



Development of Novel Herbicidal Ionic Liquids

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Authors' contributions

This work was carried out in collaboration between both authors. Author SV designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author VK managed the analyses of the study and the literatures. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: The present study involved the synthesis of small carboxylic acid based ionic liquids as potential herbicides.

Study Design: Synthesized ionic liquids.

Place and Duration of Study: Organic Synthesis Laboratory, Department of Chemistry, CBSH, G. B. Pant University of Agriculture and Technology, Pantnagar, U.S. Nagar-263145, Uttarakhand, India between September 2016 and May 2017.

Methodology: In the present studies, we synthesized ionic liquids comprising tetrabutylammonium as cation and proline, tartrate, alanate, serinate, crotonate, citrate, malonate, nicotinate, glycinate and oxalate as organic anions. The synthesized ionic liquids were screened for seed germination inhibition activity at 0.005M, 0.01M and 0.02M concentration in distilled water against radish (*Raphanus sativus*) seeds.

Results: Seed germination inhibition activity increased with increase in concentration. The compounds having an anion of tartrate, crotonate, citrate, malonate and oxalate were found at par with standard butachlor at 0.02M concentration.

Conclusion: From the above studies it clearly indicate that ionic liquids containing these organic acid anions as a part of ionic liquid may be developed as potential herbicides.

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Keywords: Tetrabutylammonium; organic anions; seed germination inhibition activity; radish (*Raphanus sativus*); butachlor.

1. INTRODUCTION

Ionic liquids have attracted attention of researchers working in various fields like analytical chemistry [1], chemical industry [2], electrochemistry [3], material chemistry [4], synthetic chemistry [5,6], gas capturing [7], agriculture chemistry [8,9], chemistry of catalysts [10], bio-catalysis [11], pharmaceutical chemistry [12], sugar industry [13] and Food industry [14].

Earlier the work on ionic liquids was confined to the development of compounds with unique tunable physical properties. These were the first generation ionic liquids. The second generation comprised the ionic liquids with targeted chemical properties in combination with selected physical properties. The third generation ionic liquids are those with targeted biological properties in combination with desired physical and chemical properties [15-22]. Presently third generation is being undertaken for the development of herbicidal ionic liquids. Recently standard herbicides have been modified to ionic liquids to increase their efficacy for example phenoxy acetic acid, dicamba, glyphosate [23-34], fomesafen [35], metasulfuron-methyl or sulfonyleurea [36], betaine, carnitine analogues [37,38] and 4-(4-chloro-2-methyl phenoxy) butanoate [39]. Some researchers have undertaken new organic molecules to synthesize their ionic liquids and to develop them as potential herbicides for example 2-chloroethyltrimethylammonium chloride (CCC) [40] and long chain alkyl ammonium ion and their esterquats as plant growth regulators [41-43].

So, there is wide scope to synthesize ionic liquids based on small organic acid molecules for the development of novel herbicides. Keeping this important aspect in view we have synthesized ionic liquids comprising tetrabutylammonium as cation and different organic acids as anions to explore their herbicidal potential.

2. MATERIALS AND METHODS

All the reagents and chemicals were purchased from Hi-Media Biosciences and were used without further purification. Butachlor was obtained from Monsanto Agriculture Products Co., USA. The radish seeds (*Raphanus sativus*)

were obtained from global seeds, Inc., Delhi, India. IR spectra were recorded on Bruker FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz JEOL JNM ECS400 instrument using CDCl_3 .

2.1 Procedure for the Synthesis of Tetrabutylammonium Hydroxide

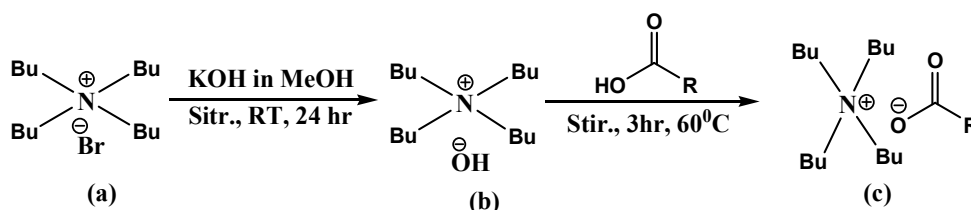
Tetrabutylammonium hydroxide [(TBA)(OH)] aqueous solution was prepared by modified literature method [44] by taking the equimolar mixture (40 mmol) of tetrabutylammonium bromide and KOH in methanol (100 ml) and the mixture was stirred on magnetic stirrer for 24 h at room temperature. Potassium bromide was precipitated. The reaction mixture was filtered to remove the KBr precipitate. The filtrate was evaporated under reduced pressure to remove the water, affording the viscous liquid of tetrabutylammonium hydroxide. The viscous liquid was extracted with ether and dried over anhydrous sodium sulfate to remove water. By distilling off ether, tetrabutylammonium hydroxide was obtained as a pale yellow liquid.

2.2 Procedure for the Synthesis of Tetrabutylammonium Organic Acids

Organic acid ionic liquids were synthesized via acid-base neutralization method [45]. The equimolar solution (40 mmol) of synthesized tetrabutylammonium hydroxide was added dropwise in aqueous solution of organic acid (40 mmol) derivatives taken in the round bottom flask with continuous stirring. The solution was further heated at 60°C for 3 h. Then reaction mixture was evaporated at reduced pressure to remove the extra water. Acetonitrile (40 ml) was added to the reaction mixture and magnetically stirred for 0.5 h. Unreacted acid precipitated. It was removed by filtration (Scheme 1). The obtained filtrate was dried over sodium sulfate and evaporated under reduced pressure to remove acetonitrile [46].

2.3 Bioassay

Seed germination inhibition of synthesized compounds was studied by using towel paper test. A test solution of concentration 0.02M, 0.01M and 0.005M were prepared by serial dilution of a stock solution of 5M in distilled



Scheme 1. Synthesis of Carboxylic acid ionic liquids

water. The test solution of standard butachlor was also prepared in distilled water. Prior to sowing, the seed of radish (*R. sativus*) were sterilized in 1% of sodium hypochlorite solution for 0.5 h. After that twenty seeds of radish were treated with each test compound overnight. Seeds treated with different compounds were taken separately in the wetted germinating sheets in triplicate manner. After rolling the germinating sheets with treated seeds, these were allowed to germinate at 25°C in the incubator. Distilled water was taken as control. The seed germination process was observed after 120 h of incubation and the number of seed germinated in each germinating sheets were counted. The length of roots and shoots were also measured. The seed germination inhibition, root inhibition and shoot inhibition values were calculated and subjected to analysis of variance (ANOVA) by STPR3 software and critical differences (CD) at $P \leq 0.05$ were calculated. The germination index values were calculated [47].

3. RESULTS AND DISCUSSION

Tetrabutylammonium hydroxide, due to its strongly basic nature, reacted readily with carboxylic acids to produced different functionalized ionic liquids [46]. Tetrabutylammonium prolinatate, tetrabutylammonium tartrate, tetrabutylammonium crotonate, tetrabutylammonium citrate, tetrabutylammonium serinate and tetrabutylammonium malonate were obtained as colorless to pale yellow viscous liquids at room temperature. Tetrabutylammonium alanate, tetrabutylammonium glycinate and tetrabutylammonium oxalate were obtained as white colored semisolid at room temperature. Tetrabutylammonium nicotinate was obtained as white solid.

3.1 Spectral Analysis

Tetrabutylammonium prolinatate: IR (KBr) cm^{-1} : 3363, 2961, 1604, 1455, 1394, 1332, 1168, 1038, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 1.00 (t, 3H), 1.46 (m, 2H), 1.65 (m, 2H), 1.84 (m, 2H),

2.20 (s, NH), 3.34 (m, 2H), 3.36 (t, 2H), 3.97 (s, 1H), ^{13}C NMR (CDCl_3 , 400MHz, δ ppm): 13.6, 19.6, 24.0, 29.0, 30.4, 45.8, 58.8, 60.9, 174.3

Tetrabutylammonium tartarate: IR (KBr) cm^{-1} : 3373, 2929, 1718, 1631, 1232, 1127, 1081, 984, 887, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 0.94 (t, 3H), 1.38 (m, 2H), 1.60 (m, 2H), 2.44 (s, OH), 3.30 (t, 2H), 4.63 (s, 1H), ^{13}C NMR (CDCl_3 , 400MHz, δ ppm): 13.6, 19.6, 24.0, 58.8, 71.9, 76.8, 174.4, 174.4

Tetrabutylammonium crotonate: IR (KBr) cm^{-1} : 3409, 2963, 2875, 1704, 1654, 1447, 1380, 1284, 1198, 970, 883, 736, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 0.88 (t, 3H), 1.33 (m, 2H), 1.73 (m, 3H), 1.75 (m, 2H), 3.17 (t, 2H), 5.82 (d, 1H), 6.78 (m, 1H), ^{13}C NMR (CDCl_3 , 400MHz, δ ppm): 13.4, 17.6, 19.4, 23.7, 58.4, 124.6, 142.9, 169.9

Tetrabutylammonium citrate: IR (KBr) cm^{-1} : 3413, 2968, 1709, 1393, 1193, 880, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 0.99 (t, 3H), 1.43 (m, 2H), 1.66 (m, 2H), 2.15 (1H, OH), 2.83 (2H), 2.94 (2H), 3.36 (t, 2H), ^{13}C NMR (CDCl_3 , 400MHz, δ ppm): 13.5, 19.5, 23.9, 43.0, 58.8, 73.1, 173.0, 176.2

Tetrabutylammonium malonate: IR (KBr) cm^{-1} : 3400, 2966, 1708, 1380, 1313, 1210, 955, 638, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 0.98 (t, 3H), 1.41 (m, 2H), 1.63 (m, 2H), 3.28 (t, 2H), 3.43 (s, 2H), 3.53 (s, OH), ^{13}C NMR (CDCl_3 , 400MHz, δ ppm): 13.6, 19.6, 21.3, 23.9, 40.2, 58.8, 170.2, 171.3

Tetrabutylammonium nicotinate: IR (KBr) cm^{-1} : 3400, 2963, 2875, 2354, 1650, 1480, 1177, 950, 741, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 0.97 (t, 3H), 1.41 (m, 2H), 1.44 (m, 2H), 3.33 (t, 2H), 7.29 (m, 1H), 8.62 (d, 1H), 8.63 (d, 1H), 9.24 (1H), ^{13}C NMR (CDCl_3 , 400MHz, δ ppm): 13.5, 19.5, 23.9, 58.7, 122.9, 130.8, 137.3, 150.6, 150.9, 168.3

Tetrabutylammonium oxalate: IR (KBr) cm^{-1} : 3417, 2963, 2875, 1713, 1464, 1343, 680, 716, ^1H NMR (CDCl_3 , 400MHz, δ ppm): 1.00 (t, 3H),

1.44(m, 2H), 1.67(m,2H), 3.35(t,2H), ¹³CNMR (CDCl₃, 400MHz, δppm): 13.6, 19.6, 23.9, 58.8, 160.9

Tetrabutylammonium hydroxide: IR (KBr) cm⁻¹: 3361, 2971, 1637, 1467, 1381, ¹H NMR (CDCl₃, 400MHz, δ ppm): 0.91 (t,3H), 1.35(m, 2H), 1.58(m,2H), 3.27(t,2H).

Mean percent germination inhibition values were calculated and subjected to analysis of variance (ANOVA). The results are present in Table 1. The perusal of Table 1 reveals that there is a significant increase in activity for maximum number of compounds with an increase in concentration from 0.005M to 0.01M. While with an increase in concentration from 0.005M to 0.02M there is significant increase in activity for all the compounds. At concentration 0.005M, standard butachlor was found to exhibit 78.33% activity. All the compounds were found to have significantly lower activity than standard butachlor. At concentration 0.01M standard butachlor exhibited 80% activity and all the compounds at this concentration also exhibited significantly lower activity than standard butachlor. At concentration 0.02M, standard butachlor exhibited 100% inhibition activity. The compounds tetrabutylammonium crotonate, tetrabutylammonium malonate and tetrabutylammonium oxalate exhibited activity at par with the standard butachlor.

Mean percent root inhibition values were calculated and subjected to analysis of variance (ANOVA) (Table 2). Increasing the concentration from 0.005M to 0.02M maximum number of

compounds exhibited significantly increased the activity. While increasing the concentration from 0.005M to 0.01M there is a significant increase in root inhibition activity. At concentration 0.005M and 0.01M all the tested compounds exhibited significantly lower root inhibition activity than standard butachlor (86.79% at 0.005M and 93.71% at 0.01M concentration) except tetrabutylammonium oxalate (80.56% at 0.005M and 90.94% at 0.01M concentration). At concentration 0.02M, tetrabutylammonium tartrate, tetrabutylammonium crotonate, tetrabutylammonium malonate and tetrabutylammonium oxalate exhibited activity at par with the standard butachlor (100%).

Mean percent shoot inhibition values were calculated and subjected to analysis of variance (ANOVA) (Table 3). With the increase in concentration from 0.005M and 0.01M, most of the compounds exhibited significantly increased shoot inhibition activity. With the increase in the activity from 0.01M to 0.02M for all the compounds except tetrabutylammonium proline and tetrabutylammonium nicotinate, there was significant increase in activity. All the tested compounds at the concentration 0.005M and 0.01M exhibited significantly lower shoot inhibition activity than standard butachlor (87.23% at 0.005M and 91.14% at 0.01M concentration) except tetrabutylammonium crotonate at 0.01M (82.72%). At concentration 0.02M tetrabutylammonium tartrate, tetrabutylammonium crotonate, tetrabutylammonium malonate and tetrabutylammonium oxalate exhibited the activity at par with standard butachlor (100%).

Table 1. Mean percent germination inhibition values of synthesized compounds

Compound code	Mean percent seed germination inhibition			CD at 5% ±SEM
	0.005M	0.01M	0.02M	
Tetrabutylammonium proline	6.66	11.66	31.66	14.10±4.08
Tetrabutylammonium tartarate	8.33	11.66	81.66	14.10±4.08
Tetrabutylammonium alanate	5.00	11.66	76.66	4.70 ±1.36
Tetrabutylammonium serinate	13.33	31.66	60.00	14.87 ±4.30
Tetrabutylammonium crotonate	8.33	46.66	100.00	11.02 ±3.19
Tetrabutylammonium citrate	11.66	23.33	75.00	7.43 ±2.15
Tetrabutylammonium malonate	16.66	23.33	100.00	4.70 ±1.36
Tetrabutylammonium nicotinate	10.00	21.66	58.33	14.87± 4.30
Tetrabutylammonium glycinate	6.66	26.66	51.66	5.75 ±1.66
Tetrabutylammonium oxalate	11.66	41.66	100.00	4.70 ±1.36
Tetrabutylammonium hydroxide	20.00	25.00	33.33	13.30 ±3.84
Standard (Butachlor)	78.33	80.00	100.00	6.65 ±1.92
CD at 5% ±SEM	8.76 ±3.00	9.83± 3.36	8.06 ±2.76	

CD=Critical difference, SEM= Standard error mean

Table 2. Mean percent root inhibition values of synthesized compounds

Compound code	Mean percent root inhibition			CD at 5% \pm SEM
	0.005M	0.01M	0.02M	
Tetrabutylammonium prolinat	45.41	45.81	54.11	15.32 \pm 4.43
Tetrabutylammonium tartarate	32.43	33.99	99.35	3.10 \pm 0.89
Tetrabutylammonium alanate	25.83	44.95	78.94	7.03 \pm 2.03
Tetrabutylammonium serinate	40.24	47.20	90.13	10.94 \pm 3.16
Tetrabutylammonium crotonate	43.39	78.16	100.00	8.78 \pm 2.54
Tetrabutylammonium citrate	39.04	51.43	84.97	11.25 \pm 3.25
Tetrabutylammonium malonate	39.84	65.19	100.00	2.09 \pm 0.60
Tetrabutylammonium nicotinate	41.63	51.67	66.03	10.48 \pm 3.03
Tetrabutylammonium glycinate	50.02	67.52	67.43	14.16 \pm 4.09
Tetrabutylammonium oxalate	80.56	90.94	100.00	2.33 \pm 0.67
Tetrabutylammonium hydroxide	30.44	34.31	67.26	15.03 \pm 4.35
Std. (Butachlor)	86.79	93.71	100.00	3.00 \pm 0.86
CD at 5% \pm SEM	10.38 \pm 3.55	7.78 \pm 2.66	6.36 \pm 2.17	

Table 3. Mean percent shoot inhibition values of synthesized compounds

Compound code	Mean percent shoot inhibition			CD at 5% \pm SEM
	0.005M	0.01M	0.02M	
Tetrabutylammonium prolinat	48.04	52.80	59.82	13.59 \pm 3.93
Tetrabutylammonium tartarate	32.84	57.26	94.61	17.54 \pm 5.07
Tetrabutylammonium alanate	40.20	55.74	85.10	10.36 \pm 2.99
Tetrabutylammonium serinate	33.68	53.47	86.38	7.53 \pm 2.18
Tetrabutylammonium crotonate	60.91	82.72	100.00	8.83 \pm 2.55
Tetrabutylammonium citrate	52.21	58.86	83.50	11.34 \pm 3.28
Tetrabutylammonium malonate	54.92	67.15	100.00	11.62 \pm 3.36
Tetrabutylammonium nicotinate	45.31	60.35	70.59	14.37 \pm 4.15
Tetrabutylammonium glycinate	50.27	52.23	74.67	10.64 \pm 3.08
Tetrabutylammonium oxalate	63.24	81.87	100.00	8.64 \pm 2.50
Tetrabutylammonium hydroxide	44.60	52.62	58.71	14.55 \pm 4.21
Std. (Butachlor)	87.23	91.14	100.00	4.60 \pm 1.33
CD at 5% \pm SEM	13.15 \pm 4.50	8.81 \pm 3.02	6.28 \pm 2.15	

Table 4. Seed germination index of synthesized compounds

Compound code	Seed germination index		
	0.005M	0.01M	0.02M
Tetrabutylammonium prolinat	26.39	22.49	13.8
Tetrabutylammonium tartarate	41.48	24.82	0.05
Tetrabutylammonium alanate	42.02	21.42	0.724
Tetrabutylammonium serinate	28.85	16.7	0.533
Tetrabutylammonium crotonate	20.18	1.98	0
Tetrabutylammonium citrate	25.44	15.11	0.61
Tetrabutylammonium malonate	22.57	8.69	0
Tetrabutylammonium nicotinate	28.64	14.9	4.36
Tetrabutylammonium glycinate	23.09	11.36	3.97
Tetrabutylammonium oxalate	6.28	1.07	0
Tetrabutylammonium hydroxide	30.74	23.27	8.94
Standard (Butachlor)	0.35	0.10	0

Seed germination index values were calculated for all tested compounds (Table 4). It is clear from seed germination index values that the compounds are having lower herbicidal potential at concentrations 0.005M and 0.01M as compared to standard butachlor. But at

concentration 0.02M, seed germination index values of the compounds tetrabutylammonium tartrate, tetrabutylammonium crotonate, tetrabutylammonium citrate, tetrabutylammonium malonate and tetrabutylammonium oxalate are comparable to butachlor. Thus seed germination index values are in close agreement with seed germination, root inhibition and shoot inhibition activity values.

4. CONCLUSION

In conclusion we can say that synthesized ionic liquids comprising tetrabutylammonium as cation and tartarate, crotonate, citrate, malonate and oxalate as different organic acid anions may be developed as potential herbicides.

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COMPETING INTERESTS

Authors have declared that there is no conflict of interest in this manuscript.

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