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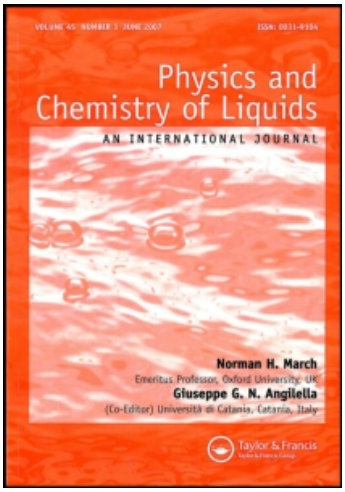

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ON THE EFFECT OF IONIC MELT COMPOSITIONS ON THEIR ACID-BASE PROPERTIES

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Analysis of the ionic solvent effect on acid-base equilibria allowed to divide them in two types distinguishing by the existence of 'inner' acid-base equilibrium and, consequently, by type of acid-base intervals. A consideration of some studies of ionic melts on the base of mixtures of $AlCl_3$ and gallium halides with alkaline halides showed that the effect of melt composition (both cation and anion) on acid-base interval extent is described in the frames of 'hard' and 'soft' acids and bases (Pearson). Oxobasicity indices of molten mixtures containing alkaline and alkaline earth chlorides at 600 and 700°C are determined, the features of oxoacidity it certain melts are discussed.

Keywords: Acids; Bases; Ionic melts; Solubility; Oxobasicity index

The donor-acceptor reactions connected with the redistribution of electron pairs are considered as acid-base by Lewis since 1923 [1]. Acids are the substances accepting the electron pairs, donors of latters are bases, the principal scheme of an acid-base reaction may be presented as follow:

$$A + : B \rightleftarrows A : B \qquad (1)$$

here and after 'A' is an acid and 'B' is a base. So wide understanding acids and bases provided extensive usage of Lewis definition for studies of different donor-acceptor processes. In particular, it was

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developed to be used for the description of chemical reactions accompanied with oxide ion exchange in high-temperature systems (solids or melts) [2]. This kind of acid-base process is known as Lux acidity or oxoacidity. In such reactions donor of O^{2-} serves as base and acceptor of oxide ions is an acid. Schematically acid-base process may be presented as follow:

$$A + O^{2-} \rightleftarrows B(\equiv A \cdot O^{2-}). \tag{2}$$

From the comparison of (1) and (2) it follows that the Lux definition is a particular case of the Lewis one.

Pure Lux acid-base processes including only acid and base take place if there are no more substances (two component or solid phase reactions, *e.g.*, $CaO + WO_3 \leftrightarrow CaWO_4$) but if process (1) occurs in liquid media, it is accompanied with the simultaneous interactions of reaction (1) participants with constituent parts of these liquids possessing acidic (basic) properties. Such interactions lead to the distortion of actual acidic and basic properties of (1) participants.

One of the purposes of the present work is to ascertain the principal features of liquid media as backgrounds for acid-base interactions.

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1. ON TWO TYPES OF SOLVENTS AS BACKGROUNDS FOR ACID-BASE EQUILIBRIA

Recently we analysed possibility to use the solvosystem definition to ionic media [3]. As it is known, this definition provides division of substances into two groups – acids and bases – on the basis of the autoionization of molecular solvent (L) [4]:

$$L \rightleftarrows Kt_L^+ + An_L^-. \tag{3}$$

In this equation Kt_L^+ is the cation particle of solvent 'L' and An_L^- is the anion one. Substances increasing Kt_L^+ (An_L^-) concentration in the solution are acids (bases). However, the practical use of this definition to molecular liquids did not lead to essential progress because of difficulties connected with indication of acidic and basic particles in liquids (especially possessing low dielectric constants) and measuring

their concentrations. Besides, this definition is unavailable for media which are not able to the autoionization.

Naturally, solvosystem definition can not be used for ionic liquids (melts) since there molecules of solvent '*L*' are practically absent. In order to extend frames of the solvosystem definition to the cases mentioned, therefore, it should be somewhat modified.

Further, the term 'acid-base reactions' is referred only to reagents being able to generate Kt_L^+ or An_L^-. It is the second disadvantage of solvosystem concept. According to it, the acid-base reaction

$$H^+ + OH^- \rightleftarrows H_2O \tag{4}$$

can not be considered as acid-base one in aprotic solvents (*e.g.*, DMSO or CCl_4).

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It is obvious that wide variety of different acid-base processes which are studied now requires the introduction of some principles allowing to consider them from the common point of view.

Undoubtedly, it should be taken into account that 'carrier' of acidity (*e.g.*, H^+) or basicity (O^{2-}) is defined primary, the second step is the solvent classification by ability to acid-base dissociation with the formation of preliminary defined acid (base). In connection with the said before, it should be mentioned, that the autoionization (3) is a particular case of acid-base autodissociation of constituent parts of the solvent, namely, molecular solvent which is able to ionisation. Ionic solvents may contain complex ions, which are able to partial dissociation with the formation of Lewis acid and base, such a case may be illustrated by the following equilibrium in molten sodium fluoroborate [5]:

$$BF_4^- = BF_3 + F^-, \quad pk = 1.8. \tag{5}$$

Here BF_3 is the acid of the solvent, F^- is the base. Since BF_4^- molar fraction in the mentioned melt remains unchanged ($N \sim 1$), the product $[BF_3] \cdot [F^-]$ is the constant describing acid-base properties of this melt as a medium for BF_3-acidity or F^--basicity.

In conclusion, we should to mention another type of solvents, which are unable to the dissociation with the formation of acidity (basicity) 'carrier'. An example of this type solvents may be found above, DMSO or carbon tetrachloride as media for the proton acidity. Such

solvents exist among ionic media, too. Chloride melts are often used as backgrounds for oxoacidity reactions (2) but they are unable to generate O^{2-}. The effect of such solvents consist, mainly, in partial fixation of 'acid' or 'base'.

So, let us define 'inner' acid-base dissociation (autodissociation) of solvent and criteria lies in the basis of the solvent classification [6]:

- Acid-base autodissociation of a solvent is any (non-Red-Ox) process of heterolytic dissociation of its constituent parts (molecules or ions) leading to the formation of Lewis acid and base.
- A solvent is referred to I type (II type) media if a process of its constituent parts acid-base autodissociation results (does not result) in formation of the corresponding acidity/basicity 'carrier'.

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Principal features of I and II type solvents as background for acid-base equilibria are schematically pictured in Figure 1. It may be seen that there are limitations of acid (base) strength caused by the interactions of constituent parts of the solvent with the 'carrier' of acidic (basic) properties.

Solvents of the first type (Fig. 1, bar 1) are characterised by sharp acidic and basic regions, since they possess neutral point where concentration of the acid and the base of solvent are equal one to another. Since these concentrations are reciprocally dependent *via* $pK_{l,i}$ acidic (basic) properties of these solvents may be described both

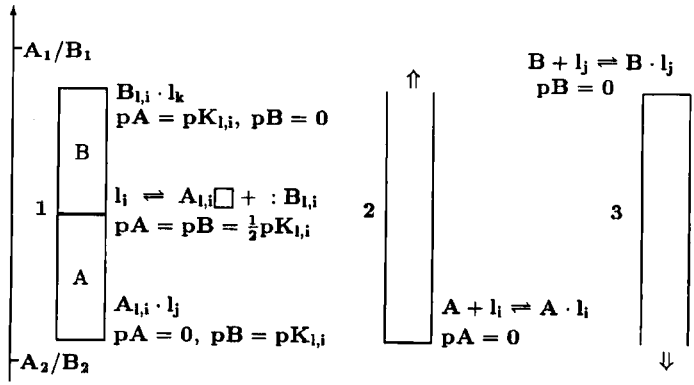

FIGURE 1 Forms of acid-base intervals in solvents: 1–of I type, 2–of II type at a defined acidity 'carrier', 3–of II type at a defined basicity 'carrier'.

by acidity and by basicity indices. For this type of solvents acid-base intervals are two-side limited.

Processes taking place in a I type solvent can be described as follows:

$$L \rightleftarrows \sum_i l_i \tag{6}$$

($L = L$ is assumed, too), and

$$l_i \rightleftarrows A_{l,i} \cdot l_j + B_{l,i} \cdot l_k \tag{7}$$

where l_i, l_j and l_k are constituent parts of a solvent (charge is unspecified), $A_{l,i}$, $B_{l,i}$ are acid and base of a solvent. Processes taking place in solutions of an acid or a base may be presented as:

$$A_1 + L \rightleftarrows B_1(A_1 \cdot B_{l,i}) \cdot l_k + A_{l,i} \cdot l_j (\text{solvo-acid}) \tag{8}$$

$$B_1 + L \rightleftarrows A_1(B_1 \cdot A_{l,i}) \cdot l_j + B_{l,i} \cdot l_k (\text{solvo-base}) \tag{9}$$

where A_1 and B_1 is a conjugated acid-base pair. Strength of acids and bases in media of I type should be limited by corresponding properties of $A_{l,i} \cdot l_j$ and $B_{l,i} \cdot l_k$, respectively. It corresponds to complete shift of Eqs. (8) and (9) to the right. In particular, acid-base pair A_1/B_1 which position is out of acid-base interval of solvent 1 (Fig. 1) should be subjected to the complete transformation in conjugated acid (A_1) in this solvent of I type. Similarly, acid-base pair A_2/B_2 is completely transformed into base B_2.

Let us illustrate these features on examples of I type solvents. Water, H_2O, is referred to solvents of this type for proton acidity, since its dissociation according to the equation reversed to (4) results in formation of H^+. Both pH and pOH (14-pH) indices are appropriate for the description of acid-base properties of the solutions. The neutral point is placed at $pH = pOH = 7$. $pH < 7$ determines the acidic region and solutions with $pH > 7$ are basic ones. The examples of levelling acidic and bases properties are presented by such equations:

$$HClO_4 + H_2O \rightarrow ClO_4^- + H_3O^+, \tag{10}$$

$$H^- + H_2O \rightarrow H_2 \uparrow + OH^-(\cdot H_2O). \tag{11}$$

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Equations (10) and (11) mean that in aqueous solutions there are no acids (bases) more strong than H_3O^+ (OH^-).

Nitrate ionic solvents, such as KNO_3-NaNO_3 as background for oxoacidity may be described by a similar way. Their ionisation is practically complete, one of constituent parts (NO_3^-) is able to dissociation with the formation of oxide ions:

$$NO_3^- \rightleftarrows NO_2^+ + O^{2-}, \quad pK \sim 31 \text{ [7] at } 225°C, \tag{12}$$

this characterised KNO_3 as a solvent of I type. It is obvious that acid-base equilibria may be described by pO and $pNO_2^+ = 31 - pO$ indices. The neutral point is placed near $pK/2 = 15.5$, the acidic region is lies at $pO > 15.5$ and the basic one – at $pO < 15.5$. As for the limitations of acidity (basicity) in this solvent it should to present the following equations:

$$2CrO_3 + NO_3^- \rightarrow Cr_2O_7^{2-} + NO_2^+, \tag{13}$$

$$O^{2-} + nNa^+ \rightarrow Na_nO^{n-2}, \tag{14}$$

from (15) it is seen that properties of bases are limited by the interactions of oxide ions with the melt cations. Levelling acidity in molten nitrates as solvents of the I type was stated at first in [5, 8] at the analysis of oxoacidity studies in molten KNO_3.

A solvent of II type is able to dissociation according to (6). But formed constituent parts do not undergo to the following heterolytic dissociation with the formation of acidity or basicity 'carrier'. There is one-side levelling of acidic properties according to the reaction

$$A + l_i \rightleftarrows A \cdot l_i \tag{15}$$

if the 'carrier' of acidic properties is defined, for bases the levelling occurs similarly – acid-base pair A_2/B_2 is completely transformed into base B_2, Figure 1 bar 2, but there is no limitation of basicity, *i.e.*, pair A_1/B_1 is not subjected to the solvolysis (here the absence of a subscript near 'A' means that the acid can not arise because of autodissociation processes in the pure solvent). To illustrate this case let us consider DMSO as a background for protic acidity. Pure DMSO do not contain protons, therefore, H^+ concentration in the pure solvent is dependent on thoroughness of its purification and may vary in wide

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interval, so, in contrary with water, pH in this solvent is not connected with the base concentration. It is obvious that the interaction of strong acids with DMSO results in the formation of adducts $DMSO \cdot H^+$. The base strength is not limited.

All the said in the previous paragraph is proper to the case of chosen basicity 'carrier' (Fig. 1 bar 3), where pair A_1/B_1 is transformed in conjugated acid, A_1, there is no acidity levelling (pair A_2/B_2 position is into the acid-base interval). Only pB index may be used for the interaction description.

In conclusion, it should be noted that interval boundaries serves as essential properties of any solvent since they predict the possibility of performing of different acid-base processes.

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2. EFFECT OF SOLVENT COMPOSITION ON ITS ACID-BASE PROPERTIES

2.1. Autodissociation Products of Mixtures 'Electronodeficite Acidic Halide – Alkaline Halide'

As it was mentioned above the Lewis definition may be used for the description of interactions in ionic melts with complex anions being able to the heterolytic dissociation. Processes reversed to (1), *i.e.*, the acid-base dissociation of A:B adducts (ions) in some solvents are considered as acid-base equilibria of these solvents.

Alkaline chloro-aluminate melts containing the excess of $AlCl_3$ *vs.* the stoichiometry are promising solvents for preparing sub-ions, *e.g.*, $Cd^+(Cd_2^{2+})$, Bi^+, Bi_5^{3+} [9, 10], the excess of acid ($AlCl_3$) favours their formation. Tremillon and Letisse [11], Torsi and Mamantov [12, 13] studied the acid-base properties of molten mixtures $AlCl_3-MCl$ (M = Li, Na, K, Cs) with $AlCl_3$ concentration exceeding 50 molar% in the temperature range 175–400°C. Equilibrium molalities of Cl^- were determined by a potentiometric method with the use of a chloride-reversible electrode. The solvents were shown to be able to the acid-base dissociation according to the following equation:

$$2AlCl_4^- = Al_2Cl_7^-(AlCl_3 \cdot AlCl_4^-) + Cl^-, \quad pK, \qquad (16)$$

in the said melts chloride-ion donors were bases and substances increasing $AlCl_3$ concentration were acids. The pK values have been found to decrease with the temperature (from 7.1 to 5.0 at temperatures 175 and 400°C, respectively, Na-based melt [12]) owing to decrease of acidic chloride complex stability. In the sequence $Li \rightarrow Na \rightarrow K \rightarrow Cs$ (at 400°C) pK of reaction (16) were 3.8, 5.0, 5.8, 7.4, respectively [13].

Taking into account the said above all the melts mentioned are I type solvents for $AlCl_3$-acidity or Cl^--basicity. The upper limit of acidity is equal to that of the complex in the right side of (16). According to (16) the basicity in this melt is limited by the properties of Cl^-, or more exact, its complexes with alkaline metal cations. We found that the pK changes may be explained from the point of view of 'hard' and 'soft' acids and bases [14–16] – Li–Cl complexes should be more stable than Cs–Cl ones as formed by 'hard' base (Cl^-) and 'more hard' acid (Li^+).

Dioum, Vedel and Tremillon [17] investigated molten $KGaX_4$ ($X = Cl, I$) as backgrounds for acid-base processes. The following acid-base equilibria in the pure solvents have been found to exist:

$$2GaCl_4^- = Ga_2Cl_7^-(GaCl_3 \cdot GaCl_4^-) + Cl^-, \quad pK = 4.25 \pm 0.05, \quad (17)$$

$$GaI_4^- = GaI_3 + I^-, \quad pK = 2.6 \pm 0.05. \quad (18)$$

The pK changes in melts based on different halide ions may be explained in the frames of the Pearson concept, too. Ga^{3+} is referred to 'hard' acids and Cl^- is the 'hard' base, therefore, adduct Ga-Cl should be more stable than Ga-I one as formed by 'hard' acid and 'soft' base (I^-). Therefore, pK of (17) should exceed pK of (18), as this actually take place.

So, acid-base intervals for molten complex halides are relatively narrow, their changes at different cation or anion composition of the melts are in a good agreement with the Pearson concept [14–16]. Practically, varying 'halide basicity' of such melts (*i.e.*, equilibrium concentration of the halide ions) is possible in the range 2–4 logarithmic units, although even such changes are enough to the obtaining of some unstable compounds with the intermediate oxidation degrees we mentioned above [9, 10].

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2.2. Oxobasicity Indices as a Quantitative Characteristic of Molten Solvents and Methods of Their Determination

Acid-base intervals in solvents of I type for oxoacidity are not widely studied. The beside of mentioned work [7] it should be mentioned paper [18, 19] which data allow to estimate acid-base product of $K_2SO_4-Li_2SO_4-Na_2SO_4$:

$$SO_4^{2-} \rightleftarrows SO_3 + O^{2-}, \tag{19}$$

as 10^{-14} at 550°C. Unfortunately, there are no data clearing the effect of melt composition on acid-base properties of these solvents.

In contrary, solvents of II type – alkaline metal halides and their mixtures – are considerably studied in this relation that allows to discuss their acid-base properties. These melts do not contain oxygen ions as constituent part of the melt, detected equilibrium oxide ion concentrations in 'pure' melts are random, usually they are within $pO = 3 \div 4$ for the melts prepared from the reagents of high purity.

Let us consider assumptions lying in the basis of the acidity studies. The initial step of estimations of relative acidic properties of alkaline halide is the choice of the 'standard melt' and the 'standard equilibrium'. The equimolar mixture KCl–NaCl at 700°C was chosen as the 'standard melt' [20], probably, owing to maximal number of studies performed in this melt.

Assumptions to choose the 'standard equilibrium' are clear from Figure 2. The interaction (2) in the molten KCl–NaCl is described by a definite free energy (ΔG^*), or equilibrium constant (K^*). In melt

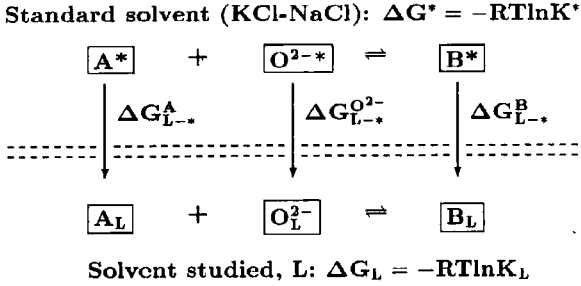

FIGURE 2 The principal scheme of a Lux acid-base interaction and constituents determining the effect of melt composition on it.

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studied corresponding magnitudes are equal to ΔG_L and K_L. ΔG (K) change is the sum of free energies of resolvation for A, O^{2-} and $B-\Delta G^{A}_{L-*}$, $\Delta G^{O^{2-}}_{L-*}$ and ΔG^{B}_{L-*}, respectively. If ΔG^{A}_{L-*} and ΔG^{B}_{L-*} or, more exact, $\Delta G^{A}_{L-*} - \Delta G^{B}_{L-*}$ are close to 0, than all the ΔG (K) change may be attributed to $\Delta G^{O^{2-}}_{L-*}$, which is caused mainly by the differences in acidity between the melts studied and the 'standard'. It is obvious that parameters of acidity based on $\Delta pK \equiv -\log(K_L/K^*) = (\Delta G_L - \Delta G^*)/2.3RT$ may be used as a measure of acid-base properties of ionic melts. These parameters are described the shift of oxoacidity intervals for solvents of II type.

One of the first attempts to estimate relative acidic properties of ionic melts was made by Tremillon *et al.* [20]. The estimations were based on studies of the following equilibrium:

$$H_2O_{gas} + 2Cl^- \rightleftarrows 2HCl_{gas} + O^{2-} \qquad (20)$$

in different chloride mixtures. Here partial pressures of H_2O (p_{H_2O}) and HCl (p_{HCl}) are known and the oxide ion concentrations are calculated on the basis of calibration data. The equilibrium constant of (20) may be represented as:

$$K_{(20),L} = (p^2_{HCl} \cdot N_{O^{2-}})/(p_{H_2O} \cdot N^2_{Cl^-}) \qquad (21)$$

where $N_{O^{2-}}$ and N_{Cl^-} ($\equiv 1$) are molar fractions of oxide- and chloride-ions, respectively. Introduced in [20] oxoacidity function, Ω, may be expressed as:

$$\Omega = 14 + \log(p^2_{HCl}/p_{H_2O}) = 14 - pK_{(20),L} + pO^{2-}. \qquad (22)$$

Low partial pressures of water and HCl (these gases may be considered as ideal) should determine good availability of (20) for practical purposes.

However, Eq. (20) can be practically studied only in chloride melts that limits Ω usage. As it was mentioned in [20, 21] Ω might be used for the prediction of oxide solubilities in molten halides, but estimations for *e.g.*, KCl–LiCl melt [22] showed, that acidity function obtained using (20) essentially exceeds actual value obtained from the solubility data. It may be caused by deviations of water vapour solubility in melts from the Henry law because of formation of H-bonds.

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The analysis of melt acidity effect on acid-base equilibria allowed us to propose the oxobasicity indices, pI_L, for estimations of equilibrium constants in ionic melts [22]. This parameter is equal to difference in pO units between standard ($m_{O^{2-}} = 1$) solutions of strong bases in the studied and 'standard' solvent. This index may be calculated from oxide solubility data and from data on equilibrium constants of homogeneous acid-base reactions, from these data it is obtained as the difference between pK in the said solvents. So, for homogeneous equilibria the oxobasicity index may be calculated as follows:

$$pI_L = pK_L - pK_{KCl-NaCl}. \tag{23}$$

The usability of oxide solubility data, *i.e.*, solubility products of oxides in a various ionic melts:

$$MeO \downarrow \rightleftarrows Me^{2+} + O^{2-}, \tag{24}$$

is apologised by the following reasons. From (24) it is clear that ΔG_{MeO} as referred to the solid phase is not dependent on the solvent composition and it is constant at a definite temperature, the change of $\Delta G_{O^{2-}}$ is in question and described by the oxobasicity index. Metal cations, Me^{2+}, in ionic melts exist as complexes with the melt anions, *i.e.*, $Me^{2+} \cdot nX^{m-}$. Therefore, $\Delta G_{Me^{2+}}$ is dependent on anionic composition of the melt. It may be assumed that the mentioned value is practically constant for melts with the same anion composition (*e.g.*, for chloride melts where $N_{Cl^-} = 1$). This assumption make possible estimations of oxobasicity indices for melts with the same anionic composition according to the following equation:

$$pI_L = pP_{KCl-NaCl} - pP_L. \tag{25}$$

The diagram of chloride melt acidities built on the oxobasicity index values from [22–29] is presented in Figure 3. It should be noted the values obtained from solubility and homogeneous reaction data are in good reciprocal accordance. The latter values are appropriate to estimations of equilibrium constants in ionic solvents from known values of the constants in molten KCl–NaCl and the corresponding oxobasicity index.

We performed a series of oxide solubility studies in melts based on alkaline and alkaline earth metal halides – KCl–NaCl(0.5 : 0.5) [23],

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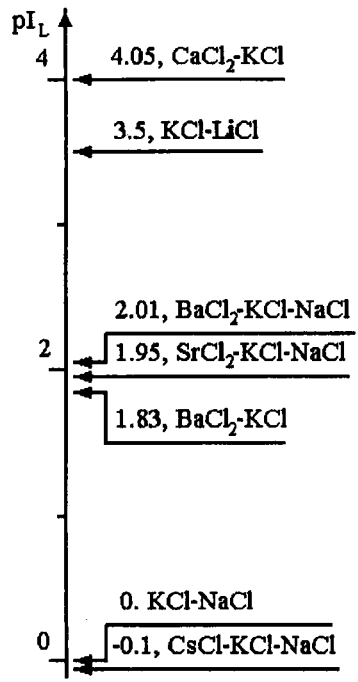

FIGURE 3 A scale of acidity (oxobasicity indices) of different alkaline–alkaline earth chloride melts at 700°C.

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KCl–LiCl (0.41 : 0.59) [22, 24], CsCl–KCl–NaCl (0.455 : 0.245 : 0.30) [25, 26], $BaCl_2$–KCl (0.26 : 0.74) and $BaCl_2$–KCl–NaCl (0.43 : 0.29 : 0.28) [27], $SrCl_2$–KCl–NaCl (0.22 : 0.42 : 0.36) [28], $CaCl_2$–KCl (0.235 : 0.765) [29]. The introduction of 'oxobasicity indices' as a measure of relative acidic properties of melts allows us to make some additional conclusions for the melts reported before [22].

The solvents studied in [22–29] can be divided in 3 groups with close oxobasicity indices: the first one includes alkaline metal halide mixtures without Li^+, their pI_L are practically equal to 0. Alkaline halide melts with addition of $BaCl_2$ or $SrCl_2$ belong to the second group and are characterised by $pI_L \sim 2$. And the third group melts – KCl–LiCl and $CaCl_2$–KCl possess most acidic properties from the ionic solvents studied.

The studies of low-acidic melt CsCl–KCl–NaCl [25, 26] showed that oxide solubilities at 700°C were practically coincident with

corresponding magnitudes for molten KCl–NaCl, oxobasicity index obtained from the solubility data was -0.07 ± 0.3, *i.e.*, statistical zero. This fact allowed to propose second 'standard melt' the beside of KCl–NaCl for oxobasicity index estimations. Indeed, a disadvantage of equimolar KCl–NaCl mixture is relatively high melting point –658°C [30] that makes impossible its usage for the practical purposes at lower temperatures (~600°C). The CsCl-based melts may be used down to 480°C, this temperature lies under commonly used ones 500 [31], 575 [32] and 600°C [33, 34]. Since some of these works contain data on MgO solubilities it is of interest to compare relative acidic properties of chloride melts at 600°C. For this purpose it should to recalculate the data of [32] and [33] in molar fractions, that results in values $pP = 7.44 \pm 0.1$ ($CaCl_2$–NaCl) and $pP = 8.15 \pm 0.1$ ($BaCl_2$–KCl–NaCl) *vs.* 12.68 ± 0.1 (CsCl–KCl–NaCl). According to (25) oxobasicity indices for $CaCl_2$–NaCl and $BaCl_2$–KCl–NaCl are estimated as 5.22 and 4.53, respectively. From the consideration of the similar data at 700°C it may be found that for the chloride melts with $CaCl_2$ molar fraction near 0.25 (0.245 for $BaCl_2$–$CaCl_2$–NaCl and 0.235 for $CaCl_2$–KCl) there is some decrease of oxobasicity index at the temperature elevation – from 4.53 to 4.12 *vs.* CsCl–KCl–NaCl. Moreover, the increase of the Ca^{2+} content from 0.245 to 0.5 leads to increase of the oxobasicity index from 4.53 to 5.22, *i.e.*, 0.69, this value is twice larger than logarithm of molar fraction ratio which is equal to 0.31.

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However, let us return to the data obtained at 700°C, just to the second group of the melts (Fig. 3). The main purpose of $BaCl_2$-based melt studies was to estimate the effect of acidic cation content on the oxobasicity index. As it is clear from Figure 3 they are $pI_{BaCl_2-KCl-NaCl} = 2.01$ and $pI_{BaCl_2-KCl} = 1.83$, *i.e.*, the increase of the acidic cation (Ba^{2+}) content causes the strengthening of the melt acidity (and pI_L). We made an attempt to quantitatively estimate this effect by comparing ($pI_{BaCl_2-KCl-NaCl} - pI_{BaCl_2-KCl}$) with $-\log(N_{Ba^{2+}, Ba, K, Na\|Cl}/N_{Ba^{2+}, Ba, K\|Cl})$ where $N_{Ba^{2+}, Ba, K, Na\|Cl}$ and $N_{Ba^{2+}, Ba, K\|Cl}$ were molar fractions of Ba^{2+} in $BaCl_2$–KCl–NaCl (0.43 : 0.29 : 0.28) and $BaCl_2$–KCl (0.26 : 0.74), respectively. The first magnitude is equal to 0.18 and the second one – to 0.21, *i.e.*, these values are practically coincident. This allows to estimate the oxobasicity indices for the melts with the contents of acidic cation

essentially different from those studied according to the following equation:

$$pI_{L_1} = pI_L + \log(N_{Me^{n+},L_1}/N_{Me^{n+},L}), \quad (26)$$

where pN_{Me^{n+},L_1} and $N_{Me^{n+},L}$ are molar fractions of the most acidic cation in non-studied and the studied melts, respectively. The results of oxoacidity studies at 600°C are not subjected to this rule, but it should be mentioned that these were obtained by different investigators. As it follows from Figure 3 $BaCl_2$-based chloride melts possess weaker acidic properties that $SrCl_2$-based ones at the acidic cation molar fraction near 0.25, however this difference is of order of experimental error.

The third group of melts (Fig. 3) includes KCl–LiCl and $CaCl_2$–KCl melts with the oxobasicity indices 3.5 and 4.05, respectively. At this level of oxoacidity we observed some features connected with the levelling acidity. So, Pb^{2+} (with pK = 3.26 in molten KCl–NaCl) and Cd^{2+} cations in the molten KCl–LiCl do not demonstrate acidic properties, their acidity is completely suppressed by acidic properties of Li^+.

Besides having efficient acidic properties, the $CaCl_2$-based melt possesses upper limit of basicity connected with the precipitation of CaO owing to saturation of the solvent by O^{2-} [29]. Similar behaviour of $CaCl_2$-based melts was observed at lower temperatures, too [20, 33].

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