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Thermodynamic analysis of processes with the participation of zeolites

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The quantum calculation of the free energy of polyatomic dipole-active polarizable particles revealed two mechanisms of free energy change during interaction with a polar medium (solvation and fluctuation mechanisms).

For charged particles the main contribution to complete free energy change is given by the solvation mechanism. Correspondingly, for simple charged particles in homogeneous isotropic polar medium without spatial dispersion this brings to Born free energy of solvation. For uncharged particles with equilibrium dipole moment, solvation mechanism also contributes to the change in system's free energy, and this contribution for spherical particles is in direct proportion to the quadratic dipole moment of the particle and in inverse proportion to its volume. In the frame of the solvation mechanism, effects of nonisotopity and nonlocality of medium (like zeolites), effects of spatial dispersion may be taken into account.

The fluctuation mechanism of free energy change of the system has usually a minor contribution to the complete change of system's free energy, but it should be considered for systems where contribution of solvation mechanism is not great and also for systems, where vibration frequencies of the impurity particle change greatly upon placing it in a polar medium.

The obtained results will promote the investigations of adsorption processes on the zeolite surface, the study of kinetics of charge transfer and particle transfer process in channels of composite materials.

Key words: thermodynamic analysis, polar medium, free energies, spatial dispersion, frequency dispersion, zeolites.

INTRODUCTION

Natural and synthetic zeolites have wide application in gas separation installations, gas generators, purification plants, for creation of ionisators, super-condensers, and accumulators. Their wide application is connected with the specific structure of zeolites, the form of their nanopores providing unique sorption properties. The surface of zeolites is very active, so they are fine catalysts for many processes. Size, form and properties of the surface of nano-sized materials may be adapted and optimized for a particular application. Placing different ions in the pores of natural and synthetic zeolites we obtain modified materials, which have unique properties. For determination of the realization possibility of processes with participation of zeolites, first of all, thermodynamic analysis of the corresponding system has to be conducted.

1. FREE ENERGIES OF POLYATOMIC POLARIZABLE DIPOLE-ACTIVE PARTICLES IN POLAR MEDIUM

Complete change of system's free energy includes the following components:

a) Work connected with cavity formation in the medium, where the impurity particle is placed;

b) Free energy connected with the translational and rotational motion of the impurity as a whole;

c) Electrostatic part connected with the interaction of the impurity particle with the medium (zeolite and liquid in canals).

Below we shall calculate the latter component, which in the majority of cases, makes the greatest contribution to the free energy change.

2. HAMILTONIAN OF THE SYSTEM

Existence of electrostatic interaction between impurity and medium causes polarization of the medium. In turn, polarized medium influences the impurity particle and polarizes it. The Hamiltonian of the system may be represented

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as:

$$H = H_m + H_p - \int \left\langle \vec{P}(\vec{r}) \right\rangle_0 \vec{E}(\vec{r}, Q_0) d\vec{r} - \int \delta\vec{P}(\vec{r}) \vec{E}(\vec{r}, Q_0) d\vec{r}, \quad (1)$$

where H_m^s - is Hamiltonian of the system; H_p - is Hamiltonian of the particle; $\langle P(r) \rangle_0$ - is the average value of medium polarization induced by the electric field of the particle, with field intensity $E(r,Q^0)$ [1], (Q^0 – is the set of intramolecular coordinates of the impurity). Going from the Hamiltonian of the nonpolarized medium H_m^s to the Hamiltonian of the polarized medium H_m, in dielectric approximation we have:

$$H = H_m + H_p - \frac{1}{2} \int \left\langle \vec{P}(\vec{r}) \right\rangle_0 \vec{E}(\vec{r}, Q_0) d\vec{r} - \int \delta\vec{P}\vec{E}(\vec{r}, Q_0) d\vec{r}, \quad (2)$$

According to the fluctuation - dissipative theorem:

$$\left\langle P_i(\vec{r}, t) \right\rangle_0 = -\int d\vec{r} \int dt' G^R_{P_i P_k}(\vec{r}, \vec{r}'; t - t') E_k(\vec{r}', t'), \quad (3)$$

where G^R_{PP} is the retarded Green function of operators of medium polarization [1].

For the intensity of the electric field of impurity particles in dipole approximation the expression may be used:

$$\varepsilon_\alpha(\vec{r}) = -\int d\vec{r} G_{E_\alpha E_\beta}(\vec{r}, \vec{r}') \sum_{i=1}^{N} \mu^i_\beta(\vec{R}_i) \delta(\vec{r} - \vec{R}_i) + G_{E_\alpha \varphi}(\vec{r}, R) \rho(\vec{R}). \quad (4)$$

Here G_{EE} and G_{E_φ} are Green functions of the operators of electric field intensity and the scalar potential of the condensed medium; they may be expressed by the Green functions $G_{\varphi\varphi}$, which may be simply defined from the solution of the electrostatic task (see [1, 2]). μ^i is the dipole moment of i-th bond of the particle, R_i is the radius-vector of the i-th dipole of the particle, ρ, *R* is the charge of the particle and the radius-vector of the charge localization point.

For a polarizable particle the value of μ^i differs from the corresponding vacuum value μ^i_0, it could be determined through:

$$\mu^i_\alpha = \mu^i_0 + \sum_{j=1}^{N} \alpha^i_{\alpha\beta} \left\{ G_{E_\beta E_\gamma} \mu^i_\gamma + G_{E_\alpha \varphi} \rho \right\}, \quad (5)$$

where $\alpha^i_{\alpha\beta}$ is the polarizability tensor of the i-th bond of the particle. It is obvious that if all components of the polarizability tensor and the vacuum values of the dipole moment of the bond are known, then all 3N values of μ may be found from system (5). As Green functions, the corresponding solutions of electrostatic tasks of model functions may be used, which allows taking into account the effects of spatial dispersion of the medium. Further, substituting the found values μ^i_α into correlation (4) we define the electric field intensity of the system $\varepsilon(r, R_i,)$ and from (3) we find the polarization of medium $\langle P(\vec{r}) \rangle_0$.

Substituting (3) into (2) we rewrite the Hamiltonian of the system in the following form:

$$H = H_m + H_p + \frac{1}{2} \int \vec{E}(\vec{r}, Q) G^R_{PP}(\vec{r}, \vec{r}') \vec{E}(\vec{r}, Q) d\vec{r} d\vec{r}' - \int \delta\vec{P}(\vec{r}) \vec{E}(\vec{r}, Q) d\vec{r}. \quad (6)$$

In this formula we expand the electric field intensity into a series by Q^0 up to linear terms,

$$H = \delta\Omega_0 + H_p + H_m - \int d\vec{r} \delta\vec{P}(\vec{r}) \vec{E}(\vec{r}, Q). \quad (7)$$

Here H_p is the Hamiltonian of the polarized solvated particle,

$$H^p = H^{p0} + \sum_n d_n Q^0_n + \sum_{nn'} h_{nn'} Q^0_n Q^0_{n'}, \quad (8)$$

where

$$h_{nn'} = \frac{1}{2} \frac{\partial E^0}{\partial Q^0_n} G^R_{PP} \frac{\partial E^0}{\partial Q^0_m}_{Q^0_n = Q^0_{n0}}, \quad (9)$$

$$d_n = \frac{1}{2} \left(E^0 G^R_{PP} \frac{\partial E^0}{\partial Q^0_n} + \frac{\partial E^0}{\partial Q^0_n} G^R_{PP} E^0 \right)_{Q^0_n = Q^0_{n0}}$$

In (7) $\delta\Omega_0$ is the free energy of the solvated particle, which has the following form:

$$\delta\Omega_0 = \frac{1}{2} \int dt dt' \int d\vec{r} d\vec{r}' E_\alpha(\vec{r}, Q^0_0) G^R_{P_\alpha P_\beta}(\vec{r}, \vec{r}', t - t') E_\beta(\vec{r}, Q^0_0) \quad (10)$$

By transformation of coordinates (shift and turn) H_p may be reduced to quadratic form with frequencies ω_s and coordinates Q_s.

$$H_p = \frac{1}{2}\sum_s \omega_s \left[(Q_s - Q_{so})^2 - \frac{\partial^2}{\partial Q_s^2} \right] + J, \quad (11)$$

where Q_{s0} is the equilibrium value of coordinate Q_s, J – the minimal energy of the particle.

It is obvious that the influence of a solvated polarized particle on the medium leads to additional polarization of the medium. Therefore, it is necessary to use the characteristics of the polar particle in (7) - (11) and introduce $E(Q_0)$ instead of E(Q).

In formula (7) we expand into series the electric field intensity E by $Q - Q_0$ up to a linear term. Consequently:

$$H = \delta\Omega_0 + H_m + H_p + H_{int}^{(1)} + H_{int}^{(2)}, \quad (12)$$

where

$$H_{int}^{(1)} = -\int \delta\vec{P}\vec{E}(\vec{r}, Q_0)d\vec{r} \quad , \quad (13)$$

is the interaction of the medium polarization fluctuations with the static field of the impurity, and

$$H_{int}^{(2)} = -\sum_s \int d\vec{r}\delta\vec{P}(\vec{r})\delta Q_s \vec{V}_s(\vec{r});$$

$$\vec{V}_s(\vec{r}) = \frac{\partial\vec{E}(\vec{r}, Q)}{\partial Q_s}\Bigg|_{Q_s = Q_{s0}} \quad , \quad (14)$$

is the interaction of the medium polarization fluctuations with intramolecular vibrations of the impurity.

The electrostatic part of the free energy change connected with introduction of polyatomic dipole-active impurities in the polar medium may be written in the following form [3]:

$$\delta\Omega = \delta\Omega_o + \delta\Omega_1 + \delta\Omega_2 + \delta\Omega_3, \quad (15)$$

where $\delta\Omega_1$ and $\delta\Omega_2$ are the changes of the system free energy connected with $H_{int}^{(1)}$ and $H_{int}^{(2)}$ interactions, correspondingly, $\delta\Omega_3$ is the change of the vibrational free energy of the impurity particle.

3. CALCULATION OF THE FREE ENERGIES OF SOLUTION $\Delta\Omega_0$ AND $\Delta\Omega_1$

The change of free energy $\delta\Omega_1$ may be expressed through the matrix

$$\delta\Omega_1 = -kT\ln\left\langle S^{(1)} \right\rangle. \quad (16)$$

Here, averaging is carried out over the states of polar medium and $S^{(1)}$ matrix has the form:

$$S^{(1)} = T_\tau \exp\left\{ \int_0^\beta d\tau \int d\vec{r}\delta\vec{P}(\vec{r}, \tau)\vec{E}_0(\vec{r}) \right\} \quad (17)$$

After $S^{(1)}$ matrix expansion into series and calculation of quantum-statistical averages of δP operators, we obtain [4]:

$$\delta\Omega_1 = -\frac{1}{2}\int d\vec{r}\left\langle \vec{P}(\vec{r}) \right\rangle \vec{E}_0(\vec{r}, Q_0) - \frac{1}{2}\int_0^\beta d\tau \int_0^\beta d\tau' \int d\vec{r}d\vec{r}'\vec{E}_{0\alpha}(\vec{r}, Q_0)\vec{E}_{0\beta}(\vec{r}', Q_0)G_{\delta P_\alpha \delta P}(\vec{r}, \vec{r}'; \tau, \tau') \quad (18)$$

Where $\beta = 1/kT$, k is the Boltzmann constant, T- temperature, $G_{\delta P_\alpha \delta P_\beta}$ - temperature Green functions of medium polarization fluctuation operators [1],

$$G_{\delta P_\alpha \delta P_\beta}(\vec{r}, \vec{r}'; \tau - \tau') = -\left\langle T_\tau \delta P_\alpha(\vec{r}, \tau)\delta P_\beta(\vec{r}', \tau') \right\rangle \quad (19)$$

Substituting $\langle P \rangle$ in the formula (18) to the value from formula (3) and integrating over τ, τ', t, t', we obtain:

$$\delta\Omega_1 = \frac{1}{2}\int d\vec{r}d\vec{r}'E_{0\alpha}(\vec{r}, Q_0)\left[G_{P_\alpha P_\beta}^{R_0}(\vec{r}, \vec{r}'; \omega = 0) - G_{\delta P_\alpha \delta P_\beta}(\vec{r}, \vec{r}'; \omega = 0) \right] E_{0\beta}(\vec{r}) \quad (20)$$

Green functions G_{PP}^0 and $G_{\delta P \delta P}$ are phonon Green functions of the medium, when ω = 0 they are equal, so

$$\delta\Omega_1 = 0 \quad (21)$$

By integrating formula (10) over τ and τ' we obtain the following expression $\delta\Omega_0$:

$$\delta\Omega_0 = \frac{1}{2}\int d\vec{r}d\vec{r}'E_\alpha^0(\vec{r})G_{P_\alpha P_\beta}^R(\vec{r}, \vec{r}'; \omega = 0)E_\beta^0(\vec{r}'). \quad (22)$$

For a homogeneous local isotropic medium, for which

$$G_{P_\alpha P_\beta}(\vec{r},\vec{r}';\omega=0) = -\frac{1}{4\pi}(1-\frac{1}{\varepsilon})\delta_{\alpha\beta}\delta(\vec{r}-\vec{r}')\,. \quad (23)$$

the free energy of the solution $\delta\Omega_0$ takes the form:

$$\delta\Omega_0 = -\frac{C}{8\pi}(1-\frac{1}{\varepsilon})\int d\vec{r}(\vec{E}^0(\vec{r}))^2 \quad (24)$$

Here ε is the static value of dielectric permeability. For spherically symmetric particles with z charge the formula (24) brings about the Born solvation energy:

$$Q = e^2/2r\varepsilon \quad (25)$$

If the particle is not charged but has an equilibrium dipole moment, then for spherically symmetric particles we obtain:

$$\delta\Omega_0 = -(1-\frac{1}{\varepsilon})\frac{\mu^2}{3r_0^3}\,, \quad (26)$$

where r_0 – radius of particle.

4. EFFECTS OF MEDIUM SPATIAL DISPERSION.

Taking into account the spatial dispersion of the medium let us rewrite (22) in the following form:

$$\delta\Omega_0 = -\frac{1}{2}\int \rho(\vec{r})G_{\varphi\varphi}(\vec{r},\vec{r}')\rho(\vec{r}')d\vec{r}d\vec{r}' \quad (27)$$

where $G_{\varphi\varphi}$ is the Green function (GF) of the medium scalar potential operators, ρ is the charge density of the impurity which creates an electric field with intensity E_o.

Effects of spatial dispersion of the medium may be considered, when calculating the free energy change of the system, if some model functions are used as Green functions of operators of polarization fluctuation or charge density or a medium scalar potential. For determination of GF $G_{\varphi\varphi}(\vec{r},\vec{r}')$ the results of solving electrostatic tasks may be used: accurate within electron charge GF $G_{\varphi\varphi}(\vec{r},\vec{r}')$ coincides with the magnitude of the electrostatic potential in point $\vec{r}$ of the system, if in point $\vec{r}'$ a unit charge is placed. Considering the above mentioned, it should be expected that allowance behavior of GF $G_{\varphi\varphi}(\vec{r},\vec{r}')$ will be of type:

$$G_{\varphi\varphi}(\vec{r},\vec{r}') = C(\vec{r})\frac{1}{|\vec{r}-\vec{r}'|}\,, \quad (28)$$

In this case, the behavior of GF $G_{\varphi\rho}$ and $G_{\rho\varphi}$ will be of type:

$$G_{\varphi\rho}(\vec{r},\vec{r}') = G_{\rho\varphi}(\vec{r},\vec{r}') = -f(\vec{r})\delta(\vec{r}-\vec{r}') \quad (29)$$

The Fourier component of $f(\vec{r})$ function may be connected with the longitudinal component of the dielectric permeability $\varepsilon^l(k)$. After standard conversions we get:

$$f(\vec{r}) = \frac{1}{(2\pi)^{3/2}}\int e^{i\vec{k}\vec{r}}f(\vec{k}) \quad (30)$$

and

$$f(\vec{k}) = \frac{1}{4\pi}\left(1-\frac{1}{\varepsilon^l(k)}\right) \quad (31)$$

Hereby, for Fourier components we have the following correlation:

$$G_{\varphi\rho}(\vec{k},\vec{k}') = -\frac{1}{4\pi}\left(1-\frac{1}{\varepsilon^l(k)}\right)\delta_{\vec{k}\vec{l}'} \quad (32)$$

In case of a local homogeneous medium, from the previous formula we get:

$$G_{\varphi\rho}(\vec{k},\vec{k}') = -\frac{1}{4\pi}\left(1-\frac{1}{\varepsilon^l(k)}\right)\delta_{\vec{k}\vec{l}'} = -\frac{C_0}{4\pi}\delta_{\vec{k},k'} \quad (33)$$

In the $\vec{r}$ space the latter formula has the form:

$$G_{\varphi\rho}(\vec{r},\vec{r}') = -\frac{1}{4\pi}C_0\delta(\vec{r}-\vec{r}') \quad (34)$$

If the impurity particle is spherically symmetric, has z charge and radius r_0, then for the change of free energy $\delta\Omega_1$ we get:

$$\delta\Omega_1 = -\frac{C_0 z^2}{2r_0} = -\frac{z^2}{2r_0}\left(1-\frac{1}{\varepsilon}\right) \quad (35)$$

For consideration of space dispersion effects, instead of δ-function in formula (34) the function may be used:

$$G^{(\lambda)}_{\varphi\rho}(\vec{r},\vec{r}') = -\frac{C_0}{4\pi}\Delta_\lambda(|\vec{r}-\vec{r}'|) \quad (36)$$

In the capacity of $\Delta_\lambda(|\vec{r}-\vec{r}'|)$ function the exponentially damped function normalized on unity must be selected:

$$\Delta_\lambda(|\vec{r}-\vec{r}'|) = \frac{1}{8\pi\lambda^3}e^{-\frac{|\vec{r}-\vec{r}'|}{\lambda}} \quad (37)$$

If for charge density of impurity particle ρ^{ex} classic approximation is used and assuming that the point of charge localization coincides with the origin of coordinates, then

$$\rho^{ex}(\vec{r}) = z\delta(\vec{r}) \quad (38)$$

In this case for $\delta\Omega_1$ we have:

$$\delta\Omega_1 = -\frac{C_0 z^2}{16\pi\lambda} = -\frac{z^2}{16\pi\lambda}\left(1-\frac{1}{\varepsilon}\right) \qquad (39)$$

Analogously, the change of free energies of the system, where space dispersion effects of the medium are described by more complicated functions, may be calculated. For example, if Δ_λ describes oscillations with attenuation:

$$\Delta_\lambda\left(\left|\vec{r}-\vec{r}'\right|\right) = \frac{\nu\left(\nu^2-3\bar{\lambda}^2\right)}{8\pi} e^{-\nu\left|\vec{r}-\vec{r}'\right|} \cos\left(\bar{\lambda}\left|\vec{r}-\vec{r}'\right|\right) \qquad (40)$$

Then for the free energy change $\delta\Omega_1$ we obtain:

$$\delta\Omega_1 = -\frac{C_0 z^2}{16\pi} \frac{\nu\left(\nu^2-3\bar{\lambda}^2\right)\left(\nu^2-\bar{\lambda}^2\right)}{\left(\nu^2+\bar{\lambda}^2\right)^2} \qquad (41)$$

Here the parameter $1/\lambda$ will be approximately equal to the diameter of the solvent molecule. If for charge density ρ^{ex} quantum approximation is used, then

$$\rho^{ex}(\vec{r}) = e\left|\Psi(\vec{r})\right|^2 \qquad (42)$$

where $\Psi(\vec{r})$ is wave function.

In the capacity of wave function we take the normalized function:

$$\Psi(\vec{r}) = \frac{\alpha^{3/2}}{(8\pi)^{1/2}} e^{-\frac{\alpha r}{2}} \qquad (43)$$

GF of operators of medium scalar potential we take in the form (36). Free energy change $\delta\Omega_1$ has the form:

$$\delta\Omega_1 = -\frac{e^2 C_0}{32\pi^2}\int d\vec{r}d\vec{r}'d\vec{r}''\Delta_\lambda\left(\left|\vec{r}-\vec{r}'\right|\right)\frac{\left|\Psi(\vec{r})\right|^2\left|\Psi(\vec{r}'')\right|^2}{\left|\vec{r}-\vec{r}''\right|} \qquad (44)$$

Using here the form of the function $\Delta_\lambda\left(\left|\vec{r}-r'\right|\right)$ (37) and the wave function $\Psi(\vec{r})$ in the form (43), we get:

$$\delta\Omega_1 = -\frac{e^2 C_0 \alpha^6}{(8\pi)^4\lambda^3}\int d\vec{r}d\vec{r}'d\vec{r}''\exp\left(-\frac{\left|\vec{r}-\vec{r}'\right|}{\lambda}-\alpha\left(\vec{r}+\vec{r}''\right)\right)\frac{1}{\left|\vec{r}'-\vec{r}''\right|} \qquad (45)$$

Omitting cumbersome calculations, we give the result in the form:

$$\delta\Omega_1 = \frac{e^2 C_0 \lambda^2}{8\pi(\alpha/2)^4}\left(32\alpha^7 - 4\alpha^9\lambda^2 + \frac{4\alpha^6}{\lambda} - \frac{55\alpha^5}{\lambda^2} - \frac{21\alpha^4}{\lambda^3} + \frac{38\alpha^3}{\lambda^4} + \frac{26\alpha^2}{\lambda^5} - \frac{20\alpha}{\lambda^6} - \frac{12}{\lambda^7}\right). \qquad (46)$$

For description of space dispersion effects of the medium, the function may be used:

$$\Delta_\lambda\left(\left|\vec{r}-\vec{r}'\right|\right) = \frac{1}{\pi^{3/2}\lambda^3}\exp\left(-\frac{\left|\vec{r}-\vec{r}'\right|^2}{\lambda^2}\right) \qquad (47)$$

If we take (43) as wave function $\Psi(\vec{r})$, then for $\delta\Omega_1$ we obtain:

$$\delta\Omega_1 = -\frac{e^2 C_0 \alpha^3}{4}\int_0^\infty dr r e^{-\alpha r}\Phi\left(\frac{r}{\lambda}\right) \qquad (48)$$

where $\Phi\left(\frac{r}{\lambda}\right)$ - is the error integral:

$$\Phi\left(\frac{r}{\lambda}\right) = \frac{2}{\sqrt{\pi}}\int_0^{r/\lambda} e^{-t^2}dt \qquad (49)$$

During numerical calculations by formula (49) it is convenient to use an approximate expression for the error integral:

$$\Phi\left(\frac{r}{\lambda}\right) = 1-\sqrt{\frac{2}{\pi}}e^{-(r/\lambda)^2}\left[b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4 + b_5 t^5\right] \qquad (50)$$

where $t = \frac{1}{1+P\sqrt{2}\frac{r}{\lambda}}$,

P = 0,2316; b_1 = 0,3194; b_2 = - 0,3566; b_3 = 1,7815; b_4 = -1,8213; b_5 = 1,3303. (51)

In quantum case for charge density of the particle also the following function may be used:

$$\rho(\vec{r}) = \frac{e\alpha^3}{56\pi}\left(1+\frac{\alpha r}{2}\right)^2 e^{-\alpha r} \qquad (52)$$

If expression (47) is used for Δ_λ function, then for $\delta\Omega_1$ we have:

$$\delta\Omega_1 = -\frac{9e^2 C_0 \alpha}{56} + \frac{e^2 C_0 \alpha^3}{14\sqrt{2\pi}}\int_0^\infty d\vec{r}\left\{r\left(1+\frac{\alpha r}{2}\right)^2\left[b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4 + b_5 t^5\right]e^{-\left(\alpha r+\frac{r^2}{\lambda^2}\right)}\right\} \qquad (53)$$

If space dispersion effects of medium are described by function (47), and for charge density the function is used:

$$\rho(\vec{r}) = \frac{4e\beta^3}{4\sqrt{2\pi}} e^{-2\beta^2 r^2} \qquad (54)$$

then the free energy change will be equal to:

$$\delta\Omega_1 = -\frac{2e^2C_0\beta}{\sqrt{2\pi}} + \frac{8e^2C_0\beta^3}{\pi}\int_0^\infty drre^{-\left(2\beta^2+\frac{1}{\lambda^2}\right)r^2}\left[b_1t + b_2t^2 + b_3t^3 + b_4t^4 + b_5t^5\right] \quad (55)$$

In the capacity of Δ_λ function describing space dispersion effects of the medium the step function may be selected:

$$\Delta_\lambda\left(\left|\vec{r}-\vec{r}'\right|\right) = \frac{3}{4\pi\,\lambda^3}\theta\left(\left|\vec{r}-\vec{r}'\right|\right)\theta\left(\lambda - \left|\vec{r}-\vec{r}'\right|\right) \quad (56)$$

If exponential function of the form (52) is selected as a wave function, then for $\delta\Omega_1$ we have:

$$\delta\Omega_1 = \frac{81}{14}\frac{e^2C_0}{\lambda^3\alpha^2} - \frac{3}{4}\frac{e^2C_0}{\lambda} - \frac{3}{56}\frac{e^2C_0}{\lambda}e^{-\alpha\lambda}\left[4\lambda^2\alpha^2 + 7\lambda\alpha + 40 + \frac{106}{\lambda\alpha} + \frac{106}{\lambda^2\alpha^2}\right] \quad (57)$$

For a model in which charge density is described by a function of the type (43), we have:

$$\delta A\Omega_1 = 3\frac{e^2C_0}{\lambda}\left[\frac{1}{(\alpha\lambda)^2} - \frac{1}{4}\right] + \frac{e^2C_0\alpha}{4}\left[2 - \frac{3}{\alpha\lambda} - \left(1 + \frac{1}{\alpha\lambda}\right)\right]e^{-\alpha\lambda} \quad (58)$$

If charge density has the form (54), then

$$\delta\Omega_1 = -\frac{3}{4}\frac{e^2C_0}{\lambda}\left[1 - \frac{1}{(2\lambda\beta)^2}\right] - \frac{4e^2C_0}{\sqrt{2\pi}}e^{-2\beta^2\lambda^2}\left\{\frac{\beta}{2} + \frac{3 - 4\lambda^2\beta^2 - 32\lambda^4\beta^4}{32\lambda^3\beta^2}\left(b_1t + b_2t^2 + b_3t^3 + b_4t^4 + b_5t^5\right) + \right.$$
$$\left. + \frac{12\lambda^2\beta^2 - 1}{4\lambda^2\beta}P\left(b_1t^2 + 2b_2t^3 + 3b_3t^4 + 4b_4t^5 + 5b_5t^6\right) - \frac{P^2}{4\lambda}\left(2b_1t^3 + 6b_2t^4 + 12b_3t^5 + 20b_4t^6 + 30b_5t^{75}\right)\right\} \quad (59)$$

Thus, for the free energy change of the system, when a polyatomic polarizable nondipole charged particle is introduced into a condensed medium, the calculations may be carried out with different precision, considering various effects: in case of quantum or classic behavior of the degrees of freedom of the impurity, effects of spatial dispersion of the medium, which may be described by a set of different model functions; interactions of intramolecular vibrations of the impurity with polarization fluctuations of the medium.

For obtaining the equilibrium dipole moment of an impurity particle in classic approximation for the charge density of a particle placed in a local homogeneous isotropic medium, we have the following expression:

$$\delta\Omega_1^d = -\int d\vec{r}d\vec{r}'\left(\vec{E}(\vec{r})\vec{E}(\vec{r}')\right)\delta\left(\vec{r}-\vec{r}'\right)\frac{C_0}{4\pi} \quad (60)$$

After corresponding integration we obtain:

$$\delta\Omega_1^d = -\left[8\pi C_0/\left(3r_0^3\right)\right]\left(\partial d/\partial Q\right)^2 \quad (61)$$

where r_0 is the particle radius.

Naturally, a total change of free energy for a charged dipole particle will be equal to the sum of changes for charged impurity (35) and dipole impurity (61):

$$\delta\Omega_1 + \delta\Omega_1^d = -\frac{8\pi C_0}{3r_0^3}\left(\frac{\partial d}{\partial Q}\right)^2 - \frac{z^2C_0}{8\pi r_0} \quad (62)$$

In regard to obtaining the space dispersion of the medium for dipole particles, representation of the free energy change of the system in one of the following forms is more convenient:

$$\delta\Omega_1 = \int d\vec{r}d\vec{r}'\nabla_{\vec{r}\alpha}\nabla_{\vec{r}'\beta}G_{\varphi\varphi}\left(\vec{r},\vec{r}'\right)P_\alpha^{ex}\left(\vec{r}\right)P_\beta^{ex}\left(\vec{r}'\right) = \int G_{E_\alpha E_\beta}\left(\vec{r},\vec{r}'\right)P_\alpha^{ex}\left(\vec{r}\right)P_\beta^{ex}\left(\vec{r}'\right)d\vec{r}d\vec{r}' \quad (63)$$

For particle polarization ρ^{ex} point approximation may be used:

$$\vec{\rho}^{ex}\left(\vec{r}\right) = \vec{d}\delta\left(\vec{r}\right) \quad (64)$$

For GF, $G_{\varphi\varphi}$ and G_{EE} different model functions may be used.

Most acceptable way for calculation of $\delta\Omega_1$ for the charge density of charged dipole particle in quantum approximation is to use correctly selected wave functions Ψ_d and to carry out integration by formula (44) for various types of Δ_λ functions.

5. CALCULATION OF THE FLUCTUATION PART OF FREE ENERGY CHANGE

Let us write the change of free energy in the following form:

$$\delta\Omega_2 = -kT\ln\left\langle S^{(2)}\right\rangle \quad (65)$$

where

$$S^{(2)} = T_\tau \exp\left\{\int_0^\beta d\tau\int d\vec{r}\delta\vec{P}(\vec{r},\tau)\vec{V}_s(\vec{r})Q_s(\tau)\right\}. \quad (66)$$

Let us formally represent the matrix as:

$$S^{(2)}(\lambda) = T_\tau \exp\left\{\lambda\int_0^\beta d\tau\int d\vec{r}\delta\vec{P}(\vec{r})\vec{V}_s(\vec{r})Q_s(\tau)\right\}. \quad (67)$$

and the corresponding free energy $\delta\Omega_2(\lambda)$, similarly to correlation (16), like this [1]:

$$\frac{\partial\Omega_2(\lambda)}{\partial\lambda} = kT\frac{\frac{\partial}{\lambda}\left\langle S^{(2)}(\lambda)\right\rangle_0}{\left\langle S^{(2)}(\lambda)\right\rangle_0}, \quad (68)$$

Integrating this correlation accordingly by λ from 0 up to 1 and taking into account the condition $\delta\Omega_{12} = \Omega(\lambda=1) - \Omega(\lambda=0)$, we express $\delta\Omega_2$ through Green function

$$\delta\Omega_2 = -\int_0^1 \frac{\partial\lambda}{\lambda}\int_0^\beta d\tau\int dr\lambda V_{s\alpha}(\vec{r})\left\{G_{\delta P_\alpha Q_s}(\vec{r},\lambda,\tau=0)\right\}, \quad (69)$$

where $G_{\delta PQ}$ - is the Green function of operators δP and Q with effective interaction $\lambda V_s(r)$.

Expanding the Green function into Fourier series by τ and integrating by τ we have:

$$\delta\Omega_2 = -kT\int_0^1 \frac{\partial\lambda}{\lambda}\int dr\lambda V_{s\alpha}(\vec{r})\sum_{n=-\infty}^{\infty} G_{\delta P_\alpha Q_s}(\vec{r},\lambda,\omega_n), \quad (70)$$

Taking into account the results [1-5] it follows that:

$$\delta\Omega_2 = -kT\int_0^1 \frac{\partial\lambda}{\lambda}\sum_n W_{ss'}(\lambda,\omega_n)G_{Q_sQ_{s'}}(\lambda,\omega_n), \quad (71)$$

where W is renormalized interaction of intramolecular vibrations with each other through the polar medium. This quantity may be calculated quantum-chemically or may be simulated by a suitable function with consideration of above mentioned formulas.

$$W_{ss'}(\lambda,\omega_n) = \int d\vec{r}d\vec{r}''\lambda V_{\alpha s}(\vec{r})G_{\delta P_\alpha\delta P_\beta}(\vec{r},\vec{r}';\omega_n)\lambda V_{\beta s}(\vec{r}'), \quad (72)$$

Green functions of normal coordinate operators of intramolecular vibrations of the solvated impurity satisfy the system of linear algebraic nonhomogeneous equations:

$$G_{Q_sQ_{s'}}(\lambda) = G^0_{Q_sQ_{s'}} + G^0_{Q_sQ_{s'}}(\lambda)W_{ss''}(\lambda)G_{Q_{s''}Q_{s'}}. \quad (73)$$

Here $G^0_{Q_sQ_s}$ are the Green functions of the oscillator.

So solving (73) for any finite number of intramolecular degrees of freedom N, the components $G_{Q_sQ_{s'}}(\lambda,\omega_n)$ may be determined and accordingly integrated by λ and summed by n in (71) for calculation of $\delta\Omega_2$.

For a simple model, when the system has one dipole-active degree of freedom, we get:

$$\delta\Omega_2 = \frac{kT}{2}\sum_n \mathrm{Sp}\ln\left|G^0_{QQ}G^{-1}_{QQ}\right| = \frac{kT}{2}\sum_n \mathrm{Sp}\ln\left|1 - G^0_{QQ}W\right| \quad (74)$$

In order to show the possibilities of the calculations in accordance with (74), we use a polar approximation (which includes Debye and resonance function) for the Green function of medium polarization fluctuation operators. In this case,

$$W(\omega_n) = \sum_{i=1}^{m}\frac{u_i}{|\omega_i - \omega_n|}, \quad (75)$$

where u_i are experimental constants, and m - the number of poles of the Green function.

Substituting (89) into (88), we get:

$$\delta\Omega_2 = \frac{kT}{2}\ln\left(1 - \frac{W(0)}{\omega_s}\right) + kT\ln\prod_{n=1}^{\infty}\left[1 - \sum_{i=1}^{m}\frac{u_i\omega_s}{(\omega_n^2+\omega_s^2)(\omega_i-\omega_n)}\right], \quad (76)$$

here ω_s is the frequency of intramolecular vibrations of the impurity. Expression in brackets in this correlation may be presented in the form of a ratio of two polynomials,

$$1 - \sum_{i=1}^{m}\frac{u_i\omega_s}{(\omega_n^2+\omega_s^2)(\omega_i-\omega_n)} = \frac{\left[\left(\frac{\omega_s}{2\pi kT}\right)^2 + n^2\right]\prod_{i=1}^{m}\left(\frac{\omega_i}{2\pi kT} - n\right) - \sum_{i=1}^{m}\frac{u_i\omega_s}{(2\pi kT)^2}\prod_{i=1}^{m}\left(\frac{\omega_i}{2\pi kT} - n\right)}{\left[\left(\frac{\omega_s}{2\pi kT}\right)^2 + n^2\right]\prod_{i=1}^{m}\left(\frac{u_i}{2\pi kT} - n\right)}. \quad (77)$$

If condition [6] is fulfilled,

$$a_1 + ... + a_l = b_1 + ... + b_l \quad (78)$$

Then, as it is known from the theory of Γ-functions

$$\prod_{n=1}^{\infty}\frac{(n-a_1)...(n-a_l)}{(n-b_1)...(n-b_l)} = \prod_{i=1}^{l}\frac{\Gamma(1-b_i)}{\Gamma(1-a_i)} \quad (79)$$

In our case condition (78) is fulfilled, so

$$\delta\Omega_2 = kT\ln\frac{kT}{\omega_s} + kT\ln\left(2sh\frac{\omega_s}{2kT}\right) + \frac{kT}{2}\ln\left(1-\frac{W(0)}{\omega_s}\right) + kT\ln\prod_{j=1}^{m+2}\Gamma\left(1-\frac{\overline{\omega}_{j\,j}}{2\pi kT}\right) - kT\ln\prod_{ii=1}^{m}\Gamma\left(1-\frac{\omega_i}{2\pi kT}\right) \quad (80)$$

where $\overline{\omega}_j$ is the root of (74). $W(\omega=0)/\omega_2$ should be always less than unit. If the ratio is close to unit, then such molecules dissociate.

CONCLUSIONS

A method of calculation of the free energy change of polyatomic polarizable dipole-active particles during their dissolution in heterogeneous polar medium is presented. Two mechanisms of interaction of these particles with the polar medium are considered: solvation and fluctuation mechanism, including ion-dipole and dipole-dipole interactions. The obtained analytic expressions allow realization of quantitative calculations for dissolved particles with any finite number of degrees of freedom of intra-molecular vibrations, under consideration of the spatial and frequency dispersion of the medium.

Thereby, at the expense of the "fluctuation" mechanism of interaction of the intramolecular vibrations of a particle with the medium polarization fluctuations, dissociation of the molecule is possible, although solvation of this molecule by the medium does not allow the molecule to dissociate to ions. This mechanism is also important for chemical adsorption – the adsorbed molecule may desorb because of the "fluctuation" mechanism. Moreover, the adsorbed molecule may dissociate to ions owing to this mechanism.

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ТЕРМОДИНАМИЧЕН АНАЛИЗ НА ПРОЦЕСИ С УЧАСТИЕ НА ЗЕОЛИТИ

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Квантово-химкичните пресмятания разкриват два механизма на изменение на вободната енергия на диполактивни поляризуеми частици при взаимодействие с полярна среда (солватация и флуктуационен механизъм).

При заредени частици главният принос за пълното изменение на свободната енергия се дава от солватационния механизъм. Съответно, при прости заредени частици в хомогенна изотропна среда без пространствена дисперсия това води до свободна енергия на солватация по Борн. За незаредени частици с равновесен диполен момент солватационният механизъм също води до промяна на свободната енергия на системата, а за сферични частици тя е право пропорционална на квадрата на диполния омент на частицата и обратно пропорционална на обема й. В рамките на солватационния механизъм ефектите на анизотропия и нелокализирането на средата (напр. при зеолити) трябва да се държи сметка за пространствената дисперсия.

Флуктуационният механизъм на изменението на свободната енергия в системата обикновено има малък принос за общото изменение. Той трябва да се отчита в системи със слабо влияние на солватационния механизъм или при които вибрационните честоти на онечистванията се променят значително при постаянето им в полярна среда..

Получените резултати ще насърчат изследванията върху адсорбционните процеси на повърхността на зеолити, кинетиката на пренос на заряда и преносните процеси в порите на композитни материали.