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New Ionic Liquids with Organic Anions

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A series of 1-alkylimidazole and 1-alkoxymethylimidazole has been converted to the ionic form. The resulting salicylates and lactates constitute a new category of ionic liquids. They are air and water stable. Some physical properties of these salts were measured, including melting point, boiling point, density and their solubility in some common organic solvents and in water. For 1-alkyl- and 1-alkoxymethylimidazolium lactates values of minimal inhibitory concentration (MIC) and of minimum biocidal concentration (MBC) were determined. Effects of lactate structure on microbiological activity were defined. In aqueous solution the obtained lactates reacted with ozone, unlike their commercially available analogs.

Key words: ionic liquids, imidazolium salicylates and lactates, antimicrobial activity

Ionic liquids (ILs) are compounds composed of cation and anion, which are either liquids at room temperature or the melting points of which are slightly higher than ambient temperature. The cation is generally bulk, organic with low symmetry and the 1,3-dialkylimidazolium based salts are predominant. As far as the anions are concerned, they can be classified into two groups. The first group includes polynuclear anions, *e.g.*, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Cu_2Cl_3^-$, $Fe_2Cl_7^-$, $Sb_2F_{11}^-$, *etc*. In general, these ILs are particularly air and water sensitive. The second group corresponds to mononuclear anions, which yield neutral stoichiometric salts, *e.g.*, BF_4^-, PF_6^-, SbF_6^-, $CF_3CO_2^-$, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $CH_3SO_3^-$, $TFSI^-$, $TSAC^-$ *etc.* In literature, it has been mentioned that many cation-anion associations are able to yield ILs. They have already been described in a number of reviews [1–13]. The most frequently studied ILs contain an imidazolium cation, in which two alkyl groups are linked to nitrogen atoms. The liquids are also described in literature which, instead of the alkyl group, contain CH_2OR [14], CH_2CH_2SR [15], $(CH_2)_3NHCONHR$ [15], $(CH_2)_XOH$ [16–18], $(CH_2)_XOMe$ [16–18], or $(CH_2)_XOCH_2CH_2OMe$ [17] group and poly(ethyleneglycol) [19]. The anion is most frequently of inorganic type. The first reports are already available, which describe IL with anion of organic character, *e.g.*, α-cyano-4-hydroxycinnamate or anthraquinose-2-sulphonate [20]. BASF has been the first company to establish a commercial process of manufacturing alkoxyphenylphosphines using IL. N-Methylimidazolium chloride or the IL containing imidazolium cation with methyl substituent and a proton has been termed the BASF's smart ionic liquid [21]. The aim

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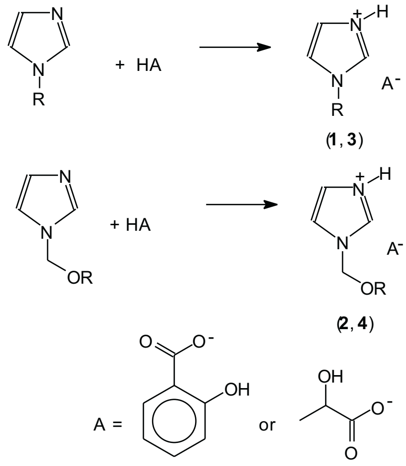
of our studies was a search for novel ILs, in which anion was of organic type and was not exceedingly expanded.

RESULTS AND DISCUSSION

We report herein our results of the investigation of new ILs with special attention paid to an anion, which has an organic character. All the prepared salts included a non-symmetrical imidazolium cation with a monosubstituent. They were analogous to commercially available imidazolium salicylate (symmetrical cation, m.p. 123–4°C, used as an anti-inflammatory agent). 1-Alkylimidazoles and 1-alkoxymethylimidazoles, which are weak bases, were protonated by salicylic or lactic acid to form salicylates **1–2** and lactates **3–4**, listed in Scheme 1. The characteristics of the synthesized salts are presented in Tables 1 and 2. Of the 42 products, 34 are Ils.

Scheme 1



Their one stage synthesis yielded no by-products. In this case, the problem of inorganic salt presence in ILs was completely eliminated. The work-up procedure of synthesis was very simple, the yield was high and the product was easily purified. In pure form, the obtained imidazolium salts could be safely stored and could be handled in air atmosphere. Purity was preliminarily determined *via* a direct biphasic titration technique (EN ISO 2871-2: 1994). The determination could be performed due to the structure of the cation; cationic surfactant was obtained. The liquids, containing 8 or more carbon atoms in the alkyl substituent, could be titrated. The results are listed in Tables 1 and 2. Lactates were titrated in aqueous solution and salicylates in methanol.

We found also that the prepared salts were stable in methanol and water up to the boiling point of the solvents. For determination of compound stability in a solution, a well-established direct biphasic titration technique was employed.

Table 1. 1-Alkyl - and 1-alkoxymethylimidazolium salicylates (**1**,**2**).

No	R	M.p. (°C)	B.p. (℃)	Yield (%)	Surfactant content (%)	Colour	Density[c] (g/mL)
1a	CH_3	90–91	–	83	–	white	–
1b	C_2H_5	liquid[a]	189.5	96	–	straw-col.	1.1911
1c	C_3H_7	89–89.5		91	–	white	–
1d	C_4H_9	liquid[a]	194.0	98	–	colourless	1.1316
1e	C_5H_{11}	46–8	–	95	–	white	–
1f	C_6H_{13}	115–116	–	94	–	white	–
1g	C_7H_{15}	121–122	–	94	–	white	–
1h	C_8H_{17}	liquid[a]	205.5	95	98.9	straw-col.	1.0691
1i	C_9H_{19}	liquid[a]	204.5	97	97.5	straw-col.	1.0653
1j	$C_{10}H_{21}$	liquid[a]	209.0	97	99.2	colourless	1.0466
1k	$C_{11}H_{23}$	37.5–39	–	89	98.5	white	–
1l	$C_{12}H_{25}$	37.5–38.5	–	91	98.1	white	–
2a	C_4H_9	liquid	199.5	95	–	colourless	1.1396
2b	C_5H_{11}	liquid	205.0	93	–	colourless	1.1153
2c	C_6H_{13}	liquid	212.0	93	–	colourless	1.0956
2d	C_7H_{15}	liquid	221.5	96	–	colourless	1.0919
2e	C_8H_{17}	liquid	240.0	95	99.2	colourless	1.0682
2f	C_9H_{19}	liquid	205.0	90	98.3	colourless	1.0578
2g	$C_{10}H_{21}$	liquid	204.0	92	98.7	colourless	1.0522
2h	$C_{11}H_{23}$	liquid	209.0	93	99.5	s. yell[b]	1.0308
2i	$C_{12}H_{25}$	34–35	–	98	98.2	white	–

[a]after cooling form glass, [b]strongly yellow, [c]density at rt.

Table 2. 1-Alkyl - and 1-alkoxymethylimidazolium lactates (**3**,**4**).

No	R	M.p. (°C)	B.p. (℃)	Yield (%)	Surfactant content (%)	Colour	Density[b] (g/mL)
3a	CH_3	liquid	196.5	92	–	w. yellow[a]	1.1231
3b	C_2H_5	liquid	207.5	95	–	straw-col.	1.1081
3c	C_3H_7	liquid	211.0	98	–	colourless	1.0825
3d	C_4H_9	liquid	244.5	96	–	straw-col.	1.0595
3e	C_5H_{11}	liquid	228.5	93	–	yellow	1.0413

Table 2 (continuation)

3f	C_6H_{13}	liquid	226.0	95	–	straw-col.	1.0374
3g	C_7H_{15}	liquid	224.5	97	–	straw-col.	1.0273
3h	C_8H_{17}	liquid	223.0	95	98.6	straw-col.	1.0026
3i	C_9H_{19}	liquid	209.0	91	97.7	straw-col.	0.9908
3j	$C_{10}H_{21}$	liquid	206.5	99	99.8	straw-col.	0.9793
3k	$C_{11}H_{23}$	liquid	197.5	93	99.4	colourless	0.9685
3l	$C_{12}H_{25}$	liquid	194.0	94	98.6	colourless	0.9591
4a	C_4H_9	liquid	188.0	93	–	colourless	1.0640
4b	C_5H_{11}	liquid	197.0	99	–	straw-col.	1.0490
4c	C_6H_{13}	liquid	211.0	94	–	colourless	1.0252
4d	C_7H_{15}	liquid	224.5	94	–	colourless	1.0207
4e	C_8H_{17}	liquid	228.0	92	98.5	colourless	1.0105
4f	C_9H_{19}	liquid	238.0	95	99.5	straw-col.	0.9906
4g	$C_{10}H_{21}$	liquid	207.5	90	98.5	colourless	0.9861
4h	$C_{11}H_{23}$	liquid	222.0	97	97.8	straw-col.	0.9854
4i	$C_{12}H_{25}$	liquid	245.5	94	98.8	yellow	0.9804

[a]weakly yellow, [b]density at rt.

All salts manifested a high solubility in common alcohols, DMSO, DMF, ethyl acetate, acetone and chloroform. As could be visually observed, salicylates **1–2** as well as lactates **3–4** were completely immiscible with hexane. All prepared lactates were miscible with water but lactates **3a–3f** and **4a–4e** were completely miscible with the solvent while the other lactates, **3g–3l** and **4f–4i**, were only partially miscible. Additionally, all 1-alkoxymethylimidazolium salicylates **2a–2i** displayed a complete immiscibility in water. 1-Alkylimidazolium salicylates could be noted to be miscible with this solvent, but only when their alkyl chain comprised between 1–6 carbon atoms. The other 1-alkylimidazolium salicylates **1g–1l** displayed a complete immiscibility in water. In general, all prepared salicylates **1–2** as well as 1-alkoxymethylimidazolium lactates **4a–4i** were miscible with toluene, 1-alkylimidazolium lactates were also soluble in toluene, but only when their alkyl chain comprised 7–12 carbon atoms. The other 1-alkylimidazolium lactates **3a–3f** were immiscible with the solvent.

In comparison to 1-alkyl-3-methylimidazolium tetrafluoroborates [12,14], the prepared imidazolium salts may be classified as "soft", thermally stable ILs. Their respective boiling points, ranging between 245° and 188°C, are presented in Tables 1 and 2. The salts did not change their colour until the above temperature was reached. Such a low boiling temperature encouraged us to attempt to distil the liquid obtained. When the boiling temperature was reached, carbonization of the compound followed, confirming the generally known fact that ILs cannot be distilled.

Densities of the obtained compounds ranged from 1.1396 to 1.0308 g/mL for salicylates **1–2** and from 1.1231 to 0.9591 g/mL for lactates **3–4**. The density of prepared ILs decreases as the bulkiness of the imidazolium cation increases and it is possible to prepare ILs lighter than water (**3i–j** and **4f–i**). Physical properties of salicylates and lactates with decyl group are presented in Table 3. Viscosities of the obtained imidazolium ILs were substantially higher than those of the majority of ILs with TFSI [bis(trifluoromethanesulfonyl)imide] anion and TSAC [22] [2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamid] anion and substantially lower than those of ILs with PF_6 [23] anion. The studied liquids proved to represent Newton liquids in the range of shearing stress: for **1j** 40.5–1312 [s^{-1}], for **2g** 72.9–1312 [s^{-1}], for **3j** 27.0–1312 [s^{-1}] and for **4g** 40.5–1312 [s^{-1}].

Table 3. Physical properties of salts with decyl substituent at 20°C.

Salt	ρ (g/mL)	η (mPa·s)	K (mS/cm)
1j	1.0466	164	0.0920
2g	1.0522	89	0.0538
3j	0.9793	218	0.1383
4g	0.9861	161	0.1045

ρ – density, η – viscosity, K – electrical conductivity.

We decided also to examine the effects of the synthesized ILs on microorganisms. We expected that the representatives of cationic surfactants would exert effects on both bacteria and fungi. The studies were performed on lactates, since they are sufficiently soluble in water. The two estimated parameters included minimal inhibitory concentration (MIC, in mg/L) and minimum biocidal concentration (MBC, in mg/L). The relationship between activity measured against 12 microbes, expressed by arithmetic means, and the length (number of carbon atoms) of the alkyl substituent is presented in Figs. 1 and 2. The results demonstrated that the obtained liquids were active against bacteria and fungi. The length of alkyl substituent exerted the highest effect on the activity; the preferred numbers of carbon atoms in the substituent were 9, 10, 11 and 12. The performed microbiological studies are of significance, when liquids are selected to serve as solvents for reactions involving enzymes or microbes. If microbes are to be applied, we should select a liquid with a short alkyl or alkoxymethyl substituent. The lactates **3a–3g** carrying methyl, ethyl, propyl, butyl, pentyl, hexyl or heptyl substituent as well as lactates **4a** with butoxymethyl substituent should be regarded inactive toward microorganisms. Four lactates, **3h**, **3k**, **4e** and **4h**, were subjected to ozone oxidation in water medium, at room temperature. Conditions of ozone treatment resembled those used in cleaning plants and water conditioning. The synthesized lactates proved to be decomposable under effect of ozone. After 40 min treatment their decay reached 84–91% (Table 4). The degree of destruction was calculated from the relationship

$$D = (1 - X/X_0)\ 100\ [\%]$$

where X are the concentrations in water after 10, 20, 30 and 40 min and X_0 is an original concentration.

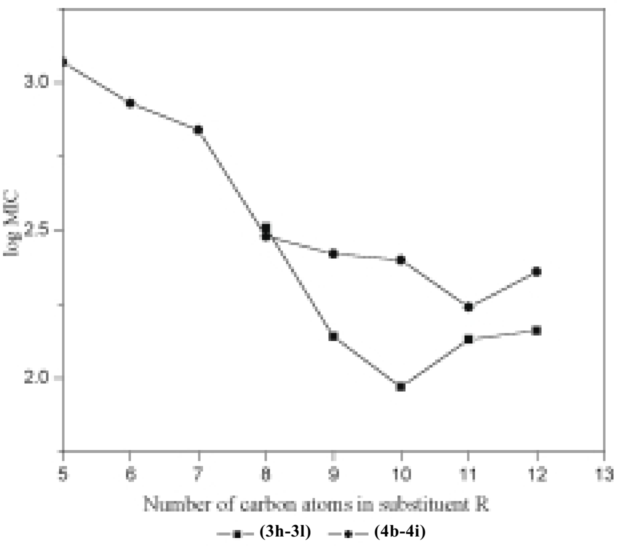


Figure 1. Relationship between alkyl chain length and antimicrobial activity (log MIC in mg/L).

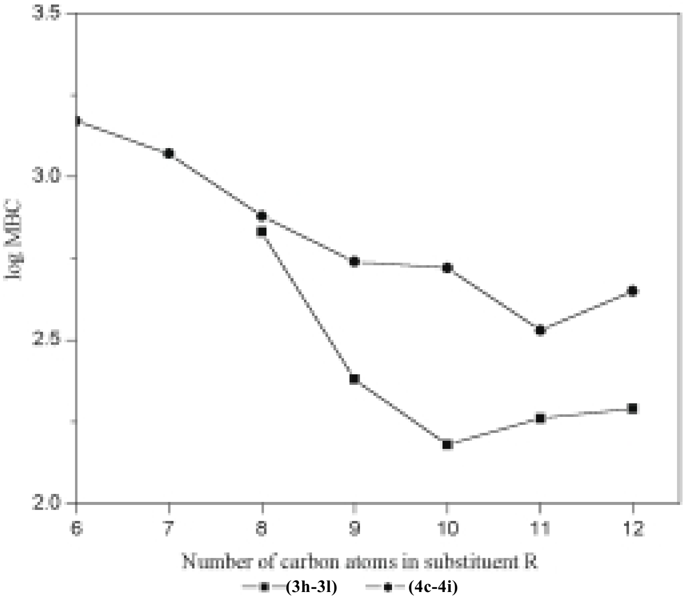


Figure 2. Relationship between alkyl chain length and antimicrobial activity (log MBC in mg/L).

Table 4. Degree of destruction D [%] of lactates **3h**, **3k**, **4e**, **4h**.

Time [min]	**3h**	**3k**	**4e**	**4h**
10	34	34	42	58
20	45	67	53	73
30	66	80	73	81
40	85	89	87	93

The highest rate of decomposition was noted within the first 10 min, as evident in Fig. 3. Thus, the first decomposable ILs were obtained. The other commercially available ILs, such as: 1-ethyl-3-methylimidazolium tetrafluoroborate or bis(pentafluoroethylsulfonyl)imide, 1-butyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate and 1-butyl-4-methylpyridinium tetrafluoroborate could not be decomposed using ozone.

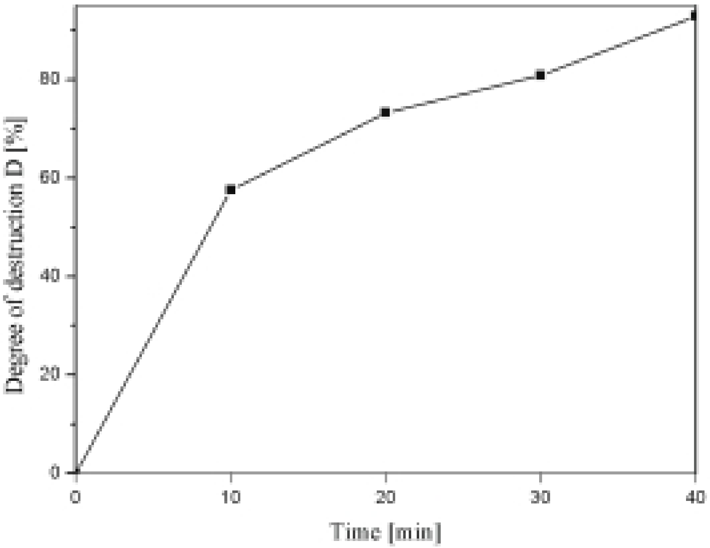


Figure 3. Decay of 1-undecyloxymethylimidazolium lactate in the presence of ozone as a function of time.

CONCLUSIONS

New ionic liquids, containing an anion of organic type, were obtained with a high efficiency in a one-stage synthesis. Physicochemical parameters of 1-alkyl- and 1-alkoxymethylimidazolium salicylates and lactates reflected the number of carbon atoms in the substituent as well as the type of anion. Selection of ionic liquids for practical applications frequently reflects their solubility in water and organic solvents. Liquids presented in this paper provide a significant scope of selection. Moreover, the group of presented compounds includes salts, which are neutral to microorganisms and salts which destroy microorganisms. The division into active and inactive compounds reflects the number of carbon atoms in the substituent. For the first time ILs were obtained, which could be utilized using ozone treatment in aqueous medium. In cases of such ILs their application poses no risk of environmental pollution with the used ILs.

The obtained liquid lactates and salicylates provide new potential media for enzymatic reactions and new agents for embalming and tissue preservation. ILs potential in embalming and tissue preservation has already been recognized [24].

EXPERIMENTAL

Melting points were measured using an electrothermal digital melting-point apparatus, model JA 9100. Boiling points were determined using Büchi automatic apparatus, model B-545. A Mettler Toledo DA 110M scale was used for the mass/density measurements (temp. 20±2°C, sample volume = 2 mL). The viscosity of each of the salts was measured using rotation rheometer, Rheotest 2. Molecular weights of studied compounds were confirmed by LSI MS (Liquid Secondary Ion Mass Spectrometry). Mass spectra were recorded in both positive and negative ion mode. The LSI mass spectra ions were obtained using AMD 604 two sector mass spectrometer of the reverse B/E geometry, made by AMD Intecra (Germany). A CsI gun supplied the primary ion beam (12 keV, Cs^+). The secondary ion beam was accelerated to 8 kV. The compounds were dissolved in NBA (3-nitrobenzyl alcohol), the matrice was obtained from Aldrich. ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO solutions with a Varian model XL 300 spectrometer at 300 MHz for ^{1}H with TMS as the standard and at 75 MHz for ^{13}C. L,D-lactic acid was obtained from Akwawit, 64-100 Leszno, Poland.

Preparation of 1-alkyl- and 1-alkoxymethylimidazolium salts: Salicylates **1–2** and lactates **3–4** were prepared in the same way: 0.1 mol of salicylic or lactic acid was dissolved in 50 mL MeOH and then 0.1 mol of 1-alkyl- or 1-alkoxymethylimidazoles in 50 mL of MeOH was added. The solution was stirred at rt for 3 h and then concentrated in a rotary evaporator. The product was purified by precipitation from acetone, toluene or ethyl acetate. Hexane was used as a precipitating agent. Satisfactory elemental analyses were obtained, C±0.29; H± 0.26 and N± 0.22.

*1-Decylimidazolium salicylate (**1j**):* ^{1}H NMR (DMSO-d_6) 0.87 (t, J= 6.7 Hz, CH_3), 1.23 (m, 14H, CH2), 1.79 (q, J= 7.1 Hz, CH_2), 4.11 (t, J= 7.1 Hz, N-CH_2), 6.82 (m, 2H, anion), 7.33 (m, 1H, anion), 7.38 and 7.54 (2s, 2H, imid.), 7.81 (d, J= 9.6 Hz, 1H, anion), 8.54 (s, 1H, imid.), 10.06 (s, wide, OH and N^+-H). ^{13}C NMR (DMSO-d_6) 13.9 (CH_3), 22.1, 25.7, 28.4, 28.6, 28.9, 29.9, 31.3 (CH_2), 47.3 (N-CH_2), 116.4, 117.0, 117.6, 130.2, 133.3, 161.9 (anion), 120.7, 123.7 and 136.1 (imid.), 172.7 (CO). LSI MS m/z: 209.4 for cation and 137.0 for anion (requires 209.4 for cation and 137.1 for anion).

*1-Decyloxymethylimidazolium salicylate (**2g**):* ^{1}H NMR (DMSO-d_6) 0.87 (t, J= 6.7 Hz, CH_3), 1.21 (m, 14H, CH_2), 1.48 (m, CH_2), 3.43 (t, J= 6.5 Hz, O-CH_2), 5.46 (s, N-CH_2-O), 6.90 (m, 2H, anion), 7.31 (s, 1H, imid.), 7.42 (m, 1H, anion), 7.52 (s, 1H, imid.), 7.85 (d, J= 9.3 Hz, 1H, anion), 8.45 (s, 1H, imid.), 13, 38 (s, wide, OH, N^+-H). ^{13}C NMR (DMSO-d_6) 13.9 (CH_3), 22.1, 25.4, 28.71, 28.72, 28.8, 28.9, 29.0, 31.3 (CH_2), 68.4 (O-CH_2), 76.4 (N-CH_2-O), 115.3, 116.7, 118.3, 130.3, 134.3, 161.6 (anion), 120.3 125.5 and 137.2 (imid.), 172.6 (CO). LSI MS m/z: 239.5 for cation and 136.9 for anion (requires 239.4 for cation and 137.1 for anion).

*1-Decylimidazolium lactate (**3j**):* ^{1}H NMR (DMSO-d_6) 0.88 (t, J = 6.7 Hz, CH_3, cation), 1.32 (m, 17H, 7 CH_2 cation and CH_3 anion), 1.74 (q, J = 7.2 Hz, CH_2), 3.98 (t, J = 7.1 Hz, N-CH_2), 4.08 (q, J = 6.9 Hz, CH anion), 6.94 and 7.20 (2s, 2H, imid.), 7.62 (s, wide, OH and N^+-H), 7.73 (s, 1H, imid.). ^{13}C NMR (DMSO-d_6) 13.9 (CH_3, cation), 20.5 (CH_3, anion), 22.1, 25.9, 28.5, 28.7, 28.95, 28.96, 30.6, 31.3 (CH_2), 46.1 (N-CH_2), 65.9 (CH, anion), 119.4, 127.7 and 137.1 (imid.), 176.7 (CO). LSI MS m/z: 209.4 for cation and 88.7 for anion (requires 209.4 for cation and 89.1 for anion).

*1-Decyloxymethylimidazolium lactate (**4g**):* ^{1}H NMR (DMSO-d_6) 0.88 (t, J = 6.7 Hz, CH_3, cation), 1.33 (m, 17H, 7 CH_2 cation and CH_3, anion), 1.49 (m, CH_2), 3.37 (t, J= 6.5 Hz, O-CH_2), 4.10 (q, J= 6.9 Hz, CH, anion), 5.39 (s, N-CH_2-O), 6.96, 7.27 and 7.83 (3s, 3H, imid.), 8.27 (s, wide, OH and N^+-H). ^{13}C NMR (DMSO-d_6) 13.9 (CH_3, cation), 20.5 (CH_3, anion), 22.2, 25.6, 28.8, 28.9, 29.07, 29.1, 31.4 (CH_2), 65.8 (CH, anion), 67.9 (O-CH_2), 75.5 (N-CH_2-O), 119.4 128.3 and 137.6 (imid.), 176.3 (CO). LSI MS m/z: 239.3 for cation and 88.7 for anion (requires 239.4 for cation and 89.1 for anion).

Antimicrobial characteristic: The following microorganisms were used: *Micrococcus luteus* ATCC 9341, *Staphylococcus epidermidis* ATCC 12228, *Staphylococcus aureus* ATCC 6538, *Staphylococcus aureus* (MRSA) ATCC 43300, *Enterococcus hirae* ATCC, *Escherichia coli* ATCC 25922, *Proteus vulgaris* NCTC 4635, *Klebsiella pneumoniae* ATCC 4352, *Pseudomonas aeruginosa* ATCC 27853, *Serratia marcescens* ATCC 8100, *Candida albicans* ATCC 10231 and *Rhodotorula rubra* PhB. The *R. rubra* was obtained from the Department of Pharmaceutical Bacteriology, University of Medical Sciences, Poznań. Antimicrobial activity was determined by the tube dilution method. Twofold dilutions of the lactates were prepared in the Mueller-Hinton broth medium (bacteria) or in the Sabouraud broth medium (fungi). A suspension of the standard microorganisms, prepared from 24 h cultures of bacteria in the Mueller-Hinton broth medium and from 48 h cultures in the Sabouraud agar medium for fungi at a concentration of 10^6 cfu/mL, was added to each dilution in a 1:1 ratio. Growth of the microorganisms (or its lack) was determined visually after incubation for 24 h at 37°C (bacteria) or 48 h at 28–30°C (fungi). The lowest concentration at which there was no visible growth (turbidity) was taken as the minimal inhibitory concentration (MIC). Then, from each tube content one loopful was smeared on an agar medium with inactivates (0.3% lecithin, 3% polysorbate 80 and 0.1% cysteine L) and incubated for 48 h at 37°C (bacteria) or for 5 days at 28–30°C (fungi). The lowest concentration of the lactates capable of preventing colony formation was defined as the minimum biocidal concentration (MBC).

Ozonation in aqueous solution: Aqueous ozone solution of approx. 5 mg/L and of pH = 4.5 was prepared by bubbling ozone-oxygen gas through a 2 g/L aqueous solution of prepared lactates. The ozone reactor was kept at rt. The concentration of lactates in the reaction mixture was determined by a direct biphasic reverse titration.

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