## Enthalpic Pair Interaction Coefficients in Aqueous and Nonaqueous Solutions

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Interpretation of calorimetric data in terms of the McMillan–Mayer theory of solutions yields enthalpic pair interaction coefficients of several solutes both in water and in N,N-dimethylformamide(DMF) as solvent.

In the solvent water, the interaction coefficients refer mostly to interactions between DMF with several electrolytes and nonelectrolytes. Attention is given to the influence of charge, size and shape of the solute molecules. Simple electrolytes have negative pair interaction coefficients with DMF, while those for hydrophobic electrolytes and non-ionic solutes are positive. Increasing size of the alkyl groups contributes in a positive sense to the interaction coefficients. Their value is decreased by introduction of hydroxy groups or a reduction of the flexibility of the alkyl chains. It appears that the different functional groups in the solute molecules contribute independently towards the values of the interaction coefficients, so that it is possible to construct a group additivity scheme.

In DMF as the solvent the measured interaction coefficients are restricted to those between water molecules and several ionic and non-ionic solute molecules. They are positive for all combinations studied and show a much smaller variation than those in water. In several cases the difference with the behaviour in water is striking. It can be related to the absence of structural effects in DMF. A group interaction scheme is applicable also and gives even better results than in water as the solvent.

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## Interaction in Ionic Exchange Systems $M^1X$–$M^nX_n$–$H_2O$

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*1*). Up to this moment there are no criteria for a quantitative prediction of solubility of chemical compounds. Neither can we make this for such systems as $M^1X$–$M^nX_n$–$H_2O$ or for more complicated systems. There are often experimental data about change of solubility in systems of this type, however, a quantitative bond of solubility and system's composition is unknown. An isotherm of solubility for systems of this type is two lines on a plane system of coordinates and one on a cross point.

2). Our Experimental data for systems $M^1X$–$M^nX_n$–$H_2O$ by solid zeolite phase as an ion exchanger are such that we can draw the following conclusions:

*a*, transition of $M^+$-ion from phase of zeolite is a stage which changes the energy of the systems a little;

*b*, interaction $M^1X$–$M^nX_n$ with molecules of liquid phase of solute or interaction of solvate ions with one another is a basic contribution to a decrease in energy of the whole system.

So, for example, for systems Na-zeolite–$CaCl_2$–$H_2O$ and Ca-zeolite–NaCl–$H_2O$ in a region of high concentration solutions, the change of salt composition takes place along an isotherm of the system to the eutectic point.

*c*, This result indicates indifference to the direction of approach to eutectic and, hence, a prevailing influence of interaction in liquid phase in comparison with the transition of a solid phase NaA to CaA or *vice versa.*

*3*). From this we can make following admissions. Let's consider that salt $M^1X$ is a strong coordinating salt, if $M^+$-ion has the more specific electrostatic charge in comparison with the charge of $M^{n+}$-ion and *vice versa.* Let's consider also, that a cation with the more specific charge corresponds to the more coordinative number. In the simplest approach a maximum coordinative number is equal to 6 and another number is 4. We can admit that a tetrahedron environment of cation $M^+$ is formed by bond of octahedron pair (1 octahedron = 1 tetrahedron cavity), and also from bond of 4 octahedrons (1 close tetrahedron cavity).

*4*). These admissions give the following results: 1 kg $H_2O$ contains $6.02 \times 10^{23} \cdot 10^3 : 18 : 6$ octahedrons, half of which has $M^+$-ion and another half contains $X^-$-ion. So, octahedrons contain $6.02 \times 10^{23} \times 10^3 : 18 : 6 : 2 = 4.63$ *gM* salt MX. This figure evidently determines the solubility of any octahedron coordinative salt of MX-composition.

Another salt, $M^nX_n$, is found in open tetrahedron cavities, formed by octahedrons, bound in pairs and its solubility will determine 2.31 *gM* or 1.15 *gM*, if ions of salt $M^nX_n$ are found only in tetrahedron cavities, formed by 4 contacting octahedrons.

In the first variant this leads to the following results for systems NaCl($M^1X$)–KCl($M^nX_n$)–$H_2O$: 18.8 wt.% NaCl, 11.9% KCl.

In the second variant: 19.9% NaCl, 6.4% KCl, while experimental data for 25 °C are: 20.4% NaCl, 11.1% KCl.

*5*). Similar results of solubility were also found for other chloride, sulphate and nitric systems of $M^1X$–$M^nX_n$–$H_2O$-type, forming individually soluble salts.