

STUDY OF THE PROCESS OF ION FRACTIONATION IN THE PART OF THE ION MELT

V.Ya. Khentov¹, E.Yu. Shachneva^{1*}, V.M. Gasanov¹, D.E. Kudinova²

¹South-Russian State Polytechnic University, Novocherkassk, Russia

²JSC «Thermo Fisher Scientific», Saint Petersburg, Russia

Abstract. The presented material describes the process of ion fractionation in the separation of part of the ionic melt. Of particular interest in the study is the effect of the imbalance of adsorption of anions and cations. It is considered on the example of potassium chloride, both for aqueous solutions and for ionic melts of a substance. It is assumed that the effect of ion fractionation is determined by their mobility. The results of the study confirm the initial idea of the study that in cumulative drops the content of anions of the substance exceeded the content of cations. It is established that the liquid cumulative drops has special properties. It should be noted that the kinetics of the described process of evaporation of cumulative drops and the kinetics of drops of a bulk liquid differed significantly in the obtained values.

Keywords: Fluid accumulation, ionic melt, fractionation of ions, the ion mobility.

Corresponding Author: E.Yu. Shachneva, South-Russian State Polytechnic University, Novocherkassk, Russia, e-mail: evgshachneva@yandex.ru

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1. Introduction

The phenomenon of ion fractionation is of great importance in the formation of gas-liquid systems and the description of their properties. It is necessary to note the importance of these processes and their role in the interaction of the ocean-atmosphere system, as well as the formation of condensation nuclei and clouds, the chemical composition of precipitation. With cumulative drops, hydrocarbon films, colloidal particles and suspension particles are removed from the water surface, and microorganisms are easily transferred. In the presence of an electrolyte, the process of removing dispersed particles with cumulative drops is enhanced. Bubbling aerosol can create a number of problems that have to be taken into account when conducting a number of technological processes.

The separation of a part of the liquid from the surface of aqueous electrolyte solutions is accompanied by ion fractionation (Hentov, 1979). The composition of cumulative drops has always been enriched with weakly hydrated ions which tend to enter into the composition of the surface layer of the electrolyte solution – gas interface. Partial acidification of the drops ($\Delta\text{pH} \sim 0,1-0,5$) could not fully compensate for the lack of cation in them (Vlasov *et al.*, 1984).

It was found out that the cumulative drops liquid has special properties. It was characterized by a lower surface tension (Hentov *et al.*, 1989; Vlasov *et al.*, 2003), and therefore, by partial ion dehydration compared to a bulk liquid. Cumulative drops wetted the surface of a solid more efficiently (Hentov *et al.*, 1988a; Hentov *et al.*,

1988b). At the final stage of evaporation cumulative drops exploded and dropped excess charge and mass.

2. Experimental

Potassium chloride (reagent grade) was used as a melt. The salt was melted in a platinum crucible, into which, after melting, a quartz capillary was lowered. Bubbling of the melt was carried out with nitrogen by single bubbles. The bubble generation frequency was extremely low. The depth of bubble rise was maintained constant – 1 cm. Drops were captured on a platinum plate, which was located at a distance of 5 cm from the surface of the melt. The plate and the crucible were placed in a quartz tube to exclude the influence of air movement on the flight path of the drops. The size of the drops on the plate was determined by using a microscope at a 7-fold increase. The measurement results were processed using the Rosen – Ramler function (Hentov *et al.*, 1973). The most probable value of the drop diameter was calculated and it was 1.8 mm.

To fix the imbalance of charges at the separation of a part of the ionic melt surface layer, X-ray spectral analysis was used. To determine the relationship between potassium and chlorine according to X-ray spectral studies, a radiation intensity coefficient was found, which is defined as the ratio of potassium radiation intensity to chlorine radiation intensity (Losev *et al.*, 1982).

3. Results and discussion

It should be noted that the obtained lines of the X-ray spectrum of the two-component KCl compound had the form of dispersion curves. Since the surface layer of the liquid of cumulative drops is enriched with electrolyte to a greater extent than the bulk, the redistribution of electron density between the ions of the surface layer and all other ions should be considered during the process of cumulation. It is known that ions with a lower charge are located closer to the liquid – gas surface (Frumkin, 1924). There is another evidence of the imbalance of charges recorded during the evaporation of a drop of sodium chloride solution. The estimate of the ion exit energy from the solution is equal to 21 kcal/mol for the Cl^- anion and 37 kcal/mol for Na^+ cation (Savchenko *et al.*, 1977).

A completely different situation appears when a part of the ionic melt liquid is separated. Therefore, it seemed quite interesting to study the composition of the cumulative drops obtained by the ion melt barbotage.

It should be noted that the obtained lines of the X-ray spectrum of the two-component KCl compound had the form of dispersion curves. Therefore, peak areas were determined with great accuracy by their triangles approximation (Martynov *et al.*, 1972). The peak areas of 7 samples were measured, and the intensity coefficient and the K/Cl ratio were determined by using the method described above (Table 1).

For samples obtained by cumulation of the melt (samples 3-5), the K/Cl ratio approximates to 2. The K / Cl ratio of the condensate samples, obtained from the vapors of the potassium chloride melt, was significantly less than 1, the same result was obtained while evaporating a drop of a sodium chloride solution (Savchenko *et al.*, 1977). As for the melt, a change in the K/Cl ratio from 1 in the reference salt to 1, 12 in the melt indicates the emission of Cl^- ions from the melt into the gas phase. A similar

Cl⁻ emission was observed upon evaporation of a drop of sodium chloride solution (Savchenko *et al.*, 1977).

Thus, in cumulative drops, the potassium content prevailed over the chlorine content. Chlorine was detected in predominant quantities in the condensate of potassium chloride vapors.

Positive and negative ions were recorded in a high temperature pair of inorganic salts (Pogrebnoi *et al.*, 1984). Me⁺ cations and Cl⁻ anions were found in a pair for alkali metal chlorides. Apparently, for the melt, as well as for the solution, the Cl⁻ output energy was also lower than for the Me⁺ cation.

Table 1. Peak areas S_{kalium} (mm²) and S_{chlorine} (mm²), integral potassium intensities I_{K} and I_{Cl} , intensity ratio $I_{\text{K}}/I_{\text{Cl}}$; ratios of potassium and chlorine in K/Cl samples

Sample	S_{kalium}	S_{chlorine}	I_{K}	I_{Cl}	$I_{\text{K}}/I_{\text{Cl}}$	K/Cl
1. Standard salt	865,3	515,8	8653	5158	1,677	1
2. Melt	859,1	454,1	8591	4541	1,890	1,12
3. Drops	324,8	100,7	3248	1007	3,240	1,93
4. Drops	480,4	162,1	4804	1621	2,960	1,76
5. Drops	476,9	161,4	4769	1614	2,950	1,75
6. Condensate on a plate with drops	706,9	443,7	7069	4437	1,659	0,94
7. Condensate from the side of the quartz tube	485,6	432,6	4856	4326	1,120	0,66

The content of anions in cumulative drops of a melt (binary system NaCl – Na₂SO₄ with an equimolar content of components) was studied using the nephelometry method. The amount of singly charged Cl⁻ anion prevailed over the amount of doubly charged SO₄²⁻ anion. This corresponds to the ideas based on the method of mirror images about the predominant incorporation of Cl⁻ ions into the surface layer of the ion – melt – gas interface compared to doubly charged SO₄²⁻ ions.

An increase in the melt temperature led to an exacerbation of the effect of separation of anions (Table 2). Table 2 shows the averaged ratio of Cl⁻ / SO₄²⁻ anions from 10–20 experiments.

Table 2. The ratio of anions Cl⁻/SO₄²⁻ in the cumulative drops for different melt overheating temperatures. The diameter of the quartz capillary is 0.08 mm

Melt temperature, °C	630	720	1100
Ratio of anions Cl ⁻ / SO ₄ ²⁻	1.11	1.26	1.57

It is important to note that for ionic melts as well as for aqueous solutions ion fractionation is observed during the accumulation of liquids. The process of liquid cumulation of an aqueous electrolyte solution can be considered as unsteady. This conclusion can be drawn from a comparison of the formation time of the jet and the relaxation time of the surface of the electrolyte solution. The relaxation time of the surface tension is $0.6 \cdot 10^{-3}$ s, the relaxation time of the surface potential is $0.4 \cdot 10^{-3}$ s (Kochurova *et al.*, 1979). Whereas the formation time of the cumulative jet formed after a gas bubble bursts is shorter than the time it takes to reach equilibrium values of the surface potential and surface tension. This circumstance is the reason for the selectivity of the electrolyte solution cumulation (Hentov & Shakirova, 1978; Hentov, 1987).

In this regard, it is necessary to highlight a number of works describing the processes of cumulation occurring in micro-layers of liquid (Hentov *et al.*, 2014), the main provisions of the theory of deposition and surfacing of solid particles, droplets and bubbles in an isotropic turbulent flow (Kelbaliev, 2015), as well as (Hentov *et al.*, 2014; Hentov *et al.*, 2013), which considers the main mechanisms of aerosol formation and classification of aerosol particles.

Since the viscosity of the ionic melt does not exceed the viscosity of the electrolyte solution, the liquid cumulation of the ionic melt is also non-stationary, which is confirmed by the fractionation of ions during cumulation of the melt. This is also confirmed by high values of electrical conductivity (Hentov, 1987).

Other transport properties of ionic melts and electrolyte solutions can be compared – thermal conductivity, diffusion, ionic mobility, and transfer numbers [20].

Particular consideration is required to the process of fractionation of Cl^- and K^+ ions during the accumulation of KCl ionic melt and KCl solution. During the accumulation of the melt, the K/Cl ratio exceeded 1. In the case of an aqueous KCl solution, this ratio was less than 1 (Hentov & Shakirova, 1978). These results correspond with the ion transport numbers in the melt and aqueous solution (Table 3) (Bagočkii, 2015; Delimarskii, 1978; Rabinovich & Havin, 1991).

An exacerbation of the separation effect (an increase in the $\text{Cl}^-/\text{SO}_4^{2-}$ ratio) with an increase in the temperature of the ionic melt can be explained by a decrease in the melt viscosity and an increase in the mobility of ions.

Table 3. Ion transfer numbers in the melt (830°C) and aqueous 0,1 M solution at room temperature

Ions	Melt [21]	Solution [22]
K^+	0.620	0.490
Cl^-	0.380	0.506

4. Conclusion

Summing up all of the above the following conclusion may be drawn. The described study examines a rather complex process of ion fractionation when a part of the ionic melt is detached. Potassium chloride is used as an example for both aqueous solutions and ionic melts of a substance. The obtained results indicate that the effect of ions fractionation is determined by their mobility. This is evidenced by the exceeding content of anions of the substance compared to the content of cations. It was found out that the kinetics of the described process of cumulative drops evaporation and the bulk liquid drops kinetics significantly differ in the obtained values.

The considered processes of ion fractionation are rather complicated. When studying them, it is necessary to take into account the influence of ion hydration energy, negative surface activity and ion diffusion coefficients. Ion fractionation occurs in the cumulative drops formed during the rupture of gas bubbles on the surface of the electrolyte solution. Film drops are enriched with highly hydrated ions, cumulative drops, on the other side, are enriched with weakly hydrated ions. The effect of ion separation during the formation of cumulative drops is also influenced by a number of physicochemical factors (like gas bubble size, bubble floating depth, bubble generation frequency, drops selection height, electrolyte concentration, temperature, surface-active substance concentration).

All of the above will allow to form a more detailed assessment of the processes of interaction in the ocean-atmosphere system, as well as, to get closer to solving the problems of metal structures corrosion and desalination of salt water.

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