ – effective rate constant of DCA conversion into ME, s^{-1}; $k_{2,ef}$ – effective reaction constant of ME conversion into DE, s^{-1}.

The reaction reversibility may be neglected.

Acid number of the reaction mixture *AN* is determined according to the procedure described in [4]. The relative error was ± 3 %.

Acid number is recalculated from mg KOH/g for mol/dm^3 (C_{AN}) according to the formula (1):

$$C_{AN} = \frac{AN \cdot 10^{-3} \cdot r}{56 \cdot 10^{-3}} = \frac{AN \cdot r}{56} \qquad (1)$$

where *AN* – acid number, mg KOH/g; ρ – mixture density, g/cm^3; 56 – KOH molar mass, g/mol.

DE content in the esterification products is determined using a gas-liquid chromatograph "Tsvet-100" with a thermal conductivity detector. To separate the components the column of 1 m length and 3 mm diameter is filled by a stationary phase of 5% Silicone SE30 over Chromaton N-AW. Helium with a flow rate of 3 dm^3/h is a gas-carrier; current strength at the detector is 120 mA; sample volume is 2 µl. Evaporator temperature is 523 K, detector temperature is 503 K. The temperature of the column was varied within 373–448 K depending on DE type. The samples (if necessary) were dissolved in propan-2-ol relative to the weight.

To determine the current concentrations of DCA and ME (mol/dm^3) the combined equation (2) is used:

$$\begin{cases} C_{DCA,0} = C_{DCA} + C_{ME} + C_{DE} \\ C_{AN} = 2C_{DCA} + C_{ME} \end{cases} \qquad (2)$$

where $C_{DCA,0}$ and C_{DCA} – DCA initial and current concentrations, respectively, mol/dm^3; C_{ME} – ME current concentration, mol/dm^3; C_{DE} – DE current concentration, mol/dm^3; C_{AN} – carboxy groups acid number to recalculate for mol/dm^3.

Hence, ME current concentration is calculated according to Eq. (3):

$$C_{ME} = 2(C_{DCA,0} - C_{DE}) - C_{AN} \qquad (3)$$

and DCA concentration:

$$C_{DCA} = C_{AN} - C_{DCA,0} + C_{DE} \qquad (4)$$

For the irreversible reaction of the first order the time of achieving ME maximum concentration is:

$$t_{max} = \frac{1}{k_{2,ef} - k_{1,ef}} \ln \frac{k_{2,ef}}{k_{1,ef}} \qquad (5)$$

and maximum yield of monoester is:

$$h_{ME,max} = \left(\frac{k_{2,ef}}{k_{1,ef}} \right)^{\frac{k_{2,ef}}{k_{1,ef} - k_{2,ef}}} \qquad (6)$$

3. Results and Discussion

The change in the yield of intermediate product – monobutyladipinate (MBA) is observed (Fig. 1) during AA esterification by butan-1-ol within the temperature range of 343–363 K with the increase in AA conversion *X*. Such change is typical for the consecutive reaction: at first MBA yield achieves maximum (42–45 %) and then decreases; the yield of the final product – dibutyladipinate (DBA) neatly increases. The same behavior is observed (Fig. 2) for SA esterification by 3-methylbutan-1-ol in the presence of stanum(II) perfluorine(4-methyl-3,6-dioxaoctane)sulfonate aprotic catalyst. However, during the catalysis in the presence of Sn(pfos)$_2$ the yield of monoester – monoisoamylsuccinate (MiAS) is considerably higher (~74%) compared with that in the presence of Bronsted-Lowry acid. SA conversion is almost 96 %. The change in temperature within a narrow range (20 K) affects the products yield only at high values of DCA conversion, namely at higher temperature the ME yield is higher (Figs. 1 and 2).

The small difference (3–7 %) between ME and DE yields is observed under the same conditions of AA esterification by butan-1-ol and penta-1-ol, as well as AA and SA esterification by butan-1-ol in the presence of TSA. This difference increases with the increase in DCA conversion (Fig. 3).

Obviously, the catalyst has a greater influence on the products composition than reagents structure (Figs. 1, 2 and 4).

The ratio between rate constants k_2/k_1 is the parameter providing the maximum concentration, time for its achieving and selectivity of the intermediate product formation. To estimate the effect of the mentioned value on the products composition we calculated the corresponding rate constants k_1 and k_2 using previously determined preexponential factor and activation energy of AA and SA esterification by C$_2$–C$_5$ alcohols [5, 6]. For the assumed classical scheme of the consecutive reaction it is typically that the higher ratio k_1/k_2, the closer ME maximum concentration to the reaction beginning and the lower its value [7].

One can see from Table 1 that time for achieving ME maximum yield and ME yield calculated according to Eqs. (5) and (6) differs from their experimental values. As a rule, the mentioned values are achieved at high values of DCA conversion (~0.6 $\pm$ 0.1), therefore the reaction reversibility influences the difference between them. Actually, during DCA esterification by large excess of alcohol under stationary conditions the ME maximum yield is achieved later and its value is higher than the calculated one. The reason is water inhibition of diester formation from monoester at the deep stages of reagents conversion. According to Ref. [5, 6] we calculated the rate constants for the temperature of esterification technolo-
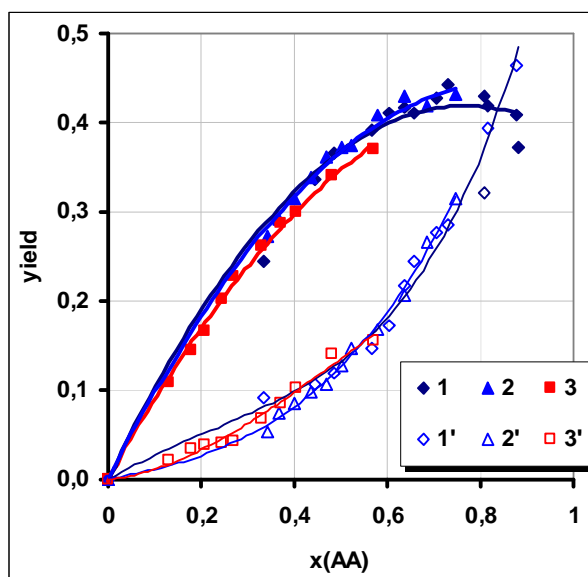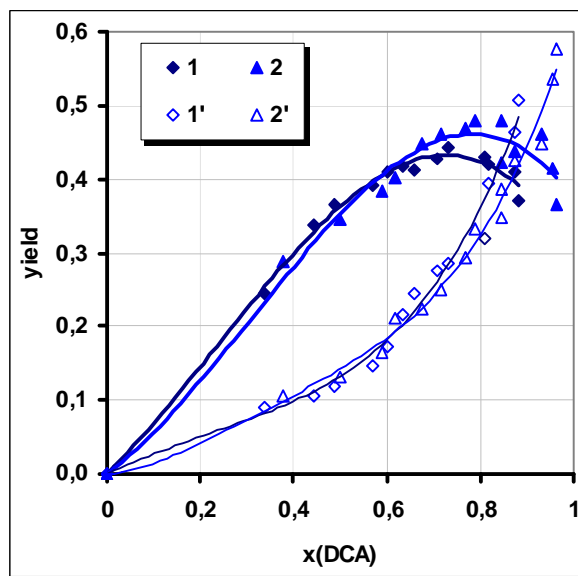
Fig. 1. Dependence of MBA (1, 2, 3) and DBA (1', 2' and 3') yields on AA conversion at different temperatures (K): 363 (1); 353 (2) and 343 (3). C(TSA) = 1.4·10^{-2} mol/dm^3, butan-1-ol (BA):AA = 20:1 (mol)
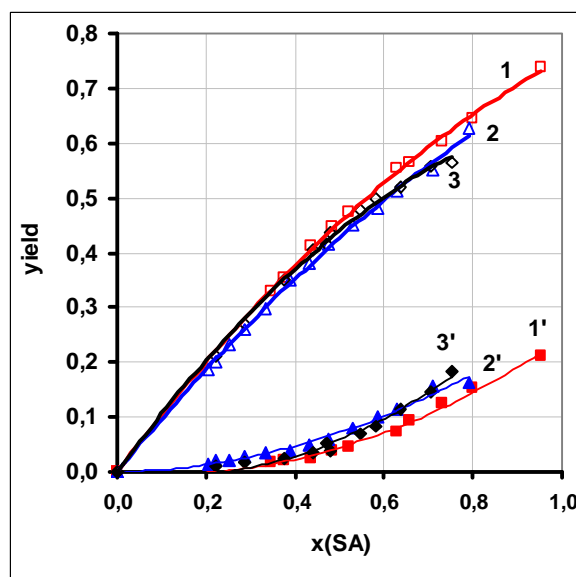
Fig. 2. Dependence of MiAS (1, 2, 3) and diisoamyl succinate (DiAS) (1', 2', 3') yields on SA conversion at different temperatures (K):1 – 364 (1); 354 (2) and 350 (3). C(Sn(pfos)$_2$) = 1.5·10^{-2} mol/dm^3, 3-methylbutan-1-ol (iAA):SA = 16:1 (mol)
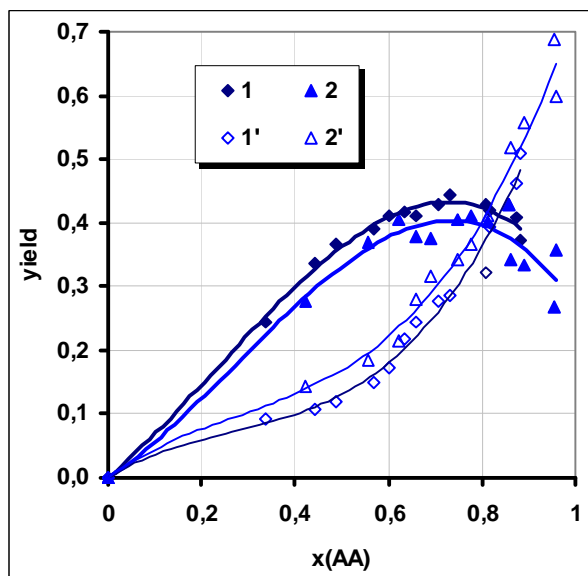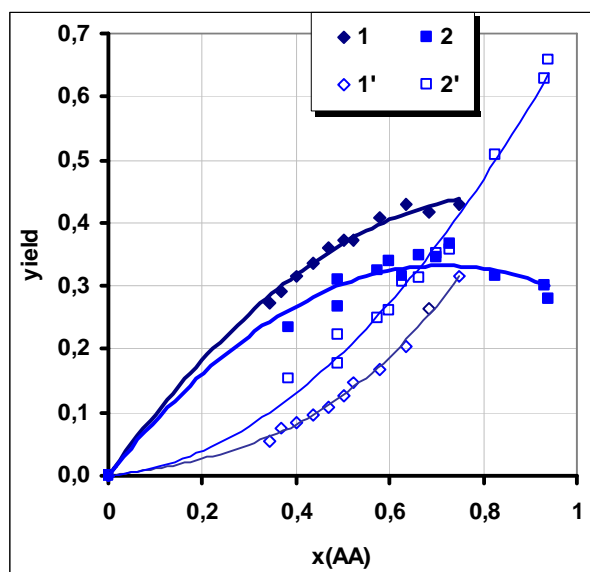

a)

b)

Fig. 3. Effect of alcohol (a) and DCA (b) composition on the dependence:
a) yield of MBA (1), MAA (2), DBA (1') and DAA (2') on AA conversion in the reaction with butan-1-ol and pentan-1-ol. T = 363 K, C(TSA) = 1.4·10^{-2} mol/dm^3, alcohol:AA = 20:1 (mol);
b) yield of MBA (1), monobutylsuccinate (2), DBA (1') and dibutylsuccinate (2') on AA and SA conversions in the reaction with butan-1-ol. T = 363 K, C(TSA) = 1.4·10^{-2} mol/dm^3, BA:DCA = 20:1 (mol)

Fig. 4. Dependence of MBA (1, 2) and DBA (1', 2')
yields on AA conversion for the esterification in the presence
of TSA (1) and H_2SO_4 (2). T = 353 K;
C(cat) = $1.45 \cdot 10^{-2}$ mol/dm^3,
BA:AA = 20:1 (mol)

Table 1

Calculated and experimental values of achieving time and ME maximum yield

T, K	Calculated		Experimental		Calculated		Experimental	
	time, min	yield	time, min	yield	time, min	yield	time, min	yield
	catalyst – TSA				catalyst – H_2SO_4			
	AA – ethanol							
338	43	0.354	60	0.420	37	0.332	60	0.422
343	34	0.357	40	0.425	28	0.308	60	0.355
348	29	0.352	30	0.376	20	0.318	35	0.333
	SA – ethanol							
338	60	0.342	50	0.284	43	0.211	60	0.236
343	45	0.344	40	0.390	29	0.209	60	0.323
348	33	0.332	30	0.336	22	0.230	23	0.246
	AA – propan-1-ol							
343	20	0.152	25	0.205	12	0.085	13	0.096
353	14	0.197	15	0.248	9	0.101	15	0.154
363	8	0.104	13	0.050	7	0.127	35	0.207
	AA – 2-methyl-propan-1-ol							
343	22	0.344	30	0.425	40	0.277	70	0.331
353	14	0.390	20	0.427	28	0.282	60	0.389
363	9	0.396	15	0.438	18	0.296	40	0.289
	AA – butan-1-ol							
343	73	0.352	60	0.369	27	0.255	50	0.382
353	43	0.382	40	0.430	18	0.307	30	0.368
363	26	0.402	30	0.443	12	0.321	25	0.379
	AA – 3-methylbutan-1-ol							
343	47	0.285	43	0.339	33	0.110	30	0.150
353	29	0.94	28	0.361	21	0.134	25	0.158
363	21	0.301	20	0.390	14	0.161	23	0.173
	SA – pentan-1-ol							
343	37	0.312	41	0.388	42	0.134	70	0.193
353	25	0.354	35	0.420	27	0.164	50	0.217
363	18	0.387	23	0.405	19	0.211	23	0.210

a)

b)
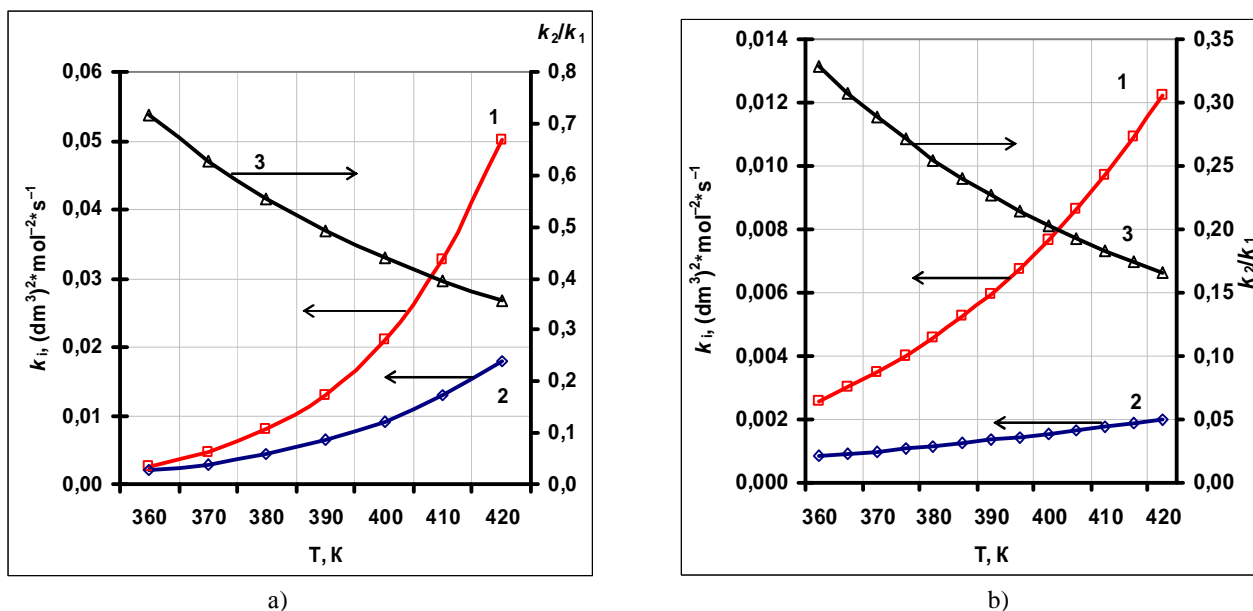
Fig. 5. Dependence of the calculated rate constants of AA esterification by butan-1-ol in the presence of TSA (a) and SA esterification by 3-methylbutan-1-ol in the presence of Sn(pfos)$_2$ (b) and their ratio on the temperature: DCA flow rate constant k_1 (1); rate constant of monoester conversion k_2 (2) and ratio between esterification rate constants k_2/k_1 (3)

gical process carried out under mixture boiling and water distillation. For example, AA esterification by butan-1-ol is carried out under mixture boiling within the temperature range from the boiling point of azeotropic mixture butan-1-ol–water (~365 K) to the boiling point of alcohol (~390 K) and higher temperatures (under the conditions of alcohol excess).

Fig. 5a represents the dependence of the calculated rate constants and the k_2/k_1 ratio on the temperature for AA esterification by butan-1-ol in the presence of TSA within 360–420 K temperature range. The increase in temperature decreases the k_2/k_1 ratio from 0.65 to 0.35. It is obvious that with the increase in temperature AA is consumed more quickly than MBA leading to the higher concentration of monoester in the reaction products. The same regularity was established for SA esterification by 3-methylbutan-1-ol in the presence of Sn(pfos)$_2$ (Fig. 5b). In that case the k_2/k_1 ratio decreases from 0.33 to 0.16 within 360–420 K.

In accordance with the data of kinetic investigations within 333–368 K [5, 6] we calculated the values of k_2/k_1 ratio for AA and SA esterification by C$_2$–C$_5$ alcohols in the presence of TSA and H$_2$SO$_4$ (Fig. 6) within the temperature range of 360–420 K. Such calculations are possible if activation energy insignificantly differs from the calculated one with temperature deviation by 30–50 K.

In all cases (except AA esterification by ethanol in the presence of H$_2$SO$_4$ and SA esterification by ethanol in the presence of TSA and H$_2$SO$_4$) the increase in

temperature decreases the k_2/k_1 ratio by higher or lesser degree. So, the increase in temperature accelerates DCA flow rate whereas the rate of ME conversion into DE increases slower. This leads to the increase in selectivity of the esterification intermediate product and its maximum yield. The higher yield of DCA monoesters and C$_3$–C$_5$ alcohols may be achieved while proceeding esterification under high pressure, because in such a case the boiling point of alcohol is higher.

For the consecutive reaction corresponding to the scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ the integral selectivity of the intermediate product B (ME) for the reagent A conversion X_A is calculated according to Eq. (7):

$$\Phi_B^A = \frac{1-X_A}{X_A} \frac{1}{k_2/k_1 - 1}\left[1 - (1-X_A)^{k_2/k_1 - 1}\right] \qquad (7)$$

The yield of the product B is calculated as a product of the reagent A conversion and selectivity of the product B formation:

$$h_B^A = X_A \Phi_B^A = \frac{1-X_A}{k_2/k_1 - 1}\left[1 - (1-X_A)^{k_2/k_1 - 1}\right] \qquad (8)$$

The selectivity of B formation for the reaction with water distillation which takes place in the technological process under equimolar ratio of reagents or small excess of alcohol according to the scheme $A + Y \xrightarrow{k_1} B + Y \xrightarrow{k_2} C$, is calculated according to Eq. (7). Therefore this equation and obtained data of kinetic investigations may be used to calculate the maximum

concentration and selectivity of monoalkylsuccinate and monoalkyladipinate formation in the reaction mixture.

The graphical dependencies (Fig. 7) plotted according to Eqs. (7) and (8) show that high values of ME selectivity and yield are achieved at very low k_2/k_1 ratio (~0.1). The increase in the k_2/k_1 ratio decreases the selectivity of ME formation and shifts its maximum toward lower value of DCA conversion. ME maximum yield is observed for k_2/k_1 ratio till 0.1 at high DCA conversion.

The obtained conclusions are in good agreement with experimental results. For SA esterification by butan-1-ol in the presence of $Sn(pfos)_2$ (Fig. 6b) the low k_2/k_1 ratio (0.16–0.35) correlates with high yield of MiAC (70–74 %) and low yield of DiAC at high SA conversion determined during the kinetic investigations (*vide* Fig. 2). Higher values of k_2/k_1 ratio (0.35–0.65) for the reaction of AA esterification by butan-1-ol in the presence of TSA (Fig. 6a) provide lower ME yield (~40 %).
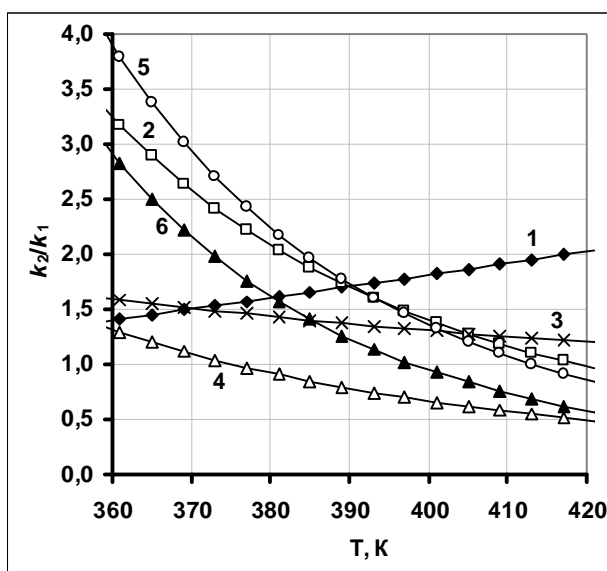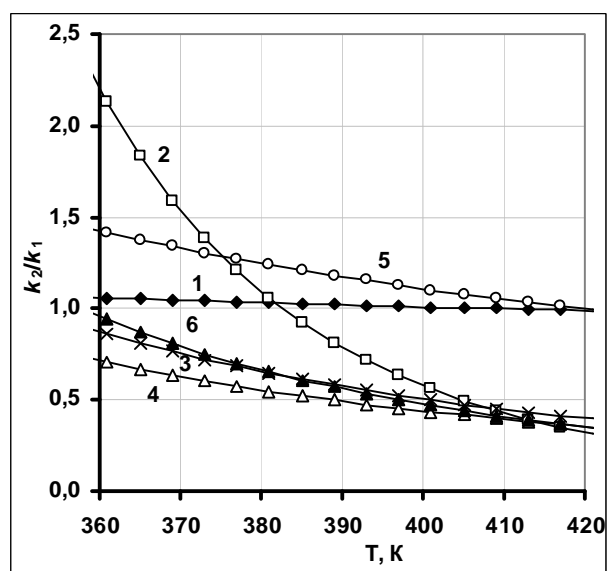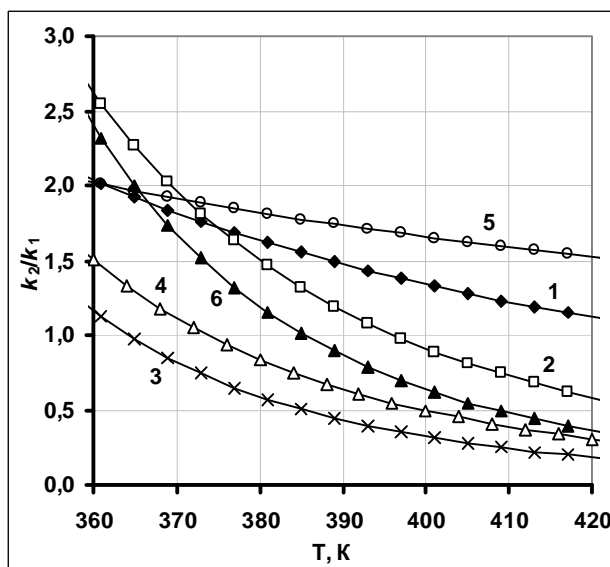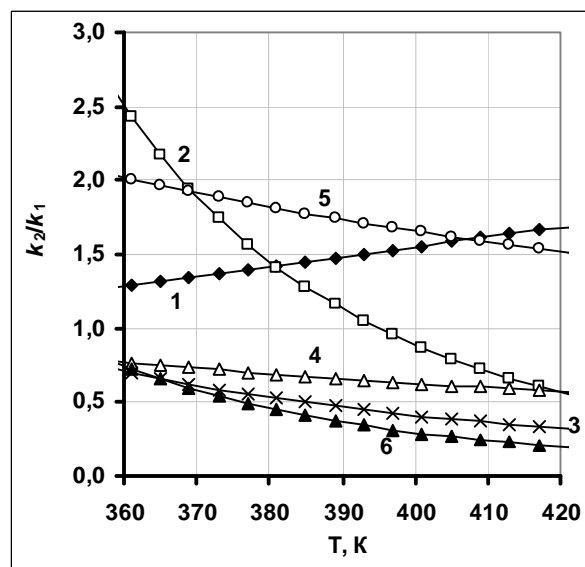

Fig. 6. Temperature dependence of the calculated ratio k_2/k_1 for AA esterification in the presence of H_2SO_4 (a) and TSA (b); for SA esterification in the presence of H_2SO_4 (c) and TSA (d) by: ethanol (1); propan-1-ol (2); 2-methylpropan-1-ol (3); butan-1-ol (4); 3-methylbutan-1-ol (5) and pentan-1-ol (6)
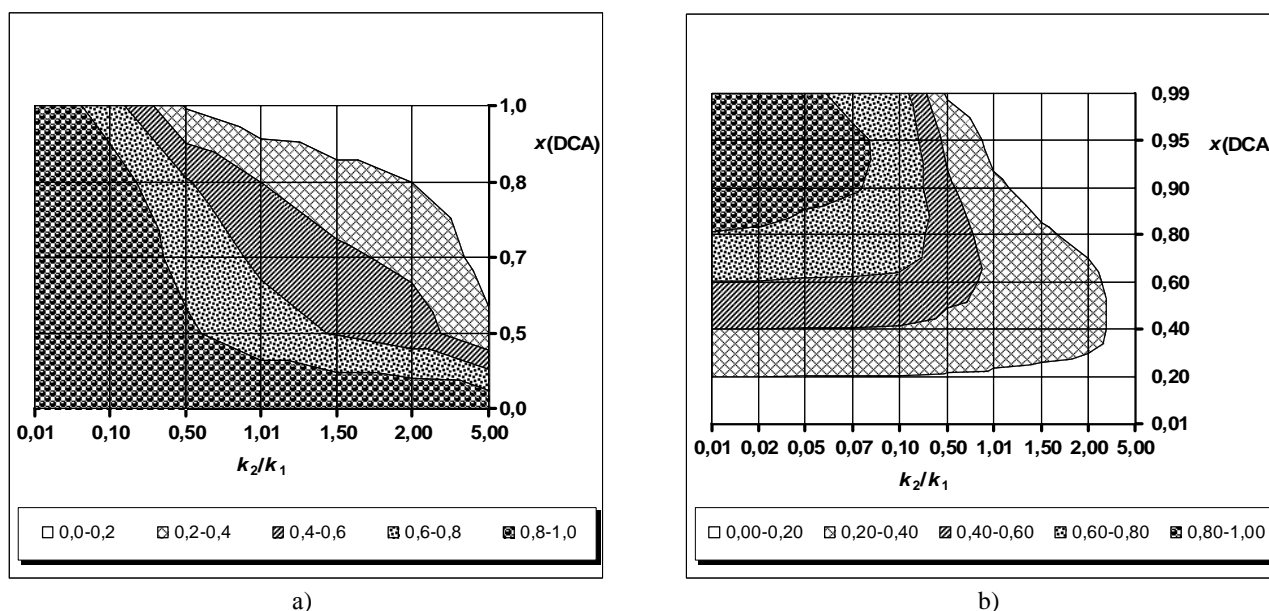
a)

b)

Fig. 7. Dependence of selectivity of intermediate product formation (a)
and its yield (b) on the rate constants ratio k_2/k_1 and DCA conversion

Thus, the maximum yields of AA and SA monoesters are achieved at the temperature ensuring the ratio $k_2/k_1 < 0.1$. However, for DCA esterification by C_2–C_5 aliphatic alcohols the high yields of monoesters (40–60 %) are possible only for some reaction systems, namely: SA–2-methylpropan-1-ol (catalysts H_2SO_4 and TSA) and SA–pentan-1-ol (TSA), for which k_2/k_1 ratio varies within 0.8–0.3 (370–410 K); 0.6–0.35 (370–410 K) and 0.45–0.2 (380–420 K) (Figs. 6c and 6d).

It is evident from Eqs. (7) and (8) that selectivity of ME formation and its yield are independent of alcohol:DCA ratio. Therefore we recommend the equimolar ratio between these reagents to provide the maximum reaction rate.

4. Conclusions

Maximum selectivity of monoesters formation during their esterification by alcohols is achieved under the ratio between monoester and DCA flow rates less than 0.1. The process temperature is one of the main parameters affecting the reaction rates, therefore the ratio between mono- and diesters may be controlled by its change during esterification. At the same time the reagents structure also affects the yield and selectivity of the reaction products. For AA and SA esterification by C_2–C_5 aliphatic alcohols the high yields of monoesters (40–60 %) are possible only for some reaction systems, namely: SA–2-methylpropan-1-ol (catalysts H_2SO_4 and TSA) and SA–pentan-1-ol (TSA). The obtained results

may be used to select optimum conditions for DCA monoesters synthesis and achieving maximum yield of ME during obtaining mixed diesters *via* stepped addition of reagents-alcohols for esterification. They are also the basis for mathematical simulation of esterification in the industrial reactor and explanation of regulations of dicarboxylic acids esterification by alcohols mixture using by-products of different productions as the reagents.

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**СЕЛЕКТИВНІСТЬ УТВОРЕННЯ Й ВИХІД МОНО-
ТА ДІЕСТЕРІВ ДИКАРБОНОВИХ КИСЛОТ
ЗА СТАЦІОНАРНИХ УМОВ**

Анотація. *Встановлено вплив температури, природи каталізатора, будови спирту й дикарбонової*

*кислоти (ДК) та співвідношення реагентів на селектив-
ності утворення та вихід моно- та діестерів у реакціях
естерифікації адипінової (АК) та бурштинової (БК)
кислот аліфатичними спиртами C_2–C_5 за стаціонарних
умов. Теоретично і експериментально доведено, що
максимальна селективність утворення моноестерів ДК
під час їх естерифікації спиртами досягається при
співвідношенні констант швидкості витрати моно-*

*естеру і ДК, меншому ніж 0,1. Встановлено, що для
естерифікації АК і БК аліфатичними спиртами C_2–C_5
високий вихід (40–60%) моноестеру можливий лише для
таких реакційних систем, як БК – 2-метилпропан-1-ол
(каталізатори H_2SO_4 і пТСК) і БК – пентан-1-ол (пТСК).*

***Ключові слова**: селективність, вихід, моноестер,
дикарбонова кислота, спирти C_2–C_5.*