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Distribution of 2-Chlorobenzoic Acid in Two-Phase Systems Aromatic Solvent – Water

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Literature on partition and dimerization of aliphatic carboxylic acids and of benzoic acid shows an essential influence of organic solvent on partition of the acids and their association [1–11]. In spite of numerous uses of 2-chlorobenzoic acid, its full characterization in two-phase systems has not been performed yet. There are some data available, based on alcohol [12,13] and ketone [14] systems. The data on the distribution of 2-chlorobenzoic acid in systems with aromatic or non-polar solvent systems are fragmentary, and refer to toluene [15] and heptane [16]. The knowledge of partition K_p and dimerization K_d constants of acids is indispensable for a quantitative description of processes with acids participation, especially of complexation equilibria and extraction of chlorobenzoic salts of metals in two-phase systems. K_p and K_d constants of an acid can be obtained by combining equilibrium constants with physicochemical parameters of solvents, especially with Hildebrand solubility parameter [17,18]. Determination of K_p and K_d of 2-chlorobenzoic acid by this method for systems with aromatic solvents becomes impossible, because empirical relationships are known only for systems with ketones [14]. Thus, investigation of partition and association of 2-chlorobenzoic acid in two-phase systems, leading to determination of K_p and K_d are necessary to understand the physico-chemical properties of these systems.

Studies were carried out for aromatic solvents: benzene, bromobenzene, chlorobenzene, ethylbenzene, nitrobenzene and toluene. The partition constants, K_p, of 2-chlorobenzoic acid in two-phase systems (aromatic solvents-water), dimerization constants, K_d, of this acid in the organic phase were determined and the influence of various parameters of the systems on the equilibria was investigated. Carboxylic acid (further denoted by HR) in two-phase systems, organic solvent – water, is described by the distribution ratio, D_{HR}:

$$D_{HR} = \frac{c_{HR,o}}{c_{HR,w}} \tag{1}$$

where: $c_{HR,o}$ and $c_{HR,w}$ – analytical concentrations of carboxylic acid in the organic and water phase, respectively. Expressing the partition constant, K_p, for the acid in the organic – water system as $K_p = [HR]_o \cdot [HR]_w^{-1}$, the dimerization constant K_d of the acid in organic phase as $K_d = [(HR)_2]_o \cdot [HR]_o^{-2}$, and dissociation constant of the acid in aqueous phase as $K_{HR} = [H^+]_w \cdot [R^-]_w \cdot [HR]_w^{-1}$, the behavior of carboxylic acid in two-phase system can be described by [3–5]:

$$\frac{c_{HR,o}}{[HR]_w} = K_p + 2K_p^2 K_d [HR]_w \tag{2}$$

Partition of 2-chlorobenzoic acid and the monomer-dimer equilibria were analyzed using

$$\log c_{HR,o} = f(\log [HR]_w) \quad \text{and} \quad c_{HR,o}/[HR]_w = f([HR]_w) \tag{3,4}$$

(3) is a linear dependence, the slope of which informs about the shift of monomer-dimer equilibrium of the acid. In extreme cases, for tg $\alpha = 1$, the only acid form in the organic phase is the monomer (then $\log c_{HR,o} = \log K_p + \log[HR]_w$), however, for tg $\alpha = 2$ it is the dimer (then $\log c_{HR,o} = \log K_p^2 K_d + 2 \log[HR]_w$). From (4) the partition constant, K_p, and dimerization constant, K_d, of the acid can be obtained. Based on the experimental data and dissociation constant of the acid ($K_{HR} = 1.2 \times 10^{-3}$ [19]), $[HR]_w$ in (3) and (4) can be obtained from (5):

$$[HR]_w = c_{HR,w} [H^+]_w / ([H^+]_w + K_{HR}) \tag{5}$$

The values of tgα, K_p and K_d constants of 2-chlorobenzoic acid determined using computer program PARTITION are presented in Table 1. As can be seen, the slopes of the straight lines are within the range of 1.32–1.80 (Table 1), which indicates the co-existence of monomeric and dimeric forms of the acid. The equilibrium monomer – dimer of the acid has been shifted towards the monomeric form in the system with nitrobenzene (tg α =1.32). The shift of equilibrium towards the dimeric form of the acid has been observed for systems with ethylbenzene (tg α = 1.80) and toluene (tg α = 1.67). For other systems with benzene, chlorobenzene and bromobenzene tg α are in the range of 1.50–1.56. In these systems the content of monomeric, HR_o, and dimeric, $(HR)_{2,o}$, forms of the acid are comparable.

The partition constant, K_p, of 2-chlorobenzoic acid increased together with the Hildebrand solubility parameter, δ, of the solvents used. The increase in K_p from 0.38 for ethylbenzene ($\delta = 17.84$ kJ$^{1/2}$cm$^{-3/2}$) to 2.19 for nitrobenzene ($\delta = 20.46$ kJ$^{1/2}$cm$^{-3/2}$) has been noticed. On the other hand, the smaller δ the more molecules of the acid dimerize. The increase in δ from 17.84 kJ$^{1/2}$cm$^{-3/2}$ (ethylbenzene) to 20.46 kJ$^{1/2}$cm$^{-3/2}$ (nitrobenzene) led to of K_d of the acid from 514 to 32, respectively.

In the two-phase systems studied, the influence of solvent, pH and the concentration of the acid on the contents of its different forms (HR_o, HR_w, $(HR)_{2,o}$, R_w^-) in the organic and water phases has been determined. As an example, Fig. 1 presents the content of the existing forms of 2-chlorobenzoic acid (c_{HR} = 0.01 mol/dm^3) in the two-phase system, with regard to pH of the aqueous phase for systems containing ethylbenzene and nitrobenzene. Significant differences in the contents of monomeric and dimeric forms of the acid occur in these systems. The largest content of the monomeric form HR_o of the acid (37.4 %; pH < 3) has been found for the system with nitrobenzene, and the lowest one (10.8 %; pH < 3) for the system with ethylbenzene.

Table 1. Values of tgα for the dependence log $c_{HR,o} = f(\log[HR]_w)$, partition constant K_p and dimerization constant K_d of 2-chlorobenzoic acid in aromatic solvent – water systems. Confidence level of K_p and K_d values was calculated for n = 3 and p = 95%.

Solvent	Hildebrand solubility parameter, δ ($kJ^{1/2}cm^{-3/2}$)	tgα	Partition constant K_p	Dimerization constant K_d
Ethylbenzene	17.84	1.80	0.38 ± 0.05	514 ± 34
Toluene	18.21	1.67	0.72 ± 0.06	426 ± 28
Benzene	18.72	1.57	0.89 ± 0.11	276 ± 17
Chlorobenzene	19.44	1.56	1.47 ± 0.15	105 ± 10
Bromobenzene	19.74	1.50	1.97 ± 0.07	89 ± 3
Nitrobenzene	20.46	1.32	2.19 ± 0.10	33 ± 2

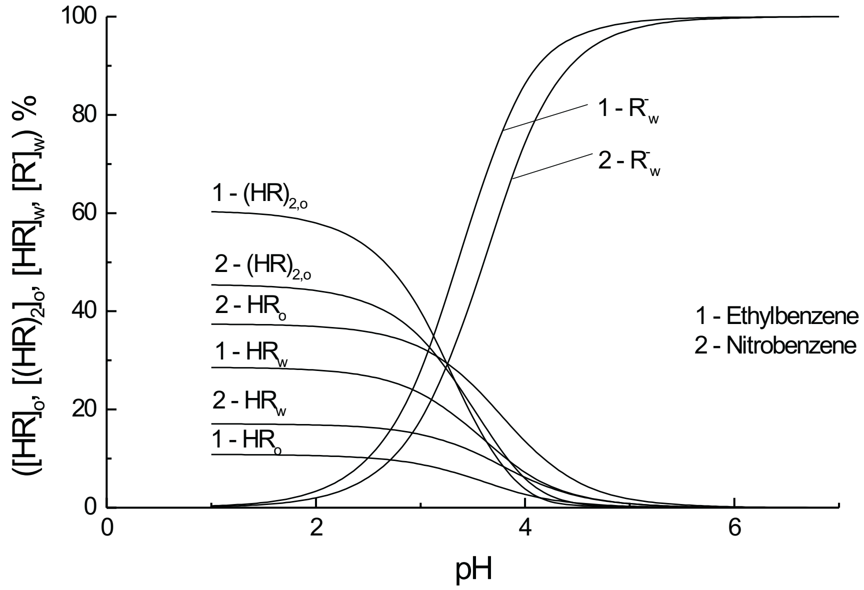

Figure 1. Dependence of the content of monomeric HR_o and HR_w, dimeric $(HR)_{2,o}$ and dissociated, R^-_w, forms of 2-chlorobenzoic acid on pH of the aqueous phase at equilibrium in aromatic solvent – water systems.

Furthermore, the largest concentrations of dimeric $(HR)_{2,o}$ and monomeric HR_w forms of the acid were observed with ethylobenzene (60.3 and 28.6 %, respectively; pH < 3), and the lowest one in the system with nitrobenzene (45.4 and 17.1 %, respectively; pH < 3). No influence of solvent polarity at pH < 2 on the content of the dissociated acid R^-_w was observed. For pH > 2 we observed a negative influence of nitrobenzene on dissociation of 2-chlorobenzoic acid in water in relation to systems with solvents of lower polarities. The reason for this is the interaction of the acid with nitrobenzene in the organic phase, which decreased the probability of the acid transfer from the organic to the water phase, and further dissociation of the acid. The influence of the concentration of the acid on the contents of its forms in two-phase system was observed as well. The increase in the acid concentration (at pH < 2.5) led to the increase in the content of HR_o and $(HR)_{2,o}$ forms, and to some extent – of HR_w and R^-_w forms.

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