

Research of extractional balance in the phase-transfer catalytic reaction of aminolysis of activated amino-acid ethers

Viktor S. Doroshkevich¹, Vasiliy A. Aleksandrov², Aleksandr S. Doroshkevich³, Oksana V. Baranova¹

¹ State Higher Educational Institution "Donetsk National University", Universitetskaya st., 24, 83001 Donetsk, E-mail: nelya_dor@mail.ru

² Dubna International University for Nature, Society and Man, 141980, Moscow region, Dubna, st. Universitetskay, 19, E-mail: valdir-02@mail.ru

³ Joint Institute for Nuclear Research, str. Joliot-Curie, 6, 141980, Dubna, Russian Federation; E-mail: doroh@jinr.ru

Introduction

At the current level of scientific and technological development, a special role is assigned to interfacial catalytic (IFC) processes. They are widely used:

- in synthetic organic chemistry
- for the disposal of ecotoxicants and highly toxic substances
- in lots of industries
- in "green" chemistry reactions

Research aims:

Studying of the distribution of reagents, products and interfacial catalyst between phases in the liquid/liquid system;

Identifying of the main kinetic patterns on the example of the aminolysis reaction of the activated N-benzyloxycarbonyl glycine ester in the presence of an interfacial transfer catalyst - cetylpyridinium chloride (CPC) and on the surface of the nanostructured ZrO_2/Y_2O_3

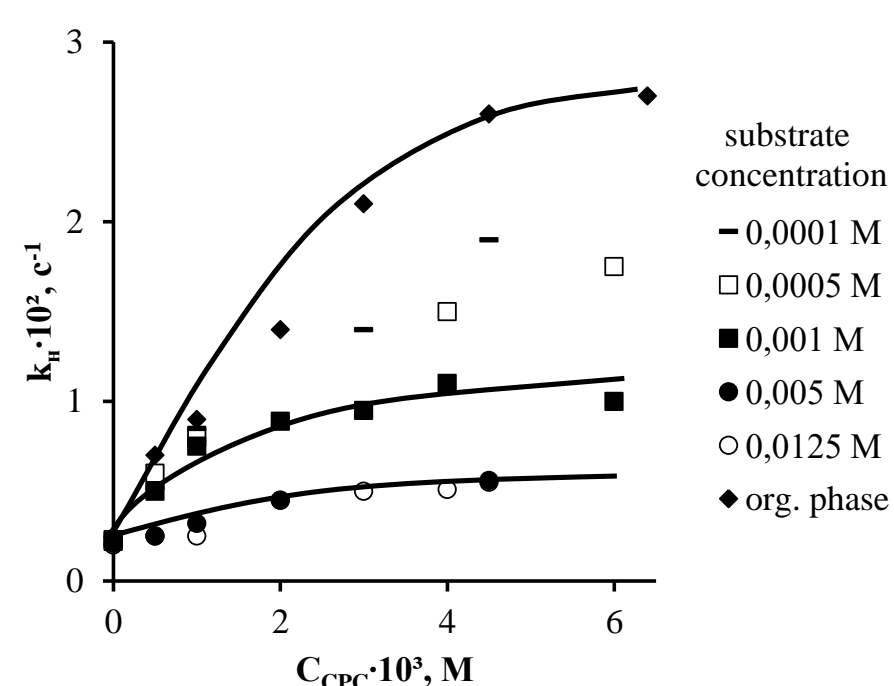


Fig. 1. Dependence of k_N (c^{-1}) aminolysis reaction of 4-nitrophenyl ester of N-benzyloxycarbonyl glycine in a two-phase system of butanol-1 / glycine buffer solution (pH = 10.5) and in the separated organic phase from the concentration of cetylpyridinium chloride, 298 K.

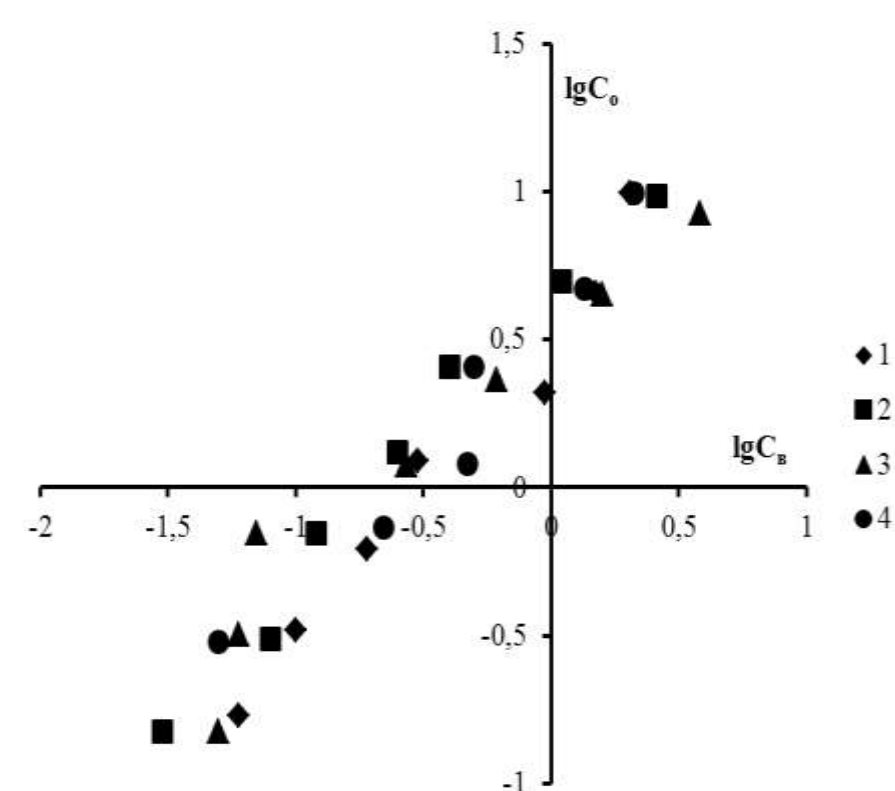


Fig. 3. The logarithmic dependence of the concentration (mol/L) of the 4-nitrophenolate ion in the separated organic phase ($lg C_O$) on the concentration (mol/L) of the 4-nitrophenolate ion in the separated aqueous phase ($lg C_B$) at different concentrations (mol/L) of CPC: $0.5 \cdot 10^{-3}$ (1); $6.0 \cdot 10^{-3}$ (2); $1.0 \cdot 10^{-3}$ (3); $3.0 \cdot 10^{-3}$ (4) in a two-phase system butanol-1/glycine buffer solution (pH 10.5), 297K.

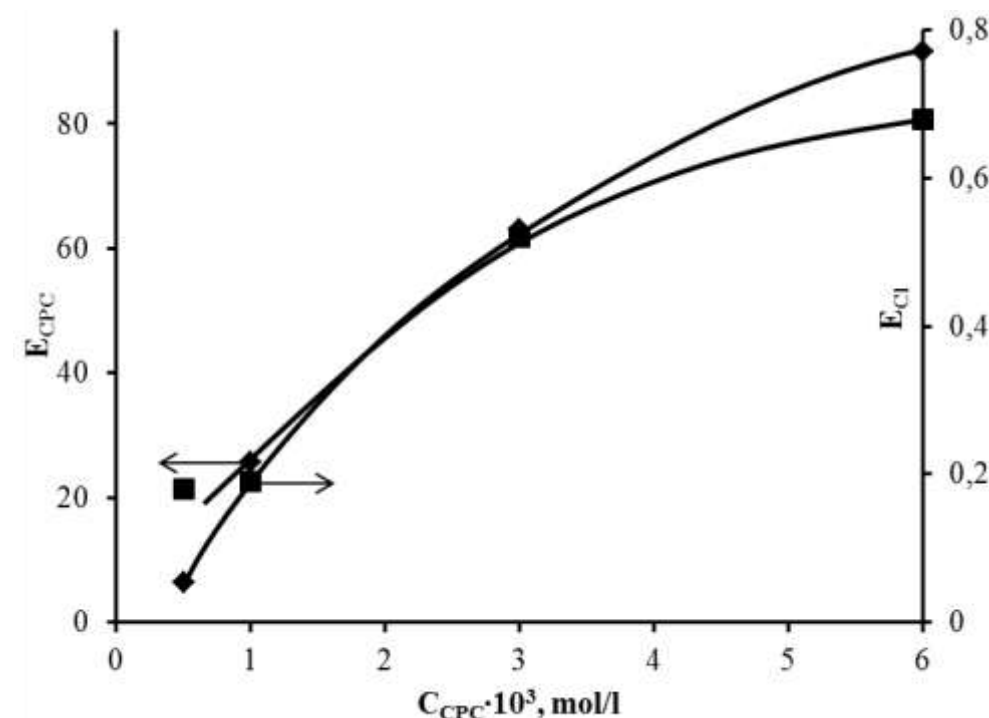


Fig. 2. Dependence of the extraction coefficient of cetylpyridinium (E_{cp}) and extraction coefficient of chloride anion (E_{Cl}) on the concentration of cetylpyridinium chloride (C_{CPC} , mol/l) in a two-phase system butanol-1/glycine buffer solution (pH=10.5), 297K.

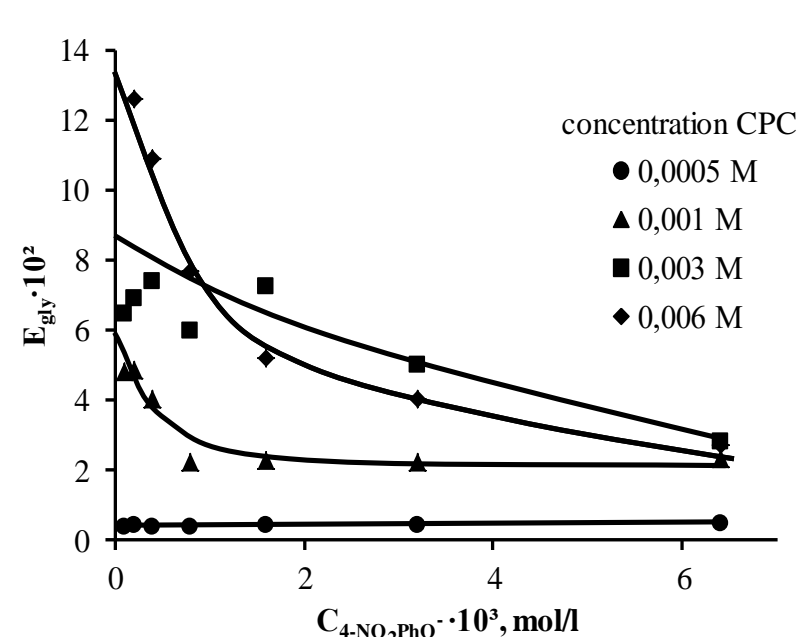
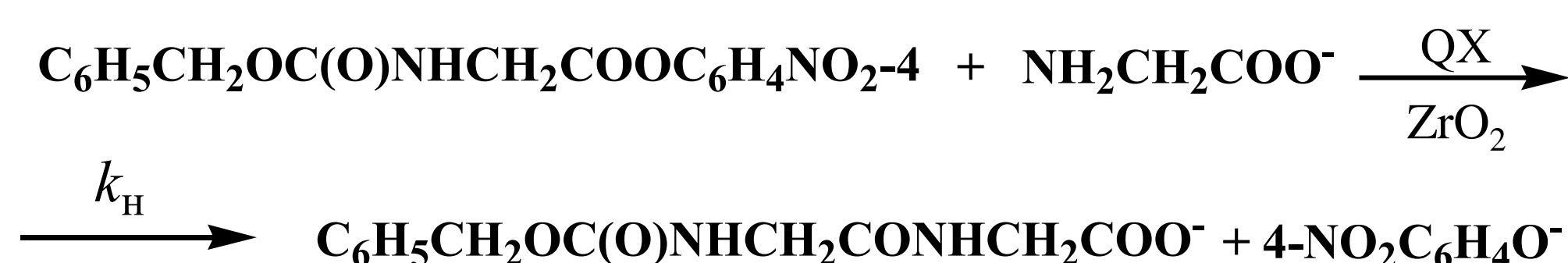


Fig. 4. Dependence of the extraction coefficient of glycinate anion (E_{gly}) on the concentration of 4-nitrophenolate ion ($4-NO_2C_6H_4O^-$, mol/L) in a two-phase system butanol-1/glycine buffer solution (pH=10.5), 297K.

Research object:



Research methods:

1. Method of spectrophotometric determination of cetylpyridinium cation, 4-nitrophenolate, glycine, chloride ions in separated aqueous and organic phases.
2. Method of studying the aminolysis rate of 4-nitrophenyl ester of N-benzyloxycarbonyl glycine in a two-phase system.
3. RBS method (Rutherford Backscattering Spectrometry). Study of the chemical composition and crystallinity of nanostructured ZrO_2 .

Results

Aminolysis reaction rate in two-phase system at equal concentration of interfacial catalyst increases with decrease of substrate concentration (fig. 1).

The extraction coefficient of cetylpyridinium does not depend on the concentration of 4-nitrophenol in the system, but depends on the concentration of the salt itself, which is explained by the transfer mechanism of cetylpyridinium - in the form of an ion pair with an anion (fig. 2).

The extraction coefficient of the glycinate anion depends on the concentration of CPC, 4-nitrophenolate ion in the two-phase system (fig. 3 and 4).

The presence of a nanosized ZrO_2 (3 mol% Y_2O_3) in the system (fig. 5) leads to an increase in the extraction of the amino acid into the organic phase.

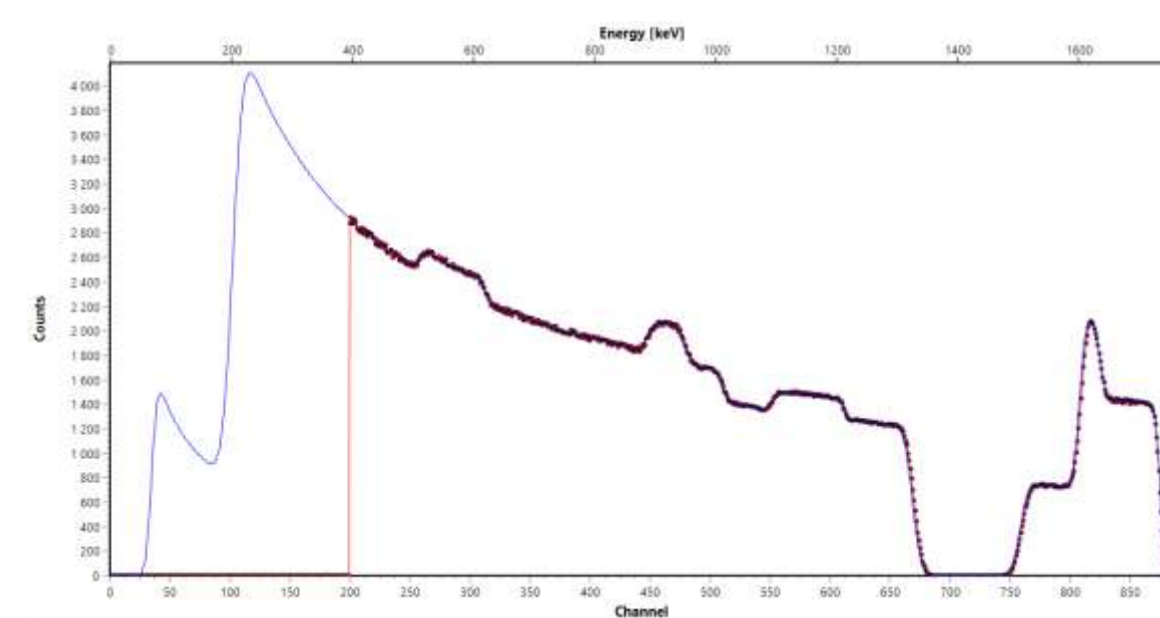


Fig. 5. Measured by RBS method and calculated by Simnra 7.02 concentration profiles of nanosized ZrO_2 (3 mol% Y_2O_3) and impurities on the SiO_2 substrate. Energy 2000 KeV, incident geometry angle - 60 deg, energy per channel - 1,9845keV/ch.

Conclusions

1. The distribution of cetylpyridinium cation, chloride, 4-nitrophenolate, glycine anions in a two-phase butanol-1/glycine buffer system (pH = 10.5) with varying concentration of the catalyst CPC and 4-nitrophenol in the aminolysis reaction of activated N-protected glycine ester was studied.
2. It has been found that the extraction coefficient of the chloride anion does not depend on the concentration of 4-nitrophenol in the system, but depends on the concentration of cetylpyridinium chloride, which indicates the same mechanism of transfer of cetylpyridinium and chloride anion, i.e. in the form of an ion pair.
3. The extraction coefficient of the 4-nitrophenolate anion does not depend on the concentration of CPC or on the concentration of 4-nitrophenol, which indicates that the 4-nitrophenolate anion is transferred by exchange with other anions at the interface.