

## THE DISTRIBUTION COEFFICIENTS OF BIS(2-CHLOROETHYL) SULFIDE BETWEEN SOME ORGANIC SOLVENTS AND WATER

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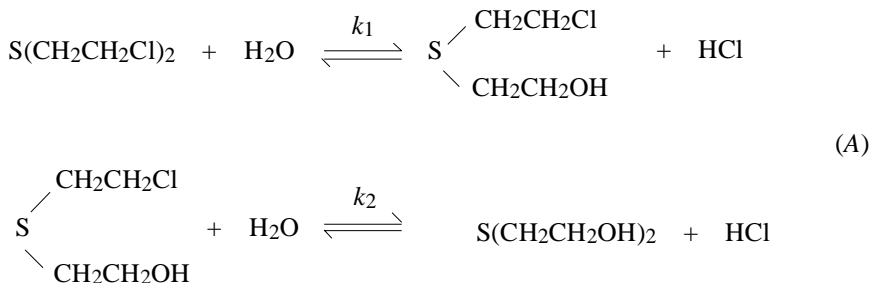
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The results of determining the distribution coefficients of bis(2-chloroethyl) sulfide between some organic solvents and water at 25 °C are presented in this paper. Two original methods for determining the distribution coefficients were applied: the kinetic method and the method of hydrolysis blocking. Values of the obtained distribution coefficients are discussed from the aspect of the calculated solubility parameters. The denoted methods can also be applied in a similar fashion to determine the distribution coefficients of other substances of similar properties.

Two phase systems based on emulsions<sup>1</sup>, microemulsions<sup>2</sup>, as well as phase boundary catalysis<sup>3,4</sup> have lately been of special interest in the field of chemical weapon degradation. Although there have been extensive investigations of the most appropriate systems for rapidly decomposing bis(2-chloroethyl) sulfide, there are no data in the literature on the distribution coefficients of this compound between organic solvents and water. They cannot be determined directly due to the relatively rapid hydrolysis of bis(2-chloroethyl) sulfide<sup>5-7</sup>. Information on distribution coefficients is necessary for investigating reactions in heterogeneous systems as well as for choosing solvents for extraction from aqueous solutions for analytical purposes.

In range  $2 < \text{pH} < 10$  the hydrolysis of bis(2-chloroethyl) sulfide is pH-independent and thus the overall reaction likely proceeds via two consecutive pseudo-first order reactions:



Values of the rate constants  $k_1$  and  $k_2$  at 25 °C in this pH range were ascertained to 0.155 min<sup>-1</sup> and 0.260 min<sup>-1</sup>, respectively<sup>5</sup>. In the range pH < 2, both reverse reactions become relevant. The synthesis of bis(2-chloroethyl) sulfide from thiodiglycol in acidic medium<sup>8</sup> is based on the distinct reverse reaction of Eq. (A). In the range pH > 10 along with hydrolysis, an elimination reaction also occurs, thus leading to formation of a mixture of various products<sup>9</sup>.

## EXPERIMENTAL

**Chemicals.** Bis(2-chloroethyl) sulfide was synthesized from thiodiglycol according to the procedure given in ref.<sup>8</sup>, purity 99.5% by GC. Hexane, cyclohexane, tetrachloromethane (Merck, p.a.) tetrachloroethylene, toluene, nitrobenzene (Fluka, p.a.) were used without further purification. Water saturated by organic solvents and organic solvents saturated by water were applied in order to minimize errors which occur due to changes in phase volumes during their mixing. Saturation was performed manually, with subsequent centrifuging and phase separation.

**Kinetic method.** Organic solvent (5 cm<sup>3</sup>) with  $1.5 \cdot 10^{-2}$  cm<sup>3</sup> of previously added bis(2-chloroethyl) sulfide was transferred to a thermostatted reaction vessel maintained under isothermal conditions. Previously distilled water (5 cm<sup>3</sup>) thermostatted at 25 ± 0.1 °C was then added. Intensive mixing of the reaction mixture was achieved using a magnetic stirrer. At defined time intervals (60, 120, 180, 240 and 300 min) the stirrer was briefly stopped (for no more than 15 s) and a 0.1 cm<sup>3</sup> aliquot of the organic phase removed and transferred to a flask containing 10 cm<sup>3</sup> of ethanol. The sample was analyzed spectrophotometrically using thymolphthalein as reagent<sup>10</sup>.

**Hydrolysis blocking method.** Bis(2-chloroethyl) sulfide ( $3.2 \cdot 10^{-2}$  cm<sup>3</sup>) was added to 5 cm<sup>3</sup> of organic solvent in a separating funnel and thermostatted for 20 min at 25 °C. Aqueous solution of HCl of known concentration (5 cm<sup>3</sup>) of the same temperature was then added, the mixture stirred intensively for 1 min and the phases allowed to separate for 2 min. An aliquot (0.2 cm<sup>3</sup>) was taken from the organic phases and transferred to a flask containing 2.5 cm<sup>3</sup> of ethanol. A 1 cm<sup>3</sup> aliquot was then taken from the aqueous phase. Before the assay, the sample from aqueous phase is neutralized with 1.0 mol dm<sup>-3</sup> solution of sodium hydroxide in ethanol. The samples were analyzed in the same fashion as in the kinetic method.

**Mathematical method.** All the linear dependencies were treated by the least squares method and characterized by the correlation coefficient ( $r$ ) and the standard deviation ( $s$ ).

## RESULTS AND DISCUSSION

### *Kinetic Method: Model Excluding the Salting out Effect*

Under the conditions of intensive mixing of the heterogeneous system organic solvent–water, the distributed bis(2-chloroethyl) sulfide is characterized by two processes: (i) chemical reaction in the aqueous phase (slow process of hydrolysis of bis(2-chloroethyl) sulfide, and (ii) transfer of bis(2-chloroethyl) sulfide from the organic to the aqueous phase (fast process). The change of concentration of bis(2-chloroethyl) sulfide in the aqueous phase due to the chemical reaction, for the period  $dt$ , is given by:

$$\frac{dc_{WF}}{dt} = -k_1 c_{WF}, \quad (1)$$

where  $c_{WF}$  is the molar concentration of bis(2-chloroethyl) sulfide in the aqueous phase, and  $k_1$  is the rate constant of the first stage of the bis(2-chloroethyl) sulfide hydrolysis.

On the other hand, if during the period  $dt$ ,  $dn$  moles of bis(2-chloroethyl) sulfide are transferred from the organic to the aqueous phase, it can be written:

$$dn_{WF} = -dn_{OF}, \quad (2)$$

where  $n_{WF}$  and  $n_{OF}$  are the amounts of substance bis(2-chloroethyl) sulfide in aqueous and organic phases, respectively. If the volumes of the aqueous and organic phase are the same, it can be written:  $dc_{WF} = -dc_{OF}$ , i.e.:

$$\frac{dc_{WF}}{dt} = -\frac{dc_{OF}}{dt}, \quad (3)$$

where  $c_{OF}$  is the concentration of bis(2-chloroethyl) sulfide in organic phase,  $\text{mol dm}^{-3}$ .

Effective change of the concentration of bis(2-chloroethyl) sulfide in the water as the function of time equals the sum of change due to the reaction and change due to the mass transfer from the organic phase:

$$\left(\frac{dc_{WF}}{dt}\right)_{ef} = \left(\frac{dc_{WF}}{dt}\right)_{\text{reaction}} + \left(\frac{dc_{WF}}{dt}\right)_{\text{mass transfer}}. \quad (4)$$

Taking into consideration the Eqs (1) and (3), Eq. (4) can be written as:

$$\left(\frac{dc_{WF}}{dt}\right)_{ef} = -k_1 c_{WF} - \frac{dc_{OF}}{dt}. \quad (5)$$

As a kinetic mode is presumed for this type of heterogeneous reaction, the effective  $c_{WF}$  is always in equilibrium with the current  $c_{OF}$ , i. e.:

$$c_{WF} = \frac{c_{OF}}{K}, \quad (6)$$

where  $K$  is the distribution coefficient of bis(2-chloroethyl) sulfide between the organic and aqueous phases in the presence of electrolyte. By differentiation of the Eq. (6) for  $dt$ , the following relation is obtained:

$$\left(\frac{dc_{WF}}{dt}\right)_{ef} = \frac{1}{K} \frac{dc_{OF}}{dt} \quad (7)$$

By substituting the Eqs (6) and (7) in the Eq. (5), we obtain:

$$\frac{1}{K} \frac{dc_{OF}}{dt} = -k_1 \frac{c_{OF}}{K} - \frac{dc_{OF}}{dt} \quad (8)$$

The rearrangement of the Eq. (8) results in:

$$\frac{dc_{OF}}{dt} = -\frac{k_1}{1+K} c_{OF} \quad (9)$$

At the beginning of the reaction the concentration of formed hydrochloric acid is low and so, neglecting the salting out effect, it may be assumed that for this period the distribution coefficient has a constant value ( $K \approx K_0$ ). Consequently, by integrating Eq. (9), an equation is obtained, which can be used to calculate the distribution coefficient:

$$\ln \frac{c_{OF}}{c_{OF}^0} = \frac{k_1}{1+K_0} t = k' t \quad (10)$$

where  $c_{OF}^0$  is the initial concentration of bis(2-chloroethyl) sulfide in the organic phase,  $\text{mol dm}^{-3}$ , and  $k'$  is the observed hydrolysis rate constant,  $\text{min}^{-1}$ .

The change of concentration of bis(2-chloroethyl) sulfide in the organic phase with time, for various systems organic solvents–water at 25 °C, described by the Eq. (10) is shown in Fig. 1.

Analysis of kinetic data of the hydrolysis of bis(2-chloroethyl) sulfide in two-phase system according to Eq. (10) enables the calculation of the distribution coefficients of bis(2-chloroethyl) sulfide between organic solvents and water from the experimentally determined value of the rate constant  $k'$  and the known value of the hydrolysis rate constant in pure water,  $k_1$ . The values of the observed hydrolysis rate constants of bis(2-chloroethyl) sulfide ( $k'$ ) at 25 °C in heterogeneous systems of various organic

solvents and water, as well as the distribution coefficients ( $K_0$ ), calculated according to Eq. (1), are shown in Table I.

*Kinetic Method: Model Including the Salting out Effect*

As a result of the hydrolysis of bis(2-chloroethyl) sulfide, the ions from the formed HCl cause a change in the distribution coefficient of the studied compound in accordance

TABLE I  
Observed hydrolysis constants ( $k'$ ) and the corresponding distribution coefficients ( $K_0$ ) of bis(2-chloroethyl) sulfide at 25 °C in various two-phase systems organic solvent–water ( $r$  is correlation coefficient)

Solvent	$k' \cdot 10^4, \text{min}^{-1}$	$r$	$K_0$
Hexane	$11.05 \pm 1.41$	0.984	$139.2 \pm 14.8$
Cyclohexane	$4.44 \pm 0.45$	0.985	$348.1 \pm 31.1$
Tetrachloroethylene	$4.93 \pm 0.33$	0.995	$313.4 \pm 18.7$
Tetrachloromethane	$3.23 \pm 0.38$	0.960	$479.0 \pm 62.9$
Toluene	$2.98 \pm 0.05$	0.990	$519.1 \pm 22.3$
Chlorobenzene	$1.64 \pm 0.14$	0.990	$944.1 \pm 73.3$
Nitrobenzene	$2.62 \pm 0.14$	0.991	$590.6 \pm 33.8$

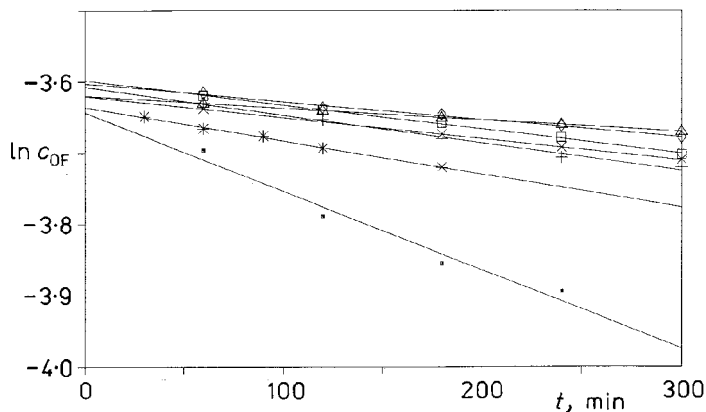


FIG. 1

Logarithmic dependance of the concentration of bis(2-chloroethyl) sulfide in the organic phase on time at 25 °C in the system organic solvent–water. Organic solvent: ■ hexane, + cyclohexane, \* tetrachloroethylene, □ tetrachloromethane, × toluene, ◇ nitrobenzene, Δ chlorobenzene

with Setchenov rule<sup>11</sup> which describes the dependence of the distribution coefficient on the concentration of electrolyte in the aqueous phase.

$$K = K_0 \cdot 10^{p(c_{\text{OF}}^0 - c_{\text{OF}})}, \quad (11)$$

where  $p$  is the salting out constant,  $\text{dm}^3 \text{mol}^{-1}$ . As the concentration  $c_{\text{OF}}^0$  and the total concentration of the solute in both phases  $c^0$  are correlated by

$$c_{\text{OF}}^0 = \frac{K_0 c^0}{1 + K_0}, \quad (12)$$

by combining Eqs (9), (11) and (12) an equation is obtained the solution of which reduces to the solution of the integral

$$\int_{c_{\text{OF}}}^{\frac{K_0 c^0}{1 + K_0}} \frac{1 + K_0 \cdot 10^{p\left(\frac{K_0 c^0}{1 + K_0} - c_{\text{OF}}\right)}}{c_{\text{OF}}} dc_{\text{OF}} = k_1 t. \quad (13)$$

Such a solution can be applied only to the initial phase of the hydrolysis of bis(2-chloroethyl) sulfide, i.e. to the case where the second stage of reaction (A) can be neglected. In the further course of the reaction the evolved hydrochloric acid must also be taken into account in the second stage of reaction (A). The change in concentration as a function of time, for this case, can be defined by the following equation<sup>7</sup>

$$c_{\text{E1}} = c^0 \left[ 2 - \frac{k_1 - 2k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right], \quad (14)$$

where  $c_{\text{E1}}$  is the concentration of electrolyte (HCl) in the aqueous phase,  $\text{mol dm}^{-3}$ . By substituting Eq. (14) into Eq. (11) and the thus obtained expression into Eq. (9) one obtains

$$\frac{dc_{\text{OF}}}{dt} = - \frac{k_1}{1 + K_0 \cdot 10^{p\left[ 2 - \frac{k_1 - 2k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right]}} c_{\text{OF}}. \quad (15)$$

By integrating this equation in the same boundaries as in expression (13) one obtains

$$\ln \frac{c_{\text{OF}}}{K_0 c^0} = -k_1 \int_0^t \frac{dt}{1 + K_0 \cdot 10^{pc^0 \left[ 2 - \frac{k_1 - 2k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right]}} \quad (16)$$

As the numerical solution of the integrals in Eqs (13) and (16) for the required parameters  $K_0$  and  $p$  based on the experimental data  $c_{\text{OF}} = f(t)$  is very complicated, these expressions are predominantly of theoretical significance.

### *The Hydrolysis Blocking Reactions*

By adding hydrochloric acid to the two-phase system organic solvent–water, the hydrolysis of bis(2-chloroethyl) sulfide is stopped. However, there is a change in the distribution of this compound in the denoted system depending on the concentration of the applied acid, in accordance with the Setchenov rule<sup>11</sup>. If the Setchenov equation is presented in its log form, the following expression is obtained

$$\log K = \log K_0 + p c_{\text{E1}} \quad (17)$$

By the direct determination of the distribution coefficient ( $K$ ) for various concentrations of hydrochloric acid in the aqueous phase, the distribution coefficient ( $K_0$ ), as well as the salting out constant ( $p$ ) for a chosen system organic solvent–water can be determined according to Eq. (17). Table II contains the experimentally determined coefficients of bis(2-chloroethyl) sulfide between hexane or tetrachloroethylene and water solutions of hydrochloric acid in various concentrations at 25 °C. On the basis data from Table II and using the least-squares method according to Eq. (17) the following values of the distribution coefficients and the salting out constants were obtained:

hexane:	$K_0 = 151.4 \pm 4.7$	$p = 0.069 \pm 0.010$	$(r = 0.981)$
tetrachloroethylene:	$K_0 = 322.6 \pm 4.4$	$p = 0.063 \pm 0.004$	$(r = 0.998)$

The various values of the distribution coefficients of bis(2-chloroethyl) sulfide between organic solvents and water, given in Table I, were analyzed by Hildebrand–Scott

solubility parameters of organic solvents and bis(2-chloroethyl) sulfide. Unknown the solubility parameters ( $\delta$ ) were calculated according to the equation<sup>12</sup>:

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V_M}}, \quad (18)$$

where  $\Delta H_v$  is the heat of vaporization,  $R$  the universal gas constant,  $T$  the temperature, and  $V_M$  the molar volume of the liquid.

TABLE II

Distribution coefficients ( $K$ ) of bis(2-chloroethyl) sulfide between organic solvents and water solutions of hydrochloric acid in various concentrations at 25 °C

$c_{\text{El}}, \text{ mol dm}^{-3}$	$K$	
	hexane	tetrachloroethylene
0.5	162	340
1.0	182	372
1.5	188	403
2.0	209	430

TABLE III

The distribution coefficients ( $K_0$ ), solubility parameters of some organic solvents ( $\delta$ ) and the difference in the solubility parameters of bis(2-chloroethyl) sulfide and organic solvents ( $|\Delta\delta|$ ) at 25 °C

Solvent	$K_0$	$\delta^a, \text{ J}^{1/2} \text{ cm}^{-3/2}$	$ \Delta\delta $
Hexane	139.2	14.9	5.0
Cyclohexane	348.1	16.8	3.1
Tetrachloroethylene	313.4	17.8	2.1
Tetrachloromethane	479.0	17.8	2.1
Toluene	519.1	18.4	1.5
Chlorobenzene	944.1	19.4	0.5
Nitrobenzene	590.6	20.5	0.6

<sup>a</sup> The solubility parameters of hexane, cyclohexane, tetrachloromethane and toluene were taken from the literature<sup>14</sup>, for chlorobenzene and nitrobenzene from ref.<sup>15</sup>, while the values for tetrachloroethylene were calculated by Eq. (18) using the literature data of the heat of vaporization and the molar volume<sup>16</sup>.



The solubility parameters of bis(2-chloroethyl) sulfide, calculated on the basis of data on the calculated heat of vaporization\* and the molar volume<sup>13</sup> at 25 °C was found to be  $19.9 \text{ J}^{1/2} \text{ cm}^{-3/2}$ . The distribution coefficients of bis(2-chloroethyl) sulfide between some organic solvents in water are presented in Table III, as well as the solubility parameters of the applied solvents and the differences in the solubility parameters of bis(2-chloroethyl) sulfide and the solvents at 25 °C.

The general rule that the mutual solubility of two liquids is greater if the absolute value of the difference of their solubility parameters ( $|\Delta\delta|$ ) is smaller was satisfied in the solvent series hexane – cyclohexane – tetrachloromethane – toluene – nitrobenzene – chlorobenzene. Something the lower value of the distribution coefficient of bis(2-chloroethyl) sulfide between nitrobenzene and water, despite the low difference ( $|\Delta\delta|$ ), is caused by the semipolar bond of the nitro group, which is reflected in the high value of the dipole moment of nitrobenzene (3.97 D).

The denoted methods, based on determining the distribution coefficients of bis(2-chloroethyl) sulfide between organic solvents and water under dynamic conditions or on blocking the hydrolysis reaction, can also be similarly applied to the determination of distribution coefficients of other substrates when, due to spontaneous hydrolysis, it is not possible to determine them by the standard procedure.

On the other hand, approximately the same value of the salting out constant ( $p$ ) for hexane and tetrachloroethylene is consistent with the results obtained for other two-phase systems, in that the change of the applied solvent usually do not, affect the experimentally determined values of salting out constants.

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\*  $\Delta H_v$  calculated according to the equation<sup>14</sup>:  $\Delta H_v = -2\,950 + 23.7 T_k + 0.020 T_k^2$ , J mol<sup>-1</sup> ( $T_k$  temperature of boiling, K).

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