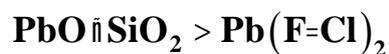


POLYANION EFFECT IN GLASSES OF THE PSEUDO-BINARE SYSTEM



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ABSTRACT

The article presents the comparative analysis of the polyanion effect at its manifestation in the pure form, i.e. with the participation in the electromigration process of only halide-ions with the polyalkali effect. It was shown that expressions used to calculate the electrical conductivity of two-alkali glasses, can not be directly applied to calculate the electrical conductivity of two-halide glasses. Analytical expressions for such calculation are proposed, giving a satisfactory compliance of calculated and experimental data.

Keywords: polyanion effect, polyalkali effect, electrical conductivity, transfer numbers, nature of conductivity, additivity of electrical conductivity.

INTRODUCTION

Since the beginning of the 80s of the last century, the polyalkali effect as an especial case of the more general phenomenon has been considered in the literature [1-8].

The question as to whether the polyalkali effect is the phenomenon inherent to only glasses, wherein charge carriers are ions of alkali metals, or it is the particular case of a more general phenomenon, was first raised in the paper [5]. Answering this question on the basis of his own researches and data available in the literature, V.E. Kogan in papers [4; 5] comes to the conclusion that the polyalkali effect is a particular case of the more general phenomenon, namely, that the change of the electric charge carrier type in various classes of glasses being in the solid state,

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Or change of glass structural fragments, throughout which the migration of the electric current carrier takes place, leads to the presence of the minimum on the dependence of the electrical conductivity as the function of the concentrations ratio of electric current carriers.

Ascertainment of the existence of the anion-halide transport in solid glasses raised the question about the possibility of manifestation in mixed halide glasses of the effect similar to the polyalkali effect. For the first time such assumption was outspoken in the work [9], but verification of the presence of such effect on glasses of fluoroberyllate systems failed due to the poor fixation of chlorides and bromides by the glass melt.

For the first time this effect, called, by the analogy with the polyalkali effect, the polyanion effect was ascertained in the halide-containing phosphate glasses of $0,3\text{Ca}(\text{F,Cl})_2 - 0,7\text{Ba}(\text{PO}_3)_2$ composition [10]. However, at the time of the polyanion effect detection, the nature of charge carriers and their transfer numbers in specified glasses were not determined experimentally, that led initially to the incorrect representation of obtained concentration dependences of the electrical conductivity.

It was shown later in the paper [11], that along with halide ions, ions, which are formed at the dissociation of the structurally bound water, are also involved in the electricity transfer process in halide-containing phosphate glasses. Thus, there failed the tracing the polyanion effect in the pure form (at experimentally confirmed participation in the electromigration process of only halide ions) in oxy-halide phosphate glasses.

A.A. Pronkin and V.E. Kogan in the paper [12] for the first time (without providing specifically studied compositions and experimental data) pointed to ascertainment of a polyanion effect in glasses of pseudo-binary system $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{F,Cl})_2$.

EXPERIMENTAL PROCEDURE

Glasses in the pseudo-binary system under study were synthesized in the corundum crucibles according to the procedure of own designed product, described in detail in the paper [13], at that, in the most cases, the synthesis was conducted in the glass melting furnace of own design [14].

Measurement of the electrical conductivity was carried out on polished plane parallel samples in the form of disks within the temperature range from 20 up to 250 °C as per GOST 6433.2-71. Measurements were carried out at the direct current by the electrometric scheme on the TR-8651 electrometer (Japan) in the TR-43C measuring cell (Japan). Transfer numbers were determined according to the technique of Hittorf, which consists in studying the concentration

changes in near-electrode spaces related to the passage of the measured amount of electricity through electrolyte.

Density was determined with the help of the successive weighing of glass samples in air and toluene.

RESULTS AND DISCUSSION

Our studies of glasses of $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{Hal})_2$ system, where $\text{Hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ pointed to the possibility of introduction in the lead metasilicate of record high concentrations of halides. Thus, the maximum content of halides throughout the synthesis reached 75.28 mol. % of PbF_2 , 23.42 mol. % of PbCl_2 , 18.81 mol. % of PbBr_2 and 17.69 mol. % of PbI_2 , at the same time, according to the data of the chemical analysis, the volatility of halogens at the maximum attainable halide content in the glass, on F, Cl, Br, I basis was respectively 0.88, 0.36, 0.66, 0.99 wt. %.

Determination of halide-ion transfer numbers showed that the unipolar anion-halide nature of the conductivity is achieved only for chloride-containing compositions with PbCl_2 content – 23.42 mol. % and for fluoride-containing glasses, beginning from PbF_2 content of 14.77 mol. %. Therefore, for the studying polyanion effect, glasses of $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{F}, \text{Cl})_2$ system with the total lead halides content of 23.42 mol. % were chosen.

Data of the chemical analysis of the synthesized glass compositions with the total lead halides content of 23.42 mol. % in the comparison with their synthetic composition are shown in Table 1, and relative losses of halogens in percent calculated as the ratio of the difference between synthetic and analytical content (% by weight) to the synthetic - in Table 2.

As it is seen from Table 1, the ratio of the content of different kinds of halogens in compositions by analysis practically correspond to that in compositions by synthesis, i.e. volatilization processes do not change the β_F value, corresponding to expression

$$\beta_F = \frac{[\text{F}^-]}{[\text{F}^-] + [\text{Cl}^-]}, \quad (1)$$

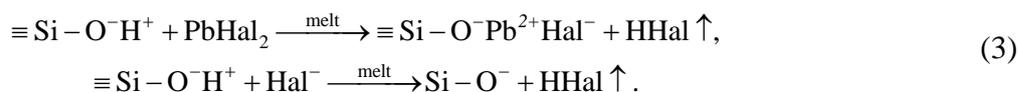
where $[\text{F}^-]$ and $[\text{Cl}^-]$ – volumetric concentrations of ions of fluorine and chlorine, respectively.

Volumetric concentrations of halide-ions ($[\text{Hal}^-]$, mol/cm³) are calculated by the formula

$$[\text{Hal}^-] = \frac{(\text{wt. \% PbHal}_2)d}{100(\text{PbHal}_2)/2}, \quad (2)$$

where d – glass density, g/cm^3 ; (PbHal_2) – molar weight of the lead halide, g/mol .

By the ratio of components of loss (Table 1), it can be assumed that the most likely compounds, in the form of which components are volatilized from the melt during the melting process are SiHal_4 , HHal and Hal_2 . At that, HHal escapes in the process of the lead metasilicate melt dehydration at the introduction of $\text{Pb}(\text{Hal})_2$ in it due to reactions behaviour, equations of which are the most likely to have the following form:



As it is seen from Table 3 and Fig. 1, in glasses under consideration, the total volumetric concentration of halide-ions $\left(\sum [\text{Hal}_j^-]\right)$ remains practically constant, while dependences of the specific electrical conductivity (σ_V) and the activation energy of the electrical conductivity (E_a) on the value β_F is characterized by the presence of extrema. At that, the unipolar conductivity by halide-ions takes place for all compositions, i.e. the sum of halide-ion transfer numbers is equal to unity $(\eta_{\text{Hal}^-} = \eta_{\text{F}^-} + \eta_{\text{Cl}^-} = 1)$.

Thus, the polyanion effect takes place in the considered system in the pure form, the depth of which by the electrical conductivity is $\Delta \lg \sigma_V \approx 1.0$ order and $\Delta E_a \approx 0.15$ eV by the activation energy of electrical conductivity (Fig. 1).

The specified made it possible to verify the applicability of the additivity rule, proposed by R.L. Mueller [15] for two-alkali glasses, and its modification for accounting specific features of the structure of two-alkali glasses with the high concentration of alkali ions, namely, the effect of dispersing single-cation structural units on the electrical conductivity of polyalkali glasses with respect to the polyanion effect.

For polyanion effect, the additivity rule and its modification will have the following form:

$$\sigma_{\Sigma[\text{Hal}_j^-]} = \sigma_{[\text{Hal}^-]} + \sigma_{[\text{Hal}^{r-}]} \quad (4)$$

and

$$\sigma_{\Sigma[\text{Hal}_j^-]} = \left(\sigma_{[\text{Hal}^-]} + \sigma_{[\text{Hal}^{r-}]} \right) \exp(-\Delta S' / 2R), \quad (5)$$

where $\Delta S'$ – entropy factor determined by the increased number of statistically possible states when transition from simple to complex glasses, corresponding to the expression

$$\Delta S' = 4,6R(m\sigma_i - m\sigma_i) = 4,6\Delta m\sigma_i; \quad (6)$$

R – universal gas constant; $m\sigma_i$ and $m\sigma_i$ – values of electrical conductivity modules, corresponding to expressions:

$$m\sigma_i = \lg \frac{\sigma_0}{[\text{Hal}^-]} \quad (7)$$

and

$$m\sigma_i = \lg \frac{\sigma_0}{[\text{Hal}^-]}, \quad (8)$$

wherein σ_0 and σ_0 – theoretical and experimental values of the pre-exponential multiplier; k – Boltzmann constant; T – absolute temperature. The experimental value of the pre-exponential multiplier is determined by the expression

$$\sigma = \sigma_0 \exp\left(-\frac{E_\sigma}{2kT}\right). \quad (9)$$

Undoubtedly, in the first place, it was necessary to check satisfiability of the expression (4). To carry out calculations by this expression, it was necessary to know values of the electrical conductivity of single-halide glasses with the volumetric concentration of the corresponding halide-ion equal to its volumetric concentration in the two-halide glass.

Concentration dependences of the electrical conductivity of single-halide glasses (in the range of the interesting for us content of PbHal_2 – 23.42 mol. %) are shown in Fig. 2.

The pattern of concentration dependences of the electrical conductivity of single-halide glasses states that the introduction of fluoride and chloride of lead in the base composition corresponding to lead metasilicate differently affects its electrical conductivity. So, if even first additives of lead fluoride result in the increase of the electrical conductivity, the introduction of lead chloride results in the significant increase only when its concentration is more than 13 mol. %.

The concentration dependence pattern of the electrical conductivity of glasses with lead chloride is outwardly similar to that obtained by R.L. Mueller for alkali-containing compositions with the unipolar cation conductivity [16-18], however, it is determined by other factors. Hereto, in particular, points the mentioned difference in patterns of concentration dependences of glasses with chloride and fluoride of lead (Fig. 2). It is the most likely that concentration dependences of the electrical conductivity of single-halide glasses are determined in preference (within the framework of considered PbHal_2 concentrations) by the degree of the glass dehydration with a certain type of halide, i.e. connected with a gradual

transition with increasing content in PbHal_2 composition from the proton conductivity, which is characteristic for the glass of lead metasilicate composition [19-21], to the unipolar anion-halide conductivity through compositions with the mixed proton-anion conductivity.

With due account for above mentioned dependencies (Fig. 2), the conclusion follows that the dehydration proceeds more intensively in compositions containing lead fluoride. The noted is confirmed by the IR spectroscopic study, carried out by us, and the concentration dependence of halide ions transfer numbers in single-halide glasses (Fig. 3).

Consideration of concentration dependences of halide-ions transfer numbers in two- and single-halide glasses (Fig. 1, 3) showed that if in a number of two-halide compositions the unipolar anion-halide type of conductivity is determined, then it is not available in the relevant single-halide glasses, i.e. in glasses with the same concentration of given type of the lead halide, as in the two-halide glass. This fact is most likely due to the fact that dehydration processes proceed more intensively in two-halide glasses, which is also confirmed by data of the IR spectroscopic study.

Based on concentration dependences of the electrical conductivity in single-halide glasses (Fig. 2) and its specific values at PbHal_2 contents of our interest, it follows that the electrical conductivity of two-halide glasses with $\beta_F < 0.36$ should primarily be determined by the electrical conductivity of corresponding chloride-containing compositions, and at $\beta_F \geq 0.36$ – by the electrical conductivity of corresponding fluoride-containing compositions. The mentioned is confirmed by concentration dependences of halide ions transfer numbers in two-halide glasses (Fig. 1), whereof it is obvious that in particular studied compositions of glasses with this particular value β_F only in the two-halide glass with $\beta_F = 0.36$ both types of halide-ions concurrently take part in the process of electromigration, at that the share of fluoride-ions participation is larger.

The calculation of the electrical conductivity of two-halide glasses, as well as its experimental study (Table 3, Fig. 1) was carried out for specific compositions of glasses with $\beta_F = 0.14; 0.36; 0.57; 0.78$, at that, all above mentioned made it necessary to use the expression (4) only in the calculation of the electrical conductivity of two-halide glass with $\beta_F = 0.36$. In other cases, the expression (4) can be simplified to expressions

$$\sigma_{\Sigma[\text{Hal}_j^-]} = \sigma_{[\text{Hal}'^-]} \quad (4 \text{ a})$$

and

$$\sigma_{\Sigma[\text{Hal}_j^-]} = \sigma_{[\text{Hal}''^-]}, \quad (4 \text{ b})$$

where $\sigma_{[\text{Hal}'^-]} \equiv \sigma_{[\text{F}^-]}$ – electrical conductivity of glasses of $\text{PbO} \cdot \text{SiO}_2 - \text{PbF}_2$ system with PbF_2 content in mol. %, equal to that in two-halide glasses with $\beta_F = 0.57; 0.78$ (see Table 3);

$\sigma_{[\text{Hal}''^-]} \equiv \sigma_{[\text{Cl}^-]}$ – electrical conductivity of the glass of $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{Hal})_2$ system with PbCl_2 content in mol. %, equal to that in bi-halide glass with $\beta_F = 0.14$ (see Table 3).

The validity of this simplification is bespoken by the data of Table 4, wherein are given values of the electrical conductivity of single-halide glasses with PbHal_2 content in mol. %, equal to that in the corresponding two-halide glasses, and electrical conductivity values obtained for all two-halide glass compositions from expressions (4), (4a) and (4b).

As it is seen from the data of Table 4, discrepancies in the electrical conductivity values calculated for glasses with $\beta_F = 0.14; 0.57; 0.78$ by the expression (4) and by expressions (4a), (4b) lie within the error of measuring the electrical conductivity (± 0.2 of order $\lg \sigma$) and amount to not more than 0.05. The same order has the difference between the electrical conductivity of the single-halide glass with PbF_2 content in mol. %, equal to that in the two-halide glass with $\beta_F = 0.36$, and the calculated value of the electric conductivity obtained by the expression (4) for the two-halide with $\beta_F = 0.36$. This is another reference to the validity of the above statement that the electrical conductivity of considered two-halide glasses with $\beta_F < 0.36$ is determined primarily by the electrical conductivity of corresponding chloride-containing compositions, and with $\beta_F \geq 0.36$ – by the electrical conductivity of the corresponding fluoride-containing compositions.

The above results bespeak that the differentiation of structural units by the anion type takes place in two-halide glasses under consideration. Thus, the principle of motion independence of charge carriers, namely of halide-ions, is realized in these glasses, i.e. migration of a halide-ion of one kind occurs primarily on polar fragments of the structure, containing the same halide-ions, and migration in the non-polar medium and in the medium of polar structural units with a halide-ion of the other kind is complicated.

In favour of the formulated conclusion bespeaks also the comparison of experimental electrical conductivity values (σ) in two-halide glasses (Table 3) with its theoretical values (σ), obtained by expressions (4), (4a), (4b), shown in Table 4, indicating extremely

unsatisfactory results. The value $\Delta(-\lg \sigma) = -\lg \sigma - (-\lg \sigma)$ for glasses with $\beta_F = 0.14; 0.36; 0.57; 0.78$ was, correspondingly, $-0.30; -1.30; -0.75; -0.40$, i.e. the average difference between the experimental and theoretical values $\overline{\Delta(-\lg \sigma)}$, determined as the arithmetic average of four values is $\approx -0,7$.

It is important to note that, if, in a number of cases [19] for the polyalkali effect, its experimentally found value is significantly greater than the theoretical one, then, for the considered case of polyanion effect, there takes place the diametrically opposite pattern, analogues of which for polyalkali effect are absent. This fact uniquely points out that, in two-halide glasses, there is no dispersion of single-halide polar groups and formation of mixed (two-halide) fragments of the structure. Thus, a situation arises wherein theoretical and experimental results can not be brought to a satisfactory compliance by using the expression (5), since it should have to take into account the dispersion of single-halide structural units, which is not the case. Thus, the expression (5) for the polyanion effect loses its physical meaning at its manifestation in the pure form.

The mentioned difference between experimental and theoretical values in cases of polyanion and polyalkali effects, in our opinion, is the most probable, this is due to such reasons as: different structural role of halide-ions in single- and two-halide glasses; absence of the unipolar anion-halide conductivity in a number of single-halide glasses, electrical conductivity values of which are used in the above calculations; presence of compositions of two-halide glasses, wherein the unipolar anion-halide type of conductivity by one halide-ion takes place, i.e. $\eta_F = 1$ or $\eta_{Cl} = 1$ (Fig. 1). To be able to use the additivity rules of R.L. Mueller as applied to the polyanion effect in its manifestation in the pure form, i.e. to use expressions (4), (4a), (4b), we introduced the empirical value k in them, defined by the expression

$$k = \frac{\lg \sigma_0 - \lg [\text{Hal}_j^-]}{\lg \sigma_0 - \lg [\text{Hal}_j^-]_\sigma}, \quad (10)$$

where $[\text{Hal}_j^-]$ – total volumetric concentration of halide-ions in the two-halide glass; $[\text{Hal}_j^-]_\sigma$ – volumetric concentration of that kind of halide-ions, which is predominantly involved in the electromigration.

It should be noted that the numerator and denominator of the expression (10) are similar to expressions (7), (8) for the electrical conductivity module. Preferential participation in the

electromigration of halide-ions of one kind or another is determined from data by transfer numbers of halide-ions in two-halide glasses.

Expressions (4), (4a), (4b), taking into account the empirical value k , should be written in the form

$$\sigma_{\Sigma[\text{Hal}^-]} = A \left(\sigma_{[\text{Hal}'^-]} + \sigma_{[\text{Hal}''^-]} \right)^k, \quad (11)$$

$$\sigma_{\Sigma[\text{Hal}^-]} = A \sigma_{[\text{Hal}'^-]}^k, \quad (11 \text{ a})$$

$$\sigma_{\Sigma[\text{Hal}^-]} = A \sigma_{[\text{Hal}''^-]}^k, \quad (11 \text{ b})$$

where A –coefficient, equal to unity, having the dimensionality $\text{S}^{1-k} \cdot \text{cm}^{k-1}$. The issue of the expression (11) simplification to expressions (11 a), (11 b) is solved for each specific glass composition on the basis of data on halide-ions transfer numbers.

The calculation carried out with expressions (11), (11 a) and (11 b), points to the satisfactory agreement with experimental results. The value $\Delta(-\lg \sigma)$ was for glasses with $\beta_F = 0.14; 0.36; 0.57; 0.78$ correspondingly $-0.10; -0.20; -0.30; -0.25$, i.e. $\overline{\Delta(-\lg \sigma)} \approx -0.20$, that is within the error of measuring electrical conductivity (± 0.2 of $\lg \sigma$ order).

CONCLUSION

Thus, we have shown that the rule of the electrical conductivity additivity of R.L. Mueller as applied to the polyanion effect in its manifestation in the pure form generally corresponds to the expression (11), wherein the empirical value k takes into account the different structural role of halide-ions in single- and two-halide glasses; absence of the unipolar anion-halide conductivity in a number of single-halide glasses, electrical conductivity values of which are used in calculations; presence of compositions of two-halide glasses, wherein the unipolar anion-halide type of conductivity by one halide-ion takes place. The issue of the expression (11) simplification to expressions (11 a), (11 b) must be solved on the basis of the study of transfer numbers of halide-ions in two-halide glasses.

Tables

Table 1. Data of the chemical analysis of $\text{PbO} \ddot{\text{SiO}}_2 > \text{Pb}(\text{Hal})_2$ system glasses with the total $\text{Pb}(\text{Hal})_2$ content of 23.42 mol. %

β_{F}	Composition by synthesis, wt. %				Composition by analysis, wt. %			
	PbO	SiO ₂	F	Cl	PbO	SiO ₂	F	Cl
0	78.07	15.95	–	5.98	78.60	15.84	–	5.56
0.14	78.46	15.87	0.59	5.08	76.63	15.85	0.57	4.05
0.36	79.25	15.17	1.95	3.63	79.42	15.14	1.90	3.54
0.57	79.56	15.64	2.30	2.50	79.88	15.62	2.26	2.42
0.78	80.11	15.50	3.15	1.24	80.55	15.20	3.06	1.19
1.00	80.61	15.41	3.98	–	81.27	15.21	3.52	–

Table 2. Relative losses of halides for glasses of $\text{PbO} \ddot{\text{SiO}}_2 > \text{Pb}(\text{F, Cl})_2$ system with the total $\text{Pb}(\text{Hal})_2$ content of 23.42 mol. %

β_{F}	Relative losses of F, %	Relative losses of Cl, %	Relative total losses of halogens
0	-	7.0	7.0
0.14	3.4	2.6	2.6
0.36	2.6	2.5	2.5
0.57	1.7	3.2	2.5
0.78	2.9	4.0	3.2
1.00	11.6	-	11.6

Table 3. Electrical properties of glasses of $\text{PbO} \cdot \text{SiO}_2 > \text{Pb}(\text{F}, \text{Cl})_2$ system with the total $\text{Pb}(\text{Hal})_2$ content of 23.42 mol. %

Composition, mol. %			Volumetric concentration of halide-ions, mol / cm ³		$d, \text{g} / \text{cm}^3$	β_{F}	$-\lg(\sigma_{\text{V}}, \text{S} \cdot \text{cm}^{-1})$ at 200 °	E_{σ}, eV	$\lg \sigma_0$
PbCl ₂	PbF ₂	PbSiO ₃	$[\text{Cl}^-] \cdot 10^{-2}$	$[\text{F}^-] \cdot 10^{-2}$					
23.42	–	76.58	0.98	–	5.91	0	7.90	1.79	1.60
20.00	3.42	76.58	0.84	0.14	5.91	0.14	8.85	1.91	1.60
15.00	8.42	76.58	0.65	0.36	6.05	0.36	8.50	1.91	1.65
10.00	13.42	76.58	0.45	0.59	6.18	0.57	8.25	1.95	2.10
5.00	18.42	76.58	0.23	0.80	6.34	0.78	7.80	1.87	2.10
–	23.42	76.58	–	1.07	6.89	1.00	7.15	1.83	2.55

Table 4. Experimental values of the electrical conductivity of glasses of $\text{PbO} \cdot \text{SiO}_2 > \text{PbHal}_2$ (Hal = F, Cl) systems and glasses of $\text{PbO} \cdot \text{SiO}_2 > \text{Pb}(\text{F}, \text{Cl})_2$ system with the total content of lead halides of 23.42 mol. %

β_{F}	$-\lg \sigma_{[\text{Cl}^-]}$ at 200 °	$-\lg \sigma_{[\text{F}^-]}$ at 200 °	$-\lg \sigma_{\sum[\text{Hal}^-]}$ at 200 ° [calculated by the expression (4)]	$-\lg \sigma_{\sum[\text{Hal}^-]}$ at 200 ° [calculated by expressions (4), (4a) and (4b)]
0.14	8.85	10.50	8.85	8.85
0.36	10.35	9.75	9.80	9.80
0.57	10.60	9.00	9.05	9.00
0.78	10.70	8.20	8.25	8.20

Figure captions

Fig.1. Variation of electrical conductivity, its activation energy, transfer numbers of halide-ions at 200 °C and the total volumetric concentration of halide-ions depending on the value β_F for glasses of $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{Hal})_2$ system with the total lead halides content of 23.42 mol. %

Fig.2. Concentration dependences of the electrical conductivity of single-halide glasses of $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{Hal})_2$ system

Fig.3. Concentration dependences of halide ions transfer numbers in glasses of $\text{PbO} \cdot \text{SiO}_2 - \text{Pb}(\text{Hal})_2$ systems at 200 °C

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Biographical sketch

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Figures

Fig.1.

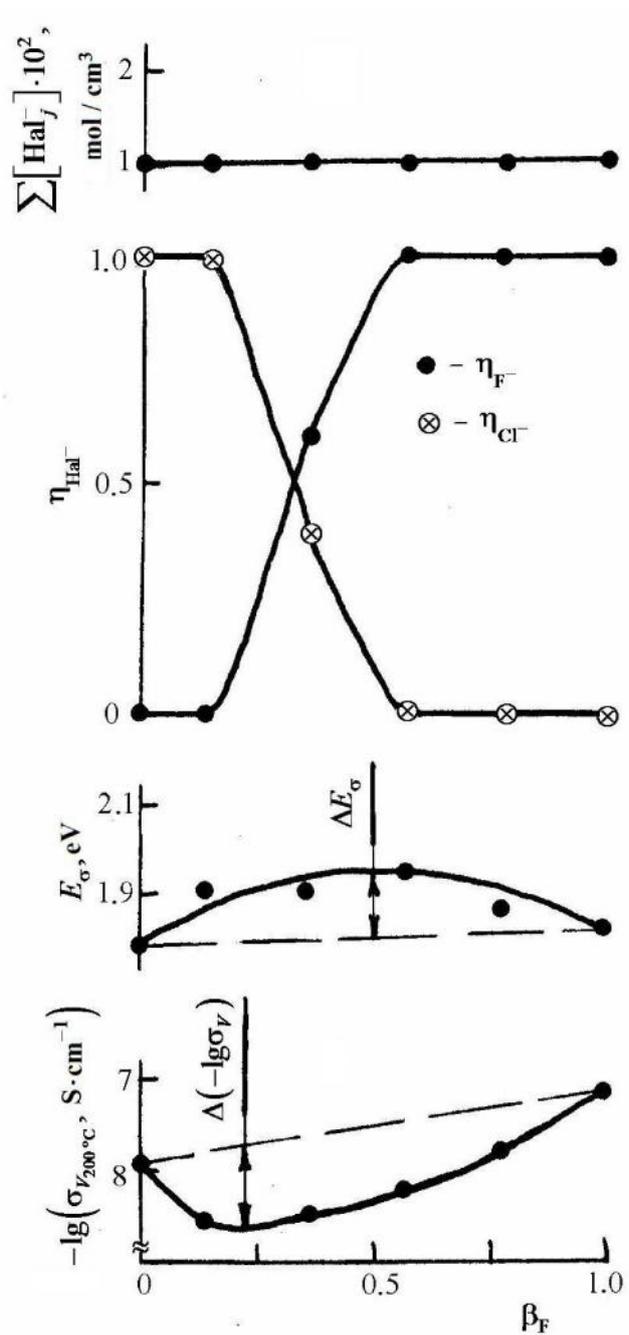


Fig.2.

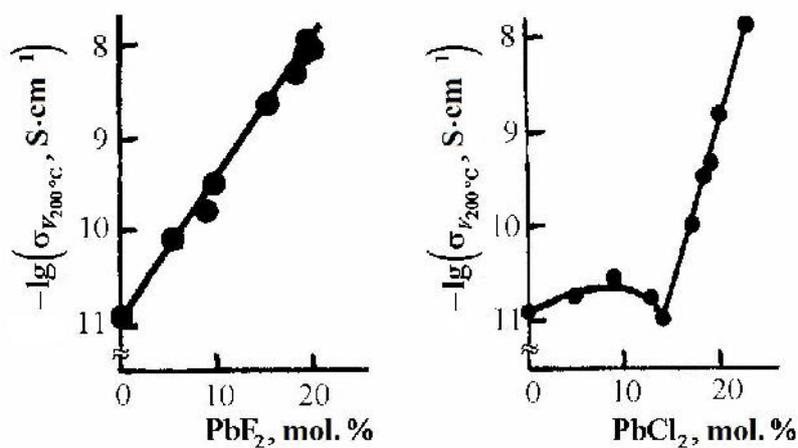
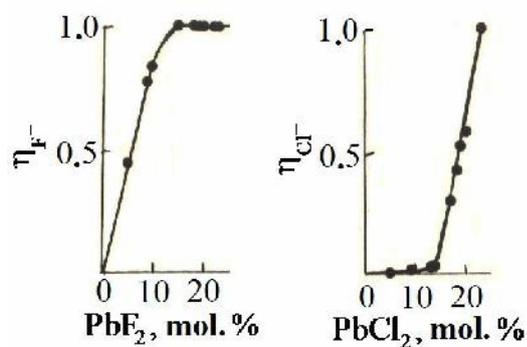


Fig.3.

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