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Equilibrium Constants of Liquid — Liquid Distribution Reactions

PART III: COMPOUND FORMING EXTRACTANTS, SOLVATING SOLVENTS AND INERT SOLVENTS

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INTRODUCTION

This report represents the third part of the compilation of Equilibrium Constants of Liquid-Liquid Distribution Reactions. The work has been sponsored by Commission V.6, Equilibrium Data, Division of Analytical Chemistry, of the International Union of Pure and Applied Chemistry (IUPAC). The work has been supported financially by the Office of Standard Reference Data, the U.S. National Bureau of Standards, and is a part of its Standard Reference Data Series.

The report consists of tables compiling equilibrium constants. All the solvents included in the list in Appendix A of the Introduction to this Series (Part I) have been looked up in the literature. In all cases, only systems in which equilibrium constants have been calculated are included in this compilation. The tables on pages 2-17 are for distribution reactions of carboyxlic and sulfonic acid extractants, for their dimerization and other reactions in the organic phase, and for extraction reactions of metal ions from aqueous solutions. The inorganic anions in these solutions are usually irrelevant, since they do not participate in the extraction reaction, hence are not properly called ligands. The extractants themselves are acids, which exchange their hydrogen ions (rarely also alkali metal ions), for the extracted metal ions, which form compounds with extractants. Since the extractants are monofunctional carboxylic or sulfonic acids, no chelates are formed.

The tables on pages 18-30 deal with the distribution of inorganic acids, salts and complexes between aqueous solutions and solvents which have oxygen donor atoms. Here the anions may act as ligands, and have been specified as such. The tables on pages 33-46 deal with the distribution of inorganic acids, salts and complexes between aqueous solutions and inert solvents, which do not have donor atoms, and which are often employed as, hopefully, inert diluents.

The literature searched covers the period 1947-1971 inclusive. The sources searched have been specified in the general introduction to the series, in Part I. The general arrangement of the tables is the same as used there and explained there in detail. In the reactions, the extractants are denoted by HS for the carboxylic and sulfonic acid extractants, and by S for the solvating and inert solvents. The ligands, if present, are denoted by A^- for univalent anions. A bar over the symbols denotes the organic phase. The equilibrium constants are in the molar scale, unless otherwise noted. The temperature is in degrees centigrade. Values of ΔH and ΔS for the extraction reactions are in kcal mol^{-1}, respectively in cal $K^{-1}mol^{-1}$ (1 cal = 4.184J), and refer to the standard states of infinite dilution of all solutes. The figures in the "conditions" columns are molar concentrations (mol dm^{-3}).

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
			Extractant Class: Compound-Forming Extractants			
Extractant: Hexanoic Acid, HS						
Distribution						
	$HS = \overline{HS}$	0.5	27	$NaClO_4$ 0.1	HS 0.3-3 in benzene	69S,67S
		0.31	25	$(Na^+,H^+)ClO_4^-$ 0.1	HS in benzene	70K
		0.9	27	$NaClO_4$ 0.1	HS 1.0, 0.3 in $CHCl_3$	69S
		0.7	27	$NaClO_4$ 0.1	HS 0.05-3.0 in $CHCl_3$	68S
		0.82	25	$(Na^+,H^+)ClO_4^-$ 0.1	HS in 1,2 dichlorobenzene	70K
		1.26	20	H_2O	HS 0-0.2 in dodecane	70A
		1.13	20	H_2O	HS 0-0.2 in hexadecane	70A
		0.8	25	H_2O	HS in hexane	69H
		1.48	25	$(Na^+,H^+)ClO_4^-$ 0.1	HS in isopropylether	70K
		1.6	27	$NaClO_4$ 0.1	HS 0.1-3.0 in 4-methyl-2-pentanone	69S
		0.77	25	$(Na^+,H^+)ClO_4^-$ 0.1	HS in nitrobenzene	70K
		1.35	20	H_2O	HS 0-0.2 in octane	70A
Dimerization						
	$2\ \overline{HS} = (\overline{HS})_2$	2.2	27(?)	$NaClO_4$ 0.1 (?)	HS 0.3-3.0 in benzene	67S,69S
		2.45	25	$(Na^+,H^+)ClO_4$ 0.1	HS in benzene	70K
		1.6	27	$NaClO_4$ 0.1	HS 0.3, 1.0 in $CHCl_3$	69S
		2.1	27	$NaClO_4$ 0.1	HS 0.05-3.0 in $CHCl_3$	68S

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
	$2\ \overline{HS} = (\overline{HS})_2$	1.19	25	$(Na^+,H^+)ClO_4^-$	HS in 1,2 dichlorobenzene	70K
		-0.19	25	$(Na^+,H^+)ClO_4^-$	HS in isopropylether	70K
		0.96	25	$(Na^+,H^+)ClO_4^-$	HS in nitrobenzene	70K
Extraction						
Tm^{+3}	$M^{+3} + 3S^- + HS = \overline{MS_3(HS)}$	7.9	27	$NaClO_4$ 0.1	HS 1.0 in 4-methyl 2-pentanone	69Sa
	$M^{+3} + 3S^- + 5HS = MS_3(HS)_5$	7.9	27	$NaClO_4$ 0.1	HS 1.0 in $CHCl_3$	69Sa
Cu^{+2}	$2M^{+2} + 3(\overline{HS})_2 = (\overline{MS_2 \cdot HS})_2 + 4H^+$	-11.48	25	$(Na^+,H^+)ClO_4^-$ 0.1	HS 1.0 in benzene	70Ka
Zn^{+2}	$M^{+2} + 2S^- + HS = MS_2(HS)$	4.3	27	$NaClO_4$ 0.1	HS 0.3-3 in benzene	69S
		4.3	27	$NaClO_4$ 0.1	HS 0.3-3 in $CHCl_3$	69S
		3.6	27	$NaClO_4$ 0.1	HS 0.1-3 in 4-methyl-2-pentanone	69S
	$M^{+2} + S^- = MS^+$	1.6	27	$NaClO_4$ 0.1	HS 0.3-3 in $CHCl_3$	69S
In^{+3}	$M^{+3} + 2S^- + 2HS = MS_2(HS)_2^-$	10.5	27	$NaClO_4$ 0.1	HS 0.05-3 in $CHCl_3$	68S,69C
	$M^{+3} + 3S^- + HS = MS_3(HS)$	9.6	27			68S,69C
	$M^{+3} + 3S^- + 2HS = MS_3(HS)_2$	12.3	27			68S,69C
	$M^{+3} + 3S^- + 3HS = MS_3(HS)_3$	14.0	27			68S,69C
	$MS_3(HS)_3 = \overline{MS_3(HS)_3}$	3.0	27			68S,69C

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.

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Extractant: Octanoic acid, (H)OT, HS

Distribution:

	$HS = \overline{HS}$	1.60	25	μ0.1($NaClO_4$)	HS 10^{-4} -6 in benzene	69S
		1.07-1.65	25	$NaNO_3$ 0.0-6.0, pH 3.0	HS (mix C_7-C_9) 6.4 in benzene	61A
		2.17	25	μ0.1 ($NaClO_4$)	HS 10^{-4} -6 in $CHCl_3$	69S
		4.3	25	HS	HS in decane	69S/65K
		-1.92	23	dil. → ∞	HS in heptane	65P
		0.63	23	μ0.16, pH 7.5	HS 0.012 in heptane	58G/65P
		0.7	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in hexane	69S
		3.3	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in hexanol	69S

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
	$HS = \overline{HS}$	1.11	25	HS → 0	HS in kerosene (mix C_7-C_9)	61Aa
		3.07	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in MiBK	69S
		2.9	27	μ0.1 ($NaClO_4$)	HS 0.01-1.0 in octanol	67S
		2.5	25	μ0.1 ($NaClO_4$)	HS 3.0 in 1-octanol	67S
		∿2	?	H_2O	HS in olive-oil	69S/28B
		1.65	?	H_2O	HS in petroleum-ether	69S/31G
		2.1	27	μ0.1 ($NaClO_4$)	HS 7.0 undil. HS	67S
Dimerization						
	$2\ \overline{HS} = (\overline{HS})_2$					
		2.5	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in benzene	69S
		2.46	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in $CHCl_3$	69S
		2.4-2.8	25	—	HS 0.01-0.2 in cyclohexane	69S/34 B
		0.0-0.4	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in decane	69S/65K
		3.50	20	—	HS 0.12 in dekaline	68S
		2.61	75	—		68S
		2.0	100	—		68S
		2.22	140	—		68S
		3.76	23	μ0.16, pH 7.5	HS 10^{-5}-10^{-3} in heptane	58E,65P
		0.63	25	HS → 0	HS in kerosene (C_7-C_9)	61Aa
		3.6-3.9	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in hexane	69S
		-1.7	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in hexanol	69S

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
	$2\ \overline{HS} = (\overline{HS})_2$	-2.0	25	μ0.1 ($NaClO_4$)	HS 10^{-4}-6 in MiBK	69S
		2.11	46	—	HS 0.05m in high-molecular-weight paraffin	69S/57S
		-0.4	179	—		69S/57S
		2.4-3.0	?	—	HS in petrol-ether	69S/31G
	$2\ S^- = S_2^{-2}$	<1.0		μ0.16, pH 7.5	HS 10^{-5}-10^{-3} in heptane	65P
	$\overline{HS} + \overline{S'} = \overline{HSS'}$	4.31	25	—	HS 10^{-5}-10^{-4} in benzene	66D
	S' = 1,3 Diphenyl guanidine					
Extraction						
Cu^{+2}	$2M^{+2} + 3\ (\overline{HS})_2 = (\overline{MS_2.HS})_2 + 4H^+$	-11.6	25	μ0.1 (Na^+, H^+)ClO_4^-	HS < 1.0 in benzene	70K
Li^+	$M^+ + (\overline{HS})_2 = \overline{MS.HS} + H^+$	-7.00	?	pH 5.5, MOH < 1.0	HS (C_7-C_9) 2.87 in benzene	67M
Na^+		-6.62	?			67M
K^+		-6.07	?			67M
Cs^+		-6.16	?			67M
	$M^+ + 4\ (\overline{HS})_2 = \overline{MA.7HS} + H^+$	-2.5	25	$NaNO_3$ 0.0-6.0 pH 3.0-2.0	HS (C_7-C_9) 0.8 in benzene	61Aa
Cu^{+2}	$2M^{+2} + 3\ (\overline{HS})_2 = (\overline{MS_2.HS})_2 + 4H^+$	-11.65	25	(Na^+, H^+, ClO_4^-) 0.1	HS 0.01-1.0 in benzene	70K

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Extractant: Naphthenic Acid(s), HS

Dissociation					
$HS = H^+ + S^-$	~-4.3	?	H_2O, HS ≡ $C_9H_{16}O_2$		68Ab
	~-5.0	?	H_2O, HS ≡ $C_{12}H_{22}O_2$		68Ab
$\overline{HS} = \overline{H}^+ - \overline{S}$	-7.5	?	—	HS ≡ $C_{10}H_{18}O_2$ from kerosene fraction	68Ab
	-6.4	?	—	HS ≡ $C_{13}H_{24}O_2$ from kerosene fraction	68Ab

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Dimerization						
	$2\ \overline{HS} = (\overline{HS})_2$	0.89	25	H_2O	HS in benzene	65Ab
		0.79	25	H_2O	HS in heptane	65Ab
		0.54	25	H_2O	HS in iso-amylalcohol	65Ab
Be^{+2}	$M^{+2} + (\overline{HS})_2 = \overline{MS_2} + 2H^+$	-8.37	?	pH 3.5, MCl 0.5 dm^{-3}	HS 1.0 in kerosene	69A
Mg^{+2}		-13.90	?	pH 6.5, MCl 0.5 dm^{-3}	HS 1.0 in kerosene	69A
Ca^{+2}		-12.63	?	pH 6.0, MCl 0.5 dm^{-3}	HS 1.0 in kerosene	69A
Sr^{+2}		-11.28	?	pH 4.2, MCl 0.5 dm^{-3}	HS 1.0 in kerosene	69A
Ba^{+2}		-9.77	?	pH 4.2, MCl 0.5 dm^{-3}	HS 1.0 in kerosene	69A
Y^{+3}	$M^{+3} + 3\ \overline{HS} = \overline{MS_3} + 3H^+$	-11.17	?	pH 4-6	HS 0.05-0.5 in kerosene	65A
Ce^{+3}	$M^{+3} + 3\ \overline{HS} = \overline{MS_3} + 3H^+$	-11.22	?	pH 4-6	HS 0.05-0.5 in kerosene	65A
UO_2^{++}	$\overline{MS_2} + (\overline{HS})_2 = \overline{MS_2 . 2HS}$	-1.46	20	—	HS 0.014-0.09 in heptane	66E
In^{+3}	$M^{+3} + 6\ \overline{HS} = \overline{MS_3 . 3HS} + 3H^+$	8.36	?	?	HS in kerosene (?)	68A

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Extractant: Versatic acid(s), HS

Cu^{+2}	$M^{+2} + 2\overline{HS} = \overline{MS_2} + 2H^+$	-9.10	22	$NaNO_3$ 2.0, pH 4.0	HS 0.35 in toluene HS ≡ Versatic 9, a tertiary carboxylic acid, M.W. = 158	67H

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Extractant: Decanoic acid, (H)DT, HS

$HS = \overline{HS}$	-0.68	23	dil. → ∞	HS in heptane	65P
	-0.68	23	μ0.16, pH 7.5	HS 10^{-3}-10^{-2} in heptane	58G,65
$2S^- = S_2^{-2}$	1.60	23	μ0.16, pH 7.5	HS 10^{-5}-10^{-3} in heptane	65P
$2\overline{HS} = (\overline{HS})_2$	2.85	25	μ0.1 (Na^+, H^+) ClO_4^-	HS < 1.0 in benzene	70K
	2.4	25	pH 6.5	HS < 0.1 in benzene	68T
	2.6	rt	—	HS in benzene	65/49W
	4.82	37	—	HS 0.02-0.1 in 1,2 $C_2H_4Cl_2$	65C

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
	$2\,\overline{HS} = (\overline{HS})_2$	3.84	23	μ0.16, pH 7.5	HS 10^{-3}-10^{-2} in heptane	58G,65
	$\overline{HS} + \overline{S'} = \overline{HSS'}$	4.34	25	—	HS 10^{-5}-10^{-4} in benzene	66D
	S' = 1,3 diphenylguanidine					
Fe^{+3}	$3M^{+3} + 4.5\,(\overline{HS})_2 = (\overline{MA_3})_3 + 9H^+$	-9.9	25	μ0.04, M^{+3} $6x10^{-4}$	HS 0.5 in benzene	68T
Co^{+2}	$M^{+2} + 3\,(\overline{HS})_2 = \overline{MS_2.4HS} + 2H^+$	-11.2	25	μ0.2, M 10^{-5}	HS 0.4-1.0 in benzene	68T
	$2M^{+2} + 4(\overline{HS})_2 = (\overline{MS_2.2HS})_2 + 4H^+$	-19.7	25	μ0.2, M 10^{-3}	HS 0.4-3.0 in benzene	68T
	$\overline{2MS_2.4HS} = (\overline{MS_2.2HS})_2 + 2(\overline{HS})_2$	2.4-3.0	25	μ0.2, M 10^{-3}	HS 0.4-3.0 in benzene	68T
Cu^{+2}	$2M^{+2} + 3(\overline{HS})_2 = (\overline{MS_2.HS})_2 + 4H^+$	-11.5	25	μ0.1 $(Na^+, H^+)ClO_4^-$	HS < 1.0 in benzene	68T,70
	$2M^{+2} + 3(\overline{HS})_2 = (MS_2.HS)_2 + 4H^+$	-11.58	25	(Na^+, H^+, ClO_4^-) 0.1		70K
	$2\overline{HS} = (\overline{HS})_2$	2.85	25	(Na^+, H^+, ClO_4^-) 0.1	HS 1.0 in benzene	70K

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