INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

EQUILIBRIUM CONSTANTS OF LIQUID–LIQUID DISTRIBUTION REACTIONS

Part 2: ALKYLAMMONIUM SALT EXTRACTANTS

Compiled by
A. S. KERTES, Y. MARCUS and E. YANIR

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ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA

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ENGLAND: BUTTERWORTH & CO. (PUBLISHERS) LTD.
LONDON: 88 Kingsway, WC2B 6AB

AUSTRALIA: BUTTERWORTHS PTY. LTD.
SYDNEY: 586 Pacific Highway, Chatswood, NSW 2067
MELBOURNE: 343 Little Collins Street, 3000
BRISBANE: 240 Queen Street, 4000

CANADA: BUTTERWORTH & CO. (CANADA) LTD.
TORONTO: 14 Curity Avenue, 374

NEW ZEALAND: BUTTERWORTHS OF NEW ZEALAND LTD.
WELLINGTON: 26–28 Waring Taylor Street, 1

SOUTH AFRICA: BUTTERWORTH & CO. (SOUTH AFRICA) (PTY) LTD.
DURBAN: 152–154 Gale Street

Published as an additional publication to

Pure and Applied Chemistry

Suggested U.D.C. number
541·123·03: 542·615

Distributed in North America by
CRANE RUSSAK & COMPANY INC.
347 Madison Avenue, New York, NY 10017

ISBN 0 408 70631 7

Printed in Great Britain by Page Bros (Norwich) Ltd, Norwich

INTRODUCTION

This volume represents the Second Part of the compilation of Equilibrium Constants of Liquid–Liquid Distribution Reactions. The work has been carried out within the frame of the activities of the Commission on Equilibrium Data, Analytical Chemistry Division, International Union of Pure and Applied Chemistry (IUPAC) and has been financially supported by the Office of Standard Reference Data, National Bureau of Standards, United States Government.

This part consists of tables compiling equilibrium constants of distribution reactions involving extractants of the long-chain alkylamine classes, primary, secondary and tertiary, as well as quaternary ammonium salts, and other 'onium' salts: tetraphenylarsonium and tetraphenylphosphonium. The literature searched covers the period 1947–1969, with some of the more recent publications, 1970–1971, also included.

The general arrangement of the tables is identical to that used in Part I, where a detailed description and explanation of the arrangement is given. The symbols used conform to those used in Part I, except that R is used to represent the non-protonated amine (the cation is then RH^+) and R^+ the quaternary ammonium ion.

CONTENTS

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
	Extractant Class: Primary and secondary amines					
Extractant: Primene JMT , $(NH_2CR_1R_2R_3$, $R_1+R_2+R_3$ = 17-23 C atoms) , R						
Ligand NO_3^- , A^-						
	$(HA)_n + \overline{R\ HA} = \overline{R\ HA(HA)_n}$	-0.57	25	HA 0.5-10	R 0.16-0.55 benzene	65S
Ligand Cl^- , A^-						
	$H^+ + A^- + \overline{R} = \overline{R\ HA}$	6.87	23	μ = 0.019 (H^+, Na^+)A^-	R 0.015 benzene	66S
		7.1	?	NaA 1.0	R 0.1 toluene	67G
Ligand Br^- , A^-						
	$H^+ + A^- + \overline{R} = \overline{R\ HA}$	7.29	23	μ = 0.019 (H^+, Na^+)A^-	R 0.015 benzene	66S
Ligand I^- , A^-						
	$H^+ + A^- + \overline{R} = \overline{R\ HA}$	7.67	23	μ = 0.019 (H^+, Na^+)A^-	R 0.015 benzene	66S

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66S Scibona, G., Orlandini, F. and Danesi, P.R., J. Inorg. Nucl. Chem., 28, 1701 (1966)

67G Grinstead, R.R., in "Solvent Extraction Chemistry," Eds. Dyrssen, D., Liljenzin, J.-O. and Rydberg, J., North-Holland, Amsterdam, 1967, p. 426

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Extractant: Amberlite LA-2 , ($C_{12}H_{25}NHCR,R_2R_3$ $R_1+R_2+R_3$=12 C atoms)						
Ligand Cl^- , A^-						
	$H^+ + A^- + \overline{R} = \overline{R\,HA}$	5.75	23	μ = 0.019 (H^+,Na^+)A^-	R 0.015 benzene	66S
		5.98	25	HA 10^{-4}-0.01	R 0.091 CCl_4	63D
		6.15	25	HA 10^{-4}-0.01	R 0.181 CCl_4	63D
		5.31	20	HA 0.05	R 0.112 kerosene	65R
		5.24	20	HA 0.05-0.1	R 0.112 kerosene	65R
		4.4-3.9	20	HA 0.2-0.5	R 0.108 kerosene	65R
	$A^- + \overline{R\,HClO_4} = \overline{RHA} + ClO_4^-$	-0.98	25	HA 0.02 , $NaClO_4$ 0.2	R $HClO_4$ 0.075-0.2 CCl_4	65D
	$HA + \overline{RHClO_4} = \overline{RHA} + HClO_4$	-1.56	20	HA 0.1	R 0.11 kerosene	65R
Pt^{+4}	$MA_6^{-2} + 2\overline{R\,H\,A} = \overline{(R\,H)_2MA_6} + 2A^-$	1.84	25	NaA 1.2-2.0	R 0.1-0.3 CCl_4	65D
Ligand ClO_4^- , A^-						
	$HA + \overline{RHCl} \rightleftharpoons \overline{R\,HA} + HCl$	-1.56	20	HA 0.09	R HCl 0.1 kerosene	65R
	$Cl^- + \overline{RHA} = \overline{R\,HCl} + A^-$	-0.98	25	HCl 0.02 , NaA 0.2	R HA 0.075-0.2 CCl_4	65D
Ligand Br^- , A^-						
	$H^+ + A^- + \overline{R} = \overline{R\,HA}$	6.20	23	μ = 0.019 (H^+,Na^+)A^-	R 0.015 benzene	66S
		6.43	25	HA 10^{-4}-0.01	R 0.091 CCl_4	63D
		6.62	25	HA 10^{-4}-0.01	R 0.181 CCl_4	63D

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand Br^- , A^- (cont.)						
Pt^{+4}	$MA_6^{-2} + 2\overline{R\,HA} = \overline{(R\,H)_2MA_6} + 2A^-$	1.02	25	$(Na^+ , H^+)A^-$ 0.4-1	R HA 0.1-0.3 CCl_4	65D
Ligand I^- , A^-						
	$H^+ + A^- + \overline{R} = \overline{R\,HA}$	6.92	23	μ = 0.019 $(H^+,Na^+)A^-$	R 0.015 benzene	66S
		7.2	25	HA 10^{-4}-0.01	R 0.091 CCl_4	63D
		7.4	25	HA 10^{-4}-0.01	R 0.181 CCl_4	63D

References

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65D Davidson, C.M. and Jameson, R.E., Trans. Faraday Soc., 61, 133 (1965)

65R Rubinstein, G., French Rept. CEA-R-2742 (1965)

66S Scibona, G., Orlandini, F. and Danesi, P.R., J. Inorg. Nucl. Chem., 28, 1701 (1966)

Extractant: Didecylamine , R

Ligand $SO_4^=$, $A^=$						
	$2H^+ + A^= + 2\overline{R} = \overline{(RH)_2A}$	11.40	?	H_2A 10^{-3}-0.06	R 0.005-0.6 benzene	58B
		10.50	?	H_2A 10^{-3}-0.06	R 0.005-0.6 CCl_4	58B

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand $SO_4^=$, $A^=$ (cont.)						
	$2HA^- + \overline{(RH)_2A} = 2\overline{(RH)HA} + A^=$	3.4	25	HA^- 0.25	0.05<R<0.1 benzene (mole fraction)	56A
	$H_2A + \overline{(RH)_2A} = 2\ \overline{(RH)HA}$	-0.4	25	H_2A<0.5	R<0.1 benzene	61M
	$H_2A + \overline{(R)_2H_2A} = 2\overline{(R)H_2A}$	1.99	25	Na_2A 0.32, H_2A 0.18	R 0.007-0.1 benzene	55B
Th^{+4}	$\overline{(RH)_7MA_{5.5}} + 3.5x\ \overline{(RH)_2A(H_2A)} =$ $= 3.5\ \overline{(RH)_2A{\cdot}MA_2} + 7x\ \overline{R\ H_2A}$ $x = [\overline{RH_2A}]/([\overline{RH_2A}] + 2[\overline{R_2H_2A}])$	2.0	25	H_2A<0.5	R<0.1 benzene	61M
UO_2^{++}	$M^{++} + 4H^+ + 3A^= + 4\ \overline{R} =$ $= \overline{[(RH)_2A]_2MA}$	21.7	19	Na_2A 0.1-1.25 , H^+<0.04	R 0.016-0.021 CCl_4	58B
Ligand Cl , A^-						
	$H^+ + A^- + \overline{R} = \overline{RHA}$	6.23	25	HA ?	R 0.001-0.02 CCl_4	63K
		7.2	?	HA 1.0	R 0.1 toluene	67G

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58B Boirie, C., Bull. Soc. Chim. France, 980, 1088 1958)

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

61M McDowell, W.J. and Allen, K.A., J. Phys. Chem., 65, 1358 (1961).

63K Kertes, A.S., Kimura, K., Schlayer, C.R. and Irvine, Jr., J.W., USAEC Rept. NYO-10063 (1963)

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Extractant: Diisononylamine, R

Ligand $SO_4^=$, $A^=$						
	$H_2A + 2\,\overline{R} = \overline{(RH)_2A}$	15.15-15.83	25	H_2A 0.001-0.5	R 0.01-0.1 isoamylalcohol	67C
	$H_2A + \overline{(RH)_2A} = 2\,\overline{(RH)HA}$	3.11-3.00	25			67C
Ligand Cl^-, A^-						
	$2H^+ + 2A^- + 2\,\overline{R} = \overline{(R\,HA)_2}$	15.48	25	$(Li,H)^+A^-$ 1.0	R 0.006-0.3 $CHCl_3$	67W,66W
	$HA + \overline{(R,HA)_2} = \overline{R_2(HA)_3}$	-5.6	25	HA 6-11.5	R 1-10% $CHCl_3$	67W
	$2HA + \overline{(R\,HA)_2} = \overline{R_2(HA)_4}$	-11.8	25			67W

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

References

66W Warnquist, B., in "Solvent Extraction Chemistry," Eds. Dyrssen, D., Liljenzin, J.-O. and Rydberg, J., North-Holland, Amsterdam, 1967, p. 416

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Extractant Class: Tertiary Amines

Extractant: Trioctylamine , R

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand OH^- , A^-						
	$HA + \overline{R} = \overline{RHA}$	-0.85	25	a_{HA} 0-1.0	R<0.5 benzene	69R
	$\overline{RHA} = \overline{RH^+} + \overline{A}$	-1.92	?		RHA<0.2 acetone	63P
		-8.35	25		R 2×10^{-3} 70% ethanol	47B
Ligand TcO_4^- , A^-						
	$A^- + \overline{RHNO_3} = \overline{RHA} + NO_3^-$	2.1-2.3	20	HNO_3 2.0	R 0.015-0.85 cyclohexane	60B
Ligand CNS^- , A^-						
	$ClO_4^- + \overline{RHA} = \overline{RHClO_4} + A^-$	-0.35	22	HA 0.2 $(Na,H)^+ClO_4^-$ 3.67	R 8×10^{-3} cyclohexane	64O

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand NO_3^-, A^-						
	$H^+ + A^- + \overline{R} = \overline{RHA}$	5.43	30	HA<2.0	R 0.1 benzene	62Va
		5.20	35			62Va
		5.04	40			62Va
		ΔH -14.9	10-40			62Va
		ΔS - 8.4	25			62Va
		6.19	10			62Va
		5.69	20			62Va
		5.76	23			62Va
		5.58	25			62Va
		5.68	25	HA 1-5	R 0.01-0.25 benzene	64V
		6.00	20	HA 0.13-0.2	R 0.22 CCl_4	62Z
		6.79	40	HA 0.01	R<0.1 $CHCl_3$	62Va
		4.92	25	HA<0.02	R 0.025,0.5 dodecane +6% octanol	62Va
		5.12	25	HA<0.07	R 0.05 xylene	65K
		7.69	40	HA 0.01	R<0.1 nitrobenzene	62Va

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand NO_3^-, A^- (cont.)						
	$H^+ + A^- + \overline{RHA} = \overline{R(HA)_2}$	-0.66	25	HA 1-5	R 0.1 benzene	64V
		-0.7	?	HA 1.5-4.5	R 0.2-0.9 benzene	63F
		-1.1	?	HA 1.4-7.4	R 0.2-1.0 CCl_4	63F
		-1.05	19	HA 1-5	R 0.5 CCl_4	60S
		-1.52	25	HA 1-5	R 0.1 $CHCl_3$	64V
		-0.59	?	HA 1-1.5	R 0.2-0.5 CCl_4	66R
		-1.05	25	HA 1-5	R 0.1 o-dichlorobenzene	64V
		-0.68	25	HA 1-5	R 0.1 toluene	64V
		-0.89	19	HA 1-5	R 0.5 o-xylene	60S
		-0.5	25	HA 0.5-1.4	R 0.05 xylene	65K
Th^{+4}	$MA_4 + 2\ \overline{RHA} = \overline{(RH)_2MA_6}$	ΔH 4.1	10-50	HA 3.0	R 0.1 benzene	68S
		ΔH 5.4	10-50	HA 6.0	R 0.1 benzene	68S
		ΔH 2.3	10-50	HA 0.1 , NaA 6.0	R 0.1 benzene	68S
UO_2^{+2}	$M^{+2} + 2A^- + \overline{(RH)A} = \overline{(RH)MA_3}$	0.31	?	HA 2.15	RHA 0.47 CCl_4 C_M<0.1	60Sb
		0.46	?	HA 2.15	RHA 0.47 xylene C_M<0.1	60Sb
		1.47	25	HA 0.75, MA_2 0.4	R<0.4 o-xylene	63V
	$MA_3^- + \overline{RHA} = \overline{RHMA_3} + A^-$	1.1	?	HA 1.0-1.5	R 0.2-0.05 CCl_4	66R
	$MA_2 + 2\ \overline{RHA} = \overline{(RH)_2MA_4}$	ΔH 2.28	10-50	HA 6.0	R 0.1 benzene	65S,64S

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand NO_3^-, A^- (cont.)						
Np^{+4}	$M^{+4} + 4A^- + 2\,\overline{RHA} = \overline{(RH)_2MA_6}$	3.7-1.8	25	HA 0.65-5.0	R 0.3 xylene	67A
		5.5	25	HA→0	R 0.3 xylene	67A
NpO_2^{+2}	$M^{+2}_{(tot)} + 2A^- + 2\,\overline{RHA} = \overline{(RH)_2MA_4}$	1.9-1.3	25	HA 0.65-2.58	R 0.3 xylene	67A
		1.4-2.0	25	HA 3.55-5.0	R 0.3 xylene	67A
		3.11	25	HA→0	R 0.3 xylene	67A
Pu^{+4}	$MA_6^{-2} + 2\,\overline{RHA} = \overline{(RH)_2MA_6} + 2A^-$	5.9	?	HA 1.0-1.5	R 0.2-0.5 CCl_4	66R
Ligand $SO_4^=$, $A^=$						
	$2H^+ + A^= + 2\,\overline{R} = \overline{(RH)_2A}$	8.5	?	H_2A 10^{-3}-0.06	R 0.005-0.6 benzene	58B
		7.9-8.4	?	H_2A 0.01-0.05	R 0.1 benzene	65D
		6.7	?	H_2A 10^{-3}-0.06	R 0.005-0.6 CCl_4	58B
		6.44	?	H_2A 0.02-0.3	R 0.05-0.25 CCl_4	61S
		8.3-8.9	?	H_2A 0.03-0.54	R 0.1-0.5 CCl_4	65D
	$H^+ + HA^- + \overline{(RH)_2A} = 2\,\overline{(RH)HA}$	1.5	?	H_2A 0.2	R 0.1 benzene	58B
		0.6 to -0.1	?	H_2A 0.09-1.0	R 0.1 benzene	65D
		-2.7	?	H_2A 1.1-2.1	R 0.1+(H_2)BP 0.1 benzene	65Da

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand $SO_4^=$, $A^=$						
		-2.9	?	H_2A 1.1-2.1	R 0.1+(H)DBP 0.1 benzene	65Da
		-3.2 to -2.9	?	H_2A 1.1-2.1	R 0.1+(H)DE-HP 0.1 benzene	65Da
		-0.5 to -0.2	?	H_2A 0.1-2.1	R 0.1+(H_2)DDP 0.1 benzene	65Da
		0.07	?	H_2A 0.02-0.3	R 0.05-0.25 CCl_4	61S
		1.02	?	H_2A 0.3-1.0	R 0.1 CCl_4	65D
		1.0-1.6	?	H_2A 0.25-2.1	R 0.25-0.5 CCl_4	65D
	$H_2A_{(tot)} + \overline{R} = \overline{(RH)HA}$	4.99	25	H_2A<1.0	R 0.5, 0.05 benzene	64W,66W
		4.82	25	H_2A 0.1-10^{-3}	R 0.25-0.1 benzene	64W/56A,58A
	$H_2A_{(tot)} + 2\overline{R} = \overline{(RH)_2A}$	8.28	25	H_2A 0.1-10^{-3}	R 0.02 benzene	56A
		8.98	11.5	H_2A<0.04	R<0.02 benzene	61V,60V
		8.27	25			61V,60V
		7.92	45			61V,60V
		7.39	55			61V,60V
		6.92	75			61V,60V
		ΔH -20.95	11-75			61V,60V
		ΔH -3.25	11-75			61V,60V
		8.15	25	H_2A<1.0	R 0.5, 0.05 benzene	64W,66W

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand $SO_4^=$, $A^=$ (cont.)						
		8.11	25	H_2A 0.1-10^{-3}	R 0.25-0.1 benzene	64W/56A,58A
		9.18	?	H_2A<0.3	R 0.1 dibutylphthalate	63C
		8.19	?	H_2A<0.3	R 0.1 n-hexadecane	63C
		9.42	20	H_2A 0.01	R 0.1 kerosene	60V
		8.72	20	H_2A 0.02-0.04	R 0.1 kerosene	60V
		7.86	20	H_2A 0.05	R 0.1 kerosene	60V
		7.04	?	H_2A<0.3	R 0.1 phenylcyclohexane	63C
	$H_2A + 3/2\ \overline{R_2{\cdot}H_2A} = 3\ \overline{RH_2A}$	3.17	25	H_2A 0.1-0.5	R 0.1, 0.25 benzene	56A
	$H_2A + \overline{(RH)_2A} = 2\ \overline{(RH)HA}$	1.48	20	H_2A 0.01	R 0.1 kerosene + 4% octyl alcohol	62V
	(Concentrations in org. phase are in mole fract. scale)	1.06	20	0.01<H_2A<0.3	R 0.1 kerosene + 4% octyl alcohol	62V
	$2H^+ + A^= + 2\overline{R(H_2)BP} = \overline{(RH)_2A} + 2\overline{(H_2)BP}$	2.2-2.5	?	H_2A 0.07-0.6	R 0.1+(H_2)BP 0.1 benzene	65Da
	$2H^+ + A^= + 2\overline{R(H)DBP} = \overline{(RH)_2A} + 2\overline{(H)DBP}$	2.1	?	H_2A 0.06-0.51	R 0.1+(H)DBP 0.1 benzene	65Da
	$2H^+ + A^= + 2\overline{R(H)DE\text{-}HP} = \overline{(RH)_2A} + 2\overline{(H)DE\text{-}HP}$	1.7-2.0	?	H_2A 0.05-2.1	R 0.1+(H)DE-HP 0.1 benzene	65Da
	$2H^+ + A^= + 2\overline{R(H_2)DDP} = \overline{(RH)_2A} + \overline{(H_2)DDP}$	5.0	?	H_2A 0.05	R 0.1+(H_2)DDP 0.1 benzene	65Da

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Ligand $SO_4^=$, $A^=$ (cont.)						
	$\overline{(RH)HA} = \overline{RH^+} + \overline{HA^-}$	-1.75	?	- -	(RH)HA 0.2 acetone	63P
	$2\ \overline{(RH)HA} = \overline{[(RH)HA]_2}$	2.30	25	H_2A<1.0	R 0.5, 0.05 benzene	64W,66W
		2.54	25	H_2A 0.1-10^{-3}	R 0.25-0.1 benzene	64W/56A,58A
		0.87	5		RH_2A 0.01-0.2 m benzene	66C
	$\overline{(RH)HA} + \overline{(RH)_2A} = \overline{(RH)_3HA_2}$	2.87	25	H_2A<1.0	R 0.5, 0.05 benzene	64W,66W
		2.82	25	H_2A 0.1-10^{-3}	R 0.25-0.1 benzene	64W/56A,58A
	$2\ \overline{(RH)_2A} = \overline{[(RH)_2A]_2}$	1.60	25	H_2A<1.0	R 0.5, 0.05 benzene	64W,66W
		1.20	25	H_2A 0.1-10^{-3}	R 0.25-0.1 benzene	64W/56A,58A
	$2\ \overline{RH_2A} = \overline{(RH_2A)_2}$	1.07	25	- -	R 0.07-0.4 benzene	67C
	$3\ \overline{RH_2A} = \overline{(RH_2A)_3}$	3.58	5	- -	RH_2A 0.01-0.2 m benzene	66C/60F,62Y
	$4\ \overline{RH_2A} = \overline{(RH_2A)_4}$	5.24	5	- -	RH_2A 0.01-0.2 m benzene	66C/60F,62Y
	$5\ \overline{RH_2A} = \overline{(RH_2A)_5}$	6.48	5	- -	RH_2A 0.01-0.2 m benzene	66C/60F/62Y
	$2\ \overline{(RH_2A)_2} = \overline{(RH_2A)_4}$	5.47	?	- -		67C
Zr^{+4}	$H_4MA_4 + 4\ \overline{RH_2A} = \overline{(RH)_4MA_4} + 4H_2A$	2.70	20	H_2A 2-6	R 0.1-10% benzene	69Y