Equilibrium and kinetic aspects of Am/Eu pair extraction by bipyridine-based N-, O- donor ligand in different solvents

Ekaterina A. Konopkina *[a], Elizaveta A. Pavlova [a], Alexander V. Gopin [a], Maria G. Chernysheva [a], Ali S. Mannaa [b], Alexander A. Guda [b], Nataliya E. Borisova [a], Petr I. Matveev [a]

Konopkina.kate@gmail.com

[a] Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russian Federation
[b] The Smart Materials Research Institute, Southern Federal University, Rostov-on-Don 344090, Russian Federation

Solvent extraction

Table S1. Properties of diluents (T=298 K, P=0.1 MPa).

Diluent	Dielectric constant (ε)	Density, g/mL	Viscosity (η), mPa × s	Polarizability (π*)*
Toluene	2.3	0.87	0.59	0.51
1,2-dichloroethane	10.4	1.25	0.83	0.58
F-3	22.3	1.44	2.35	-
FS-13	29	1.41	3.6	-
Nitrobenzene	35	1.20	2.03	0.86

Table S2. Extraction data for L, **Organic phase**: c(L) = 0.05 mol·L^{-1} in corresponding solvent, **Aqueous phase**: $C(HNO_3)$ = 3 mol L^{-1} with ^{152}Eu(III) and ^{241}Am(III) radiotracers. Temperature: 22±1 °C.

Diluent	D(Am)	D(Eu)	$SF_{Am/Eu}$
Toluene	0.12 ± 0.05	0.08 ± 0.02	1.51 ± 0.45
1,2-dichloroethane	2.14 ± 0.13	0.29 ± 0.04	7.51 ± 0.47
F-3	3.34 ± 0.01	0.42± 0.01	7.98 ± 0.20
FS-13	6.56 ± 0.03	0.73 ± 0.02	9.03 ± 0.64
Nitrobenzene	10.15 ± 0.24	1.08± 0.06	9.40 ± 0.55

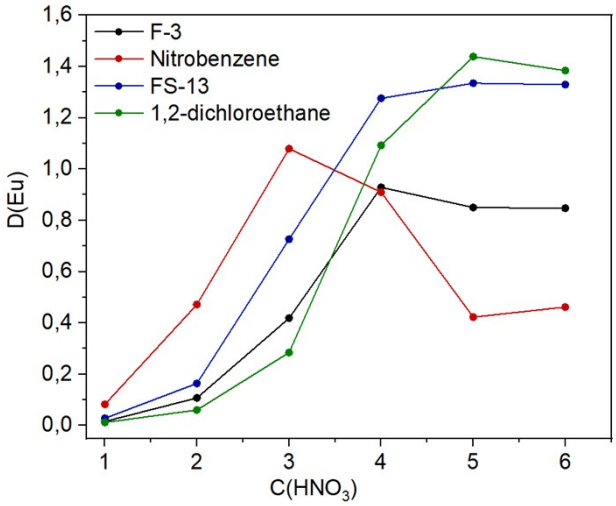


Figure S1. Extraction data for Eu, **Organic phase**: C(L) = 0.05 mol L^{-1} in corresponding diluent, **Aqueous phase**: $C(HNO_3)$ = 1-6 mol L^{-1} with ^{152}Eu(III) and ^{241}Am(III) radiotracers. Temperature: 22±1 °C. The uncertainties for D are 10% and 15% for SF.

Kinetic Features

Table S3. Eu(III) interfacial mass transfer data in various diluents. The errors are obtained from the values of the standard deviation when performing the linear approximation.

Diluent	k_{oa}, mm/s	k_{ao}, mm/s	k_{obs}, s^{-1}
F-3	$(8{,}21\pm1{,}22)\cdot10^{-4}$	$(3{,}61\pm0{,}54)\cdot10^{-4}$	$(8{,}66\pm0{,}59)\cdot10^{-3}$
FS-13	$(5{,}74\pm0{,}15)\cdot10^{-4}$	$(4{,}98\pm0{,}10)\cdot10^{-4}$	$(4{,}18\pm0{,}73)\cdot10^{-3}$
Nitrobenzene	$(2{,}72\pm0{,}20)\cdot10^{-4}$	$(2{,}61\pm0{,}19)\cdot10^{-4}$	$(3{,}36\pm0{,}38)\cdot10^{-3}$
1,2-dichloroethane	$(3{,}57\pm0{,}62)\cdot10^{-4}$	$(2{,}03\pm0{,}35)\cdot10^{-4}$	$(3{,}74\pm0{,}48)\cdot10^{-3}$

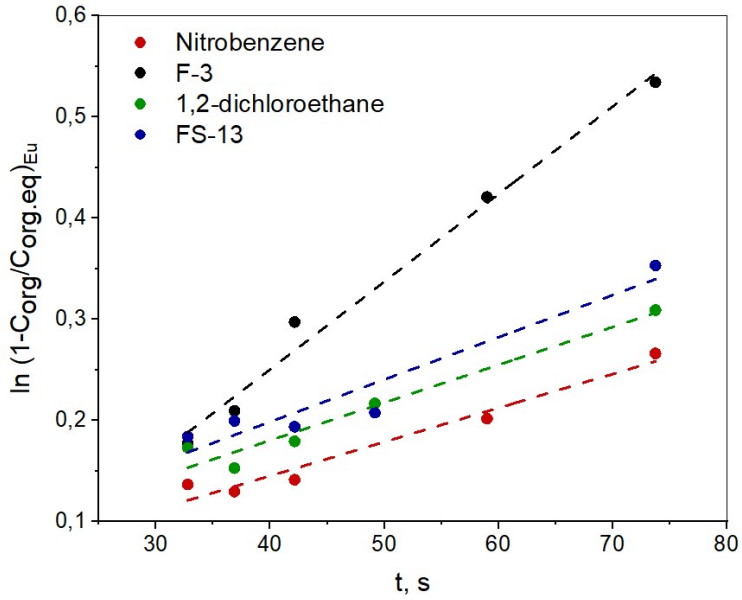
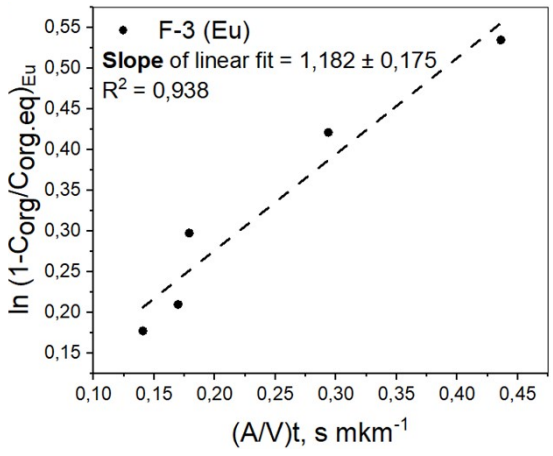
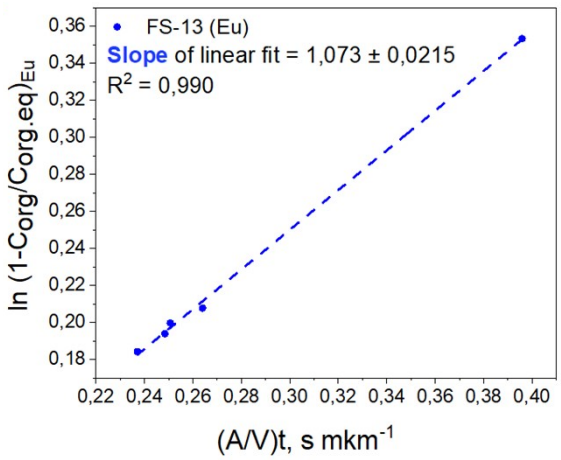


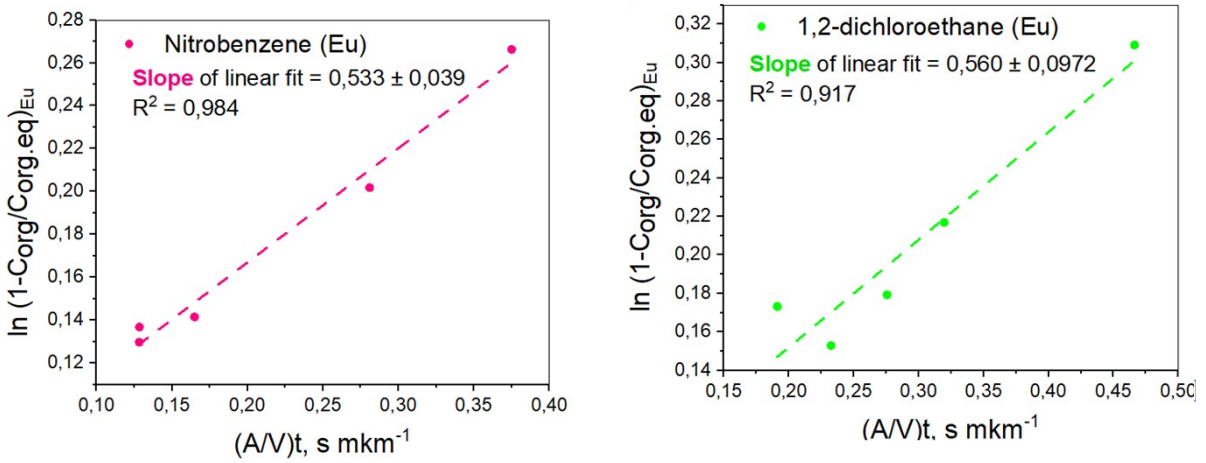
Figure S2. Observed rates for Eu(III) extraction. **Organic phase**: C(L) = 0.05 mol L^{-1} in F-3, FS-13, nitrobenzene or 1,2-dichloroethane, **Aqueous phase**: $C(HNO_3)$ = 3 mol L^{-1} with ^{152}Eu, ^{241}Am radiotracer, T = 23 ± 1 °C.



a)

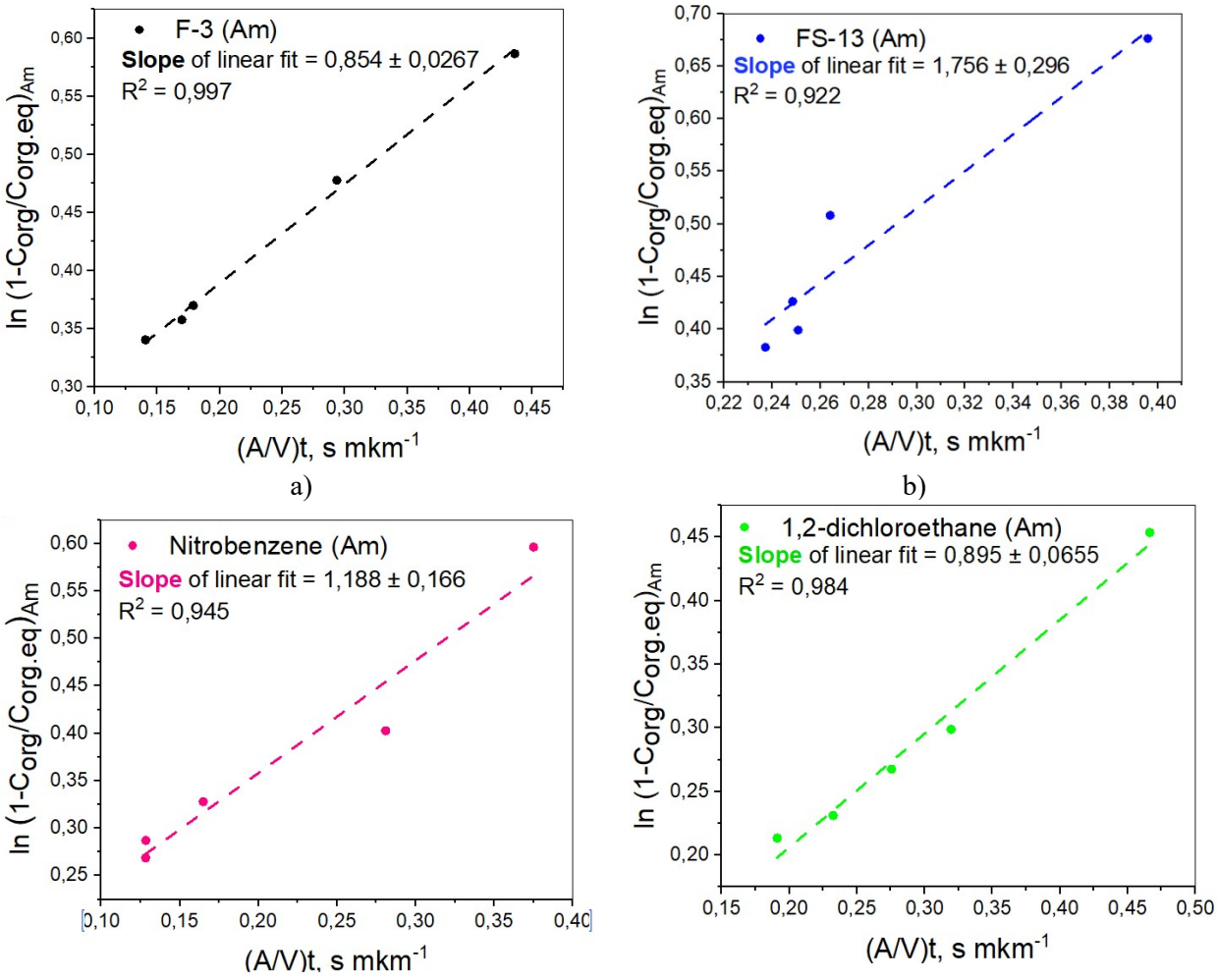


b)



c) d)

Figure S3. mass transfer rates (k_{oa}) for Eu(III) extraction. Aqueous phase: HNO_3 3 mol L^{-1} with ^{152}Eu radiotracer, organic phase: C(L) = 0.01 mol L^{-1},in a) F-3, b) FS-13, c) Nitrobenzene and d) 1,2-dichloroethane, T = 23 ± 1 °C.



a) b)

c) d)

Figure S4. mass transfer rates (k_{oa}) for Am(III) extraction. **Organic phase**: C(L) = 0.05 mol L^{-1}, in a) F-3, b) FS-13, c) Nitrobenzene and d) 1,2-dichloroethane, **Aqueous phase**: $C(HNO_3)$ = 3

mol L^{-1} with ^{152}Eu, ^{241}Am radiotracer, $T = 23 \pm 1$ °C.

Detection and Measurement of Droplets in Tubes Using Advanced Computer Vision Techniques

The measured distances (l_1, l_2, l_3, l_4) were then used to calculate the volumes of the aqueous (V_{aq}) and organic (V_{org}) phases of the droplets. These calculations were performed using the following equations:

$$A = 2\pi a^2 \left(1 + \frac{c^2}{ea^2} \tanh^{-1} e\right)$$

where $e^2 = 1 - c^2 / a^2$, a – inner radius of the capillary tube, $c = (l_1 - l_2) / 2$.

$$V_{aq} = \pi a^2 l_2 + \frac{4}{3}\pi a^2 \frac{(l_1 - l_2)}{2}$$

$$V_{org} = \pi a^2 l_4 - \frac{4}{3}\pi a^2 \frac{(l_4 - l_3)}{2}$$

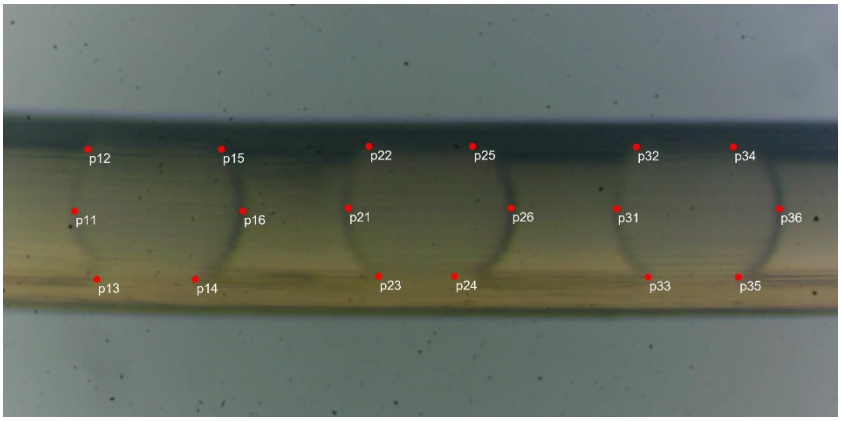


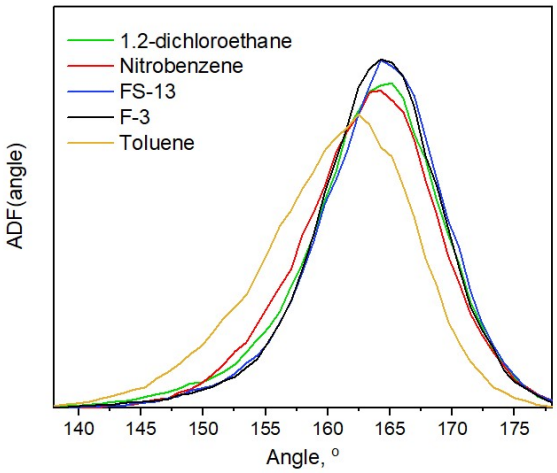
Figure S5. An example of the resulting markup for droplets

Molecular dynamics

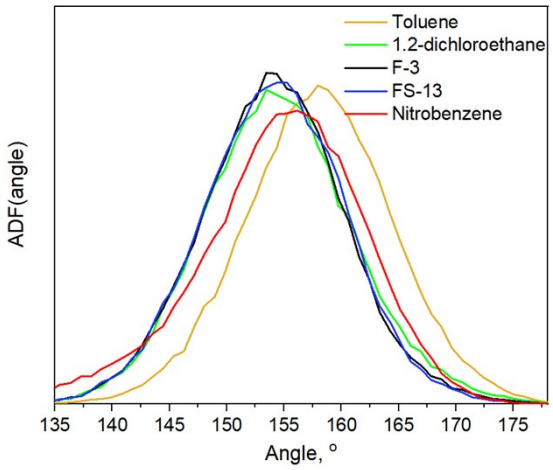
Table S4. Experimental and calculated density of solvents

Organic Name	Density		Dev, %	Ref.
	EXP	**MD**		
Phenyl Trifluoromethyl Sulfone density (**FS-13**)	1.476	1.475	0	[1]
3-nitrobenzoic trifluoride (**F-3**)	1.41	1.443	2	
Nitrobenzene	1.204	1.194	1	[2]
Toluene	0.867	0.874	1	[3]
1.2-Dichloroethane	1.235	1.289	4	

a) N-N-N angle



b) N-N-O angle



c) O-N-O angle

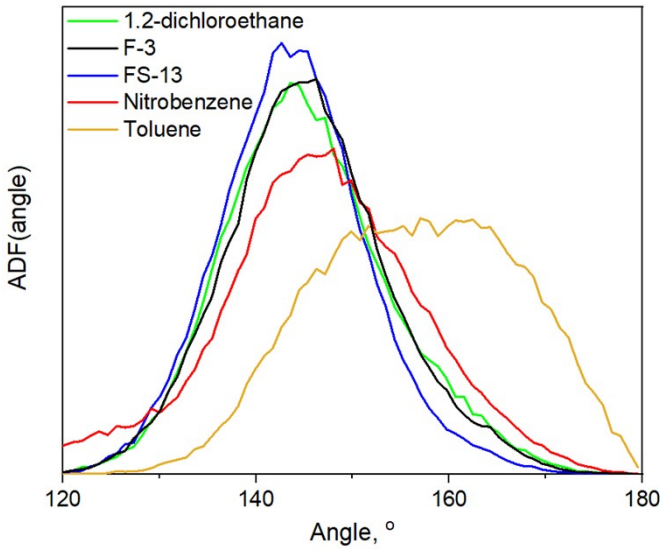
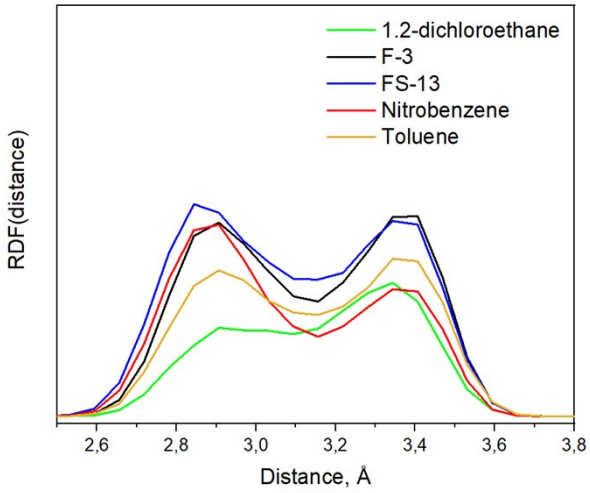
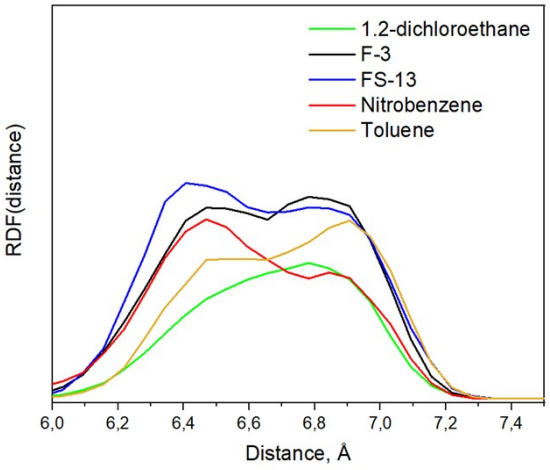


Figure S6. Angular distribution function (ADF) for ligand binding sites

a) N-O distance



b) N-O_b distance



c) O-O distance

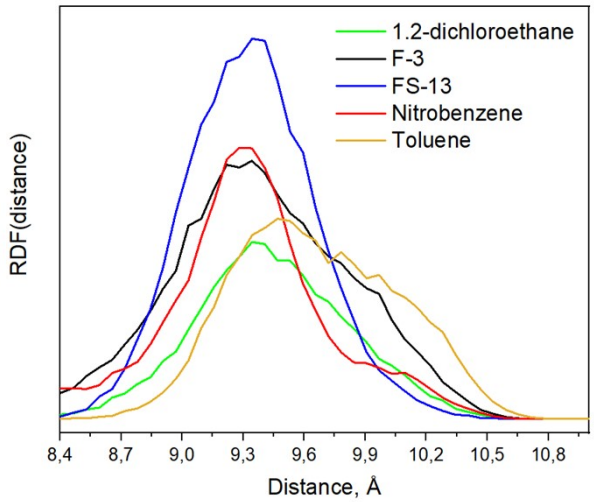


Figure S7. Radial distribution function (RDF) for ligand binding sites

Table S5. Angles and distances between the coordination centers of L obtained from the corresponding distribution functions or crystal data. The error in determining angles is 1 degree, and distances – 0.01 angstroms.

Solvent	Distance, Å			Angle,°		
	N-O (Red)	N-O_p (Blue)	O-O (Green)	N-N-N (Red)	O-N-N (Blue)	O-N-O (Green)
Nitrobenzene	2.91/3.41	6.47/6.84	9.38	164	156	147
FS-13	2.84/3.40	6.40/6.83	9.34	165	154	145
F-3	2.91/3.40	6.50/6.78	9.28/9.97	165	153	145
1,2-Dichloroethane	2.90/3.33	6.47/6.78	9.34	166	153	145
Toluene	2.93/3.38	6.47/6.91	9.53/9.97	162	158	157
Crystal data for L	3.49	6.98	10.43	160	159	170
Crystal data for $EuL(NO_3)_3$	2.64	4.45	4.76	150	114	82

1. V. Babain M. Alyapyshev C.E., Todd T. Fluorinated Diluents- A Review // Solvent Extr. Ion Exch. Taylor \& Francis, 2023. Vol. 41, № 3. P. 253–291.
2. Davies L. et al. Nitrobenzene. World Health Organization, 2003.
3. Properties of Solvents Used in Organic Chemistry [Electronic resource]. URL: http://murov.info/orgsolvents.htm.