

SORPTION
AND ION-EXCHANGE PROCESSES

Effect of Solvating Additives on Anion-Exchange Extraction of Trichloroacetate Anions from Aqueous Solutions with Trinonyloctadecylammonium Picrate in Toluene

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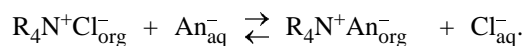
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Abstract—The solvation effect of trifluoroacetophenone derivatives on anion-exchange extraction of trichloroacetate anions from aqueous phase with trinonyloctadecylammonium picrate in toluene was studied.

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Solutions of higher quaternary ammonium salts (QASs) in organic solvents immiscible with water efficiently extract various anions from aqueous phase by the anion-exchange mechanism [1]. The extractability of anions from aqueous solutions in these systems is quantitatively characterized by the concentration equilibrium constant $K_{Cl^-}^{An^-}$ of the anion-exchange reaction



It is known that the order of extractability of anions of various kinds with liquid anion exchangers does not depend on the organic solvent [1]. Therefore, the relative extractability of anions in their series can be changed either by going to another liquid anion exchanger [2] or by adding some additional solvating agent [3]. For example, even small additions of hexyl *p*-trifluoroacetylbenzoate (approximately 10^{-2} M) increase the extraction constant of carboxylate anions $R-COO^-$ with QASs in organic solvents by several orders of magnitude [4].

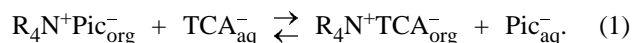
In this study we examined the effect of trifluoroacetophenone derivatives of various structures on anion-exchange extraction of trichloroacetate anions from aqueous phase with a quaternary ammonium picrate in toluene and determined the extraction and solvation constants and the average solvation numbers.

EXPERIMENTAL

We studied the extraction of trichloroacetate (TCA) anions from aqueous sodium trichloroacetate with a liquid anion exchanger, trinonyloctadecylammonium [(C₉H₁₉)₃C₁₈H₃₇N⁺] picrate, TNODA Pic, in toluene.

The extraction was carried out in test tubes with ground-glass stoppers at the volume ratio of the organic and aqueous phases of 1 : 1 at 293 ± 1 K. After completion of the extraction, the aqueous phase was separated and filtered. The content of picrate anions in the filtered solutions was determined spectrophotometrically on an SF-26 spectrophotometer [5].

The ion-exchange extraction of TCA⁻ anions from aqueous phase with TNODA Pic in toluene can be described by equation of the following heterogeneous reaction:



The concentration constant of this reaction $K_{Pic^-}^{TCA^-}$ was calculated by the equation

$$K_{Pic^-}^{TCA^-} = \frac{[Pic^-]^2}{(c_{0,R_4N^+Pic^-} - [Pic^-])(c_{0,TCA^-} - [Pic^-])} \quad (2)$$

where $c_{0,R_4N^+Pic^-}$ is the initial TNODA Pic concentration and c_{0,TCA^-} , the initial trichloroacetate anion concentration in the aqueous phase.

On addition of the solvating agent S to the organic phase, TNODA TCA is selectively solvated with S molecules by the reaction



whereas TNODA Pic is not solvated [6].

The constant $K_{Pic^-}^{TCA^-}$ [Eq. (2)] does not take into account the solvation of the extracted TCA anions by reaction (3) (Eq. 1). Therefore, this constant is considered to be an apparent quantity and hereinafter is denoted as $\tilde{K}_{Pic^-}^{TCA^-}$.

Logarithms of the apparent anion-exchange extraction constants, logarithms of the solvation constants, and average solvation numbers of TCA anions in their extraction from aqueous phase with TNODA Pic in toluene in the presence of solvating additives S (10^{-2} M)

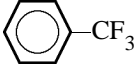
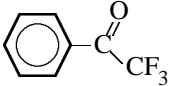
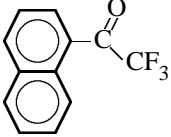
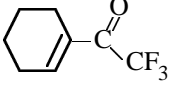
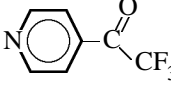
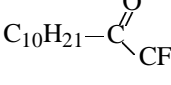
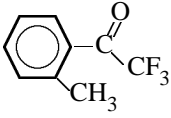
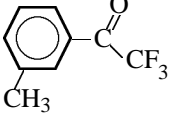
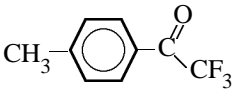
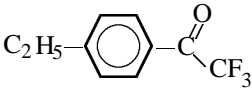
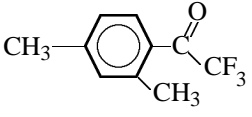
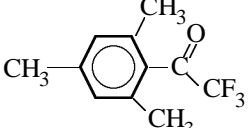
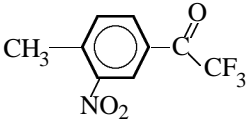
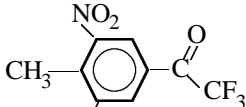
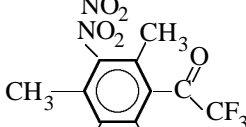
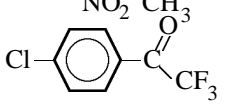
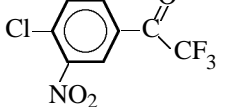
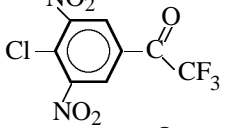
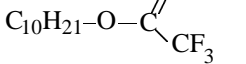
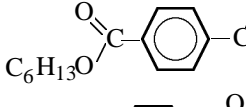
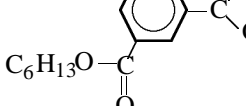
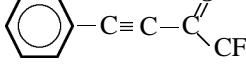
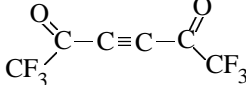
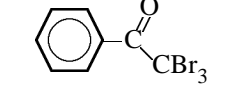
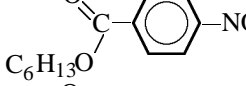
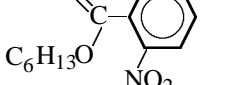
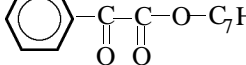
Solvating additive	$\log \tilde{K}_{\text{Pic}}^{\text{TCA}^-}$	$\Delta \log \tilde{K}_{\text{Pic}}^{\text{TCA}^-}$	$\log K_s \pm \delta$	$\bar{p} \pm \delta$
No additive	-4.67	0	-	-
 S1	-4.67	0	-	-
 S2	-4.15	0.52	2.35 ± 0.06	0.99 ± 0.04
 S3	-4.57	0.10	1.70 ± 0.28	1.01 ± 0.37
 S4	-4.59	0.08	-	-
 S5	-4.66	0	-	-
 S6	-4.71	0	-	-
 S7	-4.59	0.08	1.54 ± 0.42	1.07 ± 0.46
 S8	-4.38	0.29	2.04 ± 0.35	1.01 ± 0.23
 S9	-4.41	0.26	1.61 ± 0.54	0.81 ± 0.35
 S10	-4.40	0.27	1.83 ± 0.11	0.96 ± 0.07
 S11	-4.46	0.21	-	-
 S12	-4.49	0.18	-	-
 S13	-2.91	1.76	3.46 ± 0.28	0.92 ± 0.10

Table (Contd.)

Solvating additive	$\log \tilde{K}_{\text{Pic}^-}^{\text{TCA}^-}$	$\Delta \log \tilde{K}_{\text{Pic}^-}^{\text{TCA}^-}$	$\log K_s \pm \delta$	$\bar{p} \pm \delta$
 S14	-1.85	2.82	4.79±0.38	0.93±0.10
 S15	-4.69	0	-	-
 S16	-3.67	1.00	2.73±0.55	0.99±0.25
 S17	-2.27	2.40	4.61±0.38	1.07±0.12
 S18	-1.71	2.96	4.99±0.47	0.93±0.12
 S19	-4.70	0	-	-
 S20	-3.32	1.35	3.20±0.37	1.05±0.14
 S21	-3.76	0.91	3.06±0.60	1.11±0.27
 S22	-4.02	0.65	2.31±0.07	0.88±0.04
 S23	-4.48	0.19	1.55±0.58	0.93±0.27
 S24	-4.72	0	-	-
 S25	-4.69	0	-	-
 S26	-4.70	0	-	-
 S27	-4.70	0	-	-

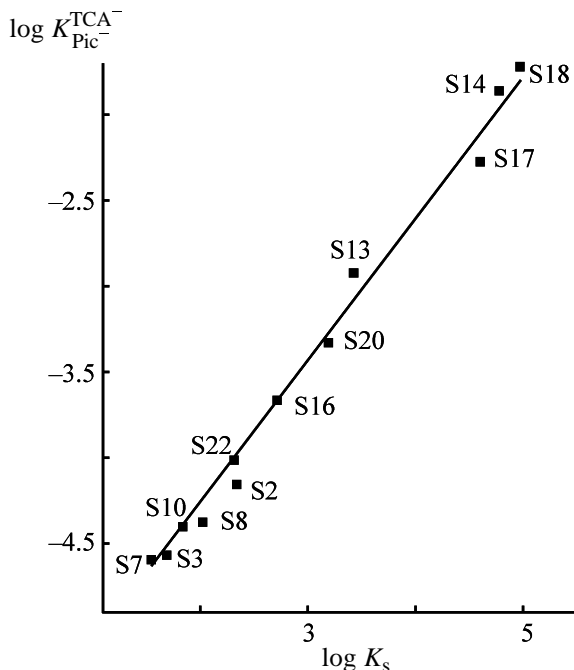


Fig. 1. Correlation between the logarithms of the anion-exchange extraction constants of TCA^- anions from the aqueous phase with TNODA Pic in toluene containing various organic additives and logarithms of the solvation constant K_s of TCA^- anions.

The relation between the concentration anion-exchange extraction constants $K_{\text{Pic}}^{\text{TCA}^-}$, the apparent anion-exchange extraction constants $\tilde{K}_{\text{Pic}}^{\text{TCA}^-}$, solvation constants K_s , and average solvation number p is described by the following bilogarithmic equation:

$$\log(\tilde{K}_{\text{Cr}}^{\text{An}^-}/K_{\text{Cr}}^{\text{An}^-} - 1) = \log K_s + p \log [S]. \quad (4)$$

The parameters K_s and p calculated by Eq. (4) using the special computer program [7] are listed in the table.

Analysis of the results listed in the table shows that the additives (trifluoroacetophenone derivatives) increasing the anion-exchange extraction of trichloroacetate anions are characterized by the following structural features.

(1) All the additives contain the CF_3 groups. This is seen from the fact that, in going from trifluoroacetophenone (structure S2) to tribromoacetophenone (structure S24), the effect of additive on the extraction completely disappears.

(2) The CF_3 group is a fragment of the trifluoroacetyl group $-\text{CO}-\text{CF}_3$. This requirement is confirmed by the fact that trifluoromethylbenzene (structure S1) does not affect the anion-exchange equilibrium. The

molecules containing the carbonyl (structure S27) or ester (structures S25 and S26) groups only do not enhance the anion-exchange extraction either:

(3) The additives containing trifluoroacetyl group bound to saturated hydrocarbon radical directly (structure S6) or via the ester oxygen atom (S19 structure) do not affect the extraction constant.

(4) Di(trifluoroacetyl)acetylene containing two trifluoroacetyl groups linked by the $\text{C}\equiv\text{C}$ group (structure S23) slightly increases the extraction constant (by 0.2 logarithmic units). This effect considerably increases (to 0.65 logarithmic units) if one of the trifluoroacetyl groups is replaced by the benzene ring (structure S22). The binding of benzene ring directly to the trifluoroacetyl group (structure S2) does not noticeably change this effect ($\Delta \log K = 0.52$).

These results show that the organic additives increasing extraction of TCA anions must contain the trifluoroacetyl group and the benzene ring. The simplest molecule of this kind is trifluoroacetophenone (structure S2). The solvation efficiency of this additive can be increased by substituting the hydrogen atoms of the benzene ring by appropriate substituent.

We found that the complete substitution of hydrogen atoms in the trifluoroacetophenone benzene ring by the methyl and nitro groups (structure S15) results in disappearance of the solvation effect. This result shows that the hydrogen atoms of the benzene ring contribute to solvation of the trichloroacetate anion with trifluoroacetophenone. The similar effect was first reported in [8].

Table shows that, for all the additives, the average solvation number is approximately 1. These data also show (Fig. 1) that the logarithms of the apparent ion-exchange extraction constants linearly correlate with the logarithms of the solvation constants. This correlation is described by the equation

$$\log K_{\text{Pic}}^{\text{TCA}^-} = (-5.91 \pm 0.08) + (0.83 \pm 0.03) \log K_s, \quad r = 0.994.$$

Figure 2 shows that the logarithms of the anion-exchange extraction constants linearly correlate with the sum of the Hammett σ -constants of substituents in solvating agents (*m*- and *p*-substituted trifluoroacetophenone). As expected, the maximal increase in extraction occurs for solvating agent of structure S18 having three substituents: *p*-chlorine and two *m*-nitro groups. In the presence of this additive, the extractive power of TNODA Pic with respect to TCA anions exceeds that in the presence of hexyl *p*-trifluoroacetylbenzoate, unsubstituted trifluoroacetophenone, and TNODA Pic in toluene by a factor of 1.61, 2.44, and 2.96, respectively.

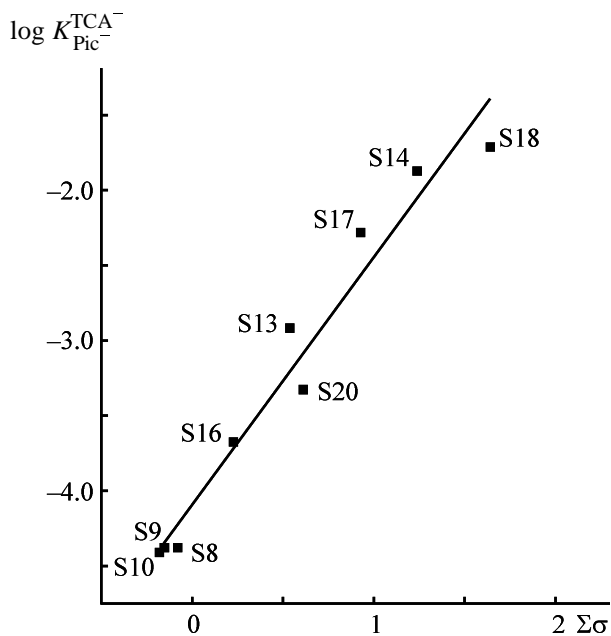


Fig. 2. Correlation between the logarithms of the anion-exchange extraction constants of TCA^- anions from the aqueous phase with TNODA Pic in toluene containing various organic additives and sum of the Hammett σ constants of substituents in the organic additives. Regression equation $\log K_{\text{Pic}}^{\text{TCA}^-} = 4.10 + 1.65 \Sigma \sigma$.

The Hammett equation $\log K = \log K_0 + \rho \Sigma \sigma$ contains the parameter ρ reflecting the sensitivity of the anion-exchange equilibrium to variation in the trifluoroacetophenone electrophilicity. We found that, for the extraction systems under consideration, $\rho = 1.65 \pm 0.13$. We believe that high ρ value in our systems is caused by low toluene polarity; it is consistent with the data on ρ values for anion-exchange equilibria in chlorobenzene ($\rho = 1.89 \pm 0.04$) and methyl butyl ketone ($\rho = 1.71 \pm 0.06$) reported in [3].

The introduction of Cl and NO_2 electron-acceptor groups into the benzene ring of trifluoroacetophenone sharply increases the anion-exchange extraction of trichloroacetate anions. We believe that this effect is caused by the fact that the introduced substituents, exhibiting strong negative inductive effect ($-I$), increase the electrophilicity of the carbon atoms of the carbonyl groups in trifluoroacetophenone molecules and, as a result, enhance their solvating power with respect to TCA anions.

We found that substituted trifluoroacetophenones are strong solvating agents increasing the extraction of trichloroacetate by three orders of magnitude even at their low content (10^{-2} M). Taking into account that the anion-exchange extraction constant increases in the direct proportion with increasing concentration of

the solvating additive, we can increase the anion-exchange extraction constant to five orders of magnitude by increasing the solvating agent concentration.

CONCLUSIONS

(1) Among 27 trifluoroacetophenone derivatives and related compounds tested as solvating additives in extraction of trifluoroacetate anions with trinonyloctadecylammonium picrate in toluene, only those containing the trichloroacetyl group bound to the benzene ring increase the extraction, provided that the benzene ring contains unsubstituted H atoms. The introduction of nitro groups and chlorine atoms into the benzene ring of the solvating additives increases this effect.

(2) Logarithms of anion-exchange extraction constants of trichloroacetate with trinonyloctadecylammonium picrate in toluene vary in direct proportion with the solvation constant of trichloroacetate with solvating additives.

(3) The apparent anion-exchange extraction constants of trichloroacetate with TNODA Pic in toluene linearly depend on the sum of the Hammett σ -constants of the solvating additives.

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