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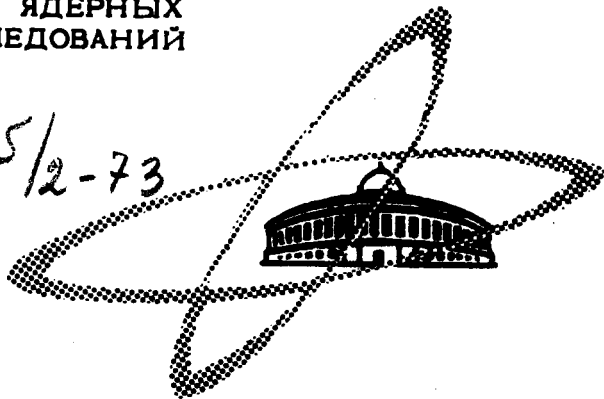
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ОБЪЕДИНЕННЫЙ  
ИНСТИТУТ  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ

Дубна.

725/2-73

E12 - 6778



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ЛАБОРАТОРИЯ ЯДЕРНЫХ ПРОЦЕССОВ

A CORRELATION BETWEEN  
THE OVERALL STABILITY CONSTANTS  
OF METAL COMPLEXES VII.

The Effect of Temperature

1972

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*Submitted to Journal  
of Inorg. Nucl. Chemistry*

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### Introduction

In the first paper of this series <sup>/1/</sup> a mathematical model of the complex formation process in aqueous solution has been developed. On the basis of that model a relation connecting the overall stability constants of the consecutive complexes in a given metal-ligand system has been derived. For a given temperature this relation has the following form

$$\beta_n = A \cdot \frac{a^n}{n!}, \quad (1)$$

where  $\beta_n$  is the overall stability constant of the species  $ML_n$ ,  $n$  is the number of ligands ( $1 \leq n \leq N$ ),  $N$  is the coordination number of the complex forming metal  $M^{m+}$ ,  $A$  and  $a$  are constants. The complexity function of the system is given by

$$F = 1 + A \sum_{n=1}^{n=N} \frac{a^n}{n!} (L)^n, \quad (2)$$

where  $(L)$  is the free ligand concentration in the solution.

The above-mentioned mathematical model has been applied to a number of systems with inorganic <sup>/1,2/</sup> and organic <sup>/3-6/</sup> ligands.

The stability constant  $\beta_n$  of the complex  $ML_n (M + nL \leftrightarrow ML_n)$  is related to the free energy changes. So, from the variations of the values of the stability constants with the temperature one can determine the free energy changes as well as the enthalpy and entropy of the complex formation reaction <sup>/7,8/</sup>. As far as no attempts have been made up to now to check the validity of the mathematical model developed in Ref. <sup>/1/</sup> for metal-ligand systems studied at a series of temperature, the present work has been initiated. The subject of our calculations were experimental data

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Корреляция между общими константами устойчивости комплексов металлов VII. Влияние температуры

Были проанализированы опубликованные экспериментальные данные для следующих двух систем: 1) кадмий-тиодинпропионатной, при температурах  $30 \pm 1$ ,  $40 \pm 1$ ,  $50 \pm 1$  и 2) таллий-этилтиогликолятной, при температурах 20 и  $30^\circ\text{C}$ . В результате анализа для этих систем были найдены константы устойчивости комплексов, которые подчиняются следующей зависимости:  $\beta_n = A \frac{\sigma^n}{n!}$ , где  $\beta_n$  - общие константы устойчивости комплекса  $ML_n$ ;  $n$  - число лигандов в данном комплексе ( $1 \leq n \leq N$ );  $N$  - координационное число комплексообразующего металла  $M$ ;  $A$  и  $\sigma$  - константы. Были рассчитаны изменения свободной энергии, энтропии и энтальпии процесса комплексообразования. Полученные значения этих величин находятся в полном соответствии с термодинамическими закономерностями.

Препринт Объединенного института ядерных исследований.  
Дубна, 1972

Mikhailov M.H., Mikhailova V.Ts., Khalkin V.A. E12 - 6778

A Correlation between the Overall Stability Constants of Metal Complexes VII. The Effect of Temperature

See the Summary on the reverse side of the title-page.

Preprint. Joint Institute for Nuclear Research.  
Dubna, 1972

reported by P.C.Rawat and C.M.Gupta for the cadmium-thiodipropionate system<sup>/9/</sup>, which had been studied polarographically at the ionic strength of 1.2, maintained by using  $KNO_3$  as an inert electrolyte and temperature of  $30 \pm 1$ ,  $40 \pm 1$  and  $50 \pm 1$  °C, as well as the experimental data reported by R.S.Saxena and U.S.Chaturvedi for the thallium-ethylthioglycolate system<sup>/10/</sup>, studied also polarographically at the ionic strength of 2 maintained by  $NaClO_4$  as an inert electrolyte and temperature of 20 and 30 °C.

### Calculation of the Stability Constants and the Thermodynamic Functions

The authors of the above mentioned papers had used the De Ford and Hume's method<sup>/11/</sup> to calculate the complexity function of the system at each temperature at which the investigation had been performed and they are presented as  $F_0$  in the corresponding Tables of those papers. We have taken the data for the experimental complexity functions directly from these sources and have analyzed them as follows: solving Eq. (2) for two values of  $F_{exp}$ , let us say  $F'_{exp}$  and  $F''_{exp}$ , taken at two ligand concentrations ( $L'$ ) and ( $L''$ ), respectively, the values of the  $A$  and  $a$  constants in Eq. (2) have been determined. The values of the corresponding overall stability constants are, then obtained from Eq. (1). For each data point two theoretical  $F$ -functions were calculated. The first of them has been obtained by using the conventional polynomial expression with the values of the stability constants reported in the corresponding Ref. /9/ or /10/, and the second one by using Eq. (2) of the present paper. The fit at each point was estimated by the quantity  $\Delta F = 1/F_{exp} (F_{calc} - F_{exp}) \cdot 100$ . As an estimate of the overall goodness of the fits the  $S$ -factor, which was used throughout the present series<sup>/2-6/</sup> has been calculated. Considering this factor we shall only remember that the smaller the values of the corresponding  $S$ -factor, the better the fit of a given theoretical function to the experimental one.

The following familiar equation has been used for the calculation of the free energy changes of the system<sup>/7/</sup>

$$\Delta F = -2,303 \lg \beta_n, \quad (3)$$

$\Delta S$  was determined using the equation

$$\Delta S = \frac{(\Delta H - \Delta F)}{T}, \quad (4)$$

$\Delta H$  was obtained on the one hand from the equation

$$\Delta H = \frac{5,76 T_1 T_2 \Delta \lg \beta_n}{(T_2 - T_1)} \quad (5)$$

and on the other hand graphically from the slope of the plot  $\lg \beta_n$  vs  $1/T$ .

### Results and Discussion

The results obtained for the cadmium-TDPA system in aqueous solution at 30, 40 and 50°C are presented in Tables 1-3 and the results obtained for the same system with 20% DMF at 30°C are presented in Table 4. For all cases the theoretical complexity functions obtained from Eq. (2) were third order polynomials in  $(L)$ . So, the results of our calculations are in agreement with Rawat and Gupta's conclusion that three consecutive cadmium-TDPA complexes are formed in the solution in the ranges of the ligand concentrations studied. The stability constants of these species reported by the authors of Ref.<sup>9/</sup> as well as those obtained in the present investigation are given in each Table, where the calculated  $S$ -factors for each fit appear also. The inspection on the values of the  $S$ -factors obtained shows that the theoretical  $F$ -functions calculated by using Eq. (2) of the present work fit the experimental data better than the  $F$ -functions obtained by the conventional polynomial expression with the set of the stability constants reported in Ref.<sup>9/</sup> except for the functions at 30°C (Table 1), where the  $S$ -factors are equal. So, for the system under consideration, the mathematical model presented in Ref.<sup>11/</sup> has the advantages of

giving a better fit to the experimental data and describing the process with smaller number of parameters than the traditional expression does<sup>/12/</sup>.

It should be remembered that the model developed in Ref.<sup>/11/</sup> was concerned with the stepwise complex formation process between a  $m$ -valent metal  $M$  and monovalent ligand  $L$  in an aqueous solution. But we have found that the same model could be successfully applied to systems in which the ligand is a neutral molecule<sup>/6/</sup>. On the basis of the results obtained in the present study we can state that it is also a good approximation for the complex formation process taking place in a system of bivalent metal and bivalent ligand. So, it seems likely that actually the application of that model could be extended to any processes in which a stepwise formation of metal complexes with metal-ligand ratios 1:1, 1:2, 1:3 and so on proceeds, irrespectively to the ligand charge. This will not be in contradiction with the original model and will not cause any fundamental changes in its scheme as presented in Ref.<sup>/11/</sup>. In Table 7 the thermodynamic quantities:  $\Delta F$ ,  $\Delta H$  and  $\Delta S$  calculated from Eqs. (3-5) respectively, on the basis of the  $\beta_n$  values obtained for the Cd-TDPA system in the present work are given. The corresponding values of  $\Delta H$  obtained from the slope of the graph  $\ln\beta_n$  vs  $1/T$  taken from Fig. 1 - a, b, and c respectively are given in Table 7 also. As could be seen from the data summarized in that Table the absolute value of  $\Delta F$  is increased with the increasing the number of ligands in the complex ranging from 2.34 to 4.10 when the number of ligands varied from 1 to 3. This is in agreement with the thermodynamic considerations underlying the complex formation process in aqueous solution<sup>/7/</sup>. As could be seen on Fig. 1 and Table 7, in the narrow temperature interval investigated,  $\Delta H$  calculated for each  $\beta_n$  remains constant. Usually this is considered as a firm indication that the mode of the complex formation process is not affected by the temperature. Inspections of the data for the entropy changes  $\Delta S$  (mean values) shows that:  $\Delta S$  for the reaction  $M + L \rightleftharpoons ML$  is -1.18 cal/deg.mole;  $\Delta S$  for the reaction  $M + 2L \rightleftharpoons ML_2$  is 1.60 cal/deg.mole and  $\Delta S$  for the reaction  $M + 3L \rightleftharpoons ML_3$  is 3.15 cal/deg.mole. It is seen also that the following inequality is hold:  $|S_2 - S_1| > |S_3 - S_2|$ . Such a trend is usually regarded as an indication that the stability of the complexes in a given series decreases with the increasing number of ligands<sup>/7/</sup>.

In Table 7 the data for the thermodynamic functions as presented in Ref.<sup>9/</sup> are given for comparison. As is seen, Rawat and Gupta have calculated the thermodynamic functions for  $M+3L \rightleftharpoons ML_3$  reaction only. Their results for the variations of  $\beta_n$  with the temperature in the range of 30 - 50°C do not make possible the calculation of these quantities for the reaction  $M+2L \rightleftharpoons ML_2$ , because  $\beta_2$  remains constant at 40 and 50°C. So, in this temperature interval  $\Delta H = 0$ . This is difficult to be explained unless a different mode of complexity is assumed for this step. Probably, to escape such an explanation the authors of Ref.<sup>9/</sup> prefer to give the results for  $\beta_3$  only. Our results are in full agreement with the basical thermodynamic relations underlying the complex formation and this could be regarded as a strong support for the validity of the mathematical model<sup>1/</sup> for the given system.

The system Cd-TDPA had been studied at three temperatures and we have tried to find how the constants  $A$  and  $a$  in Eq. (1) depend on the temperature. This dependence is shown graphically on Fig. 2 - a and b, where  $A$  and  $a$  are plotted as a function of the temperature. As could be seen in Fig. 2 both constants are linear functions of the temperature in this interval. No theoretical explanation of this finding could be advanced at present and much more data have to be analyzed before trying to give some reasonable explanation of these trends.

In the same way as it was done above, the complexity functions for the thallium-ethylthioglycolate system at 20 and 30°C have been analyzed. In Tables 5 and 6 the calculated theoretical complexity functions are compared with the experimental one. The inspection on the  $S$ -factors, which are given in those Tables also indicates that for the experimental data obtained at 20°C the fit of the theoretical complexity function calculated with the set of stability constants reported in Ref.<sup>10/</sup> is better than that one of the present work by a factor of 2. On the contrary, for the  $F$ -function at 30°C the fit of the theoretical complexity function obtained by using Eq. (2) of the present work is better by a factor of 2 than that of the corresponding function calculated with the set of stability constants found by Saxena and Chturvedi<sup>10/</sup>. So, in this case the inspection of the  $S$ -factors could not help in deciding which model is better. But we give preference to the one developed in Ref.<sup>11/</sup> because it describes the process with fewer number of parameters and with sufficient accuracy.



In Table 8 the calculated thermodynamic functions for the TI-ethylthioglycolate system are presented.  $\Delta H$  could not be determined graphically because the system had been studied at two temperatures only. The data in Table 8 demonstrate that the thermodynamic functions calculated from the  $\beta_n$  values obtained in the present study for this system display the same trends as those found for the Cd-TDPA system. So, for this system also we have sufficient justification to consider the mathematical model<sup>11</sup> as a good approximation of the complex formation process.

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Received by Publishing Department  
on October 27, 1972.

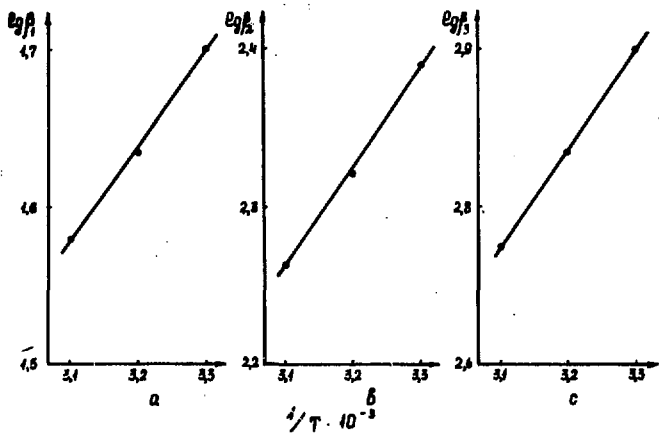


Fig. 1.  $\text{Log. } \beta_n$  as a function of  $1/T$

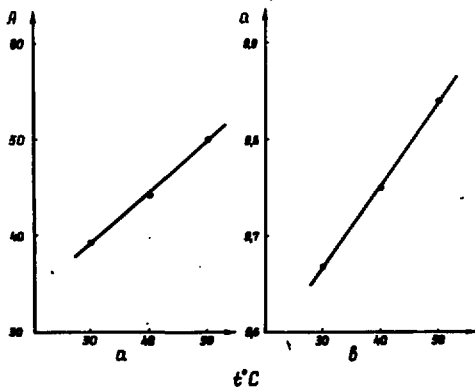


Fig. 2. a) Variation of the constant  $A$  with the temperature; b) Variation of the constant  $a$  with the temperature.

Table 1  
Comparison of the experimental and calculated complexity  
functions for the Cd-TDPA system at 30°C

(L) M	F <sub>exp</sub>	Rawat and Gupta		This work	
		F <sub>calc</sub>	Δ F <sub>calc</sub> in %	F <sub>calc</sub>	Δ F <sub>calc</sub> in %
0.025	2.689	2.688	0.04	2.417	- 10.15
0.050	4.070	4.660	14.50	4.216	3.59
0.075	7.193	7.010	- 2.54	6.474	- 9.99
0.100	12.33	9.83	- 20.27	9.27	- 24.82
0.150	16.37	17.25	5.36	16.76	2.38
0.200	27.15	27.64	1.80	27.30	0.55
0.250	41.77	41.75	- 0.05	41.48	- 0.69
0.300	61.41	60.31	- 1.79	59.93	- 2.41

\* - obtained by using the following  $\beta_n$  values reported in Ref.<sup>/9/</sup> :

$\beta_1=63; \beta_2=155; \beta_3=980;$

\*\* - obtained by using the following values of  $\beta_n$  :  $\beta_1=50;$   
 $\beta_2=246; \beta_3=807,$  which are correlated according to Eq. (1) where:

$A=5.08$  and  $\alpha=9.84.$

$S_{Ref./9/} = 1.6 \times 10^{-2}$  and  $S_{This work} = 1.6 \times 10^{-2}$

Table 2  
Comparison of the experimental and calculated complexity  
functions for the Cd-TDPA system at 40° C

(L) M	F <sub>exp</sub>	Rawat and Gupta		This work	
		F <sub>calc</sub>	$\Delta F$ in %	F <sub>calc</sub>	$\Delta F$ in %
0.025	1.995	2.289	14.74	2.217	11.13
0.050	3.165	3.810	20.38	3.760	18.80
0.075	5.635	5.646	0.19	5.694	1.05
0.100	7.814	7.880	0.84	8.081	3.42
0.150	16.62	13.87	- 16.55	14.47	- 12.94
0.200	21.61	22.44	3.84	23.45	8.51
0.250	34.40	34.25	0.44	35.51	3.23
0.300	49.97	49.96	- 0.02	51.19	2.44

\* - obtained by using the following  $\beta_n$  values reported in Ref. '9':  
 $\beta_1 = 48$ ;  $\beta_2 = 120$ ;  $\beta_3 = 880$ ;

\*\* - obtained by using the following values of  $\beta_n$ :  $\beta_1 = 43$ ;  
 $\beta_2 = 210$ ;  $\beta_3 = 681$ , which are correlated according to Eq. (1), where  
 $A = 4.42$  and  $a = 9.75$ .

$S_{Ref. '9'} = 2.3 \times 10^{-2}$  and  $S_{This work} = 1.5 \times 10^{-2}$

Table 3  
Comparison of the experimental and calculated complexity  
functions for the Cd-TDPA system at 50°C

(L) M	$F_{exp}$	Rawat and Gupta		This work	
		$F_{calc}^{**}$	$\Delta F_{calc}^{**}$ in %	$F_{calc}^{***}$	$\Delta F_{calc}^{***}$ in %
0.025	1.602	2.088	30.34	2.074	29.46
0.050	2.569	3.400	32.35	3.434	33.67
0.075	5.023	5.013	0.20	5.135	2.23
0.100	7.092	7.000	- 1.30	7.233	1.99
0.150	13.66	12.40	- 9.22	12.84	- 6.00
0.200	20.32	20.20	- 0.59	20.70	1.87
0.250	30.56	31.00	1.44	31.26	2.29
0.300	45.47	45.40	- 0.15	44.97	- 1.10

\* - obtained by using the following  $\beta_n$  values reported in Ref./9/ :  
 $\beta_1 = 40; \beta_2 = 120; \beta_3 = 800.$

\*\* - obtained by using the following values of  $\beta_n$  :  $\beta_1 = 38;$   
 $\beta_2 = 184; \beta_3 = 593,$  which are correlated according to Eq. (1) where:  
 $A = 3.92$  and  $\alpha = 9.68.$

$S_{Ref./9/} = 5.1 \times 10^{-2}$  and  $S_{This\ work} = 4.1 \times 10^{-2}$

Table 4  
Comparison of the experimental and calculated complexity  
functions for the Cd-TDPA system with 20% DMF at 30°C

(L)	$F_{exp}$	Rawat and Gupta		This work	
		$F_{calc}^*$	$\Delta F^*$ in %	$F_{calc}^{**}$	$\Delta F^{**}$ in %
0.025	3.149	3.608	14.58	3.606	14.51
0.050	7.046	7.040	- 0.05	7.021	- 0.35
0.075	11.58	11.46	- 1.04	11.42	- 1.38
0.100	17.41	17.02	- 2.24	17.35	- 0.34
0.150	32.21	32.23	0.06	32.32	0.34
0.200	53.21	53.26	1.41	54.44	2.31
0.250	84.12	83.50	- 0.74	84.75	0.75

\* - obtained by using the following  $\beta_n$  values reported in Ref. /9/ :  
 $\beta_1 = 90$ ;  $\beta_2 = 530$ ;  $\beta_3 = 1720$ .  
 \*\* - obtained by using the following values of  $\beta_n$  :  $\beta_1 = 90.4$ ;  
 $\beta_2 = 506$ ;  $\beta_3 = 1890$ , which are correlated according to Eq. (1),  
 where  $A = 16.14$  and  $a = 5.60$ .  
 $S_{Ref./9/} = 0.7 \times 10^{-2}$  and  $S_{This work} = 0.5 \times 10^{-2}$

**Table 5**  
**Comparison of the experimental and calculated complexity**  
**functions for the TI-ethylthioglycolate system at 20 °C**

(L)	$F_{exp}$	Saxena and Chaturvedi		This work	
		$F_{calc}^*$	$\Delta F^*$ in %	$F_{calc}^{**}$	$\Delta F^{**}$ in %
M					
0.02	2.237	2.174	- 2.82	2.107	- 5.81
0.04	3.526	3.515	- 0.31	3.474	- 1.47
0.06	5.136	5.109	- 0.53	5.149	0.25
0.08	6.839	7.042	2.97	7.177	4.94
0.12	12.12	12.27	1.24	12.47	2.81
0.20	30.13	30.60	1.56	29.35	- 2.59

\* - obtained by using the following values of  $\beta_n$  reported in Ref. /10/:  $\beta_1 = 56$ ;  $\beta_2 = 100$ ;  $\beta_3 = 1800$ .

\*\* - obtained by using the following values of  $\beta_n$ :  $\beta_1 = 49.6$ ;  $\beta_2 = 268$ ;  $\beta_3 = 964$ , which are correlated according to Eq. (1), where  $A = 4.59$  and  $\sigma = 10.8$ .

$S_{Ref./10/} = 0.1 \times 10^{-2}$  and  $S_{This\ work} = 0.2 \times 10^{-2}$

Table 6  
Comparison of the experimental and calculated complexity  
functions for the TI-ethylthioglycolate system at 30 °C

(L)	$F_{exp}$	Saxena and Chaturvedi		This work	
		$F_{calc}^*$	$\Delta F^*$ in %	$F_{calc}^{**}$	$\Delta F^{**}$ in %
0.02	2.070	2.069	- 0.05	2.047	- I.II
0.04	3.363	3.286	- 2.29	3.335	- 0.83
0.06	4.698	4.730	0.68	4.906	4.43
0.08	7.213	6.475	- 10.23	6.804	- 5.67
0.12	11.22	11.18	- 0.36	11.75	4.72
0.20	28.64	27.60	- 3.63	27.40	- 4.33

\* - obtained by using the following values of  $\beta_n$  reported  
in Ref./10/ :  $\beta_1= 51$ ;  $\beta_2= 90$ ;  $\beta_3= 1600$ .

\*\* - obtained by using the following values of  $\beta_n$  :  $\beta_1= 47$ ;  
 $\beta_2= 249$ ;  $\beta_3= 880$ , which are correlated according to Eq. (1), where  
 $A= 4.43$  and  $a= 10.6$ .

$S_{Ref./10/} = 0.6 \times 10^{-2}$  and  $S_{This work} = 0.3 \times 10^{-2}$



Table 7  
Calculated thermodynamic functions for the Cd-TDPA system

T °C	$f_n$	Rawat and Gupta			This work			
		$\Delta F$ kcal./M	$\Delta H$ kcal./M	$\Delta S$ cal./deg.M	$\Delta F$ kcal/M	$\Delta H$ kcal./M		$\Delta S$ cal/deg.M
						numer.	graph.	
30	$f_1$	-	-	-	- 2.34	-	- 2.71	- 1.18
40	$f_1$	-	-	-	- 2.34	- 2.84	- 2.71	- 1.30
50	$f_1$	-	-	-	- 2.34	- 2.48	- 2.71	- 1.17
30	$f_2$	-	-	-	- 3.32	-	- 2.83	1.61
40	$f_2$	-	-	-	- 3.33	- 2.98	- 2.83	1.60
50	$f_2$	-	-	-	- 3.35	- 2.66	- 2.83	1.61
50	$f_3$	$-4.15 \pm 0.02$	-	-	- 4.03	-	- 3.17	3.16
40	$f_3$	$-4.22 \pm 0.02$	$- 2.03 \pm 0.01$	$7.00 \pm 0.05$	- 4.06	- 3.15	- 3.17	3.15
50	$f_3$	$-4.29 \pm 0.02$	$- 1.92 \pm 0.01$	$7.35 \pm 0.05$	- 4.10	- 3.20	- 3.17	3.17

Table 8  
 Calculated thermodynamic functions for the TI-ethylthioglycolate  
 system

T °C	$f_1$	Saxena and Chaturvedi			This work		
		$\Delta F$ kcal/M	$\Delta H$ kcal/M	$\Delta S$ cal/deg.M	$\Delta F$ kcal/M	$\Delta H$ kcal/M	$\Delta S$ cal/deg.M
20	$f_1$	- 2.3	-	-	- 2.27	-	-
30	$f_1$	- 2.3	- 1.6	2.4	- 2.32	- 0.95	4.52
20	$f_2$	- 2.6	-	-	- 3.26	-	-
30	$f_2$	- 2.6	- 1.8	2.3	- 3.32	- 1.30	6.69
20	$f_3$	- 4.4	-	-	- 4.00	-	-
30	$f_3$	- 4.4	- 2.0	8.0	- 4.08	- 1.61	8.17