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Solubility and polarity parameters for pyridinecarboxamides and their complexes with copper(II) as determined by inverse gas chromatography

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Abstract

Pyridinecarboxamides and their complexes with copper(II) were characterized by means of inverse gas chromatography. The investigated amides were extractants of copper(II) from solutions with a high chloride concentration. Solubility and polarity parameters were used to quantitate the properties of the extractants. The influence of the extractant's structure upon its properties are presented and discussed as well as the dependence of the physicochemical parameters on the introduction of the metal ion into the molecular structure.

Keywords: Polarity parameters; Solubility parameters; Complex formation; Thermodynamic parameters; Inverse gas chromatography; Extraction parameters; Pyridinecarboxamides; Copper; Amides

1. Introduction

Copper is recovered from oxide ores and wastes in about 30 different installations using extraction with hydroxyoximes [1]. Pyridine derivatives were recently proposed by Zeneca Mining Chemicals (earlier ICI Mining Chemicals) for copper recovery from sulphidic ores and the Cuprex process was designed and verified in the pilot plant [2,3].

Pyridinecarboxamides were synthesized as potential extractants of copper from chloride solutions. The conditions of their synthesis and some basic physicochemical data were presented earlier [4]. It was demonstrated in previous works [5–9] that the extraction abilities of pyridine-type extractants can be significantly changed by the position of the substituent. The studies suggest that, besides the extractants proposed by Zeneca, several other structures may also be useful for the extraction of copper, zinc, etc., from chloride solutions. Some preliminary selection and screening of suitable structures can be achieved by comparing their dissociation constants which characterize the basicity of the pyridine nitrogen. The other possibility offers the use of topological indices as structural parameters [10–12]. Topological indices were determined for models of prospective pyridine extractants and relationships: structure–topological index and topological index–pyridine nitrogen basicity were described [13]. The second order valence molecular connectivity index, the Balaban index and the Wiener number were appropriate structural descriptors of pyridine deriva-

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tives and, in several cases, allow the pyridine nitrogen basicity to be predicted. The relationship between pK_a values and the structural descriptors were presented and discussed.

The extraction process occurs at the interface between the hydrocarbon and water phases. The amphiphilic molecules of the extractants are present at the interface, having their hydrophobic chains deeply embedded in the non-polar media while the hydrophilic heads enter the water phase. The relationship between the hydrophilic and hydrophobic properties of extractants influences their ability to form an association with the modifier molecules and adsorption at the hydrocarbon–water interface. Such a relationship may be quantitatively described by e.g., HLB number (hydrophile–lipophile balance) or by polarity parameters [14–16].

Polarity parameters have been determined by means of inverse gas chromatography (IGC) [17–19]. However, the term "polarity" is very general and according to Poole and Poole [20] refers to the capacity of a solvent for various intermolecular interactions. The potentially useful parameter seems to be the solubility parameter δ_2, introduced by Hildebrand and Scott [21] and defined as the square root of cohesive energy ratio:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \tag{1}$$

where ΔE denotes cohesive energy and V is the molar volume of the solute.

The procedure of DiPaola-Baranyi and Guillet [22,23] for the estimation of the solubility parameter δ_2 of non-volatile species has been used widely for polymers and their blends [19,23–26]:

$$\frac{\delta_1^2}{RT} - \frac{\chi^{\infty}}{V_1^0} = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^{\infty}}{V_1^0}\right) \tag{2}$$

where: δ_1 and δ_2 are the solubility parameters of the testing solute and the stationary phase, respectively; χ^{∞} and χ_s^{∞} are the Hildebrand–Scatchard interaction parameter and its entropic component, respectively; V_1^0 is the molar volume of the testing solute, R is the gas constant and T is the absolute temperature. Voelkel and Janas [27,28] proposed a modification which allowed the separation of the increments of the solubility parameter corresponding to different solute–solvent intermolecular interactions. Increments of solubility parameter corresponding to dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) interactions, were determined from Eq. (2) and were used separately for three groups of solutes, (i) *n*-alkanes, (ii) polar non-hydrogen bonding test solutes (aromatic hydrocarbons, ketones and nitropropane) and (iii) alcohols and pyridine [27,28].

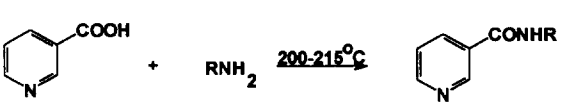
The reason for the correction of the calculation procedure was the downward curvature of Eq. (2) observed earlier by Price [29] and also found for oxyethylates examined by Voelkel and Janas [27,28,30]. In other words, the values of the solubility parameter δ_2 estimated by the use of Eq. (2) according to Guillet's original procedure were overestimated.

The aim of this paper was to: (i) examine the group of pyridinecarboxamides and their complexes with copper by means of IGC, (ii) calculate polarity and solubility parameters, (iii) discuss the influence of the structure of extractants upon the measured physicochemical parameters, (iv) discuss the temperature dependence of the solubility parameter and its increments, (v) evaluate and discuss the relationships between solubility and polarity parameters and (vi) examine the differences between the properties of extractants and their complexes and to discuss the possible implications for their behaviour in extraction systems.

2. Experimental

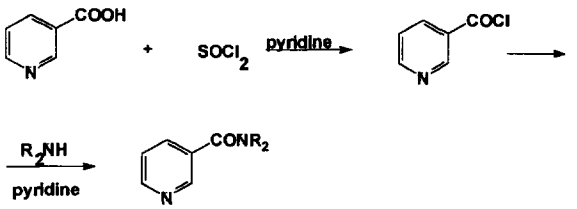
2.1. Materials

The group of amides and ester of 3-pyridinecarboxylic and 3,5-pyridinedicarboxylic acids as well as their complexes with copper(II) were used as liquid stationary phases in GC columns. N-dodecyl-3-pyridinecarboxamide (A1) and N-octadecyl-3-pyridinecarboxamide (A2) were obtained according to reaction I:

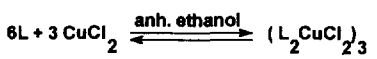


while N,N-dihexyl-3-pyridinecarboxamide (A3),

N,N-dioctyl-3-pyridinecarboxamide (A4) and N,N,N,N-tetrahexyl-3,5-pyridinedicarboxamide (A5) were obtained according to reaction II:



Dodecyl-3-pyridinecarboxylate (E1) was supplied by Szymanowski et al. [6] and was used as the reference substance often applied in industrial extraction. The corresponding complexes of compounds A1, A2, A3 and A4 were assigned as K1–K4, respectively. All complexes were obtained according to reaction III [4,31]:



The results of the elemental analysis of synthesized complexes confirm the molar ratio of metal–ligand–chloride = 1:2:2 [4].

2.2. IGC experiments

The conditions for the IGC experiments were as follows: column, 1 m×3 mm I.D.; column temperatures, 100, 110 and 120°C; column loading, 25% (w/w) of the liquid phase supported on 125–177 μm Celite (80–120 mesh); carrier gas, helium at a flow-rate of 40 ml min^{-1}; flame ionization detector; gas chromatograph, Chrom 5 (Kovo, Czech Republic). The volatile test compounds employed were: *n*-alkanes with chain lengths from C_5 to C_{13}; the aromatic hydrocarbons, benzene, toluene, xylene and ethylbenzene; the polar *n*-alkanols from C_1 to C_4; butan-2-one and pentan-2-one; 1-nitropropane and pyridine. The injection volume was 0.1 μl. Each solute was injected five times and retention times were averaged. The mean retention time was used in further calculation of net retention volume. For complexes K1 and K2 measurements were carried out at elevated temperatures (150, 160 and 170°C) due to the high melting points of these compounds. The densities of the stationary phases were measured at the temperatures of the IGC experiments with a modified picnometric procedure used earlier by Becerra et al. [32], Fernandez-Sanchez et al. [33] and Garcia-Dominguez [34].

2.3. Calculations

The void volume was calculated according to the procedure proposed by Grobler and Balizs [35]. Polarity parameters: polarity index and coefficient, ρ, were calculated with the use of the retention of ethanol as the polar probe [32,33]. Thermodynamic functions of solution: i.e., partial molar excess Gibbs free energy of solution per methylene group $\Delta G^{E}(CH_2)$ and partial molal Gibbs free energy of solution of methylene group $\Delta G_s^{m}(CH_2)$ were calculated according to the procedures given in our earlier papers [35–38]. Criterion A was calculated according to the procedure presented by Ševčik and Löwentap [39].

The solubility parameter was calculated by the procedure given by DiPaola-Baranyi and Guillet [22,23] and using Eq. (2). Increments of solubility parameter corresponding to dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) interactions, were calculated as described previously [27,30].

3. Results and discussion

Pyridinecarboxamides were characterized by empirical polarity parameters as polarity index, PI, coefficient, ρ, difference of retention index on the examined phase and the reference squalane for the first five McReynolds test solutes ΔI_i and their $\Sigma_{i=1}^{5} \Delta I_i$; criterion A; thermodynamic functions of solution partial molal Gibbs function of solution per methylene group $\Delta G_s^{m}(CH_2)$, partial molar Gibbs excess function of solution $\Delta G^{E}(CH_2)$, as well as solubility parameter δ_2, increments of solubility parameter corresponding to dispersive (δ_d), polar(δ_p) and hydrogen bonding (δ_h) interactions and the corrected solubility parameter δ_T.

Generally, the increase in polarity of the stationary phase is quantitated by an increase of the polarity index, coefficient, ρ, $\Delta G_s^{m}(CH_2)$ and $\Delta G^{E}(CH_2)$ functions, ΔI_i and $\Sigma_{i=1}^{5} \Delta I_i$ values as well as by the solubility parameters, δ_2 and δ_T. The only exception

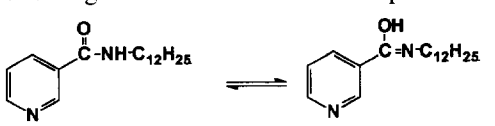
Table 1
Polarity parameters of pyridinecarboxamides and their complexes with copper(II)

Liquid phase	Polarity index PI (EtOH)			Coefficient ρ (EtOH)			Criterion A		
	100°C	110°C	120°C	100°C	110°C	120°C	100°C	110°C	120°C
A1	99.3	97.6	94.4	2.35	2.07	1.89	1.994	1.900	1.861
A2	87.0	82.8	78.2	1.56	1.39	1.27	2.033	1.958	1.888
A3	96.1	94.7	94.3	2.09	1.97	1.86	2.012	1.943	1.883
A4	88.2	86.2	84.8	1.62	1.51	1.42	2.015	1.945	1.881
AS	93.0	89.6	88.0	1.90	1.67	1.56	2.001	1.918	1.849
E1	64.5	58.7	56.6	0.92	0.86	0.87	2.095	2.009	1.936
K1[a]	108.5	106.5	104.5	–	–	–	1.976	1.889	1.821
K2[a]	93.8	91.7	89.7	–	–	–	2.007	1.927	1.883
K3	107.1	104.4	102.2	3.39	2.87	2.65	1.982	1.914	1.830
K4	93.2	90.6	85.5	2.15	1.85	1.58	2.002	1.923	1.843

[a]Extrapolated from values measured at 150, 160 and 170°C.

is criterion A, the values of which decrease with increasing polarity of the liquid stationary phase.

It was shown that the structure of the alkyl substituents significantly influences the properties of amides, e.g. nitrogen basicity and further extractive properties. Really, the increase in the length of the straight alkyl chain(s) significantly decreases compounds' polarity: A1>>A2 and A3>A4. The decrease of polarity of the liquid stationary phase is demonstrated by lower values of the polarity index and coefficient, ρ (Table 1), McReynolds constants and their sum (Table 2), ΔG^E (Table 3), as well as the solubility parameter, δ_2, and the corrected solubility parameter, δ_T (Table 5). As criterion A demonstrates the resistance of the liquid phase to dissolution of non-polar species or the non-polar part of the test substance, it decreases with the increase in polarity (Table 1). The substitution of the second alkyl chain by a nitrogen atom (total number of carbon atoms in alkyl substituent(s) remains the same) causes the decrease in polarity and the solubility parameters, i.e. A1 is more polar than A3. Moreover, in the molecule of monosubstituted amide the following tautomeric structures are possible:



Such structures may be present only in the case of amides A1 and A2. It increases the number of "active places" and, as a consequence, the probability of the formation of intermolecular hydrogen bondings with the test solutes, e.g. alcohols. In disubstituted amides, such possibilities are reduced. Therefore, on a macroscopic scale, their polarity

Table 2
McReynolds constants $\Delta I_i = I_i - I_{squalane}$ for the first five test solutes at 100°C

Liquid phase	Benzene	Butan-1-ol	Pentan-2-one	1-Nitropropane	Pyridine	$\Sigma_{i=1}^{5} \Delta I_i$
A1	101.0	354.2	203.3	258.3	234.5	1151.3
A2	75.6	294.7	161.6	206.9	188.7	927.5
A3	116.3	338.3	194.6	304.6	214.0	1167.8
A4	98.7	299.6	164.0	264.4	182.3	1009.1
A5	116.5	327.5	183.7	295.0	211.2	1133.9
E1	70.5	208.7	126.1	192.5	132.7	730.6
K1[a]	191.3	401.3	267.0	411.2	–	–
K2[a]	127.2	325.4	168.9	247.0	–	–
K3	189.7	396.7	265.2	409.3	–	–
K4	143.7	334.3	208.5	326.0	–	–

[a]Extrapolated from values measured at 150, 160 and 170°C.

Table 3
Partial molar excess Gibbs free energy of solution per methylene group for *n*-alkanes and ketones as test solutes

Liquid phase	*n*-alkanes, ΔG^E (CH_2), kJ/mol			ketones, ΔG^E (CH_2), kJ/mol		
	100°C	110°C	120°C	100°C	110°C	120°C
A1	561.5	700.1	997.5	252.9	314.6	385.6
A2	457.5	570.5	871.9	186.1	237.4	297.5
A3	527.5	587.5	894.0	227.8	300.9	342.5
A4	502.4	558.6	886.7	201.4	247.0	296.7
AS	516.0	601.0	967.6	226.2	309.8	335.7
E1	357.7	472.3	758.1	109.0	151.2	229.4
K1[a]	697.5	912.5	1216.3	570.8	581.8	592.8
K2[a]	484.8	768.5	913.0	353.0	398.8	445.5
K3	682.8	877.6	1211.2	477.2	499.3	598.4
K4	529.5	877.2	1074.5	378.7	415.7	503.5

[a]Extrapolated from values measured at 150, 160 and 170°.

decreases in comparison with monosubstituted analogs. The above suggestion is confirmed later by the analysis of structure dependence of the increment of solubility parameter corresponding to hydrogen bonding interactions (δ_h). However, A2 exhibits surprisingly low polarity. A4 is more polar than A2, probably due to the lower number of carbon atoms in two N-substituents of A4. The increase in the size (volume) of the non-polar (hydrophobic) part of A2 is so significant that its polarity is lower than A4. The contribution of the non-polar part (additional two methylene groups) prevails on the effect observed for the pair A1–A3.

The decrease of polarity may also be caused by steric effects, i.e. the screening of the nitrogen atom by long octadecyl groups. It should be noted that in solution both amides (A1 and A2) exhibit similar extraction properties. N,N,N′,N′-Tetrahexyl-3,5-pyridinedicarboxamide (A5) is the unique one in the examined group. It contains two amide groups and four *n*-hexyl chains. Its measured polarity, quantitated by all parameters, is generally lower than those of A1 and A3 (both compounds having twelve carbon atoms), but higher than those observed for A4 and A2. Although the number of carbon atoms is higher in A5 [24 (4×6) carbon atoms in comparison to sixteen (2×8) in A4 and eighteen in A2], the presence of the second polar amide group prevails and the compounds exhibit higher polarity.

All parameters indicate significantly lower polarity of the reference ester E1 when compared with amide A1, which has the same alkyl substituents. Also the solubility parameter δ_2 and the corrected solubility parameter δ_T exhibit higher values for A1. However, the dispersive component for both compounds is very close and the resulting difference is caused by much higher values of increments of the solubility parameter corresponding to hydrogen bonding and polar interactions (Fig. 1A):

$$\delta_h(E1)(5.204\ \text{units}) < \delta_h(A1)(8.189\ \text{units})$$

and

$$\delta_p(E1)(3.451\ \text{units}) < \delta_p(A1)(4.830\ \text{units})$$

Probably, the higher amide ability to polar and hydrogen bonding interactions is a result of the presence of the tautomeric structures shown earlier.

The polarity of the amides is significantly lower in comparison with their complexes with copper(II), i.e. the following order is valid when the polarity index or solubility parameters are taken into account – K1>A1, K2>A2, K3>A3 and K4>A4 (Tables 1–5). Depending on the type of environment, complexes may be present in the form of, e.g., dimers, trimers. Onan et al. [31] presented the structure of such complexes as trimers having exposed >C=O groups. Such a structure seems to have a higher possibility for polar intermolecular interactions. The influence of the alkyl substituents is similar to that observed for amides and the following relationships between the physicochemical parameters of compounds are observed: K1>K3>K4>K2. The reversed selection was found for criterion A (K1<K2)

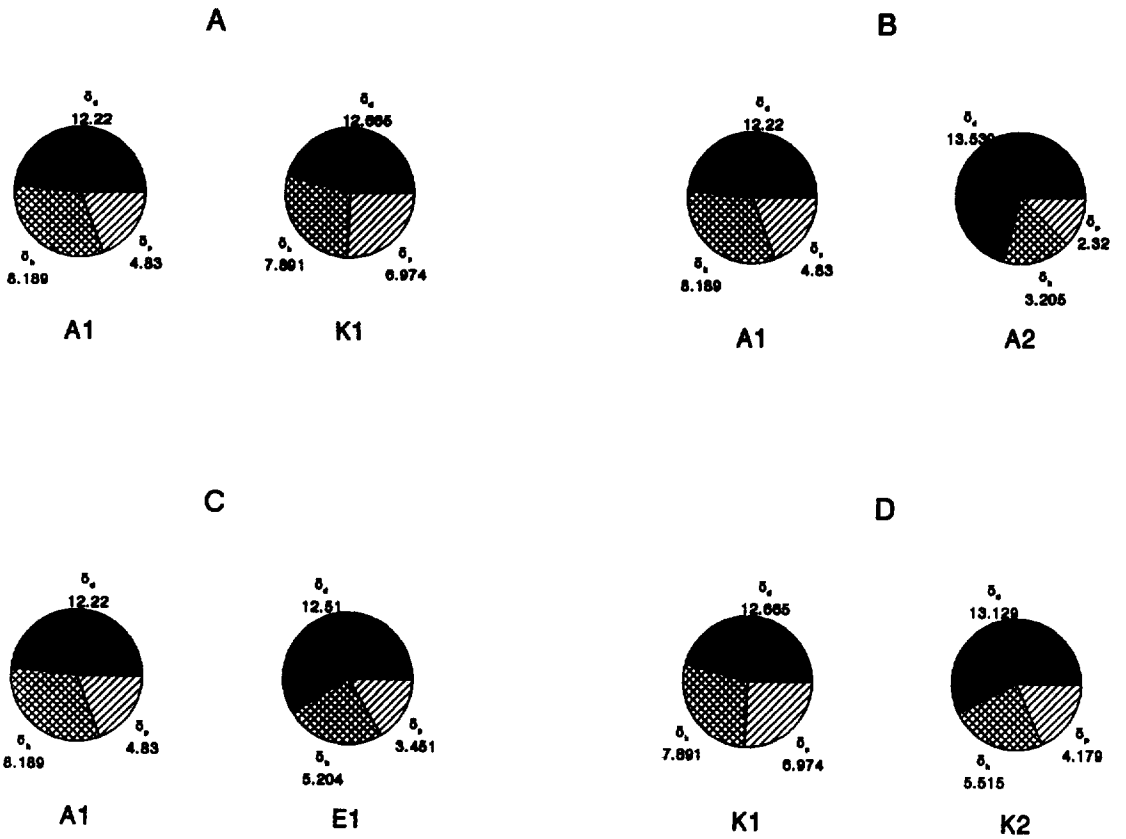


Fig. 1. Comparison of the contribution of solubility parameter components into δ_T for: (A) pyridinecarboxamide (A1) and ester (E1); (B) pyridinecarboxamide (A1) and its complex with copper (K1); (C) pyridinecarboxamides A1 and A2; (D) complexes of pyridinecarboxamides with copper K1 and K2.

Table 4
Partial molal Gibbs free energy of solution of methylene group, ΔG_s^m (CH_2), kJ/mol

Liquid phase	Temperature, °C		
	100	110	120
A1	−2.064	−1.974	−1.884
A2	−2.115	−2.08:3	−2.012
A3	−2.108	−2.042	−1.976
A4	−2.115	−2.041	−1.966
A5	−2.085	−1.991	−1.897
E1	−2.266	−2.174	−2.083
K1[a]	−1.923	−1.854	−1.785
K2[a]	−2.098	−2.001	−1.929
K3	−1.878	−1.809	−1.740
K4	−1.913	−1.841	−1.769

[a]Extrapolated from values measured at 150, 160 and 170°C.

but it also indicates increasing polarity from K1 to K2. In several cases, similar values were found for K2 and K4, e.g. for PI (all temperatures – Table 1) and for the solubility parameter, δ^2, at 120°C (Table 5). However, one should remember that values for K2 (and K1) were extrapolated from results obtained at higher experimental temperatures. Therefore, some imperfection may occur. In the case of the solubility parameter, the use of the corrected solubility parameter, δ_T, is very helpful. Its values for complexes K2 and K4 (at 120°C) are equal to 13.634 and 14.62 $(10^3\ (J/m^3)^{1/2}]$, respectively.

The use of the solubility parameters seems to be very fruitful in the analysis of extraction processes. The solubility parameters, defined by Hildebrand and Scott [21] and measured by means of IGC, exhibit a rather random variation of its values for the group of

Table 5
Solubility parameters measured at different temperatures

Temperature °C	Liquid phase	Solubility parameters, 10^3 $(J/m^3)^{1/2}$				
		δ_2	δ_d	δ_h	δ_p	δ_T
100	A1	18.099	12.220	8.189	4.830	15.483
	A2	16.098	13.539	3.205	2.320	14.105
	A3	17.530	11.866	7.616	5.925	15.294
	A4	17.064	12.050	7.795	4.396	15.010
	A5	17.636	11.399	8.329	6.533	15.556
	E1	16.007	12.510	5.204	3.451	13.982
	K1[a]	18.236	12.665	7.891	6.974	16.515
	K2[a]	17.493	13.129	5.515	4.179	14.920
	K3	17.808	12.463	6.947	5.563	15.315
	K4	17.726	12.667	6.869	4.481	15.090
110	A1	17.742	11.783	8.212	5.027	15.217
	A2	15.881	13.040	3.543	2.624	13.765
	A3	17.338	11.577	7.609	5.958	15.080
	A4	17.169	11.806	7.672	4.384	14.747
	A5	17.227	10.992	8.349	6.575	15.289
	E1	15.690	12.164	5.183	3.449	13.665
	K1[a]	18.199	11.783	8.763	5.562	15.702
	K2[a]	17.226	12.783	4.453	3.624	14.013
	K3	17.638	11.596	7.992	6.104	15.349
	K4	17.385	11.448	7.960	4.827	14.755
120	A1	17.502	11:670	8.148	4.963	15.074
	A2	15.682	12..949	3.344	2.484	13.603
	A3	17.053	11..801	6.944	5.342	14.698
	A4	16.876	11..818	7.317	4.126	14.499
	A5	16.981	11..021	8.137	6.224	15.047
	E1	15.559	12.,166	4.847	3.105	13.459
	K1[a]	17.962	11..268	8.227	6.193	15.264
	K2[a]	17.060	12.,468	4.524	3.156	13.634
	K3	17.142	11..819	7.131	5.446	14.839
	K4	16.964	11..244	7.768	5.193	14.620

[a]Extrapolated from values measured at 150, 160 and 170°C.

the examined compounds [from 16.007 to 18.236 units, i.e. 14% of the lower value (at 100°C)]. The sensitivity of a given parameter on the changes of the structure of the liquid phase describes its applicability to the physicochemical characterization of organic species. So, the solubility parameter, δ_2, may be treated as one that has medium sensitivity in comparison to the polarity index (68%) or $\Delta G^E(CH_2)$ (98%), but is much higher than for criterion A (2.9%) and $\Delta G_s^m(CH_2)$ (9%). It was indicated earlier that sometimes the ordering according to δ_2 leads to slightly different results, e.g. A4>A3 (100°C) and K4≈K3 (100 and 120°C). In all cases, the use of the corrected solubility parameter, δ_T, allowed us to sort the examined compounds into the expected order.

The corrected solubility parameter, δ_T, depends directly on the values of the increments δ_d, δ_p and δ_h and this relationship allows for the examination of the contribution of different interactions into the property called polarity. For example, higher values of δ_T measured for K1, in comparison to A1, are the result of a higher contribution of polar and hydrogen-bonding interactions, as δ_d is similar for both compounds (Fig. 1A). The δ_h value is even lower for the complex but δ_p is significantly higher (by approx. two units). The lower δ_T value for A2 (when

Table 6
Comparison of extraction constants and solubility/polarity parameters for selected extractants [40]

Compound	$\log K_{ex}$	$\log c_{ext,50}$	δ_T	PI
A3	3.25	−1.103	15.294	96.1
A4	3.13	−1.012	15.010	88.2
A5	2.50	−0.792	15.556	93.0
E1	2.2	−0.658	13.982	64.5

$c_{ext,50}$: Extractant concentration at which extraction degree $\varphi = 50\%$.

compared to A1) is caused by very low δ_h and δ_p values, while δ_d is much higher (Fig. 1B). In the case of complexes K1 and K2, the same relationship between increments of the solubility parameter is observed, although differences are not so large as in the case of amides (Fig. 1D).

The extraction equilibrium studies [40] showed that monoalkylamides (A1, A2) are stronger extractants than dialkylamides of 3-pyridinecarboxylic acid (A4, A3). The extraction declines with the addition of the second N,N-dialkylamide group into the pyridine ring (A5), but it is still higher than with the ester (E1). Our results agree well with the order of basicity of the pyridine's nitrogen. The influence of the alkyl chain length on the equilibrium extraction is small. Parameters describing the extraction process ($\log K_{ex}$ and $\log c_{ext,50}$) decrease with decreasing corrected solubility parameter (δ_T) of the extractant or its polarity index (PI) (Table 6). However, in the case of N,N,N′,N′-tetrahexyl-3,5-pyridinedicarboxamide (A5), $\log K_{ex}$ and $\log c_{ext,50}$ are much lower than for A3 and A4, although δ_T and PI are higher than those observed for dialkyl derivatives. Introduction of the second electron acceptor group into the pyridine ring decreases the electron density on the nitrogen atom and increase its basicity. This leads to a significant decrease in the extraction ability of this compound, despite the increasing polarity of A5.

4. Conclusions

IGC was found to be a useful tool in the characterization of the physicochemical properties of metal extractants and their complexes with copper(II). The examined compounds were characterized by the solubility and polarity parameters. Up to now, the extractants were not characterized in terms of the solubility parameters. The corrected solubility parameter, δ_T, of pyridinecarboxamides varies from 13.982 to 16.515 [10^3(J/m^3)$^{1/3}$] (at 100°C). It means that these compounds exhibit lower values than fluorine-containing oxyethylates (16.38–18.65 units at 90°C [28]), but values that are similar to those observed for α,ω-diaminooligoethers (14.6–16.0 units at 90°C [30]), as well as for broad and narrow distributed oxyethylates of cetyl alcohol (14.61–15.45 units at 90°C [27]). However, one should remember that the solubility parameter decreases with the increasing temperature of the experiment.

The solubility and polarity parameters strongly depend on the structure of amides and their complexes, i.e. on the number of substituents to the amide nitrogen atom and the number of carbon atoms in the alkyl chain(s). The use of the components of the solubility parameter (δ_d, δ_p and δ_h) allows one to discuss the effect of the ability to different interactions upon the total character of the extractant molecule.

The solubility and polarity parameters are higher for amide (A1) compared with the reference ester (E1). It corresponds well to better extraction properties of A1, as measured by a higher degree of extraction [40].

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