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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Comparative Assessment of the Effect of Dicarboxylic Acid Salts on the Contact Corrosion of Metals in an Aqueous-Glycolic Solution

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Abstract—Corrosion behavior of a number of materials in aqueous-glycolic solutions of sodium salts of dicarboxylic acids was studied. New formulations of ethylene glycol–based antifreeze agents possessing good anticorrosive properties are suggested.

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Modern liquid-cooling systems and, in particular, those of internal combustion engines (ICEs) use aqueous or aqueous-organic solutions of various compositions as heat-carrying agents [1]. Ethylene glycol (EG) is the most widely used organic component of cooling fluids (CFs) [2[. The main construction members of engine-cooling systems are made of steel, cast iron, aluminum alloys, brass, copper, and solder [3], i.e., of metals with different electrode potentials and other electrochemical properties. When being exposed to the medium and having no insulation, these metals can operate as galvanic cells, which leads to enhanced contact corrosion [4–6] of one of the metals.

The choice and improvement of corrosion inhibitor formulations for aqueous-glycolic heat-carriers seems to be topical and timely because of the increasingly stringent requirements to service characteristics of CFs providing reliable operation of equipment.

Recently, researchers' interest has been attracted by corrosion inhibitors capable of complexation [7, 8] and, in particular, salts of carboxylic and dicarboxylic acids [9, 10]. The mechanism of the protective action of these compounds is rather complex and is related not only to the adsorption of a complexon, as in the case of higher acid anions [11], but also to its ability to form on the metal surface difficultly soluble complexonates, which block part of defects and thereby hinder the anodic reaction [7].

However, data on the corrosion behavior of metals in aqueous-glycolic solutions of carboxylic and dicarboxylic acid salts is mostly contained in the patent literature [12–14]. It is difficult to use these data for making a conclusion about the efficiency of separate compounds and their mutual influence on the corrosion of metals because the information in patents refers to the synergetic efficiency of corrosion inhibitor formulations. In this context, the effect of dicarboxylic acid salts in aqueous-glycolic solutions on the contact corrosion of metallic construction materials used in ICE cooling systems was studied in detail. Together with being theoretically significant, these studies are also practically important because a number of countries have introduced strong restrictions on use in CFs of a number of conventional corrosion inhibitors (primarily nitrites, nitrates, and silicates of alkali metals and salts of secondary amines) in conformity with the EURO 3–5 ecological safety regulations concerning the automobile transport. For example, specifications of leading automobile manufacturers (Ford, Hyundai, Toyota) envisage use of cooling fluids of only a new generation, produced solely by the organic acid technology (OAT).

EXPERIMENTAL

Flat samples of steel 3 [GOST (State Standard) 380], GH-190 cast iron (VAZ Industrial standard

Table 1. Corrosion rate of metals in the solder–copper–brass contact system in aqueous-glycolic solutions of sodium salts of dicarboxylic acids

Na_2An, wt %	Corrosion rate, g m^{-2} day^{-1}								
	solder			copper			brass		
	Suc	Adip	Seb	Suc	Adip	Seb	Suc	Adip	Seb
0	*0.435*[*]			0.080			0.085		
0.25	*0.288*	*0.290*	0.185	*0.178*	*0.125*	*0.135*	*0.145*	*0.125*	*0.130*
0.5	0.105	0.112	0.130	*0.175*	*0.125*	*0.105*	0.065	0.092	0.073
0.75	0.080	0.083	0.105	*0.110*	*0.105*	0.080	0.063	0.085	0.068
1.0	0.070	0.060	0.068	0.100	0.073	0.020	0.060	0.075	0.035
1.5	0.050	0.057	0.018	0.061	0.053	0.005	0.063	0.070	0.005
2.0	0.043	0.018	0.015	0.055	0.035	0.004	0.060	0.070	0.003
2.5	0.040	0.015	0.013	0.038	0.022	0.000	0.056	0.066	0.000

[a] Italicized values are those for metal corrosion rates that fail to conform to GOST (State Standard) [According to GOST 28084–89, the standard values are as follows (g m^{-2} day^{-1}): solder 0.2 and the rest of the metals 0.1]; the same for Tables 2–4, 6.

Table 2. Corrosion rate of metals in the aluminum–steel–cast iron contact system in aqueous-glycolic solutions of sodium salts of dicarboxylic acids

Na_2An, wt %	Corrosion rate, g m^{-2} day^{-1}								
	aluminum			steel			cast iron		
	Suc	Adip	Seb	Suc	Adip	Seb	Suc	Adip	Seb
0	*0.108*			*0.553*			*0.865*		
0.25	*0.125*	0.045	0.100	0.055	*0.135*	*0.175*	0.075	*0.173*	*0.103*
0.5	*0.128*	0.048	*0.112*	0.043	0.070	*0.170*	0.065	0.100	0.100
0.75	*0.123*	0.088	*0.148*	0.013	0.050	*0.145*	0.028	0.078	0.073
1.0	*0.130*	*0.113*	*0.170*	0.010	0.038	0.080	0.023	0.058	0.065
1.5	*0.138*	*0.110*	*0.185*	0.007	0.005	0.002	0.005	0.010	0.030
2.0	*0.148*	*0.113*	*0.205*	0.002	0.002	0.002	0.002	0.008	0.030
2.5	*0.150*	*0.117*	*0.220*	0.000	0.002	0.002	0.000	0.002	0.022

52205), AK6M2 aluminum alloy (GOST 1583), M-1 copper (GOST 859), L-63 brass (GOST 931), and POS-35 solder [TU (Technical Specification) 48-13-10], with dimensions of 50 × 25 × 3 mm, were preliminarily polished and degreased. Corrosion tests were performed in aqueous-glycolic solutions of sodium salts of dicarboxylic acid in the concentration range 0.25–2.5 wt %, which contained 50 vol % EG. The galvanostatic dissolution method [15] and gravimetry in conformity with GOST 28084 [3] were employed. The corrosion rate was evaluated by changes in the sample masses. The following technical-grade dicarboxylic acids were used: succinic (GOST 6341), adipic (GOST 10558), and sebacic (GOST 15582). Ethylene glycol (GOST 19710, extra quality) was used without additional purification. Disodium salts were produced in EG by mixing stoichiometric amounts of the corresponding salts with sodium hydroxide at a temperature of 80–90°C in the course of 2 h.

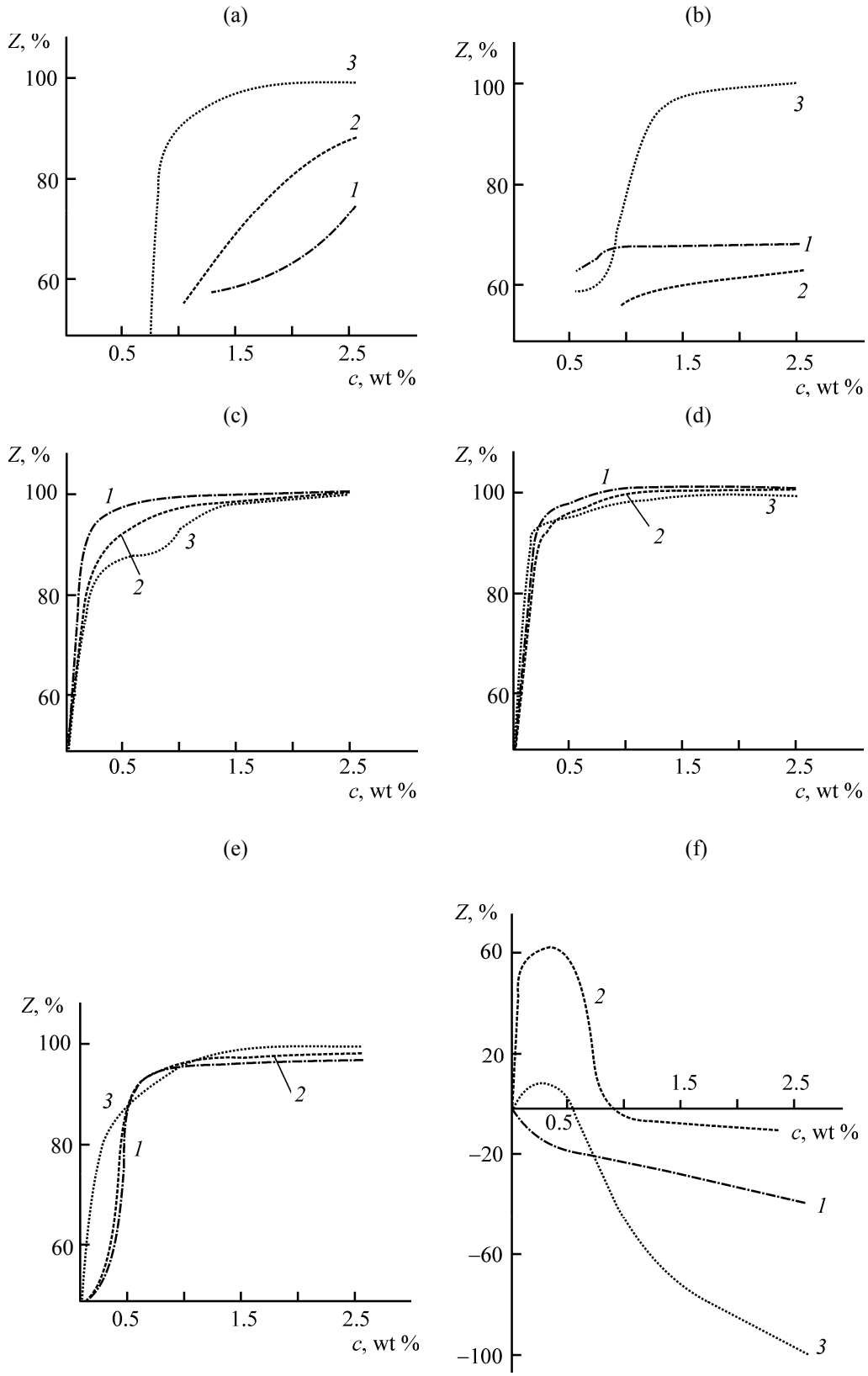

Fig. 1. Degree of protection, Z, of various materials in aqueous-glycolic solutions vs. the concentration c of sodium (*1*) succinate, (*2*) adipate, and (*3*) sebacate. Material: (a) copper, (b) brass, (c) steel, (d) cast iron, (e) solder, and (f) aluminum.

Table 3. Corrosion rate of metals in 2% aqueous-glycolic solutions of dicarboxylic acid salts at their mass ratio of 1 : 1

Dicarboxylic acid salt	Corrosion rate, g m^{-2} day^{-1}					
	solder	copper	brass	aluminum	steel	cast iron
Sodium succinate + sodium adipate	0.048	0.043	0.055	*0.110*	0.002	0.002
Sodium succinate + sodium sebacate[a]	**0.027**	**0.012**	**0.055**	***0.102***	**0.002**	**0.015**
Sodium adipate + sodium sebacate	0.035	0.038	0.013	*0.160*	0.007	0.018

[a] Boldface designates the corrosion inhibitor formulation exhibiting the highest degree of protection for all the metals under study.

Table 4. Effect of addition of sodium benzoate (0.35%), sodium tetraborate (0.45%), and their mixture on the corrosion rate of metals in 1% aqueous-glycolic solutions of dicarboxylic acid salts

Dicarboxylic acid salt	Additive	Corrosion rate, g m^{-2} day^{-1}					
		solder	copper	brass	aluminum	steel	cast iron
Sodium succinate	Sodium benzoate	0.088	0.085	0.063	0.120	0.013	0.020
	Sodium tetraborate	0.040	0.030	0.010	0.120	0.005	0.045
	Mixture	0.068	0.038	0.047	0.095	0.005	0.010
Sodium adipate	Sodium benzoate	*0.025*	*0.030*	*0.060*	*0.095*	*0.008*	*0.005*
	Sodium tetraborate	0.029	0.055	0.035	0.147	0.035	0.025
	Mixture	0.028	0.030	0.040	0.057	0.010	0.008
Sodium sebacate	Sodium benzoate	0.118	0.095	0.025	0.100	0.078	0.042
	Sodium tetraborate	0.032	0.048	0.025	0.230	0.100	0.002
	Mixture	0.000	0.022	0.020	0.078	0.080	0.005

The ICE cooling systems are polymetallic contact systems of the solder–copper–brass and aluminum–steel–cast iron polymetal contact systems. Therefore, the effect of aqueous-glycolic solutions of sodium salts of dicarboxylic acids on the corrosion behavior of the metals were studied in these polymetal contact systems. The results of corrosion tests are listed in Tables 1 and 2.

Taken in concentrations of 0.5–0.75%, the dicarboxylic acid salts under study rather reliably prevent corrosion of solder, brass, and cast iron, and at higher concentrations of up to 1.0%, that of copper and steel. At the same time, they initiate corrosion of aluminum, except sodium adipate, which somewhat diminishes the corrosion loss of the given metal in the concentration range 0.25–0.75%. Raising the concentration of sodium succinate from 1.5 to 2.5% has nearly no effect on the corrosion loss by nonferrous metals, whereas use of sodium adipate in similar concentrations can substantially reduce the corrosion rate of copper and solder (by nearly a factor of 4). Sodium sebacate completely suppresses the corrosion of copper and brass (degree of protection, Z = 100%) and strongly diminishes that of solder (Z = 97%) (see Figs. 1a, 1b, and 1e). Raising the concentration of the salts under study in aqueous-glycolic solutions to 2.0% nearly completely precludes the corrosion of steel (Z = 99.7%) (see Fig. 1c). The degree of protection of cast iron is 99.8% for sodium succinate and 99.1 and 96.5% for sodium adipate and sebacate, respectively (see Fig. 1d). Further increase in the content of dicarboxylic acid salts has nearly no effect on the corrosion loss by the metals under study.

It is known that carboxylate ions of dibasic organic acids are effective complexing agents for a wide variety of metals [16]. In the case of dicarboxylic acid salts, intracomplex salts presumably accumulate near the surface of a metal being protected, and, at concentrations exceeding the solubility limit of the complex, a film hindering the anodic reaction is formed on the metal surface. Probably, the protective mechanism of dicarboxylic acid salts is associated with the formation of difficultly soluble compounds on the surface of all the metals under study, with the exception of the aluminum alloy. Neutral octahedral aluminum complexes $\{[(CH_2)_nC_2O_4]_3Al\}^{3-}$ are insoluble in water, but readily dissolve in most of organic solvents, including alcohols [16], which presumably

Table 5. Corrosion behavior of metals in aqueous-glycolic solutions of dicarboxylic acid salts

Component (wt %)	Corrosion rate, g m^{-2} day^{-1}					
	solder	copper	brass	aluminum	steel	cast iron
Sodium adipate (2.0) + sodium benzoate (0.35)	0.089	0.031	0.028	0.014	0.017	0.038
Sodium sebacate (1.0) + sodium succinate (1.0) + sodium benzoate (0.35)	0.052	0.013	0.032	0.012	0.013	0.022

Table 6. Results of comparative corrosion tests of materials in carboxylate antifreeze agent of various compositions in accordance with GOST 28084–89, $T = 88°C$, $\tau = 336$ h

Composition no.[a]	Corrosion rate, g m^{-2} day^{-1}					
	solder	copper	brass	aluminum	steel	cast iron
1	0.05	0.01	0.03	0.01	0.01	0.02
2	0.09	0.03	0.03	0.01	0.02	0.04
3	0.03	0.03	0.04	0.05	0.01	0.01
4	0.01	0.02	0.02	0.07	0.07	0.02
5	0.08	0.06	0.07	0.02	0.07	0.06
2[b]	0.12	0.02	0.07	0.09	0.04	0.03
5[b]	0.14	0.06	0.05	0.02	*0.20*	*0.13*
Requirements by GOST 28084–89	0.20	0.10	0.10	0.10	0.10	0.10

[a] Composition no. 5: CF concentrate TOSOL–TORSA [TU (Technical Specification) 6-15-2007–98] based on disodium phosphate [15].
[b] Tests were performed at a temperature of 100°C.

hinders formation of effective protective films on the alu-minum surface in aqueous-glycolic solutions.

It can be seen from Fig. 1 that, as the length of the hydrocarbon chain of dicarboxylic acids grows, the degree of protection by their salts increases for nonferrous metals and decreases for ferrous metals. For example, in aqueous-glycolic solutions containing 2.0% sodium sebacate, the degree of protection of solder, copper, and brass is 96–97% (with sodium succinate, 90% for solder and 20–30% for brass and copper), and for similar solutions of sodium succinate, the degree of cast iron protection is 99.8% (with sodium sebacate, 96.5%). The effect of aqueous-glycolic solutions of sodium salts of dicarboxylic acids on the degree of aluminum protection is not so unambiguous because it strongly depends both on their concentration and on the length of the hydrocarbon chain (see Fig. 1f). For example, the degree of aluminum protection in a 0.25% sodium adipate solution is 59%, whereas in a 2.5% solution of sodium sebacate, the rate of metal dissolution increases by more than a factor of 2, compared with the 0.25% solution (0.22 and 0.10 g m^{-2} day^{-1}). At the same time, the corrosion rate of aluminum in sodium succinate solutions is almost independent of their concentration.

A study of the corrosion behavior of the metals in solutions of the sodium salts of dicarboxylic acids revealed the strongest protective effect for all the metals in the presence of a mixture of sodium succinate and sebacate (Table 3).

Previously, it has been found that sodium benzoate in aqueous and aqueous-glycolic solutions substantially diminishes the corrosion loss by solder and ferrous metals [15, 17, 18]. For this reason, it was of interest to study the joint effect of sodium salts of benzoic and dicarboxylic acids on the corrosion behavior of metals. It was found that the corrosion loss by steel and cast iron do decrease in aqueous-glycolic solutions of dicarboxylic acid salts combined with sodium benzoate. Used together with sodium sebacate,

sodium benzoate makes somewhat larger the corrosion loss by solder and copper, but reduces the corrosion rate of brass and aluminum and has nearly no effect on the corrosion behavior of metals when combined with sodium succinate. The most significant positive effect in protection of all the metals tested was only observed with an aqueous solution of sodium adipate and benzoate (Table 4).

At the same time, it can be seen from the data in Tables 3 and 4 that, even in the most favorable cases, the corrosion rate of aluminum remains rather high (~0.1 g m^{-2} day^{-1}). The corrosive effect of sodium carboxylates on aluminum could be diminished either by raising the concentration of sodium adipate to 2.0% in the inhibiting system constituted by sodium adipate and sodium benzoate or by using sodium benzoate together with a mixture of sodium succinate and sebacate (Table 5). The corrosion loss by aluminum in the solutions of dicarboxylic acids salts and sodium benzoate can also be reduced with sodium tetraborate, despite that its joint use with dibasic acid carboxylates fails to produce a positive effect (Table 4).

As for the corrosion behavior of the rest of the metals, a decrease in the rates of their dissolution in sodium adipate–benzoate–tetraborate and sodium sebacate–benzoate–tetraborate systems was observed. According to Evans [19], the passivation of metals by sodium tetraborate is due to formation of oxides or an oxygen layer produced via interaction of the metals with water. In addition to the influence of hydroxide ions on the formation of passivating layers, it is necessary to keep in mind the specific action of borate ions themselves, which form difficultly soluble compounds on the surface of metals.

Thus, the results of the study demonstrate that the considerable decrease in the corrosion rate of all the metals being tested and the nearly complete absence of corrosion for aluminum were observed in aqueous-glycolic solutions of the following additive mixtures: sodium adipate and benzoate; sodium adipate, benzoate, and tetraborate; and sodium sebacate, succinate, and benzoate.

The experimental data obtained made it possible to develop by the OAT technology several modifications of antifreeze formulations based on EG and sodium carboxylates under study (wt %):

Composition no.	Sodium sebacate	Sodium adipate	Sodium succinate	Sodium benzoate	Sodium tetraborate	Benzotriazole	EG
1	2.2	–	2.0	0.5	–	0.05	95.25
2	–	5.2	–	0.5	–	0.05	94.25
3	–	2.7	–	0.5	1.0	0.05	95.25
4	2.5	–	–	0.5	1.2	0.05	95.25

It can be seen in Table 6 that the suggested antifreeze formulations exhibit high protective properties with respect to all metallic construction materials of ICE cooling systems. Moreover, their test under rather severe temperature conditions (100°C) demonstrated that, in contrast to the conventional phosphate-containing formulation, the suggested formulations fully satisfy the regulation requirements (formulation nos. 2 and 5 at T = 100°C). In addition to having good anticorrosion properties, the suggested formulations preclude formation of mineral deposits on the surface of cooling system members and thereby provide effective heat transfer from the engine to the environment.

CONCLUSIONS

(1) A study of the corrosion behavior of a number of metals in aqueous-glycolic solutions of sodium salts of dicarboxylic acids demonstrated that the carboxylates studied exhibit a pronounced protective effect with respect to metallic construction materials for cooling systems of internal combustion engines.

(2) New formulations of ethylene glycol–based antifreeze agents (OAT) with high anticorrosion properties were suggested.

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