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Studies on the Distribution of Phenoxyacetic Acid in Two-Phase Systems: *n*-Aliphatic Hydrocarbon – Water

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Summary. Phenoxyacetic acid distribution in two-phase systems *n*-aliphatic hydrocarbon (C_5–C_8) – water and its dimerization in organic phase were investigated. The values of distribution coefficient (D_{HR}), distribution constant (K_D), and dimerization constant (K_{dim}) of acid were obtained. The empirical correlations of these quantities with *Hildebrand* solubility parameter of organic solvents were established. The influence of *pH* of the aqueous phase as well as the polarity of the applied organic solvents on phenoxyacetic acid physical chemistry in the two-phase systems was described.

Keywords. Carboxylic acid; Equilibrium; Phenoxyacetic acid; Solvent effect; Two-phase system.

Introduction

Phenoxyacetic acid and its derivatives are mainly used for the production of pesticides and fungicides, pharmaceuticals, and as complex factors of some metals. The acids have a considerable influence on a biological life in the natural environment, in which they permeate as crop protection products. Due to their solubility in water, phenoxyacetic acids can migrate in agricultural ecosystems causing pollution of the surface and ground waters [1–6]. In spite of numerous applications of phenoxyacetic acid, its properties and full characterization in solutions, particularly in two-phase systems, has not been examined yet. The data concerning the distribution of phenoxyacetic acid in systems with organic solvents are fragmentary, and refer exclusively to *n*-octanol and benzene [7–9], and do not allow to forecast the properties and changes of acid with other solvents.

The aim of this research was to investigate the physical chemistry of phenoxyacetic acid in two-phase systems with organic solvents and to determine the distribution constants K_D and dimerization constants K_{dim}. The influence of selected parameters of the systems on equilibria was analysed (*pH* of aqueous phase, polarity of organic solvent) with regard to creation and coexistence of different acid speciations in the examined systems.

Results and Discussion

Acid Distribution

Aliphatic and aromatic acids (further denoted as HR) in organic solvent – water systems undergo the distribution, which is quantitatively described by the distribution coefficient D_{HR} or distribution constant K_D:

$$D_{HR} = c_{HR,o} \cdot c_{HR,w}{}^{-1} \tag{1}$$

$$K_D = [HR]_o \cdot [HR]_w^{-1} \tag{2}$$

where $c_{HR,o}$ and $c_{HR,w}$ constitute the analytical concentration of carboxylic acid in the organic and water phases, whereas $[HR]_o$ and $[HR]_w$ comprise the concentration of acid monomeric forms in the organic and water phases [10, 11]. The polarity of

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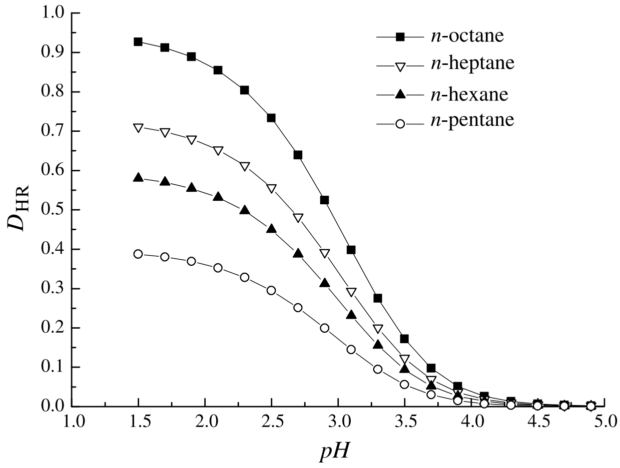

Fig. 1. Dependence of the distribution coefficient D_{HR} of phenoxyacetic acid ($c_{\mathrm{HR}} = 0.01\,\mathrm{mol \cdot dm^{-3}}$) on *pH* of the aqueous phase in organic solvent – water system, $I = 0.1$

organic solvent (*n*-aliphatic hydrocarbons by series C_5–C_8) as well as *pH* of the aqueous phase were investigated with respect to their impact on the distribution coefficient of phenoxyacetic acid in two-phase systems. Figure 1 presents the obtained results as $D_{\mathrm{HR}} = \mathrm{f}(pH)$ for applied solvents.

It was found that the highest values of the distribution coefficient are adopted for $pH < 2.5$, *i.e.* in the range where the undissociated form $\mathrm{HR_w}$ of acid exists in aqueous phase. An increase in *pH* of aqueous phase is accompanied by a decrease in the distribution coefficients. The reason for this is a gradual transfer of undissociated acid form $\mathrm{HR_w}$ in dissociated $\mathrm{R_w^-}$, the latter one is not, according to the *Born* equation [10, 12], subject to extraction to organic phase. The extraction of phenoxyacetic acid to organic phase was not observed ($D_{\mathrm{HR}} \approx 0$) for $pH > 4.5$. The effect of solvent polarity, measured by *Hildebrand* solubility parameter δ, on the distribution coefficient of phenoxyacetic acid was noticed. The distribution coefficient increases with the increase of solvent polarity according to the following series ($pH \approx 1.5$): *n*-pentane < *n*-hexane < *n*-heptane < *n*-octane.

K_D and K_{dim} Constants

Distribution coefficient does not allow the quantitative chemical forms of acid in two-phase system to be evaluated. For this purpose, distribution constants K_{D} and dimerization constants K_{dim} of acid have to be known. The K_{D} and K_{dim} constants of acid in examined two-phase systems based on experimental results and total mass balance of acid were evaluated by Eqs. (3)–(5) [13]:

$$c_{\mathrm{HR}} = [\mathrm{HR}]_{\mathrm{o}} + 2[(\mathrm{HR})_2]_{\mathrm{o}} + [\mathrm{HR}]_{\mathrm{w}} + [\mathrm{R}^-]_{\mathrm{w}} \tag{3}$$

$$c_{\mathrm{HR}} = K_{\mathrm{D}}[\mathrm{HR}]_{\mathrm{w}} + 2K_{\mathrm{D}}{}^2K_{\mathrm{dim}}[\mathrm{HR}]_{\mathrm{w}}{}^2 + [\mathrm{HR}]_{\mathrm{w}} + \frac{K_{\mathrm{a}}[\mathrm{HR}]_{\mathrm{w}}}{[\mathrm{H}^+]} \tag{4}$$

$$\frac{c_{\mathrm{HR,o}}}{[\mathrm{HR}]_{\mathrm{w}}} = K_{\mathrm{D}} + 2K_{\mathrm{D}}^2K_{\mathrm{dim}}[\mathrm{HR}]_{\mathrm{w}} \tag{5}$$

where c_{HR} is the total acid concentration, K_{dim} is the dimerization constant of acid in organic phase ($K_{\mathrm{dim}} = [(\mathrm{HR})_2]_{\mathrm{o}} \cdot [\mathrm{HR}]_{\mathrm{o}}{}^{-2}$), K_{a} is the dissociation constant ($K_{\mathrm{a}} = 6.76 \cdot 10^{-4}$ [14]), $[(\mathrm{HR})_2]_{\mathrm{o}}$ is the concentration of acid dimeric form in the organic phase, whereas $[\mathrm{R}^-]_{\mathrm{w}}$ is the concentration of acid dissociated form in water phase, for $c_{\mathrm{HR,o}}$, K_{D}, $[\mathrm{HR}]_{\mathrm{o}}$ and $[\mathrm{HR}]_{\mathrm{w}}$ see Eqs. (1) and (2). The experimental results presented in Eq. (5) as $\frac{c_{\mathrm{HR,o}}}{[\mathrm{HR}]_{\mathrm{w}}} = \mathrm{f}([\mathrm{HR}]_{\mathrm{w}})$ in *pH* range 3–4 show a linear dependence of type $y = ax + b$, where $a = 2K_{\mathrm{D}}{}^2\ K_{\mathrm{dim}}$ and $b = K_{\mathrm{D}}$. The values of K_{D} and K_{dim} constants of phenoxyacetic acid determined by use of the computer program PARTITION [13] are presented in Table 1.

Having analyzed the above presented results, it could be concluded that the increase of solvent

Table 1. Values of the distribution constant K_{D} and the dimerization constant K_{dim} of phenoxyacetic acid in organic solvent – water systems. The confidence level of K_{D} and K_{dim} values was calculated for $n = 3$ and $p = 95\%$

Solvent	*Hildebrand* solubility parameter $\delta/\mathrm{kJ^{1/2}m^{-3/2}}$	Distribution constant K_{D}	Dimerization constant K_{dim}
n-octane	15.35	$(6.97 \pm 0.30) \cdot 10^{-2}$	$(1.76 \pm 0.07) \cdot 10^4$
n-heptane	15.14	$(4.77 \pm 0.20) \cdot 10^{-2}$	$(2.36 \pm 0.09) \cdot 10^4$
n-hexane	14.94	$(3.00 \pm 0.10) \cdot 10^{-2}$	$(5.04 \pm 0.20) \cdot 10^4$
n-pentane	14.32	$(1.24 \pm 0.04) \cdot 10^{-2}$	$(2.73 \pm 0.06) \cdot 10^5$

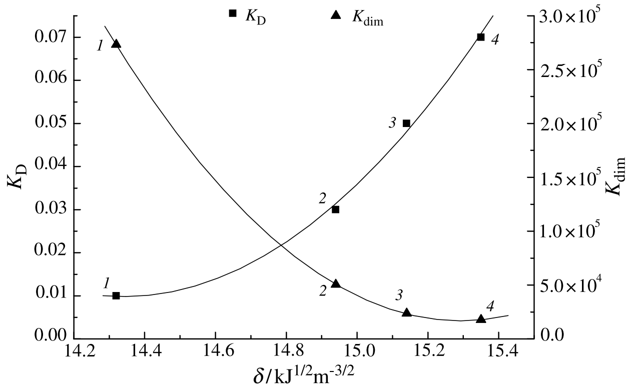

Fig. 2. Dependence of K_D and K_{dim} constants of phenoxyacetic acid in two-phase systems on *Hildebrand* solubility parameter δ of organic solvent: *1* *n*-pentane, *2* *n*-hexane, *3* *n*-heptane, *4* *n*-octane

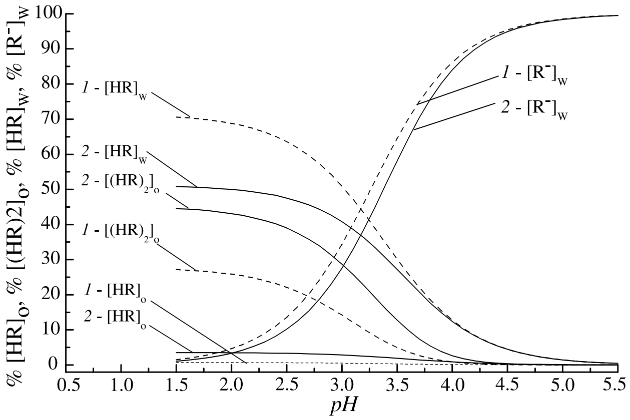

Fig. 3. Dependence of the percentage of different phenoxyacetic acid ($c_{HR} = 0.01\,\mathrm{mol \cdot dm^{-3}}$) species on *pH* of the aqueous phase at equilibrium in organic solvent – water systems. *1* *n*-pentane, *2* *n*-octane

polarity is accompanied by the increase in the distribution constants K_D from $1.24 \cdot 10^{-2}$ for *n*-pentane to $6.97 \cdot 10^{-2}$ for *n*-octane. In the case of dimerization constants K_{dim}, an inverse dependence is observed. The K_{dim} constants decrease in the series of examined solvents from $2.73 \cdot 10^5$ for *n*-pentane to $1.76 \cdot 10^4$ for *n*-octane.

Empirical correlations between K_D and K_{dim} of acid on *Hildebrand* solubility parameter δ of the used organic solvents [15] were determined (Fig. 2). It was noticed that the increase in δ is accompanied by the increase in K_D and the decrease in K_{dim}. Obtained dependences were described by Eqs. (6) and (7):

$$K_D = 0.0598\delta^2 - 1.7149\delta + 12.3066 \qquad (6)$$

$$K_{dim} = 2.7024 \cdot 10^5\delta^2 - 8.2659 \cdot 10^6\delta + 6.3224 \cdot 10^7 \qquad (7)$$

Physical Chemistry of Acid in Two-Phase Systems

Based on results of the conducted research, the influence of solvent polarity and *pH* of aqueous phase on the contents of different phenoxyacetic acid forms ($\mathrm{HR_o}, \mathrm{HR_w}, (\mathrm{HR})_{2,o}, \mathrm{R_w^-}$) in the organic and water phases was evaluated. Figure 3 presents the content of the existing forms of phenoxyacetic acid ($c_{HR} = 0.01\,\mathrm{mol \cdot dm^{-3}}$) in the two-phase system, with regard to *pH* of the aqueous phase for systems containing two solvents having extreme *Hildebrand* solubility parameter: *n*-octane ($\delta = 15.35\,\mathrm{kJ^{1/2}m^{-3/2}}$) and *n*-pentane ($\delta = 14.32\,\mathrm{kJ^{1/2}m^{-3/2}}$).

It was found that the increase of organic solvent polarity (in $pH \approx 2$) causes the following: the increase in the content of the monomeric form $\mathrm{HR_o}$ of the acid in organic phase (~0% – *n*-pentane, 4% – *n*-octane), the increased participation of dimeric form $(\mathrm{HR})_{2,o}$ of the acid (27% – *n*-pentane, 44% – *n*-octane), the slight increase in the content of dissociated form R_w^- and the decrease in participation of undissociated form $\mathrm{HR_w}$ (72% – *n*-pentane, 51% – *n*-octane). The influence of *pH* on the changes of concentration of particular acid forms is visible for values 2.5–4.5 of the investigated parameter, in which the acid distribution in the two-phase system is conducted. When *pH* of the water phase grows the percentage of dissociated form R_w^- increases while the content remaining forms decrease in both compared organic solvents. R_w^- form is exclusively present in two-phase systems for $pH > 5$.

Conclusions

Due to the fact that phenoxyacetic acid and its derivatives are widely applied in agriculture and have a great influence on the natural environment, the detailed description of their equilibria in aqueous solutions and in two-phase systems is essential. For this reason, in this paper the analysis of phenoxyacetic acid equilibria in two-phase systems was carried out and the fundamental physicochemical parameters such as distribution (K_D) and dimerization (K_{dim}) constants were determined.

Based on the conducted distribution investigations, the D_{HR}, K_D, and K_{dim} were obtained for four two-phase systems: *n*-aliphatic hydrocarbon – water solution. It follows from the experiments that the values of D_{HR}, K_{D}, K_{dim}, and the content of various acid forms depend on the organic solvent polarity. The values of D_{HR} and K_{D} increase while the values of K_{dim} decrease when the polarity of organic solvent grows. The influence of *pH* of water phase on the changes of content acid forms is visible for values 2.5–5.5 of the investigated parameter, in which the acid distribution in the two-phase system practically proceeds. The empirical correlations of K_{D} and K_{dim} with *Hildebrand* solubility parameter of applied organic solvents were established.

Experimental

The investigations of distribution and association of phenoxyacetic acid in two-phase systems organic solvent – water were performed. As organic solvent *n*-octane, *n*-heptane, *n*-hexane, and *n*-pentane were applied. The solutions of phenoxyacetic acid of $0.01\,\mathrm{mol \cdot dm^{-3}}$ concentration in water were prepared, constituting the initial aqueous phase, which was initially acidified to *pH* 1.5 by $0.1\,\mathrm{mol \cdot dm^{-3}}$ HCl. Before the acid solutions were made, the aqueous phase had been saturated by each of the organic solvents and *vice versa*. Ionic strength was maintained at 0.1 with KCl. Extraction of acid was conduced by two-phase potentiometric titration in a thermostated extraction vessel ($t = 25 \pm 0.1°\mathrm{C}$). The titrant was $0.1\,\mathrm{mol \cdot dm^{-3}}$ KOH solution. The glass electrode was standardized with aqueous buffer solutions (4.00, 7.00, 9.00). The *pH* value was continuously measured with CP-501 *pH*-meter ($pH \pm 0.01$) supplied with OSH-10-00 combined electrode. The distribution coefficients D_{HR}, the distribution constants K_{D}, and the dimerization constants K_{dim} of phenoxyacetic acid, and the content of its different forms in two-phase systems were determined by making use of PARTITION and FORM computer programs [13].

References

[1] Wells M, Yu LZ (2000) J Chromatogr A **885**: 237

[2] Schnoor JL (1992) Fate of pesticides and chemicals in the environment, Wiley, New York-Chichester-Brisbane-Toronto-Singapore

[3] Cremlyn R (1980) Pesticides: preparation and mode action, Wiley, Chichester – New York-Brisbane-Toronto

[4] Yamansarova ET, Kukovinets OS, Zainullin RA, Galin FZ, Abdullin MI (2005) Zh Org Khim **41**(4): 546

[5] Ptaszyński B, Zwolińska A (2004) J Therm Anal Cal **75**: 301

[6] Cserhăti T, Forgăcs E (1998) J Chromatogr B **717**: 157

[7] Korenman YI, Selmanshchuk NN (1982) Zh Fiz Khim **56**: 1730

[8] Fujita T, Iwasa J, Hensch C (1964) J Am Chem Soc **5**: 5175

[9] Rajesh CS, Thanulingam TL, Suresh D (1997) Tetrahedron **53**(49): 16817

[10] Sekine T, Hasegawa Y (1977) Solvent extraction chemistry, Marcel Dekker, New York

[11] Hanson C, Baird MH, Lo TC (1983) Handbook of solvent extraction, Wiley, New York-Chichester-Brisbane-Toronto-Singapore

[12] Jeżowska-Trzebiatowska B, Kopacz S, Mikulski T (1990) The rare elements occurence and technology, PWN-Warszawa, Elsevier-Amsterdam-Oxford-New York-Tokyo

[13] Kalembkiewicz J, Zapała L (2001) Polish J Chem **75**: 1797

[14] Headley AD, Stephen SD, Leland WY, Famini GR (1994) J Org Chem **59**: 8040

[15] Papciak B, Kopacz S, Kalembkiewicz J (1996) Investigations of 3-chlorobenzoic acid partition in two-phase systems. Proc. Int. Conf. "Analysis and utilization of oily wastes" Gdańsk (Poland) **2**: 421