

## Nikolai Izmailov (1907–1961): An appreciation

The International Conference on Modern Physical Chemistry for Advanced Materials was organized primarily to commemorate the centenary of the birth of Prof. Nikolai Izmailov and to pay tribute to his scientific achievements and legacy. Nikolai Arkadievich Izmailov was born in Sukhumi, in the southern region of the Russian Empire, on 22 June 1907. After his family moved to Kharkov (in Ukrainian: Kharkiv), he developed an early interest in chemistry and eventually enrolled as a Ph.D. student at Kharkov State University (at that time, it was called the Kharkov Institute of Public Education) in 1928. He initially conducted research into sorption of gases, under the guidance of Prof. Kosakevitch. Thereafter, he investigated the influence of salts on adsorption of organic molecules on water/air interface. He received his Ph.D. in 1937.

From 1934, conducting his research at the University, he started a joint appointment at Kharkov Pharmaceutical Research Institute, and his independent scientific interests developed along two main directions, namely, static and dynamic properties of sorption from solutions and the influence of the solvent on dissociation of electrolytes. It was here that he collaborated with Maria Shraiber to introduce the “drop-chromatographic method” in 1938, which later became known as thin layer chromatography (TLC). This finding is widely recognized and acclaimed, and continues to play an essential role in everyday laboratory practice. At a time when one of the most promising methods of drug analysis was titrimetry, and in the course of his work at the Pharmaceutical Institute, Izmailov also became interested in using nonaqueous 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 the differentiating influence of organic solvents on acid–base properties. Throughout the 1930s, Izmailov investigated the possibility of employing indicator electrodes, especially glass electrodes, in organic solvents.

In 1944, Izmailov headed the Department of Physical Chemistry at the University. In his Sc.D. dissertation presented in 1948, as well as in his publications during the 1950s, he proposed a scheme of dissociation of electrolytes in solutions, which is recognized as probably the most complete. The main point, in respect to acids, was based on the idea of improving the fundamental but somewhat schematic Brønsted’s theory, by considering solvation of all the equilibrium species. Just this viewpoint rationalized the differentiating action of solvents on the strength of acids (i.e., unequal changes in their dissociation constants). A seminal review published in 1950 bore the title of his dissertation, “The influence of solvents on the strength of acids”, and presented a comprehensive and lucid classification of nonaqueous solvents according to the character of their levelling and differentiating influence on acids strength. He proposed the following groupings of solvents: (i) amphoteric, such as water and alcohols; (ii) mixtures of alcohols and dioxane with water; (iii) acidic solvents, such as formic, acetic, propionic acids, sulfuric acid and its mixtures with water, and liquid hydrogen halides; (iv) basic solvents, such as ammonia, hydrazine, pyridine, etc.; (v) aprotic solvents: benzene, chlorobenzene, etc.; (vi) “differentiating” solvents. The latter category, exemplified by nitriles, nitro compounds, aldehydes, ketones, and amides, had by then been known to differentiate strength of salts due to Walden’s papers. Izmailov significantly elaborated this concept and adapted it to acids and bases, taking into consideration solvation effects. In fact, this significant group of solvents (vi) is now known as dipolar aprotic (A. Parker) or dipolar non-hydrogen-bond donor (HBD) solvents (F. Bordwell).

In order to interpret the  $pK_a$  shifts, the transfer activity coefficients of ions were divided into two parts. As a result, a general equation was proposed for the difference between the  $pK_a$  in the organic solvent and in water, which included both the so-called Born term, already used by Brønsted, and the item reflecting other solvation effects. Actually, this was a unification of electrostatic approaches (Brønsted, Wynne-Jones, Gurney) and “chemical” theory of solvation (in the spirit of Mendeleyev and Kablukov).

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. 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; later, such ideas grew very popular. These concepts enabled the different changes in dissociation constants of acids belonging to the same “charge type” to be rationalized, but to different “chemical types” on going from water to organic solvents, despite Brønsted’s theory, a general effect that had already been stressed by Verhoek. In Izmailov’s scheme of electrolytic dissociation, the possibility of the existence of ion pairs between solvated proton and anion of the acid was foreseen. Indeed, he had even alluded to this in his dissertation completed in 1947. Accordingly, for dissociation of salts CA, the scheme not only took into account solvated species  $(C^+A^-)_{\text{solv}}$ , free solvated ions  $C^+_{\text{solv}}$  and  $A^-_{\text{solv}}$ , but postulated also associates of solvated ions,  $C^+_{\text{solv}}A^-_{\text{solv}}$ . The latter can be considered as a prototype of the so-called solvent-separated, or loose, or long ion pairs  $C^+//A^-$ .

Izmailov and 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. Izmailov proposed several new methods for estimating activity coefficients of ion transfer from water to nonaqueous solvents and Gibbs energy of ion solvation and generalized the concept of unique (unified) acidity scale in different solvents. The most monumental of Izmailov’s contributions was the treatise “Electrochemistry of solvents”, which was published in Russian in 1959. Most of the original sections of this voluminous 958-page work, devoted to the detailed scheme of electrolytic dissociation, differentiating action of solvents, solvation, etc., were completely reviewed in the excellent monograph of Shatenshtein, which was translated into English and thus became available to international readership. This major contribution is well known to those working in the field of solution chemistry and is still frequently cited.

Izmailov also continued his early studies on the behavior of glass electrode in different solvents. He made a considerable contribution to the theory of physicochemical analysis. In Ukraine, Izmailov was one of the pioneers in the application of radioactive indicators to physical chemistry. The latter were used by him both for studying solubility and solvation of salts and to gain understanding of the response mechanism of glass electrodes. Izmailov was among the first who used Volta cells for determination of real solvation energies and activity coefficients of single ions. At the end of the 1950s, he applied quantum chemistry to estimate proton affinities and ionic solvation energies.

The untimely death of Nikolai Izmailov in 1961 was a loss to science, but his prolific output of over 280 publications ensures his place in the records of modern physical chemistry. This appreciation introduces a collection of works that would surely have captured his interest and will serve to honor his memory. A more detailed and personalized account of the man and the times in which he lived and achieved will be published in the September 2008 issue of *Chemistry International* and furnishes a link to a short bibliography listing some of his seminal publications.

**Nikolay O. Mchedlov-Petrosyan**  
V. N. Karazin National University