Part III

Distribution Experiments in Fused Salts

Distribution of Alkali Bromides Between Silver Bromide and Alkali Nitrates

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The distribution of alkali bromides between molten alkali nitrates and molten silver bromide has been studied by observing the distribution of both bromide and alkali metal. K was 0.116 for lithium bromide, 0.33 for sodium bromide, 1.79 for potassium bromide, and 8.6 for cesium bromide. A general expression was developed for distributions in the systems MBr–M'NO$_3$–AgBr.

THE DISTRIBUTION of $PbBr_2$ between molten KNO_3 and AgBr has been studied by adding various amounts of KBr to the system (*2*). During this investigation it was found that KBr was also distributing nearly equally between the two fused salt solvents. The same effect had been found for KCl (*2*), but since the calculation of chloride ion activity from chloride concentration involved larger corrections than in the bromide case—i.e., AgCl was more soluble than AgBr in KNO_3—the bromide system was more suited for a study of alkali halide distribution.

EXPERIMENTAL

The same apparatus used for lead bromide distributions was used for the alkali bromide distributions. The alkali metal nitrate, 50 grams, was melted and, especially in the case of lithium, allowed to dry by bubbling in nitrogen gas before the addition of 50 grams of AgBr. The temperature was controlled at 450° C. ± 3° with a Wheelco electronic temperature controller. A quantity of alkali bromide was added, the mixture was stirred for 10 minutes, and the two phases were allowed to separate. The plug of frozen salt in the capillary outlet was then melted by turning on the auxiliary heater, and the molten mixture flowed out the capillary tube into the sample collector. Several portions of each phase were collected and analyzed.

Silver bromide was prepared from A.R. silver nitrate and potassium bromide. The precipitation was carried out in the dark, and, after drying overnight, the silver bromide was stored in black bottles to prevent decomposition to silver metal. AgBr melts containing silver metal were black and occasionally clogged the capillary outlet. AgBr melts prepared in the described manner were dark brown, but clear, and flowed easily through the capillary outlet.

A.R. alkali nitrates, sodium bromide, and potassium bromide were dried overnight at 120° C. Mallinckrodt lithium bromide was dehydrated by bubbling HBr into a melted quantity for 4 hours followed by a nitrogen sweep, pouring various size samples into beakers which were subsequently covered with foil, and storing in a vacuum desiccator.

Cesium nitrate was prepared from Amend Drug C.P. cesium chloride and silver nitrate. The product obtained from evaporation of the filtrate was dried overnight at 120° C.

The concentration of bromide in the alkali nitrate phase was found by dissolving the sample in 100 ml. of water, adding 4 ml. of 6*F* HNO_3 and titrating coulometrically with a silver wire anode. A Sargent Constant Current Power Supply was used for all coulometric titrations. Potentiometric end-point detection was accomplished using a Leeds and Northrup pH Meter. This method gave total bromide minus an amount equal to the amount of silver present. The relation between the analytical value and the bromide ion concentration in the molten alkali nitrate depends on the association constants for AgBr and has been derived previously (*3*). The equation is:

$$[Br^-] = \frac{(Br) \pm [(Br)^2 + 4K_{sp}(1 + K_1K_2K_{sp})]^{1/2}}{2\,(1 + K_1K_2K_{sp})} \qquad (1)$$

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where (Br) is the analytical value. When (Br) was high (> 0.2m for KBr, > 0.1m for NaBr and LiBr), this equation simplified to:

$$[\mathrm{Br}^-] = \frac{(\mathrm{Br})}{1 + K_1K_2K_{sp}} \tag{2}$$

The values for all the constants have not been determined, but the approximate values given in Table I were used. Literature values are noted; the others were estimated from solubility data (see Table II).

The concentration of soluble bromide in the silver bromide phase was found by the following procedure. A 1-gram sample was dissolved in 100 ml. of H_2O containing 2-grams of KCN. Twenty-five milliliters of 8F H_2SO_4 was added slowly, and the mixture digested 2 to 2½ hours. At the end of this period, the volume was 60 to 70 ml. The supernatant liquid was decanted, the precipitate washed with H_2O, the solution diluted to 125 ml. with H_2O and titrated coulometrically.

Alkali metal (I) determinations were made flame photometrically with a Beckman Model B Spectrophotometer and flame attachment. Since the amount of alkali metal solute was small compared to the alkali metal nitrate, standards had to contain comparable amounts of alkali nitrate. Thus, for example, in the analysis of sodium in potassium nitrate, all samples, including standards, contained 10 grams per 100 ml. of potassium nitrate. The same problem was encountered in the analysis of silver bromide phases since they had to be dissolved in alkali cyanide. Potassium cyanide was used for sodium and lithium determinations. Sodium cyanide was used for potassium determinations.

RESULTS AND DISCUSSION

Distributions of MBr between $M'NO_3$ and AgBr where M and M' = K, Na, Li, or Cs are given in Table III. The distribution coefficient for bromide given in Table III is defined by the equation:

$$K_o = \frac{(M\mathrm{Br})_{\mathrm{AgBr}} + (M'\mathrm{Br})_{\mathrm{AgBr}}}{[\mathrm{Br}^-]_{M'\mathrm{NO}_3}} \tag{3}$$

The distribution coefficient for the metal (I) (determined flame photometrically) was determined for a number of experiments—(those in which a high concentration of MBr was present—and the results are given in Table IV and Table VI (columns 4 and 6).

In general, transport across the boundary may be formulated:

$$M^+ + \mathrm{Br}^- \xrightarrow{k_1} [M\mathrm{Br}]_{M'\mathrm{NO}_3} \xrightarrow{k_2} [M\mathrm{Br}]_{\mathrm{AgBr}}$$

$$k_1 = [M\mathrm{Br}]_{M'\mathrm{NO}_3}/[M^+][\mathrm{Br}^-] \tag{4}$$

$$k_2 = [M\mathrm{Br}]_{\mathrm{AgBr}}/[M\mathrm{Br}]_{M'\mathrm{NO}_3} \tag{5}$$

The observed alkali metal (I) distribution is:

$$K_{OM} = (M)_{\mathrm{AgBr}}/(M)_{M'\mathrm{NO}_3} \tag{6}$$

Making the assumptions that $(M)_{\mathrm{AgBr}} = [M\mathrm{Br}]_{\mathrm{AgBr}}$ and $(M)_{M'\mathrm{NO}_3} = [M^-]_{M'\mathrm{NO}_3} + [M\mathrm{Br}]_{M'\mathrm{NO}_3}$, it follows that:

$$1/K_{OM} = 1/k_2 + 1/k_1k_2[\mathrm{Br}^-] \tag{7}$$

A plot of $1/K_M$ *vs.* $[\mathrm{Br}^-]^{-1}$ for the case KBr in $LiNO_3$–AgBr is shown in Figure 1 (see Table IV for data). The line appears to intersect the origin (within experimental error). This effect can be seen more easily by examining the results for KBr in KNO_3–AgBr. In this case, the KBr concentration in AgBr was higher and, thus, could be analyzed more easily. Since KNO_3 is the solvent, the activity of potassium ion must be nearly one (standard state) in all experiments. Therefore:

$$K_{OM} \cong (K)_{\mathrm{AgBr}}$$

Figure 1 shows the results for these experiments and, again, the line intersects the origin. K_{OM} for M in $M'NO_3$ has a different standard state definition from K_{OM} for M in MNO_3.

Since the intercept was zero, $k_2 = \infty$. However, the slope was finite, which must mean that $k_1 = 0$. In other words, the transport equation should be written simply:

$$\mathrm{K}^- + \mathrm{Br}^- \xrightarrow{\mathrm{K}} [\mathrm{KBr}]_{\mathrm{AgBr}}$$

$$K = [\mathrm{KBr}]_{\mathrm{AgBr}}/[\mathrm{K}^-]_{\mathrm{KNO}_3}[\mathrm{Br}^-]_{\mathrm{KNO}_3} \tag{8}$$

Since KNO_3 was the solvent and predominantly ionized, $[K^+]$ will be in its standard state (neglecting changes in activity due to the presence of KBr) and will be at unit activity. The relation then becomes:

$$K = [\mathrm{KBr}]_{\mathrm{AgBr}}/[\mathrm{Br}^-]_{\mathrm{KNO}_3} \tag{9}$$

Referring to Equation 3, one can see that K is just K_o for the cases $M = M'$ (see Table III). K_o for this special case was essentially constant for increasing MX concentration and the average values are given. These are the K values for the system according to Equation 9. The change in distribution coefficient in going from one alkali metal to another was striking—practically no lithium was found in AgBr while the major fraction of cesium was found in the AgBr phase.

When M' was different from M, the distribution of bromide could be calculated on the basis of two competing reaction:

$$M^+ + \mathrm{Br}^- \longrightarrow [M\mathrm{Br}]_{\mathrm{AgBr}}$$

$$K_{(M)} = [M\mathrm{Br}]_{\mathrm{AgBr}}/[M^+][\mathrm{Br}^-] \tag{10}$$

$$M'^- + Br^- \longrightarrow [M'\mathrm{Br}]_{\mathrm{AgBr}}$$

$$K_{(M')} = [M'\mathrm{Br}]_{\mathrm{AgBr}}/[M'^-][\mathrm{Br}^-] \tag{11}$$

Using Equation 3 and assuming $(M\mathrm{Br})_{\mathrm{AgBr}} = [M\mathrm{Br}]_{\mathrm{AgBr}}$ and $(M'Br)_{\mathrm{AgBr}} = [M'Br]_{\mathrm{AgBr}}$, one obtains:

$$K_o = (M\mathrm{Br} + M'\mathrm{Br})_{\mathrm{AgBr}}/[\mathrm{Br}^-]_{M'\mathrm{NO}_3} = K_{(M)}[M^-]_{M'\mathrm{NO}_3} + K_{(M')}[M'^+]_{M'\mathrm{NO}_3} \tag{12}$$

Table I. Association Constants for AgBr (molal units)

Solvent	K_{sp}	K_1	K_2	$K_1K_2K_{sp}$
$LiNO_3$	2×10^{-6}	...	...	0.016
$NaNO_3$	10^{-4}	36.5(*4*)	12.9(*4*)	0.047
KNO_3	6×10^{-5}	73(*1*)	30(*1*)	0.13

Table II. Solubility of AgBr in MNO_3 (molality)

(Br)[a]	$LiNO_3$	$NaNO_3$	KNO_3
0.016	0.0012		
0.029		0.0093	
0.060			0.015
0.14	0.0026	0.0129	0.025
0.25			0.046
0.37	0.0051	0.0248	
0.40			0.069
0.73	0.011		
0.82		0.0363	

[a] Throughout this paper (Br) will refer to analytical bromide values while $[\mathrm{Br}^-]$ will refer to calculated values based on Equations 1 and 2.

Table III. Distribution of Bromide

50 grams of $M'NO_3$–50 grams of AgBr at 450° C.

KNO_3

*M*Br	Weight, Grams	$(Br)_{AgBr}$	$(Br)_{KNO_3}$	$[Br^-]_{KNO_3}$	K_o
KBr	0.5	0.049	0.029	0.027	1.81
	1.0	0.107	0.060	0.054	1.98
	2.0	0.209	0.127	0.113	1.85
	4.0	0.381	0.254	0.225	1.69
	5.0	0.488	0.315	0.279	1.75
	6.0	0.592	0.396	0.350	1.69
					Av. 1.79
NaBr	0.5	0.073	0.037	0.035	2.08
	1.0	0.130	0.075	0.067	1.94
	2.0	0.242	0.145	0.129	1.88
	4.0	0.448	0.314	0.278	1.61
	5.0	0.546	0.407	0.360	1.52
	6.0	0.627	0.505	0.447	1.40
LiBr	0.2	0.0293	0.0154	0.0142	2.06
	0.6	0.082	0.050	0.046	1.78
	1.6	0.211	0.133	0.119	1.77
	3.1	0.408	0.275	0.244	1.67
	5.2	0.648	0.478	0.423	1.53
	8.4	0.922	0.804	0.710	1.30

$NaNO_3$

*M*Br	Weight, Grams	$(Br)_{AgBr}$	$(Br)_{NaNO_3}$	$[Br^-]_{NaNO_3}$	K_o
NaBr	1.0	0.049	0.147	0.141	0.319
	2.0	0.093	0.285	0.273	0.340
	4.0	0.181	0.571	0.546	0.331
	6.0	0.265	0.824	0.788	0.335
					Av. 0.331
KBr	0.5	0.021	0.0681	0.0664	0.317
	1.0	0.043	0.128	0.122	0.352
	2.0	0.087	0.249	0.238	0.366
	4.0	0.219	0.569	0.544	0.403
	6.0	0.266	0.673	0.644	0.413
LiBr	0.2	0.0120	0.0412	0.0415	0.290
	0.6	0.0280	0.0988	0.0955	0.292
	0.9	0.048	0.155	0.148	0.324
	2.1	0.109	0.351	0.335	0.325
	6.6	0.335	1.07	1.02	0.328

$LiNO_3$

*M*Br	Weight, Grams	$(Br)_{AgBr}$	$(Br)_{LiNO_3}$	$[Br^-]_{LiNO_3}$	K_o
LiBr	0.6	0.0148	0.139	0.137	0.108
	1.4	0.0355	0.302	0.298	0.119
	1.9	0.040	0.366	0.361	0.111
	3.8	0.086	0.732	0.721	0.119
	4.0	0.092	0.763	0.752	0.122
					Av. 0.116
NaBr	0.1	0.0025	0.0212	0.0210	0.119
	0.5	0.0108	0.0863	0.0852	0.127
	1.0	0.0205	0.168	0.166	0.123
	3.0	0.068	0.483	0.475	0.143
	6.0	0.141	0.913	0.900	0.157
KBr	0.5	0.0079	0.0740	0.0728	0.109
	1.0	0.0231	0.156	0.154	0.149
	3.0	0.077	0.415	0.409	0.188
	6.0	0.156	0.773	0.763	0.205

$CsNO_3$

*M*Br	Weight, Grams	$(Br)_{AgBr}$	$(Br)_{CsNO_3}$	$[Br^-]_{CsNO_3}$	K_o
KBr	2.0	0.258	0.0336	0.030[a]	8.6

[a] Calculation based on Potassium association constants.

Table IV. Potassium(I) Distribution

KBr—LiNO$_3$-AgBr System

$(K)_{AgBr}$, m	$(K)_{M'NO_3}$, m	K_{OM}	$1/K_{OM}$	$[Br^-]$	$[Br^-]^{-1}$
0.00092	0.12	0.0077	129	0.0728	13.7
0.0030	0.20	0.015	67	0.154	6.5
0.024	0.45	0.053	19	0.409	2.4
0.075	0.82	0.092	11	0.763	1.3

KBr-KNO$_3$-AgBr SYSTEM

$(K)_{AgBr}$, m $= K_{OM}$	$1/K_{OM}$	$[Br^-]$	$[Br^-]^{-1}$
0.0506	19.7	0.027	37
0.106	9.4	0.054	18.5
0.199	5.03	0.113	8.85
0.340	2.94	0.225	4.44
0.443	2.26	0.279	3.58
0.527	1.90	0.350	2.86

Table V. Distributin of Bromide for MBr–M′NO$_3$–AgBr

M', mole fraction	M, mole fraction	K_o (Eq. 12)	K_o, exptl.
0.92Na	0.08K	0.44	0.41
0.89Na	0.11Li	0.30	0.33
0.93Li	0.07K	0.23	0.21
0.92Li	0.08Na	0.14	0.16
0.88K	0.12Na	1.61	1.40
0.82K	0.18Li	1.49	1.30

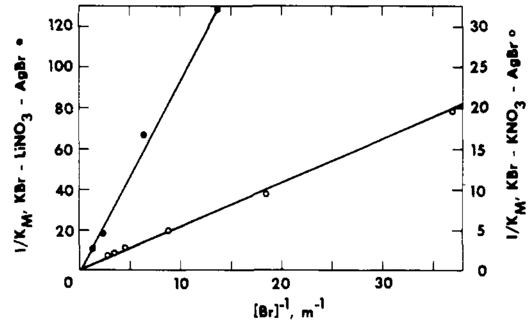

Figure 1. Potassium distribution

Table VI. Distribution of Alkali Metals(I) for M′NO$_3$–MBr–AgBr

Mole Fraction		Molality				
$[M'^+]$	$[M^+]$	$[Br^-]_{M'NO_3}$	$[MBr]_{AgBr}$ (Calcd.)	$(MBr)_{AgBr}$ (Exptl.)	$[M'Br]_{AgBr}$ (Calcd.)	$(M'Br)_{AgBr}$ (Exptl.)
0.99Li	0.01K	0.154	0.003	0.003	0.018	0.024
0.97Li	0.03K	0.409	0.022	0.024	0.046	0.055
0.93Li	0.07K	0.763	0.095	0.075	0.082	0.095
0.92Li	0.08Na	0.900	0.024	0.031	0.096	0.096
0.90K	0.10Na	0.360	0.012	0.010	0.58	0.57
0.82K	0.18Li	0.710	0.015	0.015	1.03	0.93
0.95Na	0.05K	0.544	0.048	0.042	0.17	0.17
0.92Na	0.08K	0.644	0.092	0.056	0.20	0.20
0.89Na	0.11Li	1.02	0.013	0.018	0.30	0.39

In this case, K_o should differ from $K_{(M')}$—i.e., K for the M'Br-M'NO$_3$-AgBr system—only when $[M^+]$ activity was high, and, thus, $[M'^+]$ activity was not unity. By making the approximation that the mole fraction—i.e., $M/(M + M')$ and $M'/(M + M')$—equalled the activity (ideal solutions whose alkali metal ion standard state is the pure alkali metal nitrate), calculations were made which could be checked with the experimental results. These are given in Table V.

The fact that the experimental values were somewhat low in KNO$_3$ was probably due to an activity effect which caused the mole fraction approximation to be inaccurate.

The distribution of the alkali metals (I) could also be explained on the basis of the two competing reactions, 10 and 11. The concentration of alkali metals (I) in the AgBr phase is:

$$[MBr]_{AgBr} = K_{(M)}[Br^-]_{M'NO_3}[M^+]_{M'NO_3} \tag{13}$$

$$[M'Br]_{AgBr} = K_{(M')}[Br^-]_{M'NO_3}[M'^+]_{M'NO_3} \tag{14}$$

Since, in all of the experiments, the alkali nitrate solvent was approximately 90% (or greater) of the mixture, $[M^+]$ was small compared to $[M'^+]$. This meant that, except in the case where M' was Li and M was K, bromide was transferred across the boundary predominantly as M'Br and not as the added solute MBr. Experimental and calculated values are compared in Table VI. The calculated values for $[MBr]_{AgBr}$ and $[M'Br]_{AgBr}$ were obtained from $K_{(M)}$, $K_{(M')}$ (bromide distribution values for MBr-MNO$_3$ system), $[M^+]_{M'NO_3}$, $[M'^+]_{M'NO_3}$ by flame photometry assuming $[M^+]_{M'NO_3} = (M^+)_{M'NO_3}$, and $[Br^-]_{M'NO_3}$ from Equation 2. The experimental values of $[MBr]_{AgBr}$ and $[M'Br]_{AgBr}$ refer to direct flame photometric determinations for the metals in the silver bromide phase assuming $[MBr]_{AgBr} = (M)_{AgBr}$.

These results indicate that such factors as structure and size of the solute in addition to the relative covalent tendencies of the solvents may control the distribution constants. Further experimentation with these and similar systems will be necessary before explicit relationships can be developed.

ACKNOWLEDGMENT

The author thanks Peter Bock and Robert Oldham for performing some of the experimental work reported, and the National Science Foundation for financial support.

NOMENCLATURE

K_{sp}	=	solubility product for AgBr in fused nitrate solvent
K_1	=	first association constant for AgBr in fused nitrate solvent
K_2	=	second association constant for AgBr in fused nitrate solvent

k_1 = association constant for M^+ and Br^- in alkali nitrate phase

k_2 = distribution constant for associated alkali bromide between alkali nitrate phase and silver bromide phase

K_o = experimental value, observed distribution coefficient of total alkali bromide in AgBr phase per calculated bromide ion activity in alkali nitrate phase

K_{OM} = experimental value, observed alkali metal (I) distribution coefficient between AgBr and alkali nitrate

K = distribution constant for reaction: $(M^+ + Br^-)_{MNO_3} \rightarrow (MBr)_{AgBr}$

$K_{(M)}$ = K for M solute

$K_{(M')}$ = K for M' solvent

(Br) = experimental value, total bromide in alkali nitrate–AgBr

$[Br^-]$ = calculated bromide ion activity in alkali nitrate phase

$(MBr + M'Br)_{AgBr}$ = experimental value, total alkali bromide concentration in AgBr phase = $(Br)_{AgBr}$

$(M)_{M'NO_3}$ = experimental value, alkali metal (I) concentration in $M'NO_3$ phase by flame photometry

$(M)_{AgBr}$, $(M')_{AgBr}$ = experimental value, alkali metal (I) concentration in AgBr phase by flame photometry

$[M^+]$ = activity of alkali metal ion in alkali nitrate phase

$[MBr]_{M'NO_3}$ = activity of associated MBr in $M'NO_3$ phase

$[MBr]_{AgBr}$ = activity of alkali bromide in AgBr phase, assumed equal to $(M)_{AgBr}$

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Received for review December 21, 1964. Accepted January 7, 1966.

Condensation of Some Aromatic Amines with Phenyl Glyoxal

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SOME NEW ANILS have been prepared by condensing phenyl glyoxal hydrate (*1*) with aniline, *p*-chloroaniline, *o*-, and *p*-nitroanilines, *o*-, and *p*- toluidines, and α-, and β-naphthylamines. They have been characterized by preparing their *p*- nitrophenyl hydrazones, 2,4-dinitrophenyl hydrazones, semicarbazones, and oximes. The oximes give color reactions with a number of metal ions and offer the possibility of being used as analytical reagents.

EXPERIMENTAL

Preparation of Anils. Equimolar quantities of phenyl glyoxal hydrate and the corresponding amines in 95% ethanol were refluxed on a water bath. The solid products, which separated on cooling, were crystallized from absolute alcohol and gave anils listed in Table I. These anils are soluble in methanol, ethanol, benzene, acetone, and chloro-

Table I. Anils Derived from Phenyl Glyoxal and Aromatic Amines

Anil	Color	Formula	M.P., ° C.	Yield, %	Nitrogen, %	
					Calcd.	Found
R-[a]Aniline	Yellow	$C_{14}H_{11}ON$	89–90	90.9	6.69	6.73
R- *p*-Chloroaniline[b]	Colorless	$C_{14}H_{10}ONCl$	115–116	63.6	5.74	5.89
R- *o*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	105–106	82.2	11.02	11.29
R- *p*-Nitroaniline	Yellow	$C_{14}H_{10}O_3N_2$	127–129	47.2	11.02	11.41
R- *o*-Toluidine	Reddish brown	$C_{15}H_{13}ON$	Gummy mass	85.5	6.28	6.12
R- *p*-Toluidine	Yellow	$C_{15}H_{13}ON$	97–98	89.6	6.28	6.32
R- α-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	136–137	92.2	5.40	5.24
R- β-Naphthylamine[b]	Yellow	$C_{18}H_{13}ON$	90–91	61.8	5.40	5.12

[a] R = C_6H_5—CO—CH= (phenacylidene radical). [b] No warming necessary to obtain these anils.

Table II. Characteristics of the Derivatives of Anils

Anil	*p*-Nitro Phenyl Hydrazones			2,4-Dinitro Phenyl Hydrazones			Semicarbozones			Oximes		
	M.P., ° C.	Nitrogen, %		M.P., ° C.	Nitrogen, %		M.P., ° C.	Nitrogen, %		M.P., ° C.	Nitrogen, %	
		Calcd.	Found		Calcd.	Found		Calcd.	Found		Calcd.	Found
R-[a] Aniline	185–186	16.28	16.53	236–238	17.99	17.74	190–191	21.05	20.95	58–59	12.5	12.46
R- *p*-Chloroaniline	200–201	16.16	16.46	267–269	16.52	16.46	180–181	18.63	18.44	146–147	10.83	10.35
R- *o*-Nitroaniline	233–234	17.99	17.61	255–256	19.35	19.12	197–198	22.50	22.31	189–201	15.61	15.42
R- *p*-Nitroaniline	250–252	17.99	17.54	262–263	19.35	19.40	203–205	22.50	22.25	206–207	15.61	15.48
R- *o*-Toluidine	100–101	15.64	15.56	250–251	17.36	17.25	. . .	. . .	. . .	77–78	11.76	11.56
R- *p*-Toluidine	134–135	15.64	15.32	263–265	17.36	17.16	244–245	20.00	19.95	101–102	11.76	11.43
R- α-Naphthylamine	264–265	14.21	14.13	194–195	15.94	15.63	210–211	17.72	17.56	119–120	10.22	10.20
R- β-Naphthylamine	189–190	14.21	14.09	247–249	15.94	15.83	100–101	17.72	17.43	95–96	10.22	10.32

[a] R = C_6H_5—CO—CH=.