Liquid Extraction of Copper(II) and Some Bivalent Metal Ions by Salicylidenalkylimines and N-(2-Hydroxybenzyl)alkylamines

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Extraction of Cu(II), Zn(II), Cd(II), Pb(II), Ni(II), Co(II), and Mn(II) by Schiff bases (salicylidenalkyl-imines with C_2, C_4, C_6, C_8, and C_{12} carbon atoms in alkyl chain) followed by their reduction into N-(2-hydroxybenzyl)alkylamines in chloroform was studied. High selectivity of Cu(II) extraction was confirmed. Other extraction characteristics (extraction curves, capacities, rate of the extraction equilibrium attainment) in dependence on the alkyl chain length and reduction of azomethine groups at the optimum conditions for Cu(II) extraction were studied as well. The retention of the copper extraction selectivity and improvement of extraction properties were found for the reduced forms of Schiff bases possessing longer alkyl chains.

Aggett, *Khoo*, and *Richardson* have studied the properties of a series of Schiff bases with N and O donor atoms arranged in Ar—OH and —CH=N— groups in the liquid extraction of their Cu(II) complexes [1]. They pointed at the high selectivity towards Cu(II) and Fe(III) ions when extracted by ligands with two and four donor atoms, respectively. At the same time they reported on some disadvantageous properties: easy hydrolysis and kinetic instability of Cu(II) complexes at the conditions of extraction processes. An extractability of other metal ions by Schiff bases was not yet published. With regard to these facts we aimed our work to the experimental verification of the Cu(II) extraction selectivity by Schiff bases, and especially by their reduced forms, where the suppression of disadvantageous properties should be anticipated. In the case of possible improvements some of the compounds under study may also find an application in practice, *e.g.* in the hydrometallurgy.

The synthesis of Schiff bases, their reduction, and the series of extraction experiments with salicylidenethylimine (Salet [1]) and other compounds obtained by the modification of nonfunctional parts of the Schiff base molecules were performed at the conditions which should enable to compare the properties of Schiff bases and their reduced forms in the extraction process. Also the back extraction into aqueous solutions was tested from the practical point of view, *i.e.* the preconcentration of metal ions and the possibility of agent recycling.

EXPERIMENTAL

Schiff bases of the type I, *i.e.* salicylidenethylimine (SAE), salicylidenebutylimine (SAB), salicylidene-

hexylimine (SAHX), salicylidenoctylimine (SAO), and salicylidenedodecylimine (SADD) were synthesized from salicylaldehyde and appropriate 1-aminoalkanes [2—4]; those of type II, *i.e.* N-(2-hydroxybenzyl)-butylamine (HBAB), N-(2-hydroxybenzyl)octylamine (HBAO), and N-(2-hydroxybenzyl)dodecylamine (HBADD) were obtained by the reduction of 0.1 mole of SAB, SAO, and SADD by treating their methanolic solutions with 100 % mole excess of $NaBH_4$ at ambient temperature during 30 min mixing. These were isolated from the reaction mixtures by the extraction with diethyl ether (3 × 100 cm^3), collected ethereal extracts were dried over Na_2SO_4 and evaporated to dryness in vacuum. The yields in all cases were higher than 85 % of the theoretical ones. All compounds were identified by the UV and ^1H NMR spectroscopy and elemental analysis. The refractive indexes were measured for liquid-state compounds of I and II. By the action of methanolic solution of HCl the specimens of liquid compounds were converted into the solid crystallic chlorides. The results of identification are summarized in Fig. 1 and in Tables 1—2.

By dissolving compounds I and II in chloroform there were prepared the stock solutions of extractants in concentration $c_L = 4 \times 10^{-2}$ mol dm^{-3}. The extraction properties were studied for the metal ions Cu(II), Zn(II), Cd(II), Pb(II), Co(II), Ni(II), and Mn(II). Their aqueous stock solutions were prepared from corresponding nitrates of anal. grade purity (Labora, CSFR) in approximate concentration $c_M \approx 2 \times 10^{-2}$ mol dm^{-3}. Actual content of individual metals therein was determined by the complexometry [5]. pH of water phases before extraction was adjusted by the chloroacetic (pH = 2.0—3.7) and acetic (pH = 3.7—5.7) buffers, or by the NaOH solution
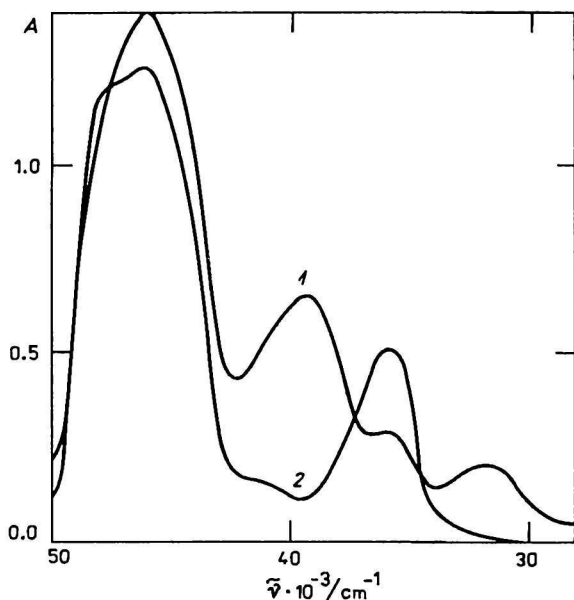
Fig. 1. A typical UV spectrum of salicylidenalkylimines (*1*. SAB) and *N*-(2-hydroxybenzyl)alkylamines (*2*. HBAB) in CH$_3$OH. c_{L1} = 3 × 10^{-6} mol dm^{-3}, c_{L2} = 2 × 10^{-5} mol dm^{-3}. $\tilde{\nu}_1$ = 46000 cm^{-1}, $\tilde{\nu}_2$ = 39600 cm^{-1}, $\tilde{\nu}_3$ = 35880 cm^{-1}: $\pi \to \pi^*$ transition. $\tilde{\nu}_4$ = 31800 cm^{-1}: $n \to \pi^*$ transition of conjugated —CH=N— [6].

ions in polythene bottles (100 cm^3 or 250 cm^3) on a laboratory shaker MEAS (Autocentrum, Prague). The evaluation of extractions was carried out by the atomic absorption spectroscopy (AAS-1, Zeiss, Jena) in the acetylene—air flame mode. The metal working solutions were prepared from 2 cm^3 of desired stock solution and 18 cm^3 of buffer solution (pH < 5.7) or 16 cm^3 of distilled water was added, pH adjusted under the pH-meter check with few drops of NaOH solution, and filled with water to the total volume of 20 cm^3 (pH > 5.7). From this solution a portion of 10 cm^3 was shaken with 10 cm^3 of extractant solution during 1 h (or more) at temperature (21.0 ± 1.0) °C. After extraction the equilibrium pH was measured, the water phase as well as the nonextracted portion of metal working solution were
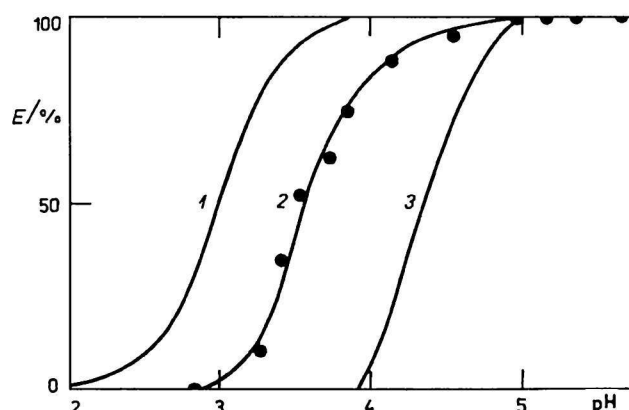

Fig. 2. Extraction of Cu(II) with SAE into CHCl$_3$ in dependence on pH. $c_M \approx$ 2 × 10^{-3} mol dm^{-3}, c_L = 2 × 10^{-2} mol dm^{-3}, θ = 22 °C. *1*. Theoretical curve, *2*. our experiment, *3*. from Ref. [1].

(*c* = 0.1 mol dm^{-3}) for pH > 5.7. The checking of adjusted and equilibrium pH values after extractions was performed by a pH-meter OP 205 equipped with a combined glass electrode OP 0808 P (Radelkis, Budapest).

All extraction experiments were carried out by shaking the two phase mixtures of working solutions of I or II and working solutions of individual metal

Table 1. ^{1}H NMR Spectra of Salicylidenalkylimines (type I). $\tilde{\nu}$ = 80 MHz, solvent CDCl$_3$, internal standard HMDSO, θ = 25 °C

δ	Proton assignment	SAE		SAB		SAHX		SAO		SADD	
		H_e	H_t	H_e	H_t	H_e	H_t	H_e	H_t	H_e	H_t
8.2—8.5 s	Ar—HC=N—	0.9	1	0.8	1	0.9	1	1.1	1	1.1	1
6.6—7.4 m	4 H$_{arom}$	3.4	4	3.6	4	3.6	4	3.5	4	3.7	4
3.5—3.6 q	=N—CH$_2$—	2.0	2	2.1	2	2.1	2	1.7	2	1.7	2
1.3—1.5 m	—(CH$_2$)$_{n-1}$—	–	–	5.0	4	8.8	8	12.5	12	20.3	20
0.8—1.2 t	—CH$_3$	3.6	3	2.6	3	2.3	3	3.0	3	3.1	3

H_e — experimental protons, H_t — theoretical number of protons, s — singlet, t — triplet, q — quartet, m — multiplet.

Table 2. ^{1}H NMR Spectra of *N*-(2-Hydroxybenzyl)alkylamines (type II). $\tilde{\nu}$ = 80 MHz, solvent CDCl$_3$, internal standard HMDSO, θ = 25 °C

δ	Proton assignment	HBAB		HBAO		HBADD	
		H_e	H_t	H_e	H_t	H_e	H_t
6.53—7.15 m	4 H$_{arom}$	3.8	4	3.5	4	4.8 x	4 x
6.07—6.22 s	—NH—	1.4	1	1.3	1	— x	1 x
3.83—3.90 s	Ar—CH$_2$—N—	2.2	2	2.1	2	2.3	2
2.54—2.60 t	—N—CH$_2$—	2.1	2	2.3	2	2.4	2
1.23—1.37 m	—(CH$_2$)$_{n-1}$—	3.7	4	11.8	12	18.9	20
0.83—0.90 t	—CH$_3$	2.8	3	3.1	3	3.5	3

H_e — experimental protons, H_t — theoretical number of protons, s — singlet, t — triplet, m — multiplet, x — common multiplet.
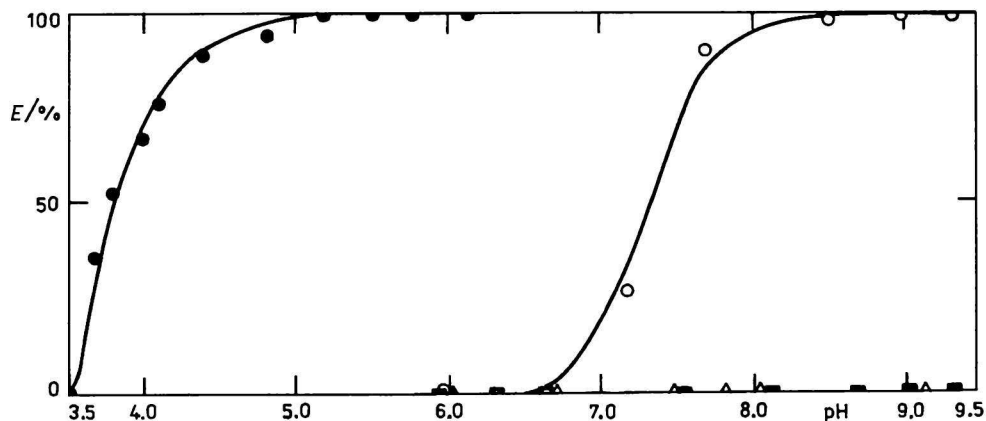
Fig. 3. Extraction of the selected M(II) with SAE into $CHCl_3$ in dependence on pH. $c_M \approx 2 \times 10^{-3}$ mol dm^{-3}, $c_L = 2 \times 10^{-2}$ mol dm^{-3}, $t = 60$ min, $\theta = 22$ °C. ● Cu, ○ Zn, △ Cd, ■ Pb.
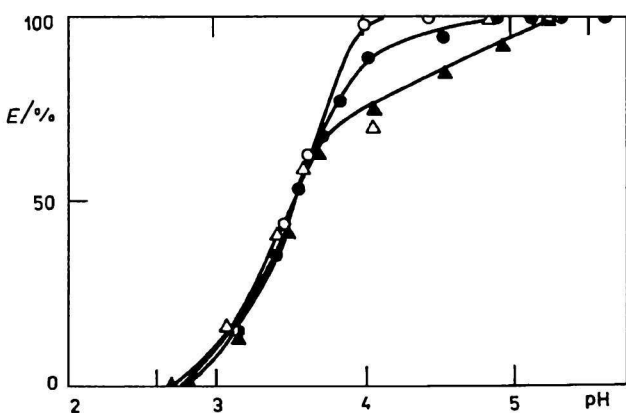

Fig. 4. Extraction of Cu(II) by I into $CHCl_3$ in dependence on pH and on the alkyl chain length. $c_M \approx 2 \times 10^{-3}$ mol dm^{-3}, $c_L = 2 \times 10^{-2}$ mol dm^{-3}, $\theta = 22$ °C. ● SAE, ○ SAB, △ SAHX, ▲ SAO.
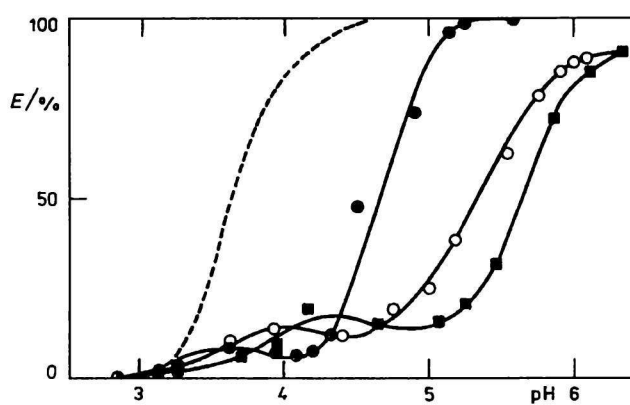

Fig. 6. Extraction of Cu(II) by II into $CHCl_3$ in dependence on pH and on the alkyl chain length. $c_M \approx 2 \times 10^{-3}$ mol dm^{-3}, $c_L = 2 \times 10^{-2}$ mol dm^{-3}, $\theta = 22$ °C. ■ HBAB, ○ HBAO, ● HBADD, - - - - - SAE.
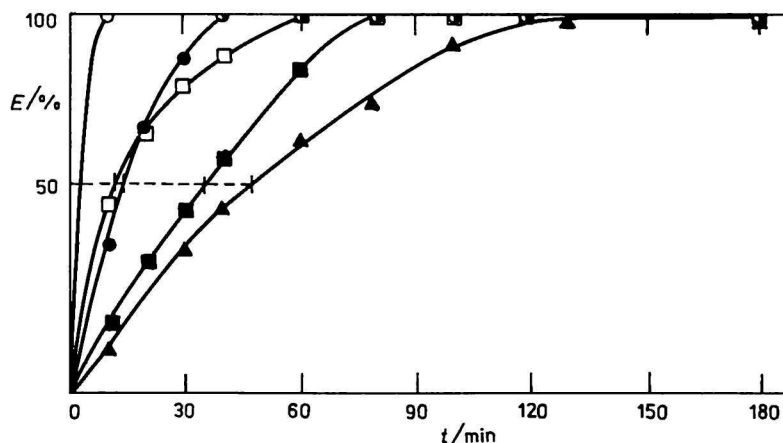

Fig. 5. Dependence of Cu(II) extraction by I on the duration of extraction at pH = 5.1 ± 0.2. $c_M \approx 2 \times 10^{-3}$ mol dm^{-3}, $c_L = 2 \times 10^{-2}$ mol dm^{-3}, $\theta = 22$ °C. ○ SAE, ● SAB, □ SAHX, ■ SAO, ▲ SADD.

adequately diluted and their atomic absorbances A_x and A_0 measured. The extracted portions of metal ion (E/%) were then calculated according to the relationship $(A_0 - A_x)/A_0$ and as dependence on the pH presented in the form of extraction curves in Figs. 2—7.

At the determination of the extraction capacities for Cu(II) 20 cm^3 of the extractant solution ($c_L = 4 \times 10^{-2}$ mol dm^{-3}) and 20 cm^3 of Cu(II) ($c_M = 2.11 \times 10^{-2}$ mol dm^{-3}) was shaken for 1 to 2 h, the above-mentioned temperature and pH = 6.0 ± 0.2 being adjusted by
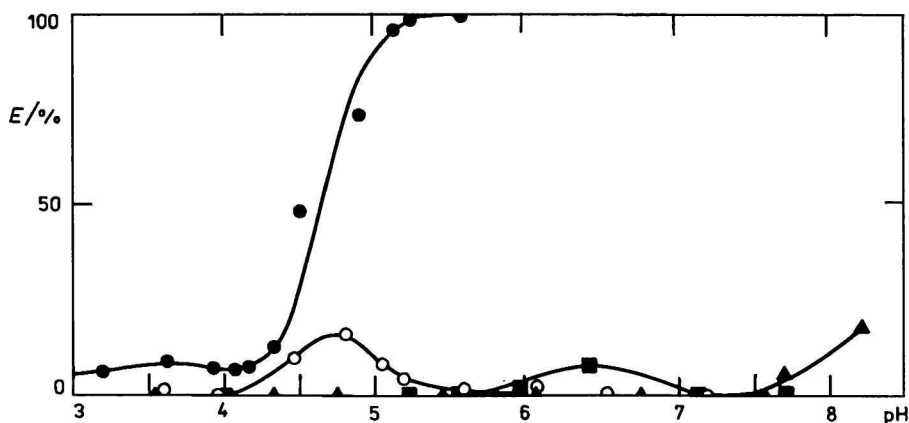
Fig. 7. Extraction of M(II) by HBADD into $CHCl_3$ in dependence on pH. $c_M \approx 2 \times 10^{-3}$ mol dm^{-3}, $c_L = 2 \times 10^{-2}$ mol dm^{-3}, $\theta = 22$ °C.
● Cu, ○ Co, ▲ Zn, ■ Pb.

few drops of NaOH solution. Nonextracted portion of copper in water phase was then determined by complexometric titration. The ratio of extracted and starting amount of copper expressed in percentage is the so-called extraction capacity. Its values for Cu(II) and individual extractants I and II are in Table 3.

Table 3. Extraction Capacities of I and II

Type	Extractant	E(Cu(II))/%
I	SAE	96
	SAB	98
	SAHX	96
	SAO	95
	SADD	87
II	HBAB	46
	HBAO	58
	HBADD	80

The study of the rate of the extraction equilibrium attainment as dependence on the alkyl chain length was carried out by shaking 50 cm^3 of extractant solution and 50 cm^3 of Cu(II) solution in approximately ten-fold lower mole concentration at the optimum pH (found in preceding experiments) for several hours. At selected time intervals there were withdrawn the

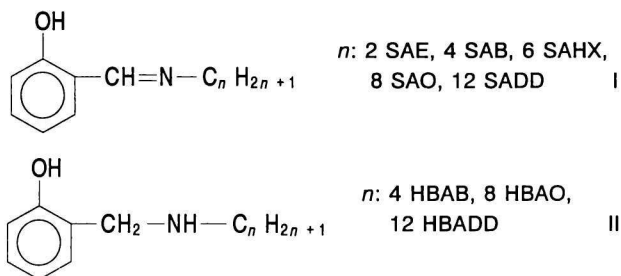**Table 4.** Dependence of the Cu(II)—II Extraction on Time and the Alkyl Chain Length

t/min	E/%		
	HBAB	HBAO	HBADD
5	77.0	69.1	82.0
10	84.7	77.8	85.2
20	90.3	82.4	89.0
30	89.5	83.5	96.5
45	88.9	82.4	99.0
60	88.9	86.0	100.0
90	90.3	83.8	99.0
120	90.2	86.2	99.4
180	90.3	84.4	99.4

specimens of 1 cm^3 from both phases, those from water phase were used for the AAS measurements and evaluation according to the relationship $(A_0 - A_t)/A_t$, where A_0 is the absorbance just before extraction and A_t at time interval t. The results are presented in Fig. 4 and in Table 4.

The back extraction (stripping) experiments were carried out by shaking 10 cm^3 of chloroform extracts containing desired Cu(II) complexes with 10 cm^3 of diluted sulfuric acid ($c \approx 0.1$ mol dm^{-3}).

RESULTS AND DISCUSSION

The following compounds were studied in this work

OH
⬡—CH=N—$C_n H_{2n+1}$ n: 2 SAE, 4 SAB, 6 SAHX,
                                        8 SAO, 12 SADD   I

OH
⬡—CH_2—NH—$C_n H_{2n+1}$ n: 4 HBAB, 8 HBAO,
                                              12 HBADD   II

i.e. Schiff bases (type I) and their reduced forms (type II), as well as their properties in the liquid-liquid extraction of their complexes with M(II) ions selected.

The main aim of our work was the experimental verification of the Cu(II) ions extraction selectivity with an emphasis on the extractants II, the comparison of properties of I and II in dependence on the alkyl chain length (C_4, C_8, C_{12}) from several aspects in order to find the optimum extraction conditions and the compounds for the potential practical use. SAE was studied as the only compound identical with Salet in Ref. [1], and together with SAHX served as the members of Schiff bases I when the attainment of extraction equilibrium of Cu(II)—I was studied.

The identity and good purity of all compounds under study was confirmed by the spectral studies (Fig. 1 and Table 1) being almost identical with those in Ref. [6], and by the interpretation of ^{1}H NMR spectra of II (Table 2).

In the preliminary extraction experiments we have tested eight organic solvents: chloroform, carbon tetrachloride, benzene, toluene, diethyl ether, 1-pentanol, 1-octanol, and methyl isobutyl ketone. These experiments proved the chloroform to be the best for all extractants and metal ions selected.

M(II) ions create with salicylidenalkylimines I complexes of the ML_2 composition [1, 7, 8], some of them are extractable into the organic solvents. Fig. 2 shows three extraction curves: theoretical one of the Cu(II) extraction by SAE being calculated from the published data and relationships [1, 9], the experimental one redrawn from Ref. [1], and our experimental curve. The differences in positions of theoretical and experimental curves may be due to the competition of hydrolytic and complex-forming actions so as it was interpreted by *Aggett, Khoo*, and *Richardson* [1]. The different positions of experimental curves with $[pH_{1/2}]_{0.01} = 4.46$ [1] and $[pH_{1/2}]_{0.02} = 3.38$ (our one) are probably caused by the fact that the increased concentration of extractant in organic phase shifts the extraction curves to the lower pH levels, which is reflected in the decrease of the $pH_{1/2}$ parameter [9]. But the difference of these two values (0.88) is rather great because we have used only two times higher concentration of SAE than that in Ref. [1], which at present we are not able to explain. Having the $pH_{1/2}$ value and other necessary experimental data and a relationship from Ref. [9], an extraction constant for the Cu(II)—SAE was calculated for our experiment as log K_{ex} = – 3.77.

Fig. 3 presents the result of extraction of the seven M(II) ions by SAE into chloroform, from which the high selectivity of Cu(II) extraction may be seen. An interesting observation is the almost quantitative extraction of Zn(II) at pH > 8.5. Other M(II) ions were not extracted at all across the whole pH range studied. The points for Ni(II), Co(II), and Mn(II) are not plotted due to the simplicity of the figure at zero extraction line.

Fig. 4 presents the results of Cu(II) extraction by I in dependence on the alkyl chain length, pH, and duration of extraction. As can be seen, the $pH_{1/2}$ for other extractants I is practically the same as that for SAE, which probably reflects the independence of the ML_2 complex stabilities on the alkyl chain length. The deviations and shapes of extraction curves above 60 % level, on the other hand, are probably connected with the alkyl chain length effect on the hydrophilicity of complex particles and the kinetics of extraction as well. The SADD extraction curve is not there drawn due to its overlap with that for SAO.

The extraction capacities of I (Table 3) will be discussed later. The rate of the extraction equilibrium attainment for the Cu(II)—I systems may be discussed from the results presented in Fig. 5, from which its dependence on the alkyl chain length is clearly seen. In the case of SADD nor the five hours lasting experiment was sufficient for the quantitative extraction (max. 97.7 %, steady from the 130th min). There are probably involved several and mutually connected effects: very low solubility of SADD in water, slow creation of the Cu(II) complexes, competitive hydrolytical, and perhaps other effects. By the way, in no case we have observed the decrease of extraction with time as it is described for the Cu(II)—SAE in MIBK [1].

Fig. 6 shows the results of the Cu(II)—II extraction experiments. The dashed curve is the same as in Figs. 3 and 4 for the Cu(II)—SAE. From this figure it is obvious that the reduction of precursors I resulting in the extractants II caused remarkable shift of the Cu(II) extraction curves into higher levels of pH. Moreover, the influence of the alkyl chain length is reflected in that shift ($pH_{1/2}$'s) and the percentage of extraction as well. These observations are probably caused by the increase of hydrophilicity of both extractants II and their Cu(II) complexes with the decrease of alkyl chain length, and also by the decreased complex stabilities due to the interruption of electron conjugation of the canceled azomethine double bond with π-orbitals of the benzene ring. Only HBADD is capable of quantitative extraction of Cu(II) with $pH_{1/2}$ = 4.7, which is of 1.12 pH unit higher than those for the Cu(II)—I systems at the same concentrations of extractants and Cu(II).

Fig. 7 presents the extractability of the seven M(II) ions selected by HBADD. Cd(II), Ni(II), and Mn(II) ions were not extracted at all across the whole pH range studied (therefore they are not plotted), other four ions were extracted in the wide range of pH to max. 18 % for Co(II), quantitative for Cu(II) at pH > 5.4. The possible selectivity of Cu(II) extraction is only in the narrow range of pH = 5.5 ± 0.1. All this is obviously different when compared with the M(II)—SAE extractions (Fig. 3).

From Table 3 the extraction capacities of I and II towards Cu(II) should be compared: while those of I are high and almost constant, those of II are substantially lower and they increase with the prolongation of alkyl chain length from HBAB to HBADD. This may also support a hypothesis concerning the role of hydrophilicity and stabilities of the Cu(II) complexes in their extractions.

Since the stability constants of Cu(II)—I complexes are by order only 10^2 [8], those for Cu(II)—II should be yet lower, there remains an open question about the extraction properties of I and II towards other M(II) and M(III) ions and with higher coordination

numbers, and therefrom the possible interferences with Cu(II) extractions.

The back extraction (stripping) of all Cu(II) complexes from the chloroform extracts may be semi-quantitatively characterized as follows: Cu(II)—I complexes are quickly and completely hydrolyzed as well as their ligands resulting in aqueous solutions of cupric ions, alkylammonium salts (sulfates), and salicylaldehyde predominantly in chloroform. In the case of Cu(II)—II complexes, HBAB and HBAO remained in greater part in aqueous solution (as sulfate salts). Only HBADD remained approximately to 90 % in the chloroform phase being capable of the next Cu(II) extraction. No hydrolysis or decomposition of II was detected.

From the point of view of possible practical use of HBADD we have made a "paper" comparison with a commercial two-component extraction agent labelled as LIX 64-N, because it possesses the same donor atoms (N in hydroxamic groups), aryls and longer alkyls, and it is already for years exploited in the hydrometallurgy [10]. If we keep in mind only the selective Cu(II) extraction, then HBADD should be there a successful competitor, because it extracts Cu(II) more than five times quicker, it is a chemical individual which is easy preparable in a two-step synthesis from not expensive starting materials, and it is well retrievable after extractions.

CONCLUSION

The study of salicylidenalkylimines I, their reduced forms, i.e. N-(2-hydroxybenzyl)alkylamines II in the series of extraction experiments directed mainly to the Cu(II) extraction besides Zn(II), Cd(II), Pb(II), Ni(II), Co(II), and Mn(II) ones under the comparison of some other properties of I and II in dependence on the alkyl chain length has brought the following results:

Verification of the selective Cu(II) extraction by I, independence of the $pH_{1/2}$ parameters, quantitative Cu(II) extraction (except of SADD); increase of ex-

tractability of the Cu(II)—II complexes up to the quantitative one with HBADD at simultaneous decrease of the $pH_{1/2}$'s.

High and steady so-called extraction capacities for the Cu(II)—I systems; remarkably lower ones for the Cu(II)—II systems and increasing from HBAB to HBADD.

The rate of the extraction equilibrium attainment remarkably decreasing for the systems Cu(II)—I with prolongation of the alkyl chain; significantly higher one for the Cu(II)—II with only slight decrease from HBAB to HBADD.

Quick and complete back extraction of Cu(II) in all cases, the possibility of good recycling only for HBADD.

All these findings may be summarized into the statement that probably only the compound HBADD representing N-(2-hydroxybenzyl)alkylamines with longer aliphatic chains should be potentially used in practice, i.e. in the treatment of the copper-containing substrates on the so-called "wet way" (in the hydrometallurgy).

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