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Conductometric and Potentiometric Studies on Zinc(II)-, Cadmium(II)- and Mercury(I, II)-Phenanthroline-Salicylaldoxime-Benzamide Complexes

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Conductometric and potentiometric studies on the complexes of Zn(II), Cd(II) and Hg(I, II) with 1,10-phenanthroline, salicylaldoxime (SD) and benzamide (BAM) in aqueous solution at 35° and 45°C provided evidence of formation of (1:1), (1:2) and (1:3) Zn(II)-, Cd(II)-, $Hg(II)_2$- and Hg(II)-Phen, SD and BAM, (1:1:1) Zn(II)-, Cd(II)-, $Hg(II)_2$- and Hg(II)-Phen-SD, Phen-BAM and BAM-SD, and (1:1:1:1) Zn(II)-, Cd(II)-, $Hg(II)_2$- and Hg(II)-Phen-SD-BAM complexes in which the metal ions are coordinated through two coordinate bonds with the two protonated nitrogen atoms of Phen, two covalent bonds with the two deprotonated atoms of phenolic OH and oximic NOH groups of SD, and one coordinate and one covalent bonds with one protonated and one deprotonated atoms of benzoyl CO and amide NH groups of BAM. Proton-ligand (pK) dissociation constants, metal-ligand and metal-mixed ligands formation stability constants (K_f) were determined in aqueous medium using 5 mL HNO_3 (1×10^{-2} M), 1:15 metal:ligand(s) ratio and 0.01 M NaOH (titrant) solution at a fixed ionic strength ($I = 0.01$ M $NaNO_3$). Free energy changes ($\Delta°G$), enthaply (ΔH) and entropy (ΔS) values at 35° and 45°C for binary, ternary and quaternary complexes were also evaluated. The data show that the magnitude of K_f, $\Delta°G$, ΔH and ΔS values increase with increasing temperature, stoichiometric ratio and with the tendency of the formation of polymeric and metal-mixed ligands' chelates. The increase of stability constants of the complexes is in the order: Cd(II) > Zn(II) > $Hg(II)_2$ > Hg(II) complexes.

INTRODUCTION

1,10-Phenanthroline (Phen) salicylaldoxime (SD) and benzamide (BAM) are good sequestering agents and react readily with Zn(II), Cd(II) and Hg(I, II). In continuation of our earlier work on transition metal complexes with heterocyclic ring compounds *viz.*, Phen, SD and BAM the present work is devoted using conductometric titrations and conductometric measurements for the determination of the stoichiometric ratios of the formed complexes and introducing the conductometric measurements method as an analytical method for the determination of trace amounts of Zn(II), Cd(II) and Hg(I, II) as well as potentiometric methods adopting the Irving and Rossotti technique[1] for the evaluation of the dissociation constants the ligands and the stability constants of free energy

changes, enthalpy and entropy values of the binary, ternary and quaternary complexes.

EXPERIMENTAL

All chemicals used were purchased from Aldrich, Sigma, BDH, E. Merck or Riedel de Haën of AnalaR quality (99.9%).

1×10^{-3} M Solutions of Zn(II), Cd(II), Hg(I, II), Phen, SD and BAM were prepared by dissolving the appropriate amounts of $ZnSO_4 \cdot 7H_2O$, $CdSO_4 \cdot H_2O$, $Hg_2(NO_3)_2 \cdot 2H_2O$ and $Hg(NO_3)_2 \cdot 0.5H_2O$ in double distilled water[2]. 1×10^{-2} M Of a carbonate-free NaOH solution was prepared by dissolving the appropriate amount of NaOH pellets in previously boiled bidistilled water and the resulting solution was standardised against standard HCl. 1×10^{-2} M HNO_3 was prepared by appropriate dilution of the conc. A.R. acid using bidistilled water, and the resulting solution was standardised against standard Na_2CO_3 solution. 1×10^{-2} M $NaNO_3$ was prepared in solution by dissolving the requisite amount of the dried crystallised salt in bidistilled water.

The conductometric titrations[3] were carried out by titrating 25 mL of 1×10^{-4} M of the ligand or a mixture of the ligands (V_1) with 0.25 mL of 1×10^{-3} M increments of the metal ion solution (V_2). The conductance values were measured at 35° and 45°C after each addition of metal ion and thorough stirring of the reaction mixture for 5 min with a magnetic stirrer and the specific conductance, λ, was corrected due to dilution effect $\left[n^{-1} = \lambda \left(\frac{V_1 + V_2}{V_1} \right) \right]$.

Conductometric Measurements

In conductometric measurements, two sets of solutions were prepared. In the first one, the metal ion solution was kept constant at 1×10^{-5} M and the ligand (1×10^{-5} M–1×10^{-4} M) or ligands mixture (biligand, 5×10^{-5} M–1×10^{-4} M; triligand 1×10^{-6} M–25×10^{-6} M) was varied. In the second series, ligand(s) concentration was maintained invariable at 1×10^{-4} M while the metal-ion concentrations were varied [Zn(II), 1×10^{-10} M–2×10^{-9} M; Cd(II), 1×10^{-10} M–3×10^{-9} M; $Hg(II)_2$, 1×10^{-10} M–3×10^{-9} M and Hg(II) 5×10^{-11} M–2×10^{-9} M.

The total volume of the reaction mixture was diluted with bidistilled water, to 25 mL using volumetric flasks. The mixtures were thermostated at 35° and 45°C for 2h using Ultrathermostat, HAAKE, Model NB-22; then the specific conductivity was measured by the aid of a conductometer, YSI Scientific, Model 35.

Potentiometric Techniques[1]

The proton-ligand and the metal-ligand(s) conditional formation constants were carried out by Bjerrum-Calvin pH titrations as recommended by Irving-Rossotti using DR-LANGE Digital pH-Meter.

The following sets of pH titrations were carried out under nitrogen atmosphere

against standard carbonate free-0.01 M NaOH solution at a fixed ionic strength ($I = 0.01$ M $NaNO_3$). The solutions were stirred for 3 min and thermostated at 35 and 45°C, and the total volume in each set was kept at 50 mL using bidistilled water:

(i) 5 mL of 1×10^{-3} M HNO_3 + 1 mL of 1×10^{-2} M $NaNO_3$, (ii) mixture (i) + 5 mL of 1×10^{-3} M of ligand (Phen, SD or BAM), (iii) mixture (ii) + 1 mL of 1×10^{-3} M M^{n+}, (iv) mixture (i) + 10 mL of 1×10^{-3} M Phen + SD, Phen + BAM or SD + BAM, (v) mixture (iv) + 1 mL of 1×10^{-3} M M^{n+}, (vi) mixture (i) + 15 mL of 1×10^{-3} M of Phen + SD + BAM, (vii) mixture (vi) + 1 mL of 1×10^{-3} M M^{n+}.

RESULTS AND DISCUSSION

The data gained by the conductometric and potentiometric studies indicate the formation of single and mixed complexes. The proton-ligand ionisation and metal-ligand stability constant values as well as the stoichiometric ratios of binary, ternary and quaternary systems obtained by conductometric titrations and conductometric measurements are recorded in Tables 2–6. The data are in good agreement with those previously reported[4].

Conductometric Experiments

The results of the conductivity titrations and conductometric measurements at constant metal ion or ligand concentration exhibit the formation of (1:1) and (1:2) Zn(II)-, Cd(II)-, $Hg(II)_2$- and Hg(II)-Phen, SD and BAM complexes at 35° and 45°C, (1:1:1) Zn(II)-, Cd(II)-, $Hg(II)_2$- and Hg(II)-Phen-BAM complexes at 35° and 45°C, (1:1:1) Zn(II)- and Cd(II)-Phen-SD and Zn(II)- and Cd(II)-Sd-BAM complexes at 35° and 45°C, (2:1:1) and (1:1:1) $Hg(II)_2$- and Hg(II)-Phen-SD and $Hg(II)_2$- and Hg(II)-SD-BAM complexes at 35 and 45°C, respectively, and (1:1:1:1) Zn(II)-, Cd(II)-, $Hg(II)_2$- and Hg(II)-Phen-SD-BAM complexes at 35 and 45°C. The conductance values increase with the increase of ligand (s) and/or metal ion concentrations as a result of the increase of the diffusion coefficients of the diffusion particles (Zn^{2+}, Cd^{2+}, Hg_2^{2+}, Hg^{2+}), SO_4^{2-}, or NO_3^- liberated from metal salts and H^+ liberated from SD or BAM having faster movements and their high mobilities (dielectric constants) through the medium (HNO_3, $NaNO_3$) reaching structure formation maxima[4]. This leads to an increase in the conductance power and the conductivity values due to complexation. The conductometric measurements technique was applied as an analytical method for assaying micro amounts of Zn(II), Cd(II), $Hg(II)_2$ and Hg(II). The data are recorded in Table-1.

Potentiometric Measurements

Proton-ligand stability constants: In the absence of metal ions, the ligand exhibits two well-separated buffer ranges, pH (3.9–9.5) and pH (4–9), pH (3.5–9) and pH (3.5–8.75), and pH (3–8.5) and pH (3.5–8.5) obviously due to successive protonation of the two nitrogen atoms of the 1,10-phenanthroline, deprotonation of the phenolic OH and the oximic OH groups of salicylaldoxime, and protonation

TABLE-1
CONDUCTOMETRIC DETERMINATION OF MICRO AMOUNTS OF Zn(II), Cd(II), $Hg(II)_2$ AND Hg(II) USING Phen, SD, BAM, Phen-SD, Phen-BAM, SD-BAM OR Phen-SD-BAM AS MICROANALYTICAL REAGENTS AT 35° AND 45°C

Metal ligand(s)	$Zn(II) \times 10^{-10}$ g		$Cd(II) \times 10^{-10}$ g		$Hg(II)_2 \times 10^{-10}$ g		$Hg(II) \times 10^{-10}$ g	
	35°C	45°C	35°C	45°C	35°C	45°C	35°C	45°C
Phen	2.50–10.00	7.50–12.50	5.00–12.50	2.50–12.50	7.50–12.50	5.00–12.50	5.00–12.50	2.50–12.50
SD	5.00–15.00	5.00–12.50	1.00–12.50	2.50–12.50	2.50–15.00	5.00–12.50	1.00–12.50	2.50–12.50
BAM	2.49–12.49	2.49–12.80	10.0–25.00	2.50–12.50	2.50–25.00	2.50–12.50	2.50–12.50	2.50–12.50
Phen-SD	5.00–12.50	1.00–12.50	5.00–12.50	5.00–15.00	2.50–12.50	5.00–12.50	2.50–12.50	2.50–15.00
Phen-BAM	5.00–12.50	2.50–12.50	7.50–15.00	5.00–12.50	7.50–12.50	7.50–12.50	5.00–12.50	5.00–12.00
SD-BAM	7.50–12.50	5.00–10.00	5.00–15.00	2.50–12.50	7.50–12.50	7.50–12.50	2.50–12.50	5.00–12.50
Phen-SD-BAM	5.00–10.00	3.50–10.00	2.50–10.00	2.50–10.00	5.00–15.00	2.50–10.00	7.50–12.50	5.00–10.00

of the benzoyl CO and deprotonation of the amide NH groups of benzamide at 35° and 45°C resepctively according to

$$\text{(a)}\quad \underset{\text{(Phen)}}{C_6H_2C_3H_3NNC_3H_3} \overset{K^H_{CN}}{\rightleftharpoons} \underset{\text{(Phen-H)}^+}{C_6H_2C_3NHNC_3H_3} \overset{K^H_{CNH}}{\rightleftharpoons} \underset{\text{(Phen-H}_2)^{2+}}{C_6H_2CH_3NHNHC_3H_3} \tag{1}$$

$$\text{(b)}\quad \underset{\text{(SD-H}_2)}{HOC_6H_4 \cdot CHNOH} \overset{K^H_{OH}}{\rightleftharpoons} \underset{\text{(SD)}^{2-}}{O^-C_6H_4CHNO^-} + 2H^+ \tag{2}$$

$$\text{(c)}\quad \underset{\text{(BAM- H)}}{OC.C_6H_5NH_2} \overset{K^H_{CO}}{\rightleftharpoons} \underset{\text{(BAM-H}_2)^+}{HOCC_6H_4 \cdot NH_2} \overset{K^H_{NH_2}}{\rightleftharpoons} \underset{\text{(BAM)}^-}{OC \cdot C_6H_4NH^-} + 2H^+ \tag{3}$$

This is evidenced that Phen is titrated as nonprotic acid, SD as biprotic and BAM as monoprotic acids under the same experimental conditions in the entire pH range 3–10. The pK's of Phen, SD, BAM, Phen-SD, Phen-BAM, SD-BAM and Phen-SD-BAM (Table-2) at 35° and 45°C are obtained from the formation curves [(representative Fig. 1 and 2), $\bar{n}_A$ vs. pH at $\bar{n}_A = 0.5$, 1.5 and 2.5 (half integral method)] and by pointwise calculations applying the following equations:

$$pK_1 = pH + \log (2 - \bar{n}_A)/(1 - \bar{n}_A) \tag{4}$$

where pH is in the range $1 < n_A > 2$

$$pK_2 = pH + \log \bar{n}_A/(1 - \bar{n}_A) \tag{5}$$

where pH is in the range $\bar{n}_A < 1$

$$pK_3 = pH + \log (3 - \bar{n}_A)/(2 - \bar{n}_A) \tag{6}$$

where pH is in the range $2 < \bar{n}_A > 3$

The $\bar{n}_A$ at different pH values can be calculated applying the following equations:

$$\bar{n}_A = \frac{y - (V_2 - V_1)(N^\circ + E^\circ)}{(V_0 + V_1)TCL^\circ} \tag{7}$$

where

Y = total number of dissociable hydrogen atoms bound to the ligand,

N° = normality of the acid (HNO_3),

V_1 = volume of alkali of normality N required for the acid at definite pH,

V_2 = volume of alkali of normality N required for the ligand(s) at a given pH,

V_0 = initial volume of the solution (25 mL),

TCL° = total ligand(s) concentration.

The $\bar{n}_A$ values are plotted versus pH and the pK values can be obtained by interpolation at $\bar{n}_A = 0.5$, 1.5 and 2.5.

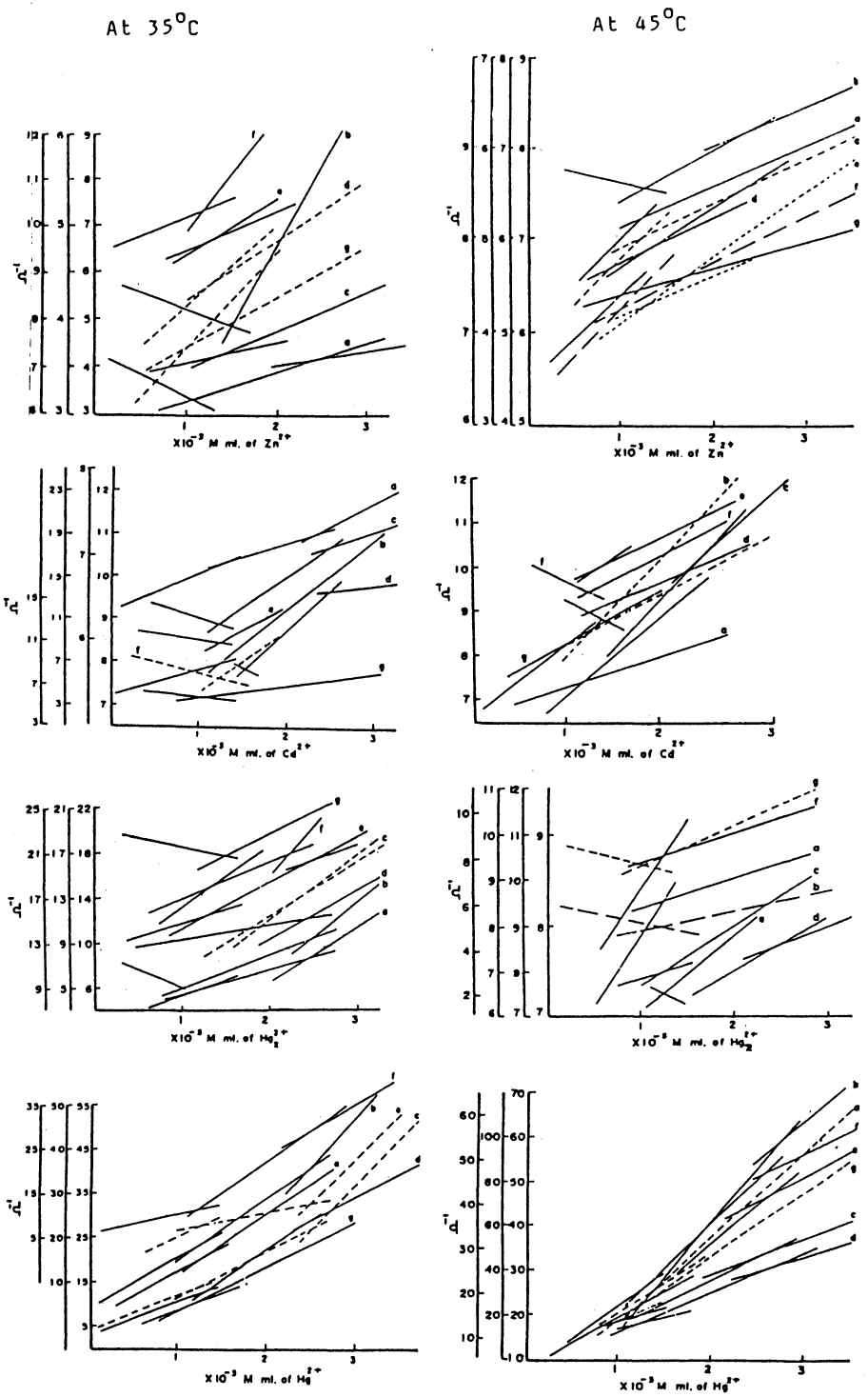


Fig. 1. Conductometric titrations of Zn(II), Cd(II) and Hg(I, II), [L] = Constant = 25 mL of 1×10^{-4} M

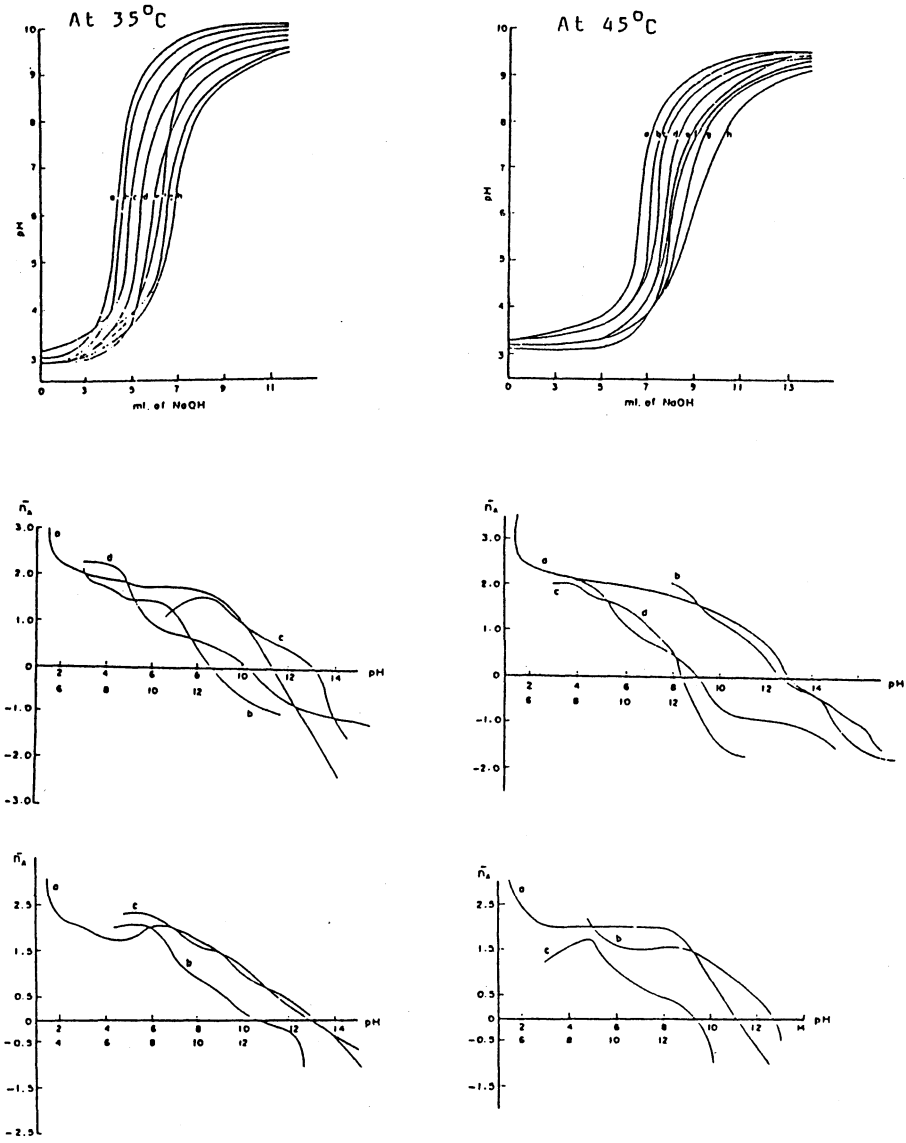


Fig. 2. Formation (pH-volume of NaOH) curve of Phen, SD and BAM:
(a) $HNO_3 + NaNO_3$
(b) $HNO_3 + NaNO_3$ + Phen
(c) $HNO_3 + NaNO_3$ + SD
(d) $HNO_3 + NaNO_3$ + BAM
(e) $HNO_3 + NaNO_3$ + Phen + SD
(f) $HNO_3 + NaNO_3$ + Phen + BAM
(g) $HNO_3 + NaNO_3$ + SD + BAM
(h) $HNO_3 + NaNO_3$ + Phen + SD + BAM

The pH regions 3.5–9.5, 3.5–9 and 3.5–8.5 corresponding to the protonation of Phen, deprotonation of SD, and protonation and deprotonation of BAM are lowered in the presence of Zn(II), Cd(II), $Hg(II)_2$ and Hg(II) (pH 4–8.5) due to the formation of binary, ternary and quaternary complexes (Fig. 3). The equilibria expected to exist in solutions are:

$$M^{n+} + Phen \rightarrow M^{n+} \cdot Phen$$

$$M^{n+} + H_2SD \rightarrow M^{(n-1)+} \cdot HSD + H^+$$

$$M^{n+} + H_2SD \rightarrow M^{(n-2)+} \cdot SD + 2H^+$$

$$M^{n+} + HBAM \rightarrow M^{(n-1)+} \cdot BAM + H^+$$

$$M^{n+} + Phen + H_2SD \rightarrow M^{(n-1)+} \cdot Phen\text{-}HSD + H^+$$

$$M^{n+} + Phen + HBAM \rightarrow M^{(n-1)+} \cdot Phen\text{-}BAM + H^+$$

$$M^{n+} + H_2SD + HBAM \rightarrow M^{(n-2)+} \cdot HSD\text{-}BAM + 2H^+$$

$$M^{n+} + Phen + H_2SD + HBAM \rightarrow M^{(n-2)+} \cdot Phen\text{-}HSD + BAM + 2H^+$$

The average number of ligand(s) molecules attached per mole of metal ion, $\bar{n}$, and the free ligand exponent, pL, can be evaluated utilising the following equations:

$$\bar{n} = \frac{(V_3 - V_2)[(N^\circ + E^\circ) + TCL^\circ(y - \bar{n}_A)]}{(V_0 + V_2) \cdot \bar{n}_A \cdot TCM^\circ} \tag{8}$$

$$pL = \log\left[\sum_{n=0}^{n=j} \frac{\beta_n^H[H]^{n+}}{TCL^\circ - \bar{n} \cdot TCM^\circ} \times \left(\frac{V_0 + V_3}{V_0}\right)\right] \tag{9}$$

or

$$pL = \log \frac{(1 + [H^+]/K_1 = [H^+]^2/K_1K_2)}{(TCL^\circ - \bar{n} \cdot TCM^\circ)} \times \left(\frac{V_0 + V_3}{V_0}\right)$$

where

TCM° = total concentration of the metal ions

V_3 = volume of alkali required to reach the acid + ligand + metal titration curve

On plotting the $\bar{n}$ values against pL values and interpolation at $\bar{n} = 0.5$, 1.5 and 2.5, the stepwise formation stability constants of the 1:1, 1:2 and 1:3 chelates can be evaluated, respectively (Fig. 3). The stability constant values are also calculated by half integral method ($\bar{n}$ vs. pL) and confirmed by the pointwise calculation and applying the equations:

$$\log \bar{n}/(1 - \bar{n}) + \log K^{\text{metal}}_{\text{metal complex}} - pL \tag{10}$$

where vlaues of $\bar{n}$ are selected between 0.2 and 0.8 (at $\bar{n} = 0.5$) for $pK_{1:1}$.

$$\log (2 - \bar{n})/(1 - \bar{n}) = \log K^{\text{metal complex (1:2)}}_{\text{metal complex (1:2)}} - pL \tag{11}$$

where values of $\bar{n}$ are selected between 1.2 and 1.8 (at $\bar{n} = 1.5$) for $pK_{1:2}$.

$$\log (3 - \bar{n})/(1 - \bar{n}) = \log K^{\text{metal complex (1:2)}}_{\text{metal complex (1:3)}} - pL \tag{12}$$

where values of $\bar{n}$ are selected between 2 and 3 (at $\bar{n} = 2.5$) for $pK_{1:3}$.

The formation constants of the mixed ligand complexes can be estimated

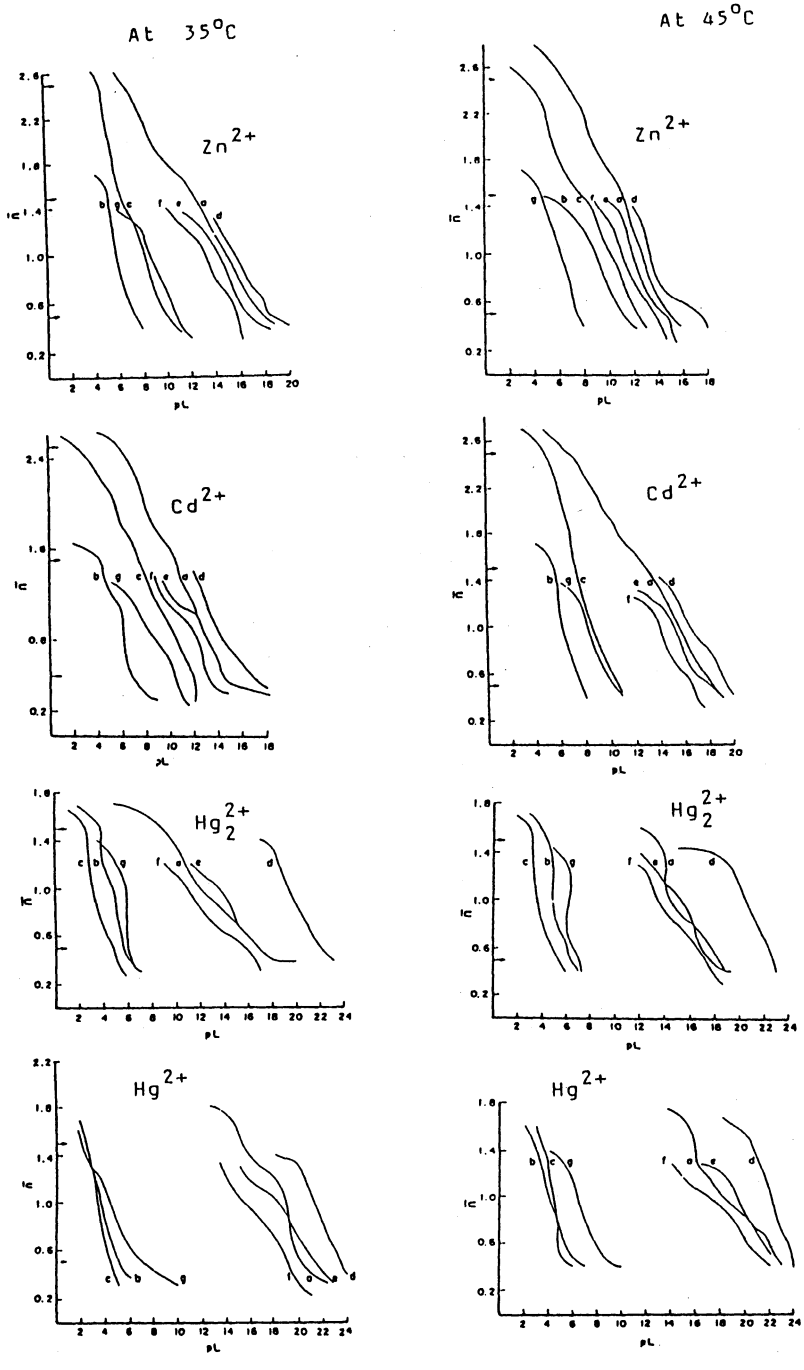


Fig. 3. $\bar{n}$-pL relationship of Zn(II)-, Cd(II)- and Hg(I, II)-Phen-SD-BAM complexes

making use of $\bar{n}$ – pL relations [equations (8), (9) and (10)]. The thermodynamic parameters $\Delta°G$, ΔH and ΔS are calculated applying the following equations:

$$\Delta°G = -RT \ln K \tag{13}$$

$$\Delta H = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1} \tag{14}$$

$$\Delta S = R \ln K + \frac{\Delta H}{(T)} \tag{15}$$

where

$\Delta°G$ = free energy changes,

ΔH = enthalpy changes (heat content),

ΔS = entropy changes,

R = gas constant,

T = absolute temperature and

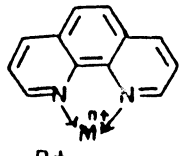
K = dissociation constant.

The results show that the dissociation constants of the ligands (Table-2) and the formation constant values of the complexes (Tables 3–6) increase with the increase of the temperature and with the ligands concentration. Release of one proton per metal in the case of 1 : 1 metal : lignand (H_2SD or HBAM) could be explained on the basis of metal promoted deprotonation of phenolic OH group moiety, while a release of two protons per metal ion in the case of H_2SD could be explained on the basis of metal-promoted deprotonation of one oximic N—OH and one phenolic OH group moieties of the ligand L^{2-} ion. Therefore, the metal ions are coordinated by two deprotonated oximic and phenolic oxygen atoms of the ligand. Formation of mixed ligand complexes (1 : 1 : 1 and 1 : 1 : 1 : 1) may thus be interpreted as involving the displacement of some of the oximic NOH and phenolic OH groups. The order of stabilities of the various metal complexes formed is Hg(II) > Cd(II) > $Hg(II)_2$ > Zn(II) with respect to $\log K_1$, $\log K_2$, and $\log K_3$ values. The small differences between $\log K_1$, $\log K_2$, $\log K_3$, $\log K^{\text{metal-ligand}}_{\text{metal-biligand}}$ and $\log^{\text{metal-ligand}}_{\text{metal-triligand}}$ complexes suggest the simultaneous formation of the 1 : 1, 1 : 2, 1 : 3, 1 : 1 and 1 : 1 : 1 : 1 complexes. The increase in the stability for Hg(II) to Zn(II) may be related to solvation and hyrophobic effects and to the decrease of ionic size (ionic potential) of metals. The positive $\Delta°G$ values indicate that all complexes are not formed spontaneously in solution. Furthermore, the negative values of enthalpy changes (ΔH) indicate exthothermic nature of chelation and their high magnitudes suggest strong metal-ligand formation. The negative values of the entropy changes (ΔS) indicate that the reaction between the metal ion and the ligand(s) suffer from a loss of some internal degrees of freedom during the complexation processes and can be attributed to the extensive solvation of metal chelates in aqueous medium. Coordination between metal ion and Phen, SD and/or BAM moieties can be suggested as:

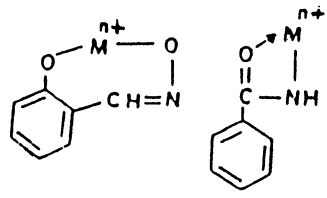
TABLE-2
PROTON-LIGAND DISSOCIATION CONSTANTS AT 35° AND 45°C

Ligand(s)	35°C			45°C		
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3
Phen	(4.8) (4.8)* [4.86]	—	—	(4.87) (4.87)*	—	—
SD	(1.6) (1.6)* [1.37]	(9.50) (9.45)* [9.18]	(12.6) (12.5)* [12.11]	(1.5) (1.5)*	(9.30) (9.25)*	(12.0) (11.95)*
BAM	(13.2) (13.2)* [13.14]	—	—	(13) (13)*	—	—
Phen-SD	(8.6) (8.6)*	(11.80) (11.86)*	—	(9.3) (9.3)*	(12.2) (12.1)*	—
Phen-BAM	(8.8) (8.8)*	(11.90) (11.85)*	—	(9.9) (9.9)*	(12) (12.1)*	(12.0) (12.1)*
SD-BAM	(9.2) (9.2)*	(12.4) (12.3)*	—	(9.4) (9.4)*	(12.6) (12.5)*	—
Phen-SD-BAM	(1.6) (1.6)*	(11.95) (11.90)*	{11.95) (11.90)*	(1.7) (1.7)*	(9.35) (9.3)*	(12.5) (12.4)*

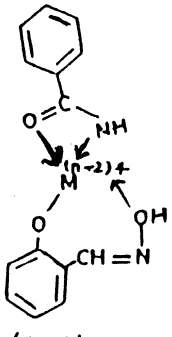
( ) values evaluated by the half integral method
( )* values evaluated by the pointwise calculation
[ ] reported values.



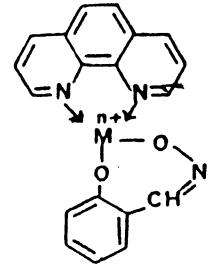
M^{n+}–phen



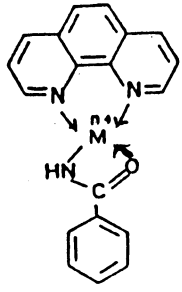
M^{n+}–SD M^{n+}–BAM



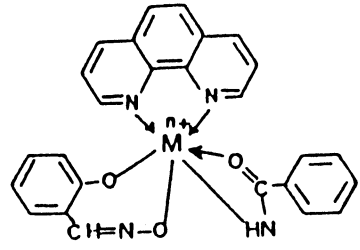
$M^{(n-2)+}$–SD–BAM



M^{n+}–phen–SD



M^{n+}–phen–BAM



M^{n+}–phen–SD–BAM

TABLE-3
STOICHIOMETRIC RATIO, STABILITY CONSTANTS, FREE ENERGY CHANGE, ENTHALPY AND ENTROPY VALUES (in kcal mol^{-1}) OF M^{n+}-Phen COMPLEXES AT 35° AND 45°C

Ratio	T, °C	Zn(II)-Phen			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(6.6) (6.6)* [6.55]	(9.36) (9.09)*	(9.02) (9.02)*	{30.43} (29.52)*
	45	(6.8) (6.8)*	(9.66) (9.39)*	(9.02) (9.47)*	(31.35) (29.52)*
1:2	35	(12.4) (12.4)* [12.35]	(17.59) (17.87)*	(40.6) (40.6)*	(57.17) (58.04)*
	45	(12.8) (12.8)*	(18.18) (18.46)*	(40.6) (40.6)*	(59.01) (58.04)*
1:3	35	(17.7) (17.7)* [17.55]	(25.11) (25.11)*	(9.02) (9.02)*	(81.6) (81.6)*
	45	(18.2) (18.2)*	(25.84) (25.48)*	(9.02) (9.02)*	(83.9) (83.9)*
		Cd(II)-Phen			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(5.8) (5.41)* [5.93]	(8.23) (7.67)*	(18.04) (36.09)*	(26.77) (61.07)*
	45	(6.2) (6.21)*	(8.8) (8.8)*	(18.04) (36.09)*	(28.61) (64.69)*
1:2	35	(10.4) (10.6)* [10.35]	(14.75) (14.75)*	(36.09) (36.09)*	(48.02) (48.91)*
	45	(11.2) (11.4)*	(15.9) (16.7)*	(36.09) (36.09)*	(51.7) (88.6)*
1:3	35	(14.4) (14.4)*	(20.43) (20.43)*	(18.04) (18.04)*	(66.38) (66.38)*
	45	(14.8) (14.8)*	(21.02) (12.02)*	(18.4) (18.4)*	(68.23) (68.23)*
		$Hg(II)_2$-Phen			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(8.8) (8.74)*	(24.68) (24.4)*	(18.04) (20.3)*	(80.2) (80)*
	45	(13.2) (13.24)*	(25.28) (25.4)*	(18.04) (20.3)*	(82.4) (82)*
1:2	35	(17) (17)*	(31.49) (31.49)*	(27.07) (27.07)*	(102.34) (102.34)
	45	(18.2) (18.2)*	(33.38) (33.38)*	(27.07) (27.07)*	(105.1) (105.1)*
		Hg(II)-Phen			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(19.6) (19.4)* [19.45]	(27.21) (26.13)*	(27.07) (22.56)*	(90.37) (90)*
	45	(20.2) (20.2)*	(28.68) (27.13)*	(27.07) (22.56)*	(93.13) (90.2)*
1:2	35	(21.4) (21.4)* [23.35]	(33.3) (33.2)*	(18.04) (18.04)*	(109.67) (109.67)*
	45	(22.4) (22.4)*	(33.8) (33.8)*	(18.04) (18.04)*	(109.68) (109.68)*

TABLE-4
STOICHIOMETRIC RATIO, STEPWISE CONDITIONAL STABILITY CONSTANT, FREE ENGERY CHANGE, ENTROPY AND ENTHAPLY VALUES (in kcal mol^{-1}) OF M^{n+}-BAM COMPLEXES AT 35° AND 45°C

Ratio	T, °C	log K	Δ°G	−ΔH	−ΔS
		Zn(II)-BAM			
1:1	35	(4.6) (4.61)*	(6.52) (6.52)*	(9.02) (9.47)*	(21.22) (11.76)*
	45	(4.8) (4.4)*	(6.81) (6.44)*	(9.02) (9.47)*	(22.14) (10.8)*
1:2	35	(6.3) (6.55)*	(8.93) (9.29)*	(40.6) (47.37)*	(29.15) (30.32)*
	45	(7.2) (7.6)*	(10.22) (11.13)*	(40.6) (47.37)*	(33.39) (32.38)*
1:3	35	(16.6) (10.6)*	(15.05) (15.05)*	(9.02) (9.02)*	(48.8) (48.9)*
	45	(10.8) (10.8)*	(15.05) (15.05)*	(9.02) (9.02)*	(49.72) (49.72)*
		Cd(II)-BAM			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(2.2) (2.01)*	(3.12) (2.85)*	(45.11) (45.27)*	(10.28) (10.53)*
	45	(3.2) (3.59)*	(4.53) (4.26)*	(45.11) (45.27)*	(14.88) (17.81)*
1:2	35	(7.4) (7.2)*	(10.5) (10.21)*	(18.04) (18.04)*	(34.14) (38.21)*
	45	(7.8) (7.6)*	(11.08) (11.13)*	(18.04) (18.04)*	(25.98) (36.05)*
1:3	35	(12) (12)*	(16.74) (16.74)*	(9.02) (9.02)*	(55.3) (55.3)*
	45	(12.2) (12.2)*	(17.35) (17.32)*	(9.02) (9.02)*	(56.22) (56.22)*
		$Hg(II)_2$-BAM			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(2.6) (2.6)*	(3.69) (3.69)*	(27.07) (29.11)*	(12.06) (18)*
	45	(3.2) (3.6)*	(4.54)(5.27)*	(27.07) (29.11)*	(14.82) (17.69)*
1:2	35	(4.5) (4.5)*	(6.81) (6.81)*	(27.07) (27.07)*	(22) (22)*
	45	(5) (5)*	(7.67) (7.67)*	(27.07) (27.07)*	(24.96) (24.96)*
		Hg(II)-BAM			
		log K	Δ°G	−ΔH	−ΔS
1:1	35	(2.6) (2.2)*	(3.69) (3.6)*	(27.07) (28.09)*	(12.06) (13.01)*
	45	(3.2) (3.6)*	(4.54) (5.27)*	(27.07) (9.11)*	(14.82) (16.6)*
1:2	35	(4.5) (4.5)*	(6.38) (6.38)*	(22.56) (22.56)*	(20.8) (20.8)*
	45	(5) (5)*	(7) (7)*	(22.56) (22.56)*	(23.1) (23.1)*

TABLE-5
STOICHIOMETRIC RATIO, STEPWISE FORMATIONS, STABILITY CONSTANTS, FREE ENERGY CHANGE, ENTHALPY AND ENTROPY VALUES (in kcal mol^{-1}) OF M^{n+}-SD COMPLEXES AT 35° AND 45°C

Ratio	T, °C	log K	Δ°G	−ΔH	−ΔS
		Zn(II)-SD			
1:1	35	(5) (4.75)* [5.27]	(7.09) (6.74)*	(18.04) (18.34)*	(23.09) (60.22)*
	45	(5.4) (5.6)*	(7.67) (8.2)*	(18.04) (18.34)*	(24.93) (64.13)*
1:2	35	(7.3) (7.3)*	(10.36) (10.36)*	(18.04) (18.04)*	(33.22) (33.22)*
	45	(7.6) (7.6)*	(10.79) (10.79)*	(18.04) (18.04)*	(35.06) (35.06)*
		Cd(II)-SD			
1:1	35	(4.3) (4.33)* [4.4]	(6.1) (6.1)*	(13.53) (9.92)*	(29.85) (30.1)*
	45	(4.6) (4.6)*	(6.53) (6.53)*	(13.53) (9.92)*	(21.23) (21.23)*
1:2	35	(6.6) (6.6)*	(9.36) (9.36)*	(36.09) (36.09)*	(30.52) (30.11)*
	45	(7.4) (7.4)*	(10.51) (10.51)*	(36.09) (36.09)*	(34.2) (34.2)*
		$Hg(II)_2$-SD			
1:1	35	(3.8) (3.94)*	(5.34) (5.5)*	(18.04) (20.2)*	(17.57) (18.24)*
	45	(4.2) (4.9)*	(5.98) (6.74)*	(18.04) (20.2)*	(19.4) (20.96)*
1:2	35	(5.6) (5.6)*	(7.94) (7.94)*	(36.09) (36.09)*	(25.91) (25.91)*
	45	(6.4) (6.4) *	(4.09) (4.09)*	(36.09) (36.09)*	(29.59) (29.59)*
		Hg(II)-SD			
1:1	35	(2.3) (2.6)*	(3.26) (3.78)*	(13.53) (13.53)*	(10.64) (11.09)*
	45	(2.6) (2.8)*	(3.39) (3.73)*	(13.53) (13.53)*	(12.02) (12.02)*
1:2	35	(5.2) (5.2)*	(7.38) (7.38)*	(27.07) (27.07)*	(24.04) (24.04)*
	45	(5.8) (5.8)*	(8.24) (8.24)*	(27.07) (27.07)*	(26.8) (26.8)*

TABLE-6A
EVALUATION OF STEPWISE CONDITIONAL STABILITY CONSTANT, FREE ENERGY CHANGES (Δ°G) ENTHALPY (ΔH) AND ENTROPY (ΔS) VALUE (in kcal mol^{-1}) OF Zn(II), Cd(II), $Hg(II)_2$ AND Hg(II) COMPLEXES AT 35°C.

Ligand(s)	log K	Δ°G	−ΔH	−ΔS
		(A) Zn(II) complexes		
Phen-SD	(16.6) (16.6)*	(23.55) (23.55)*	(63.15) (63.15)*	(139.61) (139.61)*
Phen-BAM	(15.8) (15.8)*	(22.41) (22.41)*	(36.09) (36.09)*	(108.86) (108.86)*
SD-BAM	(10.0) (10.0)*	(14.19) (14.19)*	(9.02) (9.02)*	(55.08) (55.08)*
Phen-SD-BAM	(18.2) (18.2)*	(25.82) (25.82)*	(54.13) (54.13)*	(84.01) (84.01)*
		(B) Cd(II) complexes		
Phen-SD	(14.4) (14.4)*	(20.43) (20.43)*	(9.02) (9.02)*	(75.35) (75.35)*
Phen-BAM	(13.0) (13.0)*	(18.4) (18.4)*	(27.07) (27.07)*	(86.94) (86.94)*
SD-BAM	(10.4) (10.4)*	(14.75) (14.75)*	(36.09) (36.09)*	(83.99) (83.99)*
Phen-SD-BAM	(16.8) (16.8)*	(23.83) (23.83)*	(63.83) (63.83)*	(77.59) (77.59)*
		(C) $Hg(II)_2$ complexes		
Phen-SD	(17.0) (17.0)*	(24.12) (24.12)*	(27.07) (27.07)*	(105.0) (105.0)*
Phen-BAM	(15.8) (15.8)*	(22.41) (22.41)*	(63.15) (63.15)*	(135.93) (135.93)*
SD-BAM	(6.00) (6.00)*	(8.51) (8.51)*	(54.13) (54.13)*	(81.77) (81.77)*
Phen-SD-BAM	(22.2) (22.2)*	(24.12) (24.12)*	(54.13) (54.13)*	(78.48) (78.48)*
		(D) Hg(II) complexes		
Phen-SD	(20.2) (20.2)*	(29.59) (29.59)*	(9.02) (9.02)*	(183.26) (183.26)*
Phen-BAM	(19.2) (19.2)*	(27.24) (27.24)*	(81.2) (81.2)*	(169.63) (169.63)*
SD-BAM	(7.20) (7.20)*	(10.21) (10.21)*	(54.13) (54.13)*	(87.29) (87.29)*
Phen-SD-BAM	(23.4) (23.4)*	(30.08) (30-.08)*	(54.13) (54.13)*	(97.82) (97.82)*

TABLE-6B
EVALUATION OF STEPWISE CONDITIONAL STABILITY CONSTANT, FREE ENERGY CHANGES (Δ°G), ENTHAPLY (ΔS) VALUES (in Kcal mol^{-1}) OF Zn(II), Cd(II), $Hg(II)_2$ AND Hg(II) COMPLEXES AT 45°C

Ligand(s)	log K	Δ°G	−ΔH	−ΔS
		(A) Zn(II) complexes		
Phen-SD	(18.08) (18.08)*	(26.36) (26.3)*	(63.15) (63.15)*	(146.06) (146.06)*
Phen-BAM	(16.6) (16.6)*	(24.31) (24.3)*	(36.09) (36.09)*	(112.55) (112.55)*
SD-BAM	(10.2) (10.2)*	(14.94) (14.9)*	(9.02) (9.02)*	(56.00) (56.00)*
Phen-SD-BAM	(19.4) (19.4)*	(27.55) (27.5)*	(54.13) (54.13)*	(89.53) (89.53)*
		(B) Cd(II) complexes		
Phen-SD	(14.6) (14.6)*	(21.38) (21.3)*	(9.02) (9.02)*	(76.27) (76.27)*
Phen-BAM	(13.6) (13.6)*	(19.92) (19.9)*	(27.07) (27.07)*	(89.71) (89.71)*
SD-BAM	(11.2) (11.2)*	(16.40) (16.4)*	(36.09) (36.09)*	(87.68) (87.68)*
Phen-SD-BAM	(17.2) (17.2)*	(24.87) (24.8)*	(63.15) (63.15)*	(71.13) (71.13)*
		(C) $Hg(II)_2$ complexes		
Phen-SD	(17.6) (17.6)*	(25.78) (25.7)*	(27.07) (27.07)	(108.14) (108.14)*
Phen-BAM	(17.2) (17.2)*	(25.19) (25.1)*	(63.15) (63.15)*	(142.37) (142.37)*
SD-BAM	(7.20) (7.20)*	(10.55) (10.5)*	(54.13) (54.13)*	(87.29) (87.29)*
Phen-SD-BAM	(22.6) (22.6)*	(25.84) (25.8)*	(54.13) (54.13)*	(83.99) (83.99)*
		(D) Hg(II) complexes		
Phen-SD	(22.2) (22.2)*	(32.52) (32.5)*	(9.02) (9.02)*	(192.47) (192.47)*
Phen-BAM	(21.0) (21.0)*	(30.76) (30.7)*	(81.2) (81.2)*	(177.93) (177.93)*
SD-BAM	(8.40) (8.40)*	(12.30) (12.3)*	(54.13) (54.13)*	(92.82) (92.82)*
Phen-SD-BAM	(23.8) (23.8)*	(31.08) (31.0)*	(54.13) (54.13)*	(103.34) (103.34)*

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