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## The role of size effects in microextraction

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Size effects during phase transformations change the composition of coexisting phases in ternary mixtures. The consequence is a change in the distribution coefficients of the components, which is of interest for microextraction. The concentration dependence of the degree of extraction for separable mixtures (aniline–methylcyclopentane–hexane and water–phenol–toluene) in submicron drops was simulated by the methods of equilibrium chemical thermodynamics. The concentration dependence of the degree of extraction during microextraction for submicron droplets is constructed.

**Keywords:** phase equilibria, microextraction, thermodynamic modeling, size effect, ternary system.

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Liquid-liquid extraction is one the key tools of analytical chemistry and chemical engineering. The process of microextraction based on phase equilibrium; its efficiency is attributable to an increase in the interfacial area and the rate of interfacial exchange induced by extraction, concentration, or purification of substances under analysis. The current state of droplet, membrane, and dispersive liquid-liquid microextraction in analytical chemistry was characterized in detail in [1,2]. The microextraction efficiency depends on the quality and methods of dispersion [3,4]. The role of size effects in phase equilibria [5–7] is examined in the present study in order to interpret this dependence. These effects manifest themselves in phase diagrams as shifts of characteristic temperatures and phase equilibrium lines [7–11]. A change in the composition of coexisting phases alters the distribution coefficients of components and the degrees of microextraction.

The first description of size effects in ternary systems has been presented in [8–10]. It relies on the analysis of closed ternary systems with a core–shell configuration. The state of such systems is characterized by the Gibbs energy, which includes the interfacial surface energy:

$$G = \frac{n_c G_c^m + n_s G_s^m + \sigma_s A_s + \sigma_{cs} A_c}{n_0}, \quad (1)$$

where  $G_j^m$  are Gibbs functions of a real solution in phase  $j = c, s$  (core and shell, respectively),  $n_0 = n_c + n_s$ ,  $n_j = \sum_i n_{ij}$  is the sum number of moles of components in the system and coexisting phases,  $i = 1, 2, 3$  is the component number,  $\sigma_s$  and  $\sigma_{cs}$  are outer and inner boundary tensions, and  $A_c, A_s$  are surface areas of the corresponding phases.

The composition of phases is tied by matter conservation conditions to the shape and size of phase interfaces. If the initial composition is set ( $n_i$ ),  $G(n_{1c}, n_{2c}, n_{3c})$  (1) is a function of three independent variables. The minima of

$G(n_{1c}, n_{2c}, n_{3c})$  correspond to equilibrium states. Small-volume systems may have several equilibrium states, some of them being metastable [7–11]. The composition of the system, the properties of components (molar volume, surface tension), the equation of state of a real solution, and the shape of phase interfaces are model parameters. Both mixtures considered here are characterized by the NRTL (non-random two-liquid) equation

$$G^m = RT \sum_{i=1}^3 x_i \left( \frac{\sum_{j=1}^3 x_j g_{ji} \tau_{ji}}{\sum_{k=1}^3 x_k g_{ki}} + \ln x_i \right), \quad g = e^{-\alpha\tau}.$$

Here,  $x_i$  is the molar fraction,  $\alpha$  and  $\tau$  are parameters of the equation of state,  $T$  is temperature, and  $R$  is the universal gas constant. The surface tension was calculated in linear approximation  $\sigma_j = \sum_i x_{ij} \sigma_i$ , where  $x_{ij}$  is the molar fraction in phase  $j$  and  $\sigma_i$  is the surface tension of pure components; boundary tension  $\sigma_{cs} = 0.5(\sigma_c + \sigma_s)$ . More accurate estimates of the surface energy were used in [11]. The search for minima was performed numerically.

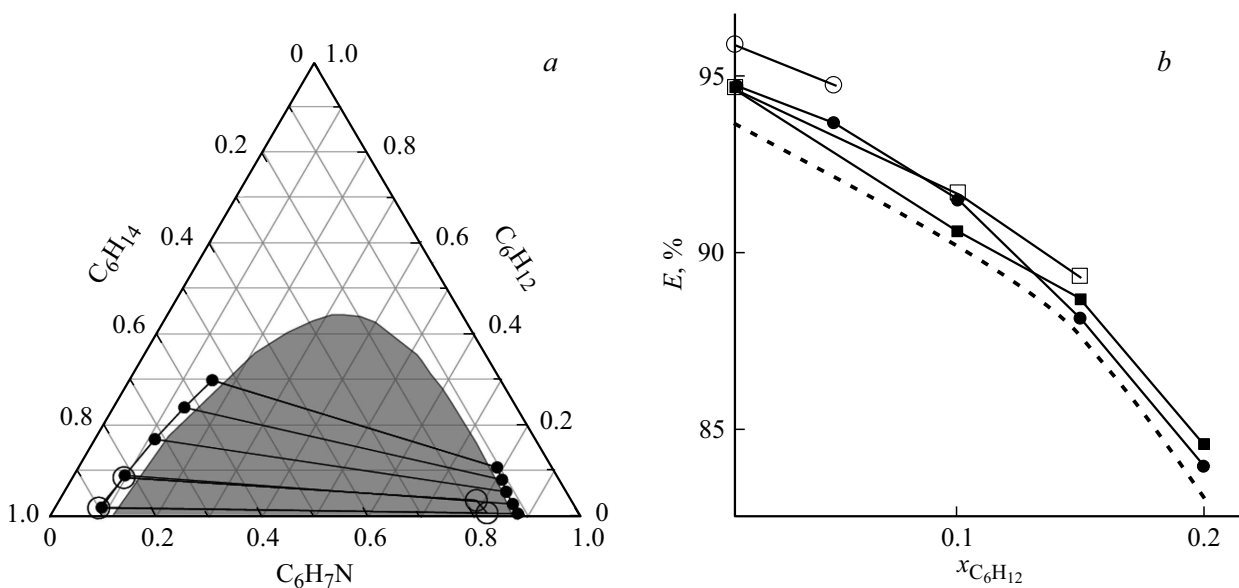
Two mixtures were simulated.

1. Aniline ( $C_6H_7N$ )–methylcyclopentane ( $C_6H_{12}$ )–hexane ( $C_6H_{14}$ ) system. Its phase diagram was provided in [12], the NRTL parameters for  $T = 318.15$  K were taken from [13]:

$$\alpha = \begin{pmatrix} 0 & 0.2 & 0.3 \\ 0.2 & 0 & 0.3 \\ 0.3 & 0.3 & 0 \end{pmatrix}, \quad \tau = \begin{pmatrix} 0 & 0.7256 & 1.6321 \\ 1.1995 & 0 & 0.5977 \\ 1.9550 & -0.4839 & 0 \end{pmatrix},$$

and reference values were used for molar volumes and the surface tension of components.

The phase diagram for a macrosystem and tie-lines for droplets with a radius of 100 nm are shown in Fig. 1, a. Tie-lines were plotted for a series of compositions with different concentrations of methylcyclopentane ( $0.01 \leq x_{C_6H_{12}} \leq 0.99$ ) and  $x_{C_6H_7N}/x_{C_6H_{14}} = 1.5$ . It



**Figure 1.** *a* — Phase diagram of an aniline ( $C_6H_7N$ )–methylcyclopentane ( $C_6H_{12}$ )–hexane ( $C_6H_{14}$ ) mixture at  $T = 318.15$  K (dark region) and tie-lines of core–shell states of droplets with a radius of 100 nm: open circles — aniline in the core phase, filled circles — aniline in the shell; *b* — concentration dependence of the degree of aniline extraction for a macrosystem (dashed line) and droplets with a radius of 200 and 100 nm (squares and circles, respectively). Filled symbols correspond to states with aniline in the core phase.

should be noted that the region of heterogeneity of a small-volume system depends on the choice of ratio  $x_{C_6H_7N}/x_{C_6H_{14}}$  [8]. The composition of coexisting phases defines distribution coefficients  $D = C_A/C_B$  or extraction degrees  $E = \frac{D}{D+V_B/V_A} \cdot 100\%$ . If aniline forms the core phase,  $A \equiv$  core and  $B \equiv$  shell; if aniline forms the shell,  $A \equiv$  shell and  $B \equiv$  core. The concentration dependence of the degree of aniline extraction for droplets with a radius of 200 and 100 nm is presented in Fig. 1, *b*. Only thermodynamically stable states ( $\Delta_{tr}G = G(n_{1c}, n_{2c}, n_{3c}) - G(0, 0, 0) < 0$ ) are shown. In the general case, small-volume systems may have several metastable states, including those outside the bounds of the region of macrosystem heterogeneity and with  $\Delta_{tr}G > 0$ . States with aniline in the core phase are advantageous for the discussed series of compositions. The states with aniline in the shell are metastable. Figure 1, *b* shows concentration dependences of the degree of aniline extraction both for submicrometer droplets and for a macrosystem. In the considered series of compositions, the degree of aniline extraction corresponding to a macrosystem is lower for both stable (aniline in the core) and metastable (aniline in the shell) states.

In the general case, stable and metastable states may compete [8–10]. Since the deviation from a macrostate is specified by the properties of components (molar volume, surface tension), the droplet size may affect the degree of extraction in a different way, and the next analyzed system proves that.

2. Water ( $H_2O$ )–phenol ( $C_6H_6O$ )–toluene ( $C_7H_8$ ) system (at  $T = 303.15$  K). Its phase diagram was provided in [14], the NRTL parameters were taken from the same

study

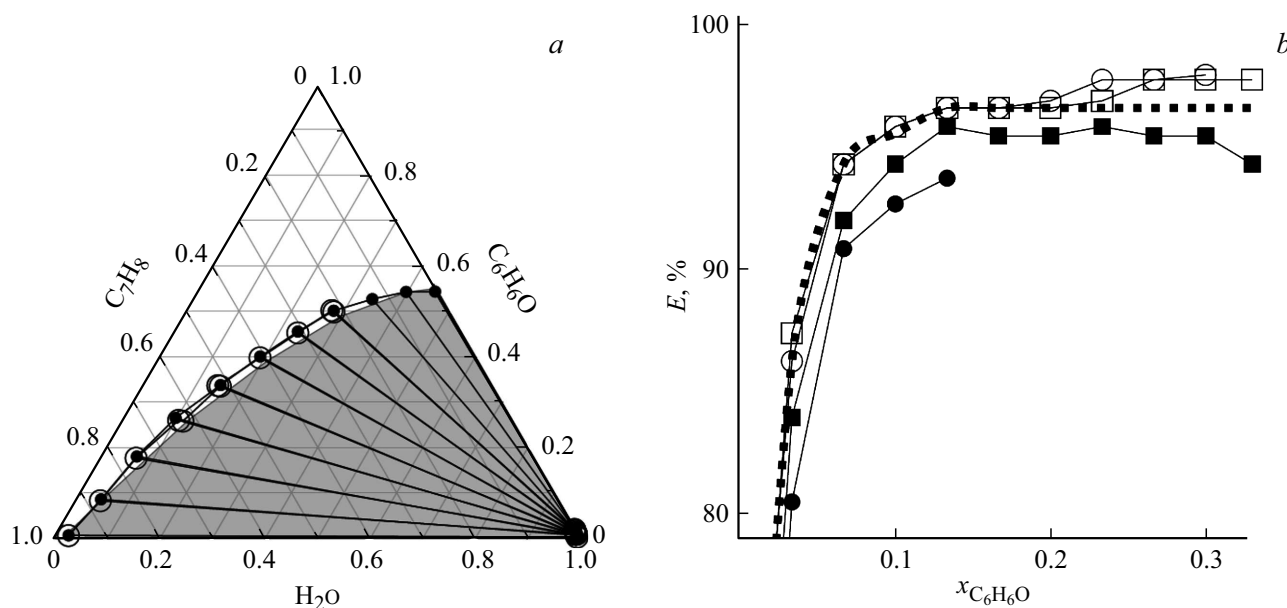
$$\alpha = \begin{pmatrix} 0 & 0.2116 & 0.2566 \\ 0.2116 & 0 & 0.2385 \\ 0.2566 & 0.2385 & 0 \end{pmatrix},$$

$$\tau = \begin{pmatrix} 0 & 4.5201 & 4.5413 \\ -0.6878 & 0 & -1.5717 \\ 2.7123 & 5.0567 & 0 \end{pmatrix}$$

and reference values were used for molar volumes and the surface tension of components.

The phase diagram for a macrosystem and tie-lines for droplets with a radius of 50 nm are shown in Fig. 2, *a*. Tie-lines were plotted for a series of compositions with  $x_{H_2O} = 2/3$ . The concentration dependence of the degree of phenol extraction for a macrosystem and droplets with a radius of 50 and 25 nm is presented in Fig. 2, *b*. Only the states with  $\Delta_{tr}G < 0$  are shown. States with a water layer in the core phase are advantageous. This system behaves in a less straightforward fashion. The degree of extraction for thermodynamically stable (water layer in the core phase) and metastable (water layer in the shell phase) states is lower and higher, respectively, than the one for a macrosystem. The size effect is more pronounced for metastable states.

A change in the degree of extraction is a natural manifestation of size effects under phase equilibria. The microextraction efficiency is sensitive both to an increase in the mass-transfer surface area and to changes in the equilibrium composition of coexisting phases. The degree of extraction may change in either direction. The nature of change is specified by the positioning of coexisting phases in the core–shell structure, the mixture composition, and the



**Figure 2.** *a* — Phase diagram of a water ( $\text{H}_2\text{O}$ )–phenol ( $\text{C}_6\text{H}_6\text{O}$ )–toluene ( $\text{C}_7\text{H}_8$ ) mixture at  $T = 303.15\text{ K}$  (dark region) and tie-lines of core–shell states of droplets with a radius of 50 nm: open circles — phenol in the core phase, filled circles — phenol in the shell phase; *b* — concentration dependence of the degree of phenol extraction for a macrosystem (dashed line) and droplets with a radius of 50 and 25 nm (squares and circles, respectively). Filled symbols correspond to states with phenol in the shell phase.

properties of components (molar volume, surface tension). With these relations taken into account, one may formalize the process of selection of extraction agents and methods of dispersion.

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### Conflict of interest

The author declares that he has no conflict of interest.

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