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BRIEF COMMUNICATIONS

Effect of Substituents in 1,2-Disubstituted Imidazolines on Properties of Concrete Mixtures

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Abstract—Physicochemical properties of concrete mixtures and concretes was studied as influenced by the structure of salts of 1,2-disubstituted imidazolines with C_1–C_4 monocarboxylic saturated acids.

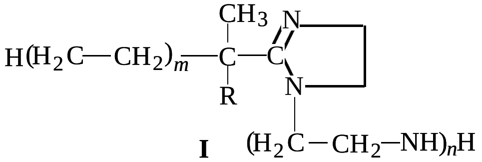
The products of condensation of higher carboxylic acids and polyethylenepolyamines are widely used in production of building materials. The hydrophobic properties of concrete mixtures are improved by modifying agents prepared by condensation of synthetic carboxylic acids with polyethylenepolyamines [1, 2]. The strength properties are enhanced by the products of reaction of 1-polyethylenepolyaminoethyl-2-alkyl-(C_6–C_{25})-2-imidazoline with orthophosphoric, sulfuric, or acetic acid [3–5]. *N,N*-Bis(2-hydroxyethyl)-2-alkyl-2-imidazoline [6] or polyamidoimidazoline resin [7] decrease water adsorption and permeability and increase the resistance of the concrete.

However, the products of cyclocondensation of linear carboxylic acids with polyethylenepolyamines are hydrolytically unstable (in contrast to 1,2-disubstituted imidazolines containing branched substituents in position 2 of the imidazoline ring [8–10]), and thus they are inefficient.

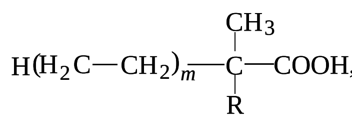
In this study we examined the mobility and water separation of concrete mixtures and strength properties of the concrete monolith as influenced by the nature of substituents in positions 1 and 2 of the imidazoline ring.

EXPERIMENTAL

1,2-Disubstituted imidazolines of the general formula



where R is ethyl, butyl; n = 1–3; m = 0–22, were prepared by heating in a nitrogen atmosphere of α,α'-branched monocarboxylic saturated acids of the general formula



II

where R is ethyl, butyl; n = 1–3; m = 0–22, with diethylenetriamine (DETA), triethylenetetramine (TETA), and polyethylenepolyamine (PEPA) at 280 ± 10°C for 10–12 h at the acid : polyamine molar ratio of 1 : 2 with subsequent vacuum treatment at 180–200°C. The salts of 1,2-disubstituted imidazolines (**I**) with formic, acetic, propionic, and butyric acids were prepared by heating of the equimolar amounts of imidazoline and acid in ethanol at 60–78°C for 1–2 h, followed by subsequent evaporation of solvents and vacuum drying of the salt at 80–90°C on a 350 R rotary evaporator (Poland).

The concrete mixture was prepared from a Portland cement and carbonate stone with coarseness of 5–10 and 10–20 mm (1 : 1.5 weight ratio). The salt was added to the concrete mixture with water. The concrete samples were hardened in the 4 + 3 + 6 + 2 mode (preliminary setting + heating + isothermal heating at 80 ± 3°C + cooling). The properties of the concrete mixtures and concrete monoliths were evaluated by the standard procedures.

In all the cases, addition of the salts of 1,2-disubstituted imidazolines with C_1–C_4 carboxylic acids increases their mobility and decreases the water separation (Table 1); the compression strength also increases.

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Table 1. Properties of concrete mixtures and concrete monoliths as influenced by 1,2-disubstituted imidazolines

Composition of concrete mixtures	Content of components in sample, wt %								
	1	2	3	4	5	6	7	8	9
Portland cement	10.40	14.20	17.50	14.20	10.40	14.20	17.50	14.20	14.20
Filler	82.60	78.80	75.50	78.76	78.78	78.76	78.74	78.76	78.76
Water	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00
Salt of 1-[2-(2-aminoethyl)aminoethyl]-2-alkyl(C_8–C_{18})-2-imidazoline with acids:									
formic	–	–	–	0.04	–	–	–	–	–
acetic	–	–	–	–	0.02	0.04	0.06	–	–
propionic	–	–	–	–	–	–	–	0.04	–
butyric	–	–	–	–	–	–	–	–	0.04
Properties of concrete mixtures									
Mobility from cone draft, cm	3	3	3	14	12	14	16	14	13
Water separation, g l^{-1}	20.0	15.0	7.0	3.0	4.5	2.0	0	2.0	0
Ultimate compression resistance, MPa	18.8	25.4	32.4	28.2	22.4	29.6	34.6	26.8	27.6

Table 2. Properties of concrete mixtures and concrete monoliths as influenced by the structure of 1,2-disubstituted imidazolines

Composition of concrete mixtures	Content of components in sample, wt %						
	1	2	3	4	5	6	7
Portland cement	14.20	14.20	14.20	14.20	14.20	14.20	14.20
Filler	78.76	78.76	78.76	78.76	78.76	78.76	78.76
Water	7.00	7.00	7.00	7.00	7.00	7.00	7.00
Salt of 1-(2-aminoethyl)-2-alkyl(C_4–C_8)-2-imidazoline with acetic acid	0.04	–	–	–	–	–	–
Salt of 1-[2-(2-aminoethyl)aminoethyl]-2-alkyl-(C_4–C_8)-2-imidazoline with acetic acid	–	0.04	–	–	–	–	–
Salt of 1-(polyethylenepolyaminoethyl)-2-alkyl-(C_4–C_8)-2-imidazoline with acetic acid	–	–	0.04	–	–	–	–
Salt of 1-(2-aminoethyl)-2-alkyl(C_8–C_{18})-2-imidazoline with acetic acid	–	–	–	0.04	–	–	–
Salt of 1-[2-(2-aminoethyl)aminoethyl]-2-alkyl-(C_8–C_{18})-2-imidazoline with acetic acid	–	–	–	–	0.04	–	–
Salt of 1-polyethylenepolyaminoethyl-2-alkyl-(C_8–C_{18})-2-imidazoline with acetic acid	–	–	–	–	–	0.04	–
Salt of 1-[2-(2-aminoethyl)aminoethyl]-2-alkyl-(C_{20}–C_{50})-2-imidazoline with acetic acid	–	–	–	–	–	–	0.04
Properties of concrete mixtures							
Mobility from cone draft, cm	8.0	9.0	9.6	12.8	14.0	14.8	14.6
Water separation, g l^{-1}	6.0	5.4	5.0	2.8	2.0	0.0	0.0
Decrease in water demand, %	13.9	14.8	16.0	18.6	20.2	20.0	21.6
Ultimate compression resistance, MPa	26.8	26.4	27.0	28.4	29.6	29.8	28.0
Resistance to type I corrosion (content of Ca^{2+} ions, g l^{-1})	0.20	0.25	0.22	0.18	0.16	0.20	0.18

It should be noted that the length of the C_1–C_4 alkyl substituent of saturated monocarboxylic acids does not affect the properties of the concrete mixtures. This indicates that the performance of the additive is determined by the structure of 1,2-disubstituted imidazoline. Our experimental results show that the increase in the length of the aminoethyl radical in position 1 of the imidazoline ring only slightly changes the mobility of concrete mixtures and water separation and does not noticeably affect the strength properties of the concrete monolith (Table 2).

With increasing length of alkyl substituents in position 2 of the imidazoline ring, the mobility of concrete mixtures sharply increases, whereas their water separation decreases (Table 2). The strength properties of the concrete also increase. Thus, the salts of 1,2-disubstituted imidazolines **I** with C_1–C_4 saturated monocarboxylic acids are efficient cationic surfactants, which, being adsorbed on the surface of Portland cement clinker, exert the plasticizing effect. Steaming of the concrete mixtures causes degradation of the concrete–additive complexes, but the rates of formation of hydroaluminates and hydrosilicates do not decrease, and the strength properties of the concrete are preserved.

It should be noted that addition of salts of 1,2-disubstituted imidazolines increases the resistance of concretes with respect to aggressive solutions that cause leach corrosion (Table 2).

CONCLUSION

(1) Salts of 1,2-disubstituted imidazolines with C_1–C_4 saturated monocarboxylic acids, when added to a concrete mixture, increase its mobility and decrease the water separation, which allows transportation of the concrete mixture at long distances without deterioration of its quality.

(2) Longer alkyl substituents in position 2 of the imidazoline ring strongly enhance the plasticizing effect of the salts of 1,2-disubstituted imidazolines.

REFERENCES

1. USSR Inventor's Certificate no. 0 638 564.
2. USSR Inventor's Certificate no. 0 727 591.
3. USSR Inventor's Certificate no. 0 908 764.
4. USSR Inventor's Certificate no. 0 958 374.
5. USSR Inventor's Certificate no. 01 030 334.
6. USSR Inventor's Certificate no. 0 931 278.
7. USSR Inventor's Certificate no. 0 962 253.
8. Kolomiets, B.S., German, V.K., Suchkov, V.V., and Kudryavtseva, M.I., *Zh. Prikl. Khim.*, 1978, vol. 51, no. 12, pp. 2758–2762.
9. Savignac, A., Kabbage, T., Dupin, P., and Calmon, M., *J. Heterocyclic Chem.*, 1978, vol. 15, no. 5, p. 897.
10. Bondareva, S.O., Lisitskii, V.V., Yakovtseva, N.I., and Murinov, Yu.I., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2004, no. 4, pp. 767–771.