INVESTIGATION OF THE OIL-EMULSIFYING AND OIL-DISPERSING PROPERTIES OF QUATERNARY AMMONIUM SALTS FORMED FROM TRIETHANOLAMINE WITH HEXADECANOIC AND HEPTADECANOIC ACIDS, AND THEIR APPLICATION AS ANALYTICAL REAGENTS

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Abstract: *The presented article is devoted to the study of oil-collecting and oil-dispersing properties of the quaternary ammonium salt (DAD), formed by hexadecane (6-DT) and heptadecanoic acid (7-DT) with triethanolamine (TEA) {triethanolammonium salt of hexadecanoic acid (6-DAD) and triethanolammonium salt of heptadecanoic acid (7-DAD)}, as well as its use as an analytical reagent for the extraction-photometric determination of manganese in the form of a mixed-ligand complex (MLC) with 2-hydroxy-5-chlorothiophenol (H_2L, L) and DAD in various objects. DAD solutions with a concentration of 0.025%, 0.05%, 0.75%, 0.1% form a colloidal solution in water, and are readily soluble in ethyl and isopropyl alcohols. From a comparison of DADs, it is clear that 6-DAD is superior in its ability to disperse oil in drinking and sea water (6-DAD: C_D=82.2; 7-DAD: 86.2%). 6-DAD exhibited high surface activity, showing a decrease in surface tension from 62.2 mN/m to 34.4 mN/m (and for 7-DAD from 59.8 mN/m to 33.3 mN/m). DAD was studied as an oil collector and oil dispersant when treating the surface of water that was turbid due to an oil layer 0.17 nm thick. The spectrophotometric method was used to study the complex formation of manganese(II) with L and DAD. The maximum absorption of MLC Mn(II)-L-DAD is observed at λ = 545-550 nm ($pH_{op.}$3.5–5.9). The molar absorption coefficients range from (2.58-2.71)·10⁴. With a single extraction using chloroform, 99.1–99.3% of manganese is extracted as MLC. The optimal conditions for the formation and extraction of MLC are $1.3\cdot10^{-3}$ M L and $(1.2–1.5)\cdot10^{-3}$ M-DAD. Beer's law is followed within the range of 0.2–100 μg/mL of manganese. Large amounts of alkali, AEM, and REE do not interfere with the determination of manganese. The interfering effect of Fe(III) was eliminated using thioglycolic acid or a 20% solution of $SnCl_2$, Cu(II) and Cr(VI) were addressed with thiourea, Ti(IV) was treated with ascorbic acid, and Zr(IV), Nb(V), and Ta(V) with fluoride ions. The results of the studies on the formation and extraction of Mn(II) MLC with L and DAD were applied for the extraction-photometric determination of manganese in water.*

Key words: *manganese, quaternary ammonium salt, triethanolammonium salt of hexadecanoic acid, triethanolammonium salt of heptadecanoic acid, 2-hydroxy-5-chlorothiophenol*
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Introduction

Like other water basins in the world, the Caspian Sea also has problems with water pollution and, as a result, the deterioration of the environmental situation here. Examples of sources of pollution of this sea are tankers transporting oil, accidents during oil production and transportation. Characteristic features of pollution by oil and its products are their spills over large water areas, accumulation of sediments on the bottom and pollution of environmental components. Oil spills worsen the quality of water and disrupt the balanced

connection of the upper layers of water with the atmosphere, causing a disruption in the effect of oxygen on living things [1, 2]. Oil-based substances that reflect sunlight prevent water from absorbing energy. Removal of such stains is especially necessary for the life of marine life, since more than a hundred species of fish live in the Caspian Sea, 95% of the world's sturgeon population [3]. Surface-active substances (SAS) used to remove thin layers of oil from the surface of water are divided into oil dispersants and oil skimmers [4-10].

The concentration of hazardous substances such as chromium, iron, aluminum, manganese, etc., must be below the established standard values [11-14].

The development of modern industrial society creates the need for prompt and reliable control of the content of heavy metals that have toxic properties and inevitably enter the environment. The content of manganese is one of the main indicators in the chemical analysis of natural water. At the same time, an increased concentration of manganese is one of the main reasons for the unpleasant taste of water and the negative impact on human health.

The heteroligand complex of manganese with 1,10-phenanthroline and o-nitrobenzenesalicylic acid has been investigated spectrophotometrically. The method for the extraction-photometric determination of manganese using PAN and xylenol orange is more sensitive [15]. A method for determining manganese in tap water using sulfosalicylic acid, salicylfluorone, and cetylpyridinium, and in wastewater using 1,3,3-trimethyl-2-[3-(1,3,3-trimethyl-1,3-H-indol-2-ylidene)propenyl]-3H derivatives, has been proposed [15]. Recently, sorption methods have been widely used for trace element determination. Imidazolate framework structures (IFS) attract particular attention as effective sorbents, not only due to their high specific surface area but also due to the feasibility of obtaining them under “mild” conditions [16]. The development of coordination chemistry involves the development of new methods for the synthesis and investigation of coordination compounds, as well as the search for new ligands to obtain compounds with desired properties.

The presented article is devoted to the study of oil-collecting and oil-dispersing properties of quaternary ammonium salt (DAD), formed by hexadecane (6-DT) and heptadecanoic acid (7-DT), with triethanolamine (TEA) {triethanolammonium salt of hexadecanoic acid (6-DAD) and triethanolammonium salt of heptadecanoic acid (7-DAD)} and its use as an analytical reagent for the extraction-photometric determination of manganese in the form of a mixed-ligand complex with 2-hydroxy-5-chlorothiophenol (H_2L, L) and DAD in various objects.

Experımental part

Reagents and solutions. In the work, 0.01 M solutions of L and DAD in chloroform were used. The standard solution of Mn (II) (1 mg/l) was prepared by dissolving anhydrous $MnSO_4$ in water containing 1 ml conc. H_2SO_4, and then diluted to 1 liter with water [15]. The anhydrous salt is obtained from $MnSO_4$ crystalline hydrate by drying at 150°C and subsequent calcination at 400°C. Working solutions with a concentration of 0.1 mg/ml were obtained by diluting the stock solution. To create the required pH value, fixanal HCl (pH 1-2) and acetate-ammonia buffer solutions (pH 3-11) were used. All reagents used were of at least analytical grade.

All the substances used in the work were of analytical reagent grade (a.r.) and chemically pure (c.p.).

Apparatus. The optical density of the organic phase was measured on a KFK-2 (in Russian). Spectrophotometric studies of colored extracts were carried out on a SF-26 spectrophotometer (in Russian).The pH value of the solutions was controlled using an I-130 ion meter (Russia) with a glass electrode. IR spectra were recorded on a Bruker spectrophotometer (Germany).

Method. 0.1-0.8 ml of Mn(II) solution, 2.4 ml of 0.01 M solution L, 2.6 ml 0.01 DAD and 2.8 ml of 1 M HCl solution were added to the test tubes. The volume of the organic phase was brought to 5 ml with CH_3Cl, the total volume was brought to 25 ml with distilled water. After 10 min, the extract was separated and the light

absorption was measured at 540 nm (l = 0.5 cm) in KFK-2.

Determination of Mn (II) in sewage water and bottom sediments. 1L taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 ml of HNO_3, was transferred to a 50 ml flask and diluted to the mark with water.

General procedure for the synthesis of DAD. For the synthesis of DAD, the reaction of 6-DT and TEA in a molar ratio of 1:1 was carried out under laboratory conditions at 60-70°C (100°C in the case of 6-DT and TEA) for 1 day with intensive stirring. The reaction scheme is as follows:

$$R\text{-}COOH + N(C_2H_4OH)_3 \rightarrow [\ R\text{-}COO^-\ N^+H(C_2H_4OH)_3]\quad (R = -C_{15}H_{31},\ -C_{16}H_{33})$$

6-DAD: IR spectrum (KBr) ν, cm^{-1}: 3245 (-OH); 2849, 2916, 2954 (-CH); 1466, 1559 (COO-) 2527, 2676 (N+ -H) [17]. Found, %: C 65.1, H 11.6, O 19.7, N 3.6. Calculated, %: C 64.09, H 10.18, 19.04, N 2.97.

7-DAD: IR spectrum (KBr) ν, cm^{-1}: 3243 (-OH); 2852, 2920, 2951 (-CH); 1462, 1563 (COO-) 2528, 2673 (N+ -H) [17]. Found, %: C 66.80, H 11.70, O 19.10, N 3.30. Calculated, %:66.03, H 11.25, O 20.09, N 3.16.

The IR spectrum of 6-DAD is represented in Fig. 1.

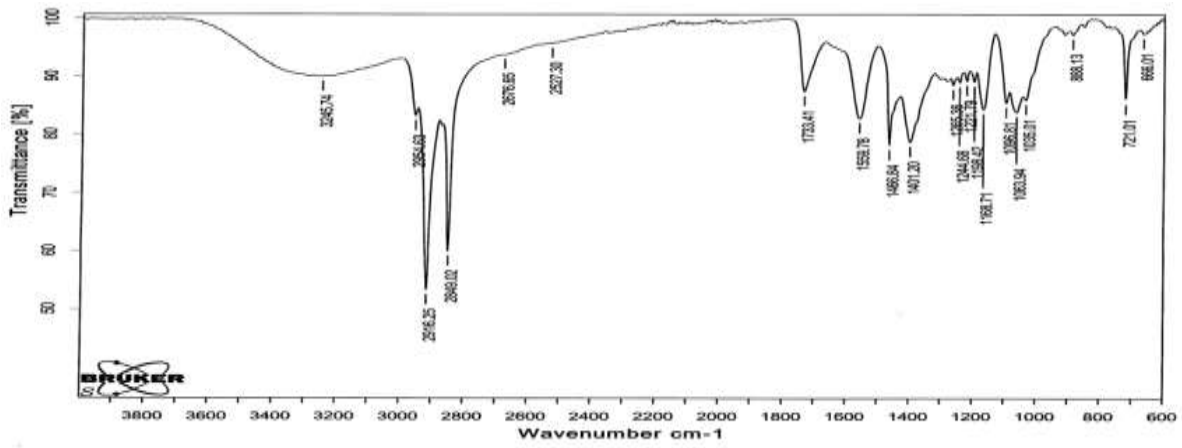


Fig. 1. IR spectrum of 6-DAD.

Study of surface activity and oil-collecting and dispersing properties of DAD. DAD is an amber-colored solid that freezes at room temperature. Its solutions with a concentration of 0.025%, 0.05%, 0.75%, 0.1% form a colloidal solution in water, and are readily soluble in ethyl and isopropyl alcohols. The surface activity of DAD solutions of various concentrations at 21°C was determined using a tensiometer at the water-air interface (Table 1).

Table 1. The value of the surface activity of DAD at the air-water interface (t=21°C)

$\omega, \%$		0.00025	0.0005	0.00075	0.001	0.0025	0.005	0.0075	0.01	0.025	0.05	0.075	0.1
$\sigma, mN \cdot m^{-1}$	6-DAD	62.2	54	50.5	48.2	42.4	39.4	37.5	36.9	34.9	34.7	34.6	34.4
	7-DAD	59.8	52	48.5	46.4	41.4	38.2	36.5	35.4	33.9	33.6	33.4	33.3

As can be seen from Table 1, 6-DAD exhibited high surface activity due to a decrease in surface tension from 62.2 mN/m to 34.4 mN/m (and for 7-DAD from 59.8 mN/m to 33.3 mN/m). DAD was studied as an oil collector and oil dispersant when treating the surface of water turbid with an oil layer 0.17 nm thick [18]. The effectiveness of this reagent was studied in laboratory conditions on waters of varying degrees of mineralization using a sample of Balakhan light oil. The reagent was used both in pure form and as a 5% aqueous solution. A decrease in the area of the initial oil layer due to reagent penetration into oil-contaminated water determines its effectiveness. The oil accumulation coefficient (K) is a value characterizing this effect. K is calculated as the ratio of the initial area of the oil layer to the area of the oil slick formed under the influence of the reagent.

Table 2. Results of studies of oil-gathering and oil-dispersing capacity of DAD

Reagent	The state of supply of reagent to the oil surface	Distilled water		Drinking water		Sea water	
		τ, hour	K(K_D,%)	τ, hour	K(K_D,%)	τ, hour	K(K_D,%)
6-DAD (Balakhany oil, thickness 0.17 mm)	Undiluted product	0 1.0-5.0 42.0-70.0 86.0	7.6 11.5 15.6 12.4	0 1.0-4.0 20.0-60.0 84.0	7.6 17.2 8.6 is destroyed	0 1.0-4.0 20.0-60.0 84.0	6.0 8.6 Dis.89.0% Dis.79.9%
	5% aqueous dispersion	0 1.0-42.0 70.0	6.7 17.6 16.2	0 6.0-20.0 44.0	6.0 Dis.82.2% Dis.76.8%	0-4.0 20.0-44.0 60-84.0	10.1 Dis.86.2% Dis.82.2%
7-DAD (Ramana oil, thickness 0.17 mm)		0 1.0-42.0 70.0	8.2 15.2 10.2	0 6.0-20.0 44.0	7.8 Dis.72.2% Dis.76.8%	0-4.0 20.0-44.0 60-84.0	11.1 Dis.82.2% Dis.76.8%

As can be seen from Table 2, 6-DAD exhibits oil-accumulating capacity in distilled water in both forms of reagent application. K_{max} is 15.6 in undiluted reagent form and 17.6 mN/m in the form of a 5% solution. The reagent exhibits oil accumulation in undiluted product form in drinking water (K_{max}=17.2), oil accumulation in the first hours in the form of a 5% solution and oil dispersibility after the 6th hour (K_D=82.2% in the case of the maximum dispersion rate). As an oil collector-dispersant, the reagent exhibits a mixed effect in both forms of application in sea water (K_{max}=10.1, K_D=86.2%). 7-DAD in the form of a 5% solution has an oil-accumulating capacity of K_{max}=15.2 mN/m. The reagent exhibits a mixed effect as an oil collector-dispersant in drinking and sea water (K_{max}=7.8 and 11.1; K_D=76.8 and 82.2%, respectively). The reagents retains its effect for 4 days.

From a comparison of DADs, it is clear that 6-DAD is superior in its ability to disperse oil in drinking and sea water (6-DAD: CD=82.2; 7-DAD: 86.2%).

Results and discussion

Charge of the complexes and choice of organic solvent. The binary complexes Mn(II)-L, cannot be extracted in chloroform or other slightly polar organic solvents. Experiments with KU-2 and AV-17 ion-exchangers showed that these species are charged negatively. Electroneutral ternary complexes can be formed in the presence of DAD.

The following organic solvents were tested for the extraction of these complexes: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, toluene, xylene, *iso*-butanol, and *iso*-pentanol. Chloroform was found to be the most effective.

The manganese content in the organic phase was determined photometrically using 8-oxyquinoline after reextraction, and in the aqueous phase – by difference. Based on the extracted complexes, the distribution coefficient (D) and the degree of extraction (R, %) were estimated [15]:

$$D = \frac{[Mn]_{org}}{[Mn]_{aq}}; \qquad R = \frac{100 \times D}{(D + \frac{V_{aq}}{V_{org}})}$$

Under optimal conditions, chloroform provides degrees of extraction R=99.1–99.3% (Table 3).

Table 3. Optical characteristics, precision and accuracy of the spectrophotometric determination of Mn(II) with L and DAD

Compound	$pH_{op.}$	R,%	λ_{max} (nm)	$\varepsilon \cdot 10^{-4}$	lgK_{eq}	lgβ	lgK_{ex}	Working range / μg mL^{-}
Mn-L-6-DAD	3.5-5.8	99.3	545	2.58	8.46	10.34	13.63	0.2-100
Mn-L-7-DAD	3.6-5.9	99.1	550	2.71	8.49	8.91	12.42	0.5-90

Influence of the pH of the Aqueous Phase. The effect of pH on the formation of Mn(II)- L-DAD complex was studied, in order to find a suitable pH that can be adopted in the determination of cobalt(II) (Fig. 2). The absorbance was found to be maximum in the pH range 1.8-5.8. Extraction of Mn(II) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrease of recovery, which was obviously associated with a decrease in the concentration of the ionized form of L. Probably, it is present in the solution in the nondissociated state. At pH ≥ 7.6, the complexes were hardly extracted, obviously because of the decrease in the degree of DAD protonation.

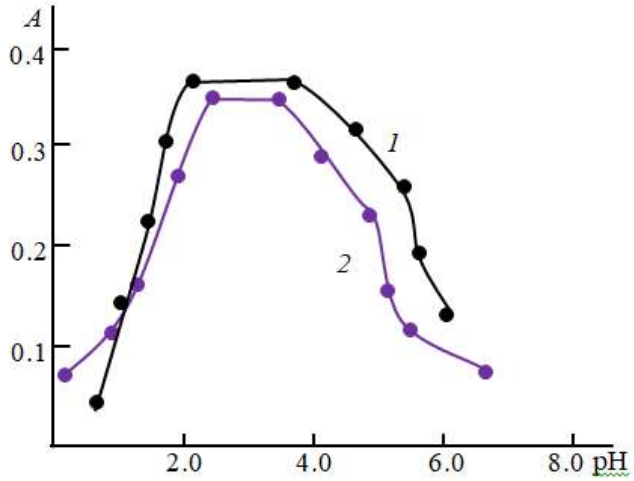


Fig. 2. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase
1- Mn-L-6-DAD, Mn-L-7-DAD
$C_{Mn(II)}= 3.63 \cdot 10^{-5}$M, $C_L = C_{DAD}=1.0 \cdot 10^{-3}$ M, λ=540 nm, ℓ=0.5 cm

Absorption maxima, reagents concentrations, molar absorptivities, influence of phase volume ratios and effect of time. The absorption maxima of the ternary Mn(II)-L-DAD complexes lie in the range of 540-545 nm (Table I). Complete extraction is achieved at reagent concentrations not lower than 1.3×10^{-3} mol mL^{-} H_2L and $(1.2\text{-}1.5) \times 10^{-3}$ mol mL^{-} DAD. Mn(II) concentration ranges in which the Beer's law is obeyed are listed in Table 1. The calculated molar absorptivities (ε_{max}) belong to the interval $(2.58\text{-}2.71) \times 10^4$. Colour develops almost immediately after the reagents addition. The absorbance of the extracts is stable for at least 48 hours. The optimum shaking time is 5 min.

The degree of extraction of M(II) in the form of MLC does not depend on the ratio of the volumes of aqueous and organic phases in a wide range (from 5:5 to 100:5), which allows for simultaneous concentration and photometric determination of Me(II). Thus, an increase in the volume of aqueous phase 20 times relative to the organic one does not affect the completeness of extraction.

Stoichiometry of the complexes and the mechanism of complexation. The molar ratios of the components of the ternary complexes were established by the equilibrium shift method and the method of Asmus [19]. The results show a complex composition of 1:2:2 (Mn(II):L:DAD). The formation of ternary complexes can be presented in the following way. When manganese interact with two molecules of H_2L, they form doubly charged anionic complexes, which are extracted with two molecules of protonated Am. (Fig. 3). Hence, the complexes can be regarded as ion associates between doubly

charged anionic chelates $[Mn(HL)_2]^{2-}$ and two protonated Am species: $[Mn(HL)_2](DADH^+)_2$. The stability constant of Mn(II)-L-DAD complexes was calculated and found to be lgβ = 8.91-10.37 at room temperature.

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3460 sm^{-1} observed in the spectrum of H_2L, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2580 sm^{-1} shows that -SH group involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 2380 cm^{-1} indicates the presence of a protonated DAD [17]. Based on the data obtained, the composition of the extracted complexes can be represented by the formula $[MnL_2](DADH^+)_2$:

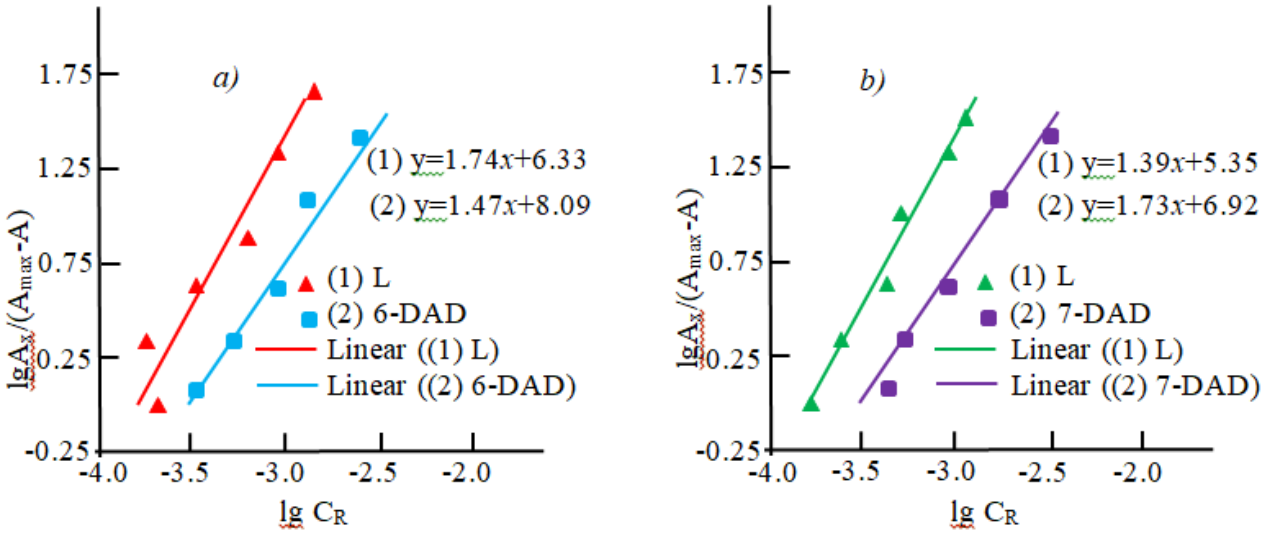
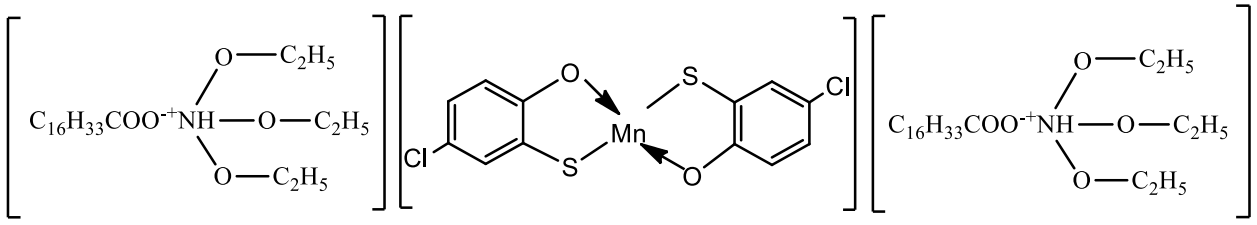
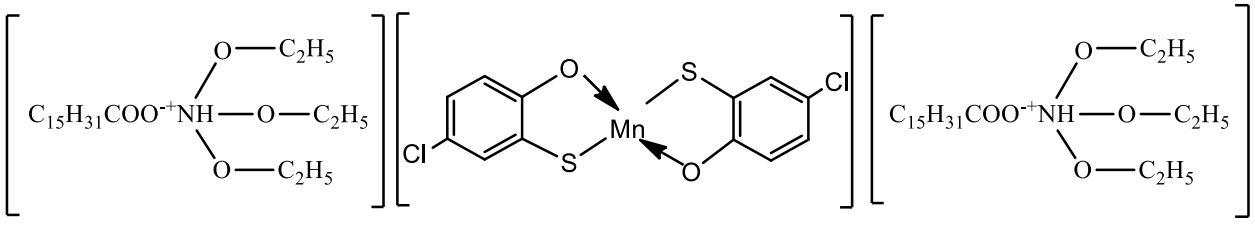


Fig. 3. Determination of the H_2L-to-Mn (straight line 1) and the DAD-to-Mn (straight line 2) molar ratios by the mobile equilibrium method. $C_{Mn(II)}= 3.63\cdot10^{-5}$M, $C_L = C_{DAD}=1.0\cdot10^{-3}$ M, SF-26, ℓ=1.0 cm.





Equilibrium constants. Several processes should be taken into account for the system of $[MnL_2]^{2-}$, $(DADH^+)_2$, H_2O and $CHCl_3$:

I) Association in the aqueous phase between anionic chelate, $[Mn(HL)_2]^{2-}$, and the hydrophobic aminescation, $(DADH^+)_2$, with the equilibrium constants $\{(AmH^+)_2[Mn(HL)_2]\}$:

$$[Mn(HL)_2]^{2-}{}_{(aq)} + 2DADH^+{}_{(aq)} \leftrightarrow [Mn(HL)_2](DADH)_{2\,(aq)}$$

$$\beta = \frac{[\mathrm{Mn(HL)_2}](\mathrm{DADH})_2}{[\mathrm{Mn(HL)_2}]^{2-}[\mathrm{DADH^+})_2]}$$

II) Distribution of the complexes between the aqueous and the organic phase

$$[\mathrm{Mn(HL)_2}](\mathrm{DADH})_{2\,(aq)} \leftrightarrow [\mathrm{Mn(HL)_2}](\mathrm{DADH})_{2\ (org)}$$

with the distribution constants

$$K_D = \frac{[\mathrm{Mn(HL)_2}](\mathrm{DADH})_{2\,(org)}}{\{[\mathrm{Mn(HL)_2}]^{2-}[\mathrm{DADH^+})_2]\}_{aq}}$$

III) Equilibrium constant (K_{eq}) of the reaction

$$\mathrm{K_{eq}} = \frac{\{[\mathrm{Mn(HL)_2}](\mathrm{DADH})_2\}_{(org)}}{\{[\mathrm{Mn(HL)_2}]^{2-}\}_{(aq)}\{[\mathrm{DADH^+})_2]\}_{aq}} = \lg\frac{A_x}{A_o - A_x} = D$$

$$\mathrm{K_{eq}} = \frac{\mathrm{D}}{[(\mathrm{DADH})^+]^2}$$

Where, A_x is the optical density for this experiment; A_o – optical density at complete binding of cobalt ion into a colored complex; *D* – distribution coefficient. Taking logarithm of the last expression, we get

$$\mathrm{lgK}_{eq} = \mathrm{lgD\text{-}2lg[DADH^+]}$$

IV) Extraction of the ternary complexes from water into chloroform

$$[\mathrm{Mn(HL)_2}]^{2-}{}_{(aq)} + 2\mathrm{DADH^+}_{(aq)} \leftrightarrow [\mathrm{Mn(HL)_2}](\mathrm{DADH})_{2\,(org)}$$

org with the extraction constants

$$K_{ex} = K_D + \beta = \frac{\{[Mn(HL)_2](DADH)_2\}_{(org)}}{\{[Mn(HL)_2]^{2-}\}_{(aq)}\{[DADH^+)_2]\}_{aq}}$$

The constants of the association β were determined by several independent methods: Mobile equilibrium method [19,20], Holme-Langmihr method [19,20], Komar-Tolomachev Method [19,20] and Harvey-Manning method [19,20]. The constants of the distribution K_D were determined by comparison of the absorbance values obtained after single extraction at the optimum conditions (A_1) and triple extraction (A_3): $K_D = A_1/(A_3 - A_1)$. The extraction constants were calculated by the equation $K_{ex} = \beta + K_D$ [19,20]. All calculations were carried out at a probability of 95%. The obtained values are presented in Table 4.

Table 4. Values of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β) and recoveries (R%) for the Mn(II)-L-DAD-H_2O-CH_3Cl systems

Extraction system	**lgβ**	**lgK_D**	**lgKeq**	**lgK_{ex}**	**R%**
Mn(II)-L-6-DAD-H_2O-CH_3Cl	10.18±0.32[a]	3.45±0.4	9.17±0.82	13.63±0.33[e]	99.1
	10.07±0.84[b]			13.52±0.31[f]	
	10.05±0.57[c]			13.50±0.39[c]	
	10.34±0.72[d]				
	8.39±0.41[a]	3.51±0.4	8.69±0.51	11.90±0.27[e]	99.3

Mn(II)-L-7-DAD-H_2O-CH_3Cl	8.91±0.62[b]			12.42±0.53[f]	
	8.45±0.35[c]			11.96±0.18[c]	
	8.34±0.19[d]				

Note: [a]Calculated by the Holme-Langmyhr method [19,20]; [b]Calculated by the Harvey-Manning method [19, 20]; [c]Calculated by the Komar-Tolmachev method [19, 20]; [d]Calculated by the mobile equilibrium method [19,20]; [e]Calculated by the formula $K_{ex}= K_D+\beta$ where is determined by the Holme-Langmihr method [19, 20]; [f]Calculated by the formula $K_{ex}= K_D+\beta$ where b is determined by the Harvey-Manning method [19, 20].

Effect of foreign ions (FI) and reagents. The effect of various ions and reagents on the extraction-spectrophotometric determination of 20 μg Mn (II) is summarised in Table 5. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH_4^+, W(VI), Mo(VI), $Cl^–$, $S_2O_3^{2–}$, $F^–$, $NO^{3–}$, $SO_4^{2–}$, $PO_4^{3–}$, tartrate, citrate, oxalate and tiron; moderate amounts of Cr(VI), Cr(III), Zn(II) and Cd(II); and small amounts of Mn(II), Sn(II), Cu(II), Al(III), ascorbic acid and $SCN^–$ are tolerable. Ni(II), Fe(II,III), V(IV,V), Ga(III), In(III), and Tl(III) interfere seriously at a ratio of 1:1 with respect to Mn(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (see Table 2). Mn – L–DAD–H_2O–$CHCl_3$ system are given in Table 5.

Table 5. Effect of foreign ions on the extraction of 20 μg Mn (II) (n = 6, P = 0.95).

FI	mg	FI-to-Mn ratio	Mn found	R, %	FI	mg	FI-to-Mn ratio	Mn found	R, %
$Citrate^{3-}$	5	250	20.03	100.5	Fe(II)	0.5	2.5	19.25	85.0
$Oxalate^{2–}$	10	200	20.13	102.6	Fe(III)	0.5	2.5	20.90	118.0
$Tartrate^{2-}$	2.5	250	5.05	101.0	V(IV)	0.05	2.5	20.55	111.0
Ascorbic acid	0.5	25	5.15	103.1	V(V)	0.05	2.5	19.25	85.0
EDTA	0.5	25	5.10	102.0	Cd^{2+}	0.2	10	19.86	97.2
CDTA	0.005	0.25	19.73	94.6	Cu^{2+}	0.06	3	20.17	103.4
Tiron	2.5	125	20.11	102.5	Al^{3+}	5	250	20.08	101.6
SCN^-	0.025	10	20.13	102.6	Zn^{2+}	0.5	25	20.04	100.8
Cl^-	20	100	20.20	104.0	Zr(IV)	3.0	150	20.18	103.5
$S_2O_3^{2-}$	10	200	19.92	98.5	Nb(V)	0.5	2.5	19.25	85.0
F^-	10	500	20.20	104.0	Ti(IV)	2.5	125	20.17	103.4
NO_3^-	20	1000	20.02	100.3	Ni^{2+}	2.5	125	19.91	98.2
SO_4^{2-}	20	500	20.03	100.5	Co^{2+}	2.5	125	19.91	98.2
PO_4^{3-}	7	225	20.10	102.0	Cr(III)	1.5	75	19.80	96.0
ClO_4^-	0.1	0.5	20.73	94.6	W(VI)	5	250	19.88	97.7
NH_4^+	20	500	20.02	100.3	Mo(VI)	5	250	19.85	97.0

Effect of manganese (II) concentration. Table 6 shows the calibration characteristics. Compliance with Beer's law was studied by measuring the absorbance value of a number of solutions containing different concentrations of metal ions. Mn(II) can be determined in the range of 0.2-100 μg /mL (Table 6).

Table 6. Analytical characteristics of some ternary complexes of Mn with L and DAD

Compound	Limit of detection: ng ·mL^{-1}	Limit of quantification: ng ·mL^{-1}	Sandell's sensitivity: μg· cm^{-2}	Beer's law range (μg· mL^{-1})	The equation of calibration curves
Mn-L-6-DAD	15	53	2.30	0.2-100	0.045+0.110*x*

Mn-L-7-DAD	14	46	2.22	0.5-90	0.056+0.107*x*

Table 7 presents data that allow us to compare the analytical characteristics of the photometric methods for determining manganese that we have developed with some already known ones [15, 21].

Table 7. Comparative characteristics of methods for determining manganese

Reagent [Ref.]	pH (solvent)	λ, nm	ε·10^{-4}	Beer's law range (μg mL^{-})
Formaldoxime [15, 26]	10–13	455	1.12	0.7-29
8-mercaptoquinolinate [15,26]	6.0–6.5($CHCl_3$)	413	0.7	0.8-56
8-hydroxyquinoline [15,26]	7.2–12.5 ($CHCl_3$)	395	0.85	0.2 - 75
1,10 fenantrolin + 2,4-dinitrobenzolazosalisil turşusu [21]	5.0-11.0 (C_2H_2Cl4)	400	0.893	0.15-22.5
PAN + aniline [22]	2.4-7.0 (CCl4)	560	3.95	0.2-120
1-(2-pyridylazo)-2-naphthol and the new reaction with 2-(2-quinolinazo)-5-diethylaminophenol [23]	3.1-5.0	430	2.7	0.2-80
1,10-phenanthroline and alizarin yellow R [24]	5.0-11.0	510	4.2	0.2-60
1,10-phenanthroline and 2,4-dinitrobenzenesalicylic acid [25]	5.0-11.0	530	4.0	0.2-110
L-6-DAD	3.5-5.8 ($CHCl_3$)	545	2.58	0.2-100
L-7-DAD	3.6-5.9 ($CHCl_3$)	550	2.71	0.5-90

Analytical Applications. The proposed method under the already established optimum conditions was applied for the determination of Mn(II) in Sewage water and Bottom sediments (Table 8). The results were compared with the well-known methods of formaldoxime [26] and 8-hydroxyquinoline [26] from the literature.

Table 8. Determination results of cobalt (II) in the Sewage water and Bottom sediments (n = 6, P = 0.95)

Compound	Analysis object		Added, μg	Found, μg	Found in the sample, μg/kg $\bar{X} = \pm\frac{t_p S}{\sqrt{n}}$	S_r
Mn-L-6-DAD	Sewage water	Sample 1	2.0	2.45	0.45±0.05	0.06
Mn-L-7-DAD		Sample 2	5.0	6.14	1.14±0.11	0.07
Formaldoxime		Sample 1	2.0	2.43	0.43±0.09	0.04
8-hydroxyquinoline		Sample 2	5.0	6.16	1.16±0.05	0.06
Mn-L-6-DAD	Bottom sediments	Sample 1	5.0	6.26	1.26±0.05	0.05
Mn-L-7-DAD		Sample 2	5.0	6.92	1.92±0.04	0.08
Formaldoxime		Sample 1	5.0	6.74	1.70±0.09	0.07
8-hydroxyquinoline		Sample 2	5.0	6.25	1.25±0.05	0.05

Conclusions

1. The oil-collecting and oil-dispersing properties of a quaternary ammonium salt (DAD) formed by hexadecane (6-DT) and heptadecanoic acid (7-DT) with triethanolamine (TEA) {triethanolammonium salt of hexadecanoic acid (6-DAD) and triethanolammonium salt of heptadecanoic acid (7-DAD)}, as well as its use as an analytical reagent for the extraction-photometric determination of manganese in the form of a mixed-ligand complex (MLC) with 2-hydroxy-5-chlorothiophenol (L) and DAD in water were studied. DAD was studied as an oil collector and oil dispersant when treating the surface of water that was turbid due to an oil layer 0.17 nm thick.
2. The maximum absorption of MLC Mn(II)-L-DAD is observed at λ = 545-550 nm ($pH_{op.}$ 3.5–5.9). The molar absorption coefficients range from (2.58-2.71)×10⁴. With single extraction using chloroform, 99.1–99.3% of manganese is extracted as MLC. The optimal conditions for the formation and extraction of MLC are 1.3×10^{-3} M L and $(1.2–1.5)\times10^{-3}$ M-DAD. Beer's law is followed within the range of 0.2–100 μg/mL of manganese.
3. Large amounts of alkali, AEMs, and REE do not interfere with the determination of manganese. The interfering effect of Fe(III) was eliminated using thioglycolic acid or a 20% solution of $SnCl_2$, Cu(II) and Cr(VI) were addressed with thiourea, Ti(IV) was treated with ascorbic acid, and Zr(IV), Nb(V), and Ta(V) with fluoride ions. The results of the studies on the formation and extraction of Mn(II) MLC with L and DAD were applied for the extraction-photometric determination of manganese in water.

References

1. Mariano A.J., Kourafalou V.H., Srinivasan A., Kang H., Halliwell G.R., Ryana E.H., Roffer M. On the modeling of the 2010 Gulf of Mexico Oil Spill. *Dinamics of Atmospheres and Oceans.* 2011, **Vol. 52(1-2)**, p. 322-340.
2. Clark R.B., Frid Ch., Attrill M. The Waters Around the British Isles: Their Conflicting Uses. *Marine Pollution,* Clarendon Press: Oxford; 1997.
3. Tolosa I., Mora S., Sheikholeslami M.R., Villeneuve J.P., Bartocci J., Cattini Ch. Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediment. *Marine Pollut. Bull.* 2004, **Vol. 48**, p. 44-60. doi.org/10.1016/S0025-326X(03)00255-8
4. Asadov Z.H., Rahimov R.A., Salamova N.V. Synthesis of animal fats ethylolamides, ethylolamide phosphates and their petroleum-collecting and dispersing properties. *J. Amer. Oil. Chem. Soc.*, 2012, **Vol. 89(3)**, p. 505-511. DOI 10.1007/s11746-011-1931-8
5. Asadov Z.H., Salamova N.V., Eyyubova S.K., Yolchuyeva U.J. Methyl iodide salts of aminoesters of vegetable oils fatty acids. *Processes of petrochemistry and oil refining*, 2020, **Vol. 21(4)**, p. 388-398.
6. Asadov Z.H., Salamova N.V., Poladova T.A., Ahmedova S.F. Sintezirovaniye neftesobirayusheqo amino-efira iz triqliseridov soevoqo masla i metildietanolamina. *Азербайджанское нефтяное хозяйство,* 2020, **№3**, p. 39-43.
7. Salamova N.V. Obtaining, physical and chemical characteristics, oil extraction and oil dispersal of their new surface-active substances based on soybean triglycerides, ethylamine and alkyl dialkylidenes. *Bashkir chemical journal*, 2023, **Vol. 30(3)**, p. 85-90.
8. Wang Z., Fingas M.F., Page D.S. Oil spillidentification. *J. Chromatog. A*, 1999, **Vol. 843(2)**, p. 369–411. DOI: 10.4236/ijamsc.2013.11001.
9. Hamdan L.J., Fulmer P.A. Effects of COREXIT EC9500A on bacteria from a beach oiled by the Deepwater Horizon spill. *Aquatic microbial ecology*, 2011, **Vol. 63(3)**, p. 101-109. doi: 10.3354/ame01482.
10. Vorobyov Yu.L., Akimov V.A., Sokolov Yu.I. Prevention and elimination of emergency spills of oil and oil products. M: In-oktavo, 2005. 368 p.
11. Zalov A.Z., Asgarova Z.G., Yakhshieva Z.Z., Abasguliyeva U.B., Mamedova Sh.A., Huseynova P.F. Extractıon-spectrophotometrıc study of the system nıckel(II) – halogenasemercaptophenol -

amınophenol - water – chloroform. *Chemical Problems,* 2024, **Vol. 22(4)**, p. 436-446. DOI: 10.32737/2221-8688-2024-4-436-446
12. Mammadova Sh.A., Abasqulieva U.B., Zalov A.Z., Novruzova N.A. Spectrophotometric research into complexation of tungsten(VI) with o-hydroxythiophenol derivatives in the presence of hydrophobic amines. *Chemical Problems,* 2022, **Vol. 20(2)**, p. 164-174. DOI: 10.32737/2221-8688-2022-2-164-174
13. Asgarova Z.G., Zalov A.Z., Rasulov Ch.K. Highly selective and sensitive extraction-photometric method for the determination of nickel (II) in water, oil and petroleum products of Baku. *Processes of Petrochemistry and oil Refining,* 2022, **Vol. 23(4)**, p. 544-555.
14. Rasulov Ch.G., Zalov A.Z., Mammadova S.A., Huseynova G.A. Spectroscopic studies of complexation Cu, Co, Ni using aminophenols. determination of Cu(II), Co(II) and Ni(II) in wastewater, bottom sediments, oil and oil products Baku. *Processes of Petrochemistry and oil Refining,* 2022, **Vol. 23(2)**, p. 163-174.
15. Marchenko Z., Balcezhak M.K. Methods of spectrophotometry in UV and visible regions in inorganic analysis. Moscow. Binomial. Knowledge Lab. 2007. 711 p.
16. Fufaeva V.A., Filippov D.V. Highly efficient extraction of copper(II) ions from aqueous solutions using nickel 2-ethylimidazolate. *News of Higher Education Institutions. Chemistry and Chemical Technology,* 2021, **Vol. 64(5)**, p. 24-29.
17. Anisimova N.A. Identification of organic compounds. Gorno-Altaisk: RIO Gorno.-Alt. gosun-ta, 2009. 118 p.
18. Gumbatov G.G., Dashdiyev R.A. Application of PAVs for liquidation of accidental oil spills on water surfaces. - Baku: Elm, 1998, 210 p.
19. Bulatov M.I., Kalinkin I.P. A practical guide to photocolorimetric and spectrophotometric methods of analysis. Ed. Chemistry. Moscow. 1972. 426 p.
20. Zalov A.Z., Gasimova Y.C., Ibrahimova Sh.A. Liquid-liquid extraction and spectrophotometric characterization of some new ternary ion-association complexes of cobalt (II) and nickel (II). *Journal of Applied Science,* 2016, **Vol. 2(6)**, p. 1-11.
21. Rustamov N.Kh., Abbasova G.G., Mustafayev N.M. Extractive-photometric determination of manganese(II) with 1,10 phenanthroline and 2,4-dinitrobenzolasalicylic acid. *Azerbaijan chemical journal*, 2011, **No. 4**, p. 112-114.
22. Safari Z., Gholivand M.B., Hosseinzadeh L. Spectrophotometric study of complex formations between 1-(2-pyridylazo)-2-naphthol (PAN) and some metal ions in organic solvents and the determination of thermodynamic parameters. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.* 2011, **Vol. 78(5)**, p. 1606–1610.
23. Grechnikov A.A., Borodkov A.S., Simakina Ya.I., Arabova Z.M., Mikhailova A.V., Kuzmin I.I., Dedkov Yu.M., Minin V.V. Complexation of heterocyclic azo-compound with transition metal ions as found by laser-induced desorption/ ionization method. *Izvestiya Akademii nauk. Seriya khimicheskaya (Russian Chemical Bulletin: Chemical series).* 2016, **No. 12**, p. 2789–2794.
24. Rustamov N.Kh., Velieva G.G. Synthesis and study of the coordination compound of manganese(II) with 1,10-phenanthroline and alizarin yellow R. *Azerbaijan chemical journal*, 2010, **No. 3**, p. 44-47.
25. Rustamov N.Kh., Abbasova G.G. Synthesis and research of coordination compounds of manganese(II) with 1,10-phenanthroline and 2,4-dinitrobenzenesalicylic acid. *"Izvestia VUZov" Chemistry and chemical technology,* 2013, **Vol. 56(12)**, p. 44-48
26. Lavrukhina A.K., Yukina L.B. Analytical chemistry of manganese. M.: Nauka, 1974, C. 54.