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This paper reports the synthesis of ionic liquids through the interaction between diethanolamine and orthophosphate and boric acids in order to establish the possibility of replacing volatile coalescents in a formulation for paints and varnishes with ionogenic compounds. The results from studying the influence of polymeric coalescents based on ionic liquids on the rheological properties of water-dispersion paints and varnishes of different nature are presented. It has been established that the synthesized coalescents could be used to modify the properties of paints and varnishes based on polyurethane and styrene-acrylic aqueous dispersions. It has been shown that the product of the interaction between diethanolamine and boric acid in aqueous solutions forms an ionogenic complex compound with a unipolar conductivity in terms of OH- ions. It was also established that when introduced to the formulation of water-dispersion paints and varnishes, the solutions of modifiers produce a diluting action. The influence of ionic liquids on the process of film formation of aqueous dispersions of polymers and pigmented paints and varnishes based on them was investigated. It was established that the synthesized ionogenic compounds are not inferior, in terms of their effectiveness, to the widespread conventional industrial coalescents of the Texanol[®] type.

Therefore, there is reason to assert the possibility of replacing the industrial coalescent Texanol[®] in the formulation of pigmented water-dispersion paints and varnishes based on styrene-acrylic and polyurethane dispersions with fundamentally new synthesized ionogenic modifiers. Thus, the coatings with a coalescent based on ion liquid of diethanolamine borate have a higher level of conditional hardness, which exceeds by 17 % the hardness index of the paint made on the basis of the conventional Texanol[®] type coalescent, without changing its decorative properties, such as color and shine

Keywords: ionic liquid, diethanolamine, boric acid, orthophosphate acid, coalescent, paints and varnishes

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1. Introduction

Over the past two decades, the demand for water-dispersion paints and varnishes (WDPVs) has been steadily increasing. This is due to the low content of volatile organic compounds (VOC) in their composition, the absence of an unpleasant odor when applying a coating, low toxicity, explosion- and fire safety. At the same time, it is possible with their participation to manufacture coatings with high enough barrier properties that could be used both indoors and when exposed to environmental factors. High-performance wood coatings have been developed on the basis of WDPVs. It is also possible to produce special-purpose PVs: for anti-corrosion protection of metal structures, their protection under the action of flames and high temperatures [1], to prevent the growth of marine organisms on underwater surfaces of vessels, etc. These and other properties of coatings based on WDPVs are ensured by the introduction of pigments, fillers, and special functional additives into their formulation. These additives include plasticizers, coalescents, emulsifiers, stabilizers, and dispersers (SAS), thickeners and structural additives, foam extinguishers, biocides, water repellents, corrosion inhibitors, etc. [2]. The need to use certain additives is determined by the requirements for the operating conditions of coatings based on them.

VOCs of different nature are used as functional additives, in particular plasticizers and coalescents, which adversely affect human health. Reducing the content of VOCs by replacing them with less volatile additives is one of the priority areas of research in the paint and varnish industry. At the same time, the scope of application of ionogenic compounds in the formulation of WDPVs is limited to components of stabilizing systems and individual dispersants.

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DEVELOPMENT OF COALESCENTS FOR PAINTS AND VARNISHES BASED ON IONIC LIQUIDS – THE PRODUCTS OF DIETHANOLAMINE AND INORGANIC ACIDS INTERACTION

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Investigating the interaction between ionogenic additives and the components of WDPVs could make it possible in the future to develop multifunctional additives with low volatility to replace conventional VOCs.

2. Literature review and problem statement

Given the availability of raw materials, one of the promising areas of research is the development of coalescents additives that increase the ability of aqueous dispersions to film formation, reducing the minimum film-formation temperature (MFT) of their high molecular component [2]. Most studies in the field of development of new functional additives are carried out by their manufacturers, and the results of such studies underlie the scientific and technical literature. At different times, low-molecular organic compounds were proposed to be used as coalescents. Among them are N-methyl pyrrolidone, alkyl ethers of polyethylene glycol, polyether alcohols and their mixtures [3], volatile organic solvents in an amount sufficient to induce the swelling of film-forming particles [4], glycol ethers [5], and others. The disadvantage of most such coalescents is their volatility, which makes their application undesirable given the need to produce and use environmentally clean and environmentally friendly coatings.

Over the past two decades, work has been underway to develop new PVs with a low VOC content. Glycerin and diglyceryl diethers [6] and mono- and di-benzoates [7, 8] have been offered for use in PVs with a low VOC content.

There are also so-called "reactive" coalescents, which simplify the formation of the coating, and then react with the film-forming macromolecules, entering the coating film composition. These compounds include acetoacetates [9], esters of levulinic acid [10], hydroxyethyl sulfone [11], and so on. Reactive coalescents were not widely used in the industry mainly due to the high price compared to conventional VOCs.

Our analysis of [2–11] suggests the feasibility of developing fundamentally new coalescents based on ionogenic organic compounds. Such compounds are ionic liquids, which belong to the "green solvents" with a high boiling point. They are used as plasticizers for formulations based on thermoplastic polymers [12–15], in particular, polyvinyl chloride [12] and polymethyl methacrylate [13], polylactide [15], and as thermoplastic starch plasticizers [16, 17].

It should be noted that work [12] investigated the plasticization of polyvinyl chloride by a series of aprotic ionic liquids. It has been established that the most effective plasticizers are ionic liquids based on tetra alkyl phosphonium and tetraalkylammonium. It was found that phosphonic fluids also showed high compatibility with the polymer and almost were not released when heated. The authors also note an increased rate of the release of ionogenic additives into the buffer solution of sodium chloride compared to conventional plasticizers. However, the issue related to determining the mechanism of the process remained unresolved.

Study [13] investigated the properties of polymethyl methacrylate (PMMA) synthesized in the environment of ionic fluid, namely [bmim]PF₆. It has been shown that the plasticizer has excellent compatibility with PMMA. It was found that the loss of mass, at 300 °C, by the formulation developed by the authors, whose content of ionic liquids

was 50 %, was much less than that by the formulation with dioctyl phthalate.

Work [15] reported a series of the developed formulations of polylactide, plasticized by trihexyl (tetradecyl) phosphonium decanoate [thtdPh]deca and tetrafluorobed orate [thtdPh]BF₄. It has been established that the ion liquids studied, especially [thtdPh]deca, reduce the glass transition temperature of the polymer. The reason for this may be the compatibility of ionic liquids with polylactide. It has been shown that modification of polymeric compositions with ionic liquids leads to a decrease in decomposition temperature.

The authors of [16] compared the plasticizing effect of glycerin, butyl methylimidazole chloride [bmim]Cl, and their mixture when plasticizing starch. It was found that the starch that is plasticized by ionic liquids has less water absorption, the Young modulus, and significantly larger elongation when ruptured compared to starch, which is plasticized with glycerin. Dry starch (with [bmim]Cl) glass transition temperature is shown to be less than that of starch with glycerin (48 °C and 80 °C, respectively).

The results of studying the dissolution and plasticization of starch with aprotic ionic liquids are considered in detail in [17]. The authors demonstrated the property of some ionic liquids with chloride anion to destroy the crystalline structure of starch, and, in some cases, with a change in the molecular weight of amylopectin molecules.

Available papers indicate a growing interest by the scientific community to plasticizing polymers with ionic liquids. Despite the practical importance of these results, the processes of interaction between polymers and protonic ionic liquids have not been considered enough. In other words, it is expedient to conduct a study addressing the processes of interaction between polymer dispersions and protonic ionic liquids.

3. The aim and objectives of the study

The purpose of this study is to synthesize ionic liquids based on the products of interaction between amino alcohols and inorganic acids. These compounds would be less volatile and, accordingly, could be safer compared to the widespread VOC-based industrial coalescents.

To accomplish the aim, the following tasks have been set:

- to investigate the effect of ionic liquids based on diethanolamine, boric and orthophosphate acids on the rheological properties of polyurethane and acrylic aqueous dispersions;

 to estimate the physical-mechanical properties of mode ified film materials in order to predict the possibility of their use as part of water-dispersion paints and varnishes.

4. Materials and methods to synthesize ionic liquids and modify film materials and paints and varnishes

For the synthesis of diethanolamine borate (boric acid amino ester) and diethanolamine phosphate, we used diethanolamine (DEA, 98%), boric acid (chemically pure), and orthophosphate acid (85%) without additional purification.

The synthesis of diethanolamine borate (boric acid amino ester). The synthesis of diethanolamine borate (I) proceeded according to the scheme in Fig. 1.

$$HN \xrightarrow{CH_2 - CH_2 - OH} + B(OH)_3 \xrightarrow{120-125 \circ C} HN \xrightarrow{CH_2 - CH_2 - O} B - OH$$

$$CH_2 - CH_2 - OH \xrightarrow{CH_2 - CH_2 - O} HN \xrightarrow{CH_2 - CH_2 - O} HN$$

Fig. 1. Scheme of synthesis of boric acid amino ester (diethanolamine borate) (I)

32.18 g (0.3 mol) of diethanolamine, 18.56 g (0.3 mol) of boric acid, and 35 ml of distilled water were added to the round-bottom flask with a volume of 100 ml. The mixture was stirred until the boric acid crystals were completely dissolved; it was then placed in a glycerin bath for the reaction over 2 hours at 120–125 °C while water was taken out of the reaction zone. We received 37.22 g (an output of 94.74 %) of transparent colorless viscous liquid, which dissolves in water, partly in p-xylol and white spirit, and does not dissolve in butanol, ethyl acetate. The pH of a 10 % aqueous solution of the compound (I) is 9.57.

FT-IR spectroscopy was performed using the AVATAR 370 FT-IR spectrometer; the measurement range was 4,000-400 cm⁻¹; separating capacity, 4 cm⁻¹; simulation of the film on the plate silver chloride.

Fig. 2 shows the FT-IR spectroscopy data on boric acid amino ester (I).



Fig. 2. IR spectra of boric acid amino ester (I)

The IR spectrum of dried boric acid amino ester (I) demonstrated absorption bands in the frequency domain of $3,354 \text{ cm}^{-1}$, $1,636 \text{ cm}^{-1}$, 2,968, and $2,858 \text{ cm}^{-1}$, $1,256 \text{ cm}^{-1}$, corresponding to -OH and -NH groups, hydrocarbon fragments of the diethanolamine molecule, the bond -C-N-C-, respectively. The bands of $1,414 \text{ cm}^{-1}$ and $1,102 \text{ cm}^{-1}$ are the characteristic absorption bands of the B–O and C–O bonds in organoborates [18].

Our conductivity and pH-metric studies have shown that in aqueous solutions the compound (I) is able to carry OH^- ions and is an ionogenic substance of structural formula (II) with a unipolar type of electrical conductivity. The confirmation that an ionogenic compound has been received is the high level of its ionic conductivity (~0.009 Cm/cm) with an almost 100 % OH⁻-ion transfer number in an aqueous solution.

In this regard, it should be assumed that the coalescent used in this work was the ionic liquid of general formula (2), whose scheme of formation is shown in Fig. 3.

The synthesis of diethanolamine phosphate. The synthesis of diethanolamine phosphate (III) proceeded according to the scheme in Fig. 4.



Fig. 3. Scheme of complex formation of diethanolamine borate (II) in water

$$HN \begin{pmatrix} CH_{2}^{-}CH_{2}^{-}OH \\ + H_{3}PO_{4} \end{pmatrix} \xrightarrow{115-120 \circ C} \begin{bmatrix} OH-CH_{2}^{-}CH_{2} \\ + H_{3}PO_{4} \\ OH-CH_{2}^{-}CH_{2} \end{bmatrix} H_{2}PO_{4}^{-}$$



107.99 g (1.006 mol) of diethanolamine were added to a 500 ml round bottom flask equipped with a stirrer and a thermometer; it was placed on an ice bath and stirred for 5 minutes to pre-cool.

With the help of a drip funnel, 115.98 g (1,006 moles) of orthophosphate acid (OPA) were slowly added to the flask during active stirring. After that, the flask was placed in a glycerin bath to perform a reaction at a temperature of 115-120 °C for two hours.

The yield of the target product III was 94.2 % of the theoretically possible. Diethanolamine phosphate (2,2'-iminobis-ethanol phosphate) is well soluble in water, weakly – in isopropanol, butanol, and butyl acetate, it does not dissolve in p-xylol and white spirit. The pH of a 10 % aqueous solution is 4.22.

Fig. 5 shows the results of IR spectroscopy of diethanolamine phosphate (III).



Fig. 5. IR spectra of diethanolamine phosphate (III)

The spectrum is characterized by the presence of characteristic absorption bands of the $R_2NH_2^+$ group (2,420 cm⁻¹), secondary amines (1,620 cm⁻¹), the fragments of $-CH_2-$ hydrocarbon radical (2,845 cm⁻¹ and 1,455 cm⁻¹), and hydroxyl groups (3,060 cm⁻¹ and 1,365 cm⁻¹). Orthophosphate acid is manifested by a peak of P=O group (1,225 cm⁻¹), peaks in the region of 1,100–950 cm⁻¹, corresponding to the oscillations of PO₄³⁻, HPO₄²⁻ and H₂PO₄⁻.

Modification of WDPVs with ionic liquids. Polyurethane and styrene-acrylic water dispersions were selected as objects for modification. Specifically, the acrylic-urethane anion dispersion Neopac E-106 (IV), the mixture Neopac E-106 (The Netherlands) with acrylic-urethane hybrid dispersion Joncryl HYB-6336, The Netherlands (in mass ratio 70:30, respectively) (V), and the styrene-acrylic dispersion Tritex SA-50, Turkey (VI).

The rheological characteristics of the modified aqueous dispersions were determined using a Brookfield viscosimeter (Myr V1-062, manufactured by OHAUS (USA)) [19].

Coating films were obtained according to the procedures given in GOST 8832-76, the physical appearance was estimated according to ISO 4628-1, the hardness was determined according to DSTU ISO 1522:2015.

We combined aqueous dispersions of the studied polymers, the regular coalescent Texanol [®] USA, and ionic liquids at room temperature (20–25 $^{\circ}$ C), and stirred using the Biuged BGD 750/1 dissolver, made in China, at a rotation rate of 120 rpm.

5. Results of studying the influence of ionogenic modifiers on the rheological and physical-mechanical properties of paints and varnishes

5. 1. The influence of ionogenic modifiers on the rheological properties of aqueous dispersions

To assess the possibility of using ionogenic modifiers in the formulation of water-dispersion paints and varnishes, it was necessary to investigate the effect of synthesized ionic liquids on the rheological properties of aqueous dispersions of polymers.

We modified aqueous dispersions by adding the 10-% aqueous solutions of diethanolamine borate (II) and diethanolamine phosphate (III) in droplets to their volume at stirring and at a temperature of 20-25 °C. The amount of coalescent solution for modification was calculated as a percentage relative to the dry residue of the aqueous dispersion.

The dependence of the dynamic viscosity of water dispersions on the content of modifiers is illustrated in Fig. 6-8.



Fig. 6. Dependence of dynamic viscosity of the styrene-acrylic water dispersion Tritex SA-50 on the content of the following in its formulation: a – diethanolamine borate; b – diethanolamine phosphate



Fig. 7. Dependence of dynamic viscosity of the acrylic-urethane water dispersion Neopac E-106 on the content of the following in its formulation: a – diethanolamine borate (II); b – diethanolamine phosphate (III)



Fig. 8. Dependence of dynamic viscosity of a mixture of the polyurethane aqueous dispersions Neopac E-106 and Joncryl HYB 6336 (70:30 wt.%) on the content of the following in its composition: *a* – diethanolamine borate (II); *b* – diethanolamine phosphate (III)

5. 2. Comparative analysis of the physical-mechanical properties of modified film materials

To assess the effectiveness of ionic liquids as coalescents, we performed a comparative analysis of the hardness of coating films modified by ionogenic and non-ionogenic coalescents. The results from our comparative analysis of the hardness of coating films, modified by ionogenic coalescents – diethanolamine borate (II) and diethanolamine phosphate (III) – and the widespread industrial coalescent Texanol[®] (2,2,4-trimethyl-1,3-pentanediol mono isobutyrate, $T_{boil}=254$ °C) are shown in Fig. 9–11.

During the study, we compared the influence of the conventional coalescent Texanol[®] and the ionogenic coalescent of diethanolamine borate (II) on the properties of the pigmented paint and varnish material based on the styrene-acrylic aqueous dispersion Tritex SA-50 (Tables 1, 2).



Fig. 9. Dependence of hardness of the coating films based on the styrene-acrylic dispersion Tritex SA-50 on the content of coalescents: a - II; b - III; $c - Texanol^{\circledast}$



Fig. 10. Dependence of hardness of the coating films based on the acrylic-urethane dispersion Neopac E-106 on the content of coalescents: a - II; b - III; $c - Texanol^{(8)}$



Fig. 11. Dependence of hardness of the coating films based on a mixture of the polyurethane dispersions Neopac E-106 and Joncryl HYB 6336 = 70:30 % by weight of the content of coalescents: a - II; b - III; $c - Texanol^{®}$

Comparing the formulations of the studied pigmented artistic paints of white color

No.	Component	Standard paint, mass parts, % by weight	Paint with ionogenic coalescent, % by weight
1	Film-forming agent (Tritex SA-50)	47.6	47.3
2	Pigment (TiO ₂)	16.6	16.5
3	Filler (Calcite 3)	5.7	5.7
4	Propylene glycol	5.7	5.7
5	Additives (biocide, defoamer, thick- ener, dispersant, rheology modifier)	1.5	1.4
6 Texanol [®]		0.6	-
7	Diethanolamine borate solution (II)	_	1.2
8	Water	22.3	22.2

the studied aqueous dispersions is diethanolamine phosphate (III). As a rule, the viscosity of all studied aqueous dispersions, subject to their modification by ionic liquids, stabilized on day 3.

In determining the effectiveness of reducing the dynamic viscosity of dispersions, as it follows from our results, it is natural to modify polymer dispersions with 10% aqueous IP solutions. The inability to determine the causes of abnormal independence of dynamic viscosity of the mixture Neopac E-106 and Joncryl HYB-6336 on the content of diethanolamine borate within the framework of this study gives rise to a potentially interesting direction of further research.

The result of our analysis of the influence exerted by modifiers of different nature on the hardness of coating films is the fact that the proposed coalescents at a concentration of 0.5 % are not inferior to Texanol[®] in their modifying effect. However, when used as part of the styrene-acrylic water dispersion Tritex SA-50, they have significant advantages

Comparative properties of white artistic paint samples

Table 1

	No.	Indicator	Unmodified paint (the content of Texa- nol [®] – 2.4 %*)	Modified paint (dieth- anolamine borate (II) content) – 0.5 %*)	Regulatory document under which control is carried out
	1	Coating physical appearance	Homogeneous surface without craters and wrinkles		ISO 4628-1
ĺ	2	Color	Acceptable		ISO 3668
	3	Mass share of non-volatile sub- stances	50.47	49.17	ISO 3251
	4	Drying duration to stage 3, hour	2	2	DSTU ISO 9117-1, DSTU ISO 9117-3, DSTU ISO 9117-6
	5	Rubbing degree, µm	25	25	DSTU ISO 1524
	6	The hardness of coating on a pendu- lum device, a.u.	0,18	0,21	DSTU ISO 1522-2015
ĺ	7	Coating shine, %	72	71	ISO 2813:2014

Note: the amount of a coalescent for modification was calculated as a percentage relative to the dry residue of water dispersion

6. Discussion of results of studying the rheological properties of PVs and the physical-mechanical properties of coatings

The result of modifying aqueous dispersions of the studied polymers with the Texanol[®] coalescent and ionic liquids is the obtained homogeneous dispersions, without any signs of possible sediment formation. Introduction to dispersions of ionogenic coalescents leads to a significant decrease in the dynamic viscosity of the styrene-acrylic dispersion Tritex SA-50 and the acrylic-urethane water dispersion Neopac E-106 and the mixtures of polyurethane dispersions (Fig. 6–8). The ionogenic coalescents used were ionic fluids II, III in the form of 10 % aqueous solutions.

The exception to this rule is the indicators of the dynamic viscosity of a mixture of the polyurethane water dispersions Neopac E-106 and Joncryl HYB 6336 (70:30 % by weight) modified by diethanolamine borate (II) (Fig. 8, *a*). It should be noted that the more effective thinner of Table 2

over the use of the industrial Texanol[®] coalescent. It should be noted that when using both Texanol[®] and new ionogenic coalescents (at a concentration of 0.5%), there formed transparent homogeneous coating films without defects in the form of craters, shagreen, swells, or cracks.

Coatingsthat are based on the polyure than e dispersion Neopac E-106 at the content of diethanolamine borate (II) of 0.7–1.0 % were partially turbid, and, at a concentration of 1.0 %, sticky to the touch. That may be evidence of its limited compatibility with the polymeric film-forming agents of a given aqueous dispersion.

At the same time, coatings that are based on a mixture of the polyurethane dispersions Neopac E-106:Joncryl HYB 6336 (70:30 % by weight) showed no signs of incompatibility over the entire range (0.5-1.0 %)of the applied ionogenic coalescents (diethanolamine borate (II), phosphate (III), and Texanol[®]).

Thus, we have demonstrated the possibility of using ionic liquids as coalescents in the formulation of aqueous dispersions of polymers; in this case, in terms of their modifying effect, they are not inferior to the industrial coalescent Texanol[®]. However, it is necessary to test the proposed ionogenic coalescents for compatibility with polymeric film-forming agents and SAS (cationic, anionic, or nonionic type) or protective colloids used to stabilize the aqueous dispersions of polymers.

When comparing the properties of pigmented paints and varnishes modified by coalescents of different nature (Tables 1, 2), it was established that the use of ionic liquid – diethanolamine borate (II) – as a coalescent makes it possible to produce coatings with a higher level of their conditional hardness, which exceeds the paints by 17 %, without changing the decorative properties such as color and shine.

The limitations inherent in this study are the possibility of using the proposed additives only to modify the properties of aqueous solutions or dispersions of polymeric materials and film-forming systems based on them.

The disadvantage of this work is the lack of information about the mechanism of coalescence of polymer particles of the studied aqueous dispersions with the participation of diethanolamine borate (II) and phosphate (III). These shortcomings can be successfully eliminated during further research, in particular on model systems and applying modern research methods (electron microscopy of coating films at different stages of their formation, differential scanning calorimetry to study phase transitions in borate-modified polymeric materials, etc.).

Further advancement of the current study may involve a more detailed elucidation of the mechanism of interaction between synthesized ionic liquids and aqueous dispersions of various compositions, including model dispersions. It is also advisable to study the interaction of aqueous dispersions and reaction products of other amino alcohols with mineral acids.

7. Conclusions

1. The synthesized ionic liquids significantly affect the change in the rheology of aqueous dispersions of various types. The dynamic viscosity of aqueous dispersions with the introduced synthesized compounds decreased in all experiments. Thus, with the modification of Tritex SA-50 by diethanolamine borate and diethanolamine phosphate, the dynamic viscosity at the modifier content of 1 % decreased more than twice. When modifying Neopac E-106 by diethanolamine borate viscosity decreased by 23 %, and, when modifying by diethanolamine phosphate – by 51 %. The viscosity of a Neopac E-106 and Joncryl HYB 6336 mixture (70:30 % by weight), when modifying by diethanolamine borate, decreased by 8 %; when modifying by diethanolamine phosphate, by 35 %. This phenomenon could be explained by the interaction of modifiers with the components of dispersions and their liquefaction given the application of IP solutions. At the same time, over time, there is no structuring of water dispersions of various types.

2. The comparison of the physical-mechanical and decorative properties of films based on the modified aqueous dispersions and pigmented PVs with films based on a conventional volatile coalescent allows us to assert efficiency of using the synthesized ionic liquids as a modifier. This is evidenced by the fact that the film hardness of the pigmented material modified by diethanolamine borate exceeds the hardness of the films made from the material with a volatile coalescent by 0.3 a.u. At the same time, the decorative properties (color, shine, and physical appearance) of the coating remained unchanged. This indicates the possibility of directed control over the operational characteristics of paint and varnish formulations based on styrene-acrylic and polyurethane aqueous dispersions by using ionic liquids from the class of diethanolamine borate and phosphates as coalescents.

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