

Andrej V. Kiselev's contributions to the science of adsorption, molecular interaction and chromatography

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A.V. Kiselev's first scientific investigation was carried under the supervision of Prof. Schilov, when Kiselev was a student of the second year of the High Technical School of Moscow (ref.1), and this certainly influenced his future scientific career which he continued at the Department of Physical Chemistry of Moscow Textile Institute. It was then that his investigations on adsorption (ref. 2,3), structure of silica gel (ref. 4), heats of adsorption and of adsorption forces (ref. 5) appeared. During the World war Kiselev began to work at the Physical Chemistry Department with Prof. B.V. Iliin and in 1943 he set up his Adsorption Laboratory at the Chemical Department of M.V. Lomonosov State University. From the very beginning Kiselev started energetically the organization of this laboratory and his work on the theory of adsorption. It had two directions: the investigation of the structure of highly dispersed porous adsorbents and catalysts, (ii) the investigation of the dependences between both adsorption and adsorption forces energy on the surface, and chemical nature and the structure of the adsorbents as well as on the nature of substances adsorbed. These directions needed unique equipment both for adsorption and for calorimetry. A calorimeter for the investigation of differential heats of adsorption was constructed; its precision was higher than that of the best known calorimeters used for this purposes (ref. 6,7), with time it attained perfection (ref. 8).

ADSORPTION AND SURFACE CHEMISTRY

Numerous investigations of adsorbents, catalysts and other highly disperse materials led to the creation of a method, which was called "adsorption-structural method" (refs. 9,10). At this time Kiselev organized a group at the Institute of Physical Chemistry of the Academy of Sciences, which became later a laboratory of surface sciences.

Great work was done in the field of adsorption thermodynamics, adsorption calorimetry and the investigation of the adsorption both of vapours and dissolved substances. The adsorption on real adsorbents established new phenomena and allowed one to systematize the great experimental data accumulated and to create a rational classification of structural types of adsorbents (ref. 11). This facilitated the possibility of governing the structure of adsorbents during their synthesis (ref. 12).

According to this classification the adsorbents were divided into (i) non-porous, (ii) highly and homogeneously porous, (iii) finely and homogeneously porous, and (iv) mixed. The use of the adsorption-structural method allowed one to investigate the structure of different adsorbents and catalysts and their influence on adsorption properties. Kiselev wrote: "In practice it is necessary to choose correctly the structural type, optimal for a given sorption process or catalytic reaction". The adsorption structural method must be developed in close connection with other structural methods: microscopic, electron-microscopic, spectroscopic, thermodynamic and others.

The second direction concerned a theoretical investigation of the thermodynamic processes. It was a unique thermodynamic system of adsorption investigation of gases, vapours, pure liquids and solutions on solid surfaces. It made possible the use of absolute adsorption values/relative to the surface unity (ref. 13). It allowed one to compare adsorption properties of different adsorbents, including crystals and porous bodies of the same chemical nature (ref. 14,15).

It was found that the adsorption potential energy rises with pore narrowing and is connected with the chemical nature and molar volume of the molecules adsorbed. It was of great theoretical importance because it depended upon the nature of adsorption forces (ref.16).

The wealth of experimental material accumulated allowed one to propose a theory of corpuscular structure of xerogels (ref. 17,18,19). The form and packing of skeleton particles are of great importance. A complex adsorption and electron-microscopic investigation of different adsorbents with corpuscles of globular and crystalline structure allowed one to obtain the picture of their structure and to examine the changes by different treatment.

A general thermodynamic theory of capillary-condensation hysteresis for adsorbents of globular structure was developed. The heat maxima on adsorption curves in vicinity of the completion of the capillary condensation in homogeneous porous adsorbents were carefully examined and a detailed theoretical interpretation of this phenomena given (ref. 21,22).

At the same time a detailed investigation of adsorption from solution was made (ref.23,24). It was found that the limiting adsorption depends upon the pore narrowing and the structure of the molecules adsorbed; a capillary stratification phenomenon was discovered (ref.25).

Surface chemistry and intermolecular interaction with the adsorbates connected with it were paid much attention in the works of Kiselev and co-workers. In his first paper in 1936 (ref.4) on the structure of silica, a chemical interpretation of the "structural water" of silica was given. It was pointed out that the skeleton of silica is covered with hydroxyl groups and a scheme of dehydroxylation was given. This scheme was confirmed by spectroscopic investigations of Terenin and co-workers, and until now they are generally accepted.

Besides thermal dehydration of the surface A.V. Kiselev with co-workers had other types of chemical surface modifications investigated and their influence on adsorption properties of different substances (ref.26,27). Their results were based on poisoning and regeneration of silica surface by adsorption of methyl alcohol vapours. The poisoning of the surface was connected with the formation of surface-ethers, which caused a sharp change in the heat of adsorption.

The influence of surface dehydration of silica on its adsorption properties was the subject matter of his numerous works of that time (ref. 29,30,31). It was stated that the change in hydroxyl surface coverage influences the form of the isotherm. It was especially noted in the case of substances able to form hydroxyl bonds with hydroxyl groups of silica - CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and even C_6H_6 . Kiselev came to the conclusion that the form of the isotherm strongly depended upon the chemical state of the surface (ref.32).

A.V. Kiselev and his co-workers were the first to use chemical modification of the surface to change their adsorption properties in the necessary direction. It was shown that the chemical modification of the surface is a powerful factor which can change the adsorption values ten fold, change the form of the isotherm, the sign of the net heat of adsorption and destroy the capillary condensation. These works are immediately connected with the possibilities of creation new materials. By selection of adsorbents it is possible to regulate the selectivity of gas-adsorption columns, even in the case of non-specific adsorbed components (ref.33).

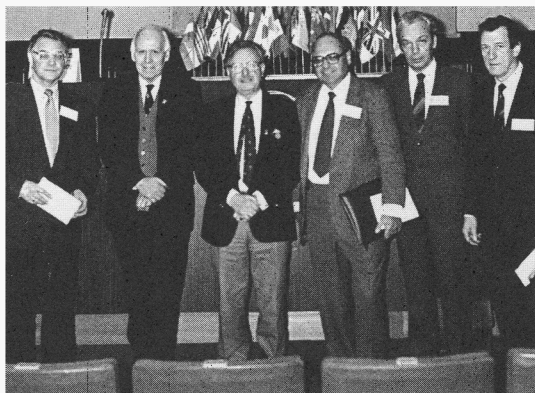
By the method of quasichemical equilibria equations of mono- and poly-molecular adsorption were set up, taking into consideration both vertical and horizontal interactions adsorbate-adsorbate and it was shown that using these equations it is possible to describe satisfactorily all the cases of adsorption on adsorbents known with homogeneous surfaces (ref.34,35,36).

CHROMATOGRAPHIC SCIENCE AND MOLECULAR INTERACTIONS

Deep knowledge of adsorption processes allowed A.V. Kiselev to study the chromatographic processes, which allowed him to create a new direction - gas-adsorption chromatography. First of all it was necessary to make adsorbents for chromatography, because adsorbents used before could not satisfy the needs of chromatography. These adsorbents were to have small surface area and to be homogeneous enough to satisfy the basic requirement of chromatography "catch, keep and let go" (ref.37).

The main problem of the laboratory (at this time it consisted of about 50 persons) was the investigation of molecular interactions and specificity in adsorption and chromatography and on their bases; the creation of new adsorbants and supports.

A classification of molecules and adsorbents according to their capacity of unspecific and specific interaction was given (ref.38). This classification was based on a different character of peripheral electron density distribution on bonds and links of molecules. It is convenient to divide molecules into groups A, B, C and D, adsorbents being divided into three types. This classification is shown on Table 1. The surface chemistry determines the nature and energy of the interactions with the adsorbate. So, type I consists of nonspecific nonpolar adsorbents/saturated hydrocarbons - crystalline, polymers or densed monolayers on the support surfaces and also of chemically inert surfaces of atom lattices, for example the basal face of graphite, BN/. Type II - specific adsorbents with positive charges localised on the surface and other electron-acceptor centers. These are for example salts as BaSO_4 or aluminosilicates, which have positive charge in the cations of small radius promoted on the surface and negative - in big complex anions. Here belongs also silica with hydroxylated surface. To the III type belong specific adsorbents having negative charges on the surface: crystal facet, constructed especially by anions or surfaces of porous polymers with nitril, carbonyl or epoxy-groups. Adsorbing surfaces of the III type can be obtained by disposition of dense monolayers of molecules of the group B on the surface of the adsorbent-support (for example nitrile groups).



Members of International Scientific Committee of Kiselev Symposium: from left to right : W. Engewald (GDR); D.H. Everett (UK); K.S.W. Sing (UK; also Chairman of IUPAC Commission on Colloid and Surface Chemistry including Catalysis); R.A. Pierotti (USA); Yu.S. Nikitin (USSR); O.G. Larionov (USSR; also Symposium Chairman)



A.V. Kiselev delivering a lecture in 1966



Group Photograph of (mostly) Invited Lecturers and Members of the Organizing Committee at Kiselev Memorial Symposium

Table 1. Capacity for Nonspecific and Specific Interactions

Molecules	Adsorbates (see footnote for explanation to types)		
	Type I	Type II	Type III
Group A: with spherically symmetrical shells of σ -bonds (inert gases, saturated hydrocarbons)	Nonspecific interactions governed mainly by dispersion forces.		
Group B: electron density locally concentrated on bonds or links, π -bonds (N_2 , unsaturated and aromatic hydrocarbons) and lone electron pairs (esters, ketones, tertiary amines, nitriles, etc.)	Nonspecific interactions	Nonspecific + specific interactions	
Group C: with positive charge localized on peripheral links (e.g. some organometallic compounds).			
Group D: with functional groups having locally concentrated electron density and positive charge on adjacent links (molecules with OH and NH groups).			
Type I : without ions or active groups (GTCB, BN, surfaces bearing only saturated groups)			
Type II : with localized positive charges (acidic OH, exchangeable cations of small radius)			
Type III : with localized negative charges (esters, nitrile and carbonyl groups, exchangeable anions of small radius)			

The geometric and chemical modification of the surface allows one to obtain the surface needed, as well as mosaic, combining properties of different types of adsorbents.

The combination of different surface chemistry of the adsorbents with different geometry allows one to optimize the adsorption processes of chromatography and on the other hand, to investigate molecular interactions.

A.V. Kiselev was of the opinion that if the adsorption properties of the component of the mixture and the adsorption isotherms are known, it is possible to predict the separation. It is possible to answer the question why some hydrocarbons are adsorbed better or worse than others, how the nature of the adsorbent influences its adsorption properties - for instance the chemical and geometric modification of the surface, their pore structure (ref.40).

The adsorption investigation helped the development of the theory and practice of chromatographic separation. In 1967 appeared the book by A.V. Kiselev and Y. Yashin "Gas-adsorption chromatography" (ref.38). It was the first book in the world literature in this field. The book was translated into German, English and French. The book deals with problems of gas-adsorption chromatography based on molecular interactions in adsorption. It is shown that gas-adsorption chromatography can be utilized for physical-chemical investigations of the surfaces and their properties. The possibilities of gas-adsorption chromatography in analytical purposes are mentioned.

Detailed investigation of intermolecular interaction by adsorption allowed one to find atom-atom potential functions of intermolecular interactions (ref.36) which manifest themselves most simply in gas-solid chromatography on the adsorbent with homogeneous surface such as graphitized carbon black (GTCB). This work allowed Kiselev to introduce a novel method for structural characterisation of molecules, called chromatocopy or chromatostructural analysis (ref.41). This direction was especially liked by Prof. Kiselev. According to this method if the structure of the adsorbent (GTCB) and the structure of the molecule adsorbed are known it is possible to calculate by molecular statistics the Henry's constants K_1 . The theoretical values of Henry's constants, calculated this way, are then compared with K_1 values measured at different temperatures by the chromatographic method. This permits us to introduce the correction factors into the parameters of atom-atom potential functions.

Using this method it is possible to identify isomer substances of known structure on the chromatogram. On the scheme given below this question can be solved by the movement from the left to the right. The reverse problem is to find experimentally Henry's constant for molecules of unknown structure and determine structural parameters on which the Henry's constant mainly depends. On the scheme this is represented by the movement from the right to the left. The possibilities of gas chromatography on GTCB can be illustrated by some examples.

The similarity of physical properties of structural isomers often makes difficult their separation and identification with gas liquid chromatography. Especially great difficulties arise in the case of cyclic and polycyclic hydrocarbons with numerous structural isomers. On the chromatogram we see a mixture containing all isomers of perhydroanthracene and perhydrophenanthrene. A great selectivity of GTCB to structural isomers allowed us to separate and identify them. The identification could be done by molecular-statistical calculation of the retention volume (the straight problem). The reverse problem - the structure of molecules from chromatographic data (retention volume from zero sample size). This problem is especially suitable for rigid and quasi-rigid molecules. An example of the use of chromatography is the determination of the angle of alternate declination of methyl groups from the plane of benzene ring in the molecule of hexamethylbenzene and the evaluation of the parameters of the potential function of inner rotation in the molecules of biphenyl and methylsubstituted biphenyls and also the determination of the structure of tetraline (ref.42).

At present there are found potential functions of interaction with GTCB not only for carbon in different electronic configuration determined but also for oxygen, nitrogen, sulphur and selenium. Chromatography can be a useful addition to existing methods for the investigation of the structure of molecules, particularly complicated molecules having many isomers as in the case of steroids. Chromatography on specific adsorbents of known structure (in particular on zeolites) permits us also to solve some questions concerning the electron configuration of molecules (dipole moments or quadrupole moments).

A.V. Kiselev widely used the adsorption effects in liquid chromatography to increase the selectivity of separation and stability of the column. The development of the modification of the surface of the adsorbent led to the wide use of the adsorption-adsorption chromatography, based on co-utilization of adsorption and solubility or processes close to solubility. During his last years Kiselev and co-workers intensively developed the liquid-adsorption chromatography. This development is also connected with the foundation of the molecular basis of selectivity for liquid chromatography. In 1979 appears another book by A.V. Kiselev and Y. Yashin "Adsorption gas and liquid chromatography" (ref.43). In the book we find the novel molecular theory of adsorption chromatography. Great attention is paid to the influence of the nature and geometrical structure of the adsorbents on the selectivity and efficiency of chromatographic separation. The ways of regulation of efficiency and selectivity of adsorbents and optimisation of the separability of adsorption columns, molecular interaction in adsorption chromatography being considered are also to be found there.

It is impossible just to mention all the numerous achievements of A.V. Kiselev, his managerial activity, his workability. He was extremely devoted to science, but together with this the scope of his interests outside it was extremely wide; he was keen on arts, architecture, history, he liked nature and travelling - he always preferred the so-called "active rest", that is walking, boating or motoring excursions, and he never failed to carry away his fellow-travellers by telling them of the sights and the history of the places they chanced to come across.

Professor A.V. Kiselev was the author of 8 monographs and of more than 900 papers. He was on the Editorial Advisory Boards of Chromatographia, Kolloidnyi Zhurnal, Advances in Colloid and Interface Sciences and Zeolites.

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