Professor Nikolai IZMAILOV (1907–1961): Scientific career, main results and achievements

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Nikolai Arkadievich Izmailov headed the Department of Physical Chemistry in Kharkov State University (now: V. Karazin National University) from 1944 to 1961.

Kharkov University has got long-standing traditions in physical chemistry [1]. A great Russian chemist, Professor Nikolai Beketov (1827–1911) established the physico-chemical division as early as 1864. In 1865, Beketov delivered the first course of lectures on physical chemistry, and still earlier, in 1860, he delivered lectures on "Special course of organic chemistry and interrelation between physical and chemical phenomena".

At the end of the XIX century and beginning of the XX century, Professors P. D. Khrushchov, V. F. Timofeyev, N. D. Pilchikov, D. P. Turbaba, G. E. Timofeyev, and many other scientists contributed to the field of physical chemistry, mainly in solution chemistry. A number of outstanding chemists elaborated physical chemistry in Kharkov before the World War II. Among them were G. E. Mukhin, A. N. Shchukarev, I. S. Teletov, P. P. Kosakevitch, E. N. Gapon, S. S. Urazovskiy, I. N. Frantsevich, and N. A. Izmailov.

Nikolai Arkadievich Izmailov was born in Sukhumi, in the South region of Russian Empire, on June 22, 1907. He was a typical self-made man. His father died when Nikolai was two years old. In 1917, when the October revolution befell, Nikolai with his family happened to be in Kharkov. He had to support his mother, grandmother, and sister. Hence, at the age of ten he started his battle for survival.

In 1922, he entered the Financial-economic technical school, where he got to know something about chemistry. He took deep interest in this science, and after graduating in 1926 he started instructing chemistry at primary school.

In 1928, Nikolai Izmailov became a PhD student of Kharkov State University (at that time it was called Kharkov Institute of Public Education), and since then his scientific career was realized there.

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Izmailov's first research, connected with sorption of gases, was carried on under the guidance of Professor Kosakevitch [2]. His next study was devoted to the influence of salts on adsorption of organic molecules on water/air interface [3].

Soon Izmailov started his independent research. Since 1934, he worked simultaneously at Kharkov Pharmaceutical Research Institute. The two main directions of his scientific interests were (i) static and dynamics of the sorption from solutions; (ii) the influence of the solvent on dissociation of electrolytes. Both branches of pure chemistry were caused by the needs of applied science.

Izmailov was an inventive thinker, with great scientific insight. In search of new methods for pharmaceutical analysis, he introduced the 'drop-chromatographic method , later called thin layer chromatography (TLC), in the work performed together with Maria Shraiber in 1938 [4]. This finding has been widely recognized [5]. [2]

Another direction of research was devoted to acid-base equilibria. At that time, one of the most promising methods of drug analysis was titrimetry. In the course of his work at the Pharmaceutical Institute Izmailov became interested in utilization of non-aqueous solvents for this purpose. He recognized that water is the most atypical of solvents, and tried to rationalize the origin of the then-novel concept of differentiating influence of organic solvents on acid-base properties [6]. Thereafter, Izmailov was contributing a lot to the physical chemistry of electrolyte solutions. In thirties Izmailov investigated the possibility of application of various indicator electrodes, especially glass electrodes, in organic solvents [7].

In 1937, Izmailov received PhD. degree in chemistry at Kharkov State University. Shortly thereafter, he got down to preparing his ScD Dissertation.

However, its submitting was postponed by the World War II. In October 1941, Izmailov and family were evacuated to Sukhumi, were he stayed for the next three years. This was a period of hard work for needs of defense.

Once the occupation of Kharkov was over in 1943, Izmailov received Government decree to leave for Kharkov and to head the Department of Physical Chemistry. In May 1944, Izmailov with his wife and two children[3] returned.

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[2] In 2007, Professor V. G. Berezkin published a book devoted to the discovery of TLC; this book also contains a detailed experimental reproduction of Izmailov's original work, accompanied by interesting comments.

[3] Izmailov and his wife Alexandra Izmailova (Glukhovtseva) had a daughter Victoria and a son Alexander. Victoria Nikolayevna Izmailova (1930-2002) afterwards worked at Moscow State University, became Professor and a well-known expert in the field of colloid chemistry. Alexander Nikolayevich (1938-1990) was physicist.

The restoration period was hard, because Kharkov was strongly destroyed during 1941-1943. However, Izmailov managed to combine his duties as Head of Department with performing research in the Pharmaceutical Institute and preparing his ScD Dissertation 'The influence of solvents on the strength of acids'. The latter was presented in January 1948 in Ukrainian Academy of Sciences in Kiev. In the same year he became Professor.

The scientific interests of Nikolai Izmailov were centered on the behavior of electrolytes, first of all acids and bases, in solutions. In his Dissertation as well as in his publications during the fifties, he proposed his scheme of dissociation of electrolytes in solutions, which is recognized as probably the most complete [8]. The main point, in respect to acids, was based on the idea of improving the fundamental but somewhat schematic Brönsted's theory by considering the solvation of all the equilibrium species. Just this viewpoint allowed to explain the differentiating action of solvents on the strength of acids, i.e., unequal changes in their dissociation constants [8a, 9].

In the principal review [9], entitled like his Dissertation and recognized as most complete at that time [10], Izmailov presented a comprehensive and lucid classification of non-aqueous solvents according to the character of their levelling and differentiating influence on acids strength. He proposed the following groups of solvents: (1) amphoteric, such as water and alcohols; (2) mixtures of alcohols and dioxane with water; (3) acidic solvents, such as formic, acetic, propionic acids, sulfuric acid and its mixtures with water, and liquid hydrogen halides; (4) basic solvents, such as ammonia, hydrazine, pyridine, etc.; (5) aprotic solvents: benzene, chlorobenzene, etc.; (6) 'differentiating' solvents.

The latter, namely nitriles, nitrocompounds, aldehydes, ketones, amides,[4] had by then been known to differentiate strength of salts due to Walden's papers. Izmailov significantly developed this concept and adapted it to acids and bases, taking into consideration solvation effects. The transfer activity coefficients of ions were divided into two parts. As a result, a general equation was proposed for the difference between the $\mathrm{p}K_\mathrm{a}$ in the organic solvent and in water, which included both the so-called Born term, already used by Brönsted, and the item reflecting other solvation effects.

Actually, this was a unification of electrostatic approaches (Brönsted, Wynne-Jones, Gurney) and 'chemical' theory of solvation (in spirit of Mendeleyev and Kablukov) [12].

[4] In fact, most of these 'differentiating' solvents are now known as protophobic sub-group [11] of dipolar aprotic (according to Parker), or non-hydrogen bond donor (non-HBD, according to Bordwell) polar solvents; acid-base equilibria in protophilic non-HBD solvent dimethyl formamide were studied by Izmailov somewhat later, while the brilliant solvent DMSO became popular only in sixties.

This was a decisive step toward the understanding of the multiplicity of solvent effects. In order to reveal the peculiarities of solvation of molecules, Izmailov compared interaction between acids (carboxylic acids and phenols) and alcohols on the one hand and ketones, nitriles, etc., on the other, using the 'inert' solvents as media. Cryoscopy, IR and Raman spectra were used for revealing the stability and structure of molecular compounds of acids with the 'active' solvents.

Besides, Izmailov underlined the significance of degree of charge delocalization in conjugated anions (i.e., carboxylate and phenolate) with respect to alterations in the strength of corresponding acids in organic solvents [12]; later such ideas grew very popular [13].

These concepts allowed rationalizing the different changes in dissociation constants of acids belonging to the same 'charge type' but to different 'chemical types' on going from water to organic solvents, despite Brönsted's theory; this general effect was stressed on already by Verhoek [14].

In Izmailov's scheme of electrolytic dissociation, the possibility of existence of ion pairs between solvated proton and anion of the acid was foreseen. For example, it was pointed to even in his Dissertation completed in 1947. Accordingly, for dissociation of salts CA the scheme not only took into account solvated species $(C^+A^-)_{solv}$, free solvated ions C^+_{solv} and A^-_{solv}, but postulated also associates of solvated ions, $C^+_{solv}A^-_{solv}$. The latter can be considered as prototype of the so-called solvent-separated, or loose, or long ion pairs $C^+//A^-$ [8d, 15].

Izmailov with his associates continued studying acids, bases, and salts in alcohols, polar and non-polar aprotic (non-HBD) solvents, acidic and basic solvents, mainly by potentiometry; the results of their exhaustive research were presented in a vast series of papers under the title 'Thermodynamic properties of electrolytes in nonaqueous solutions' published in the Russian Journal of Physical Chemistry, as well as in other publications [16]. [5]

Izmailov proposed several new methods for estimating activity coefficients of ion transfer from water to non-aqueous solvents and Gibbs energy of ion solvation and generalized the concept of unique acidity scale in different solvents [12, 16f, 17]. Of course, ever since a lot of new data have been reported [18].

Simultaneously, he elaborated some new methods of acid-base titration and polarography of various substances in organic media [12, 19]. Izmailov also kept on his studies on statics and dynamics of sorption processes, including ion exchange processes [20]. These investigations were devoted mainly to the problems of pharmaceutical chemistry; a technology of obtaining morphine from oil-bearing poppy was also proposed [21].

[5] It is certainly impossible to mention here all the work carried out by Izmailov and his pupils. It must be only noted that Izmailov's publications are well referred to in Chemical Abstracts.

Izmailov also continued his early studies on behavior of glass electrode in different solvents [22]. In 1973, in recognition of his achievements in this field, he was posthumously included into the group of State prizewinners of the USSR. He made a considerable contribution to the theory of physico-chemical analysis [23]. In Ukraine, Izmailov was one of the pioneers in application of radioactive indicators to physical chemistry. The latter were used in the Physical Chemistry Department both for studying solubility and solvation of salts [24] and to gain understanding the mechanism of response of glass electrodes [25].

Izmailov was among the first who used Volta-cells for determination of real solvation energies and activity coefficients of single ions [26]. At the end of fifties, he applied quantum chemistry to estimate proton affinities and ionic solvation energies [27].

The most monumental of Izmailov's contribution was his 'Electrochemistry of Solvents' [12]. This voluminous 958-page book appeared as a result of lectures delivered by the author for students and post-graduates, which were specializing in the field of solution chemistry.

This book was written in Russian, but the most original sections, devoted to the detailed scheme of electrolytic dissociation, differentiation action of solvents, solvation, etc., were completely reviewed in the excellent monograph of Shatenshtein, which was translated into English [28] and thus became available to foreign readers [8a].

A couple of words must be said about Izmailov's scientific style. There was no time to be lost. He would begin his workday at five o'clock a. m. He spent a lot of time for consulting his PhD students and co-workers, and also organized regular sittings of a scientific seminar at the Physical Chemistry Department. Izmailov led an active social life; a set of his publications was devoted to the history of physical chemistry in Kharkov University. Over a period of several years (1948-1953) he was Vice-Rector of the University. During his entire career, Izmailov worked hard, but it must be noted, that he also was quite a sportsman, enjoying swimming, alpinism, and tennis.

Izmailov is the author of over 270 publications; his treatise 'Electrochemistry of Solutions' (1959), honored by the Mendeleyev award, is well known to those working in the field of solution chemistry and is still frequently cited. 31 persons got PhD degree under Izmailov's supervision and 11 of his co-workers later got ScD degree (V. N. Eremenko, A. M. Shkodin, V. D. Bezugliy, V. V. Aleksandrov, E. F. Ivanova, E. V. Titov, Yu. A. Krugliyak, O. M. Konovalov, V. P. Georgievskiy, V. I. Lebed, V. D. Chmil).

In 1955, Izmailov was awarded by the title 'Honored scientist of Ukraine', and in 1957 he was elected to the Academy of Sci. of the Ukrainian Soviet Republic.

On October 2, 1961, Izmailov suddenly died at the moment when he was discussing scientific problems with one of his co-workers.

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