

Conductivity study of Bulk and Nano CuSO₄ with organochalcogenic ligand (H₄L_{Chal})

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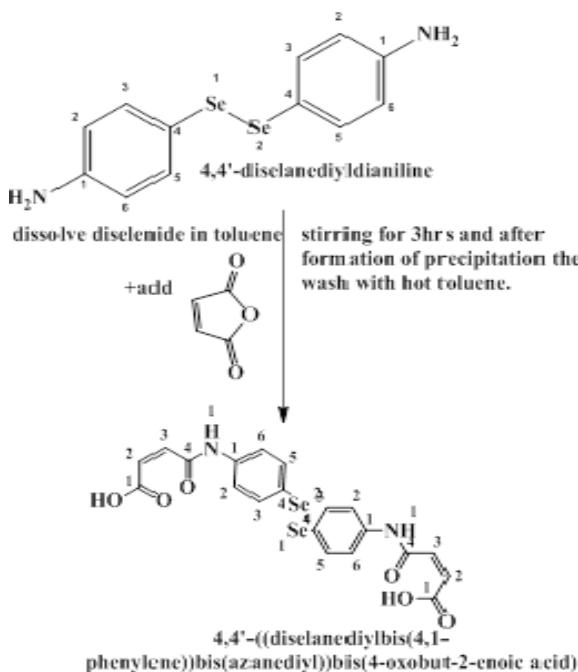
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1. Introduction

Electrical conductivity of materials in water as can be evaluated which depends on ions nature, temperature, and concentration of ions. Conductivity defined as the measurement of ions in solution [1-4]. Conductivity method routinely used because of fast, cheap (61). Conductometric measurements are largely used in industry. For example, treating water or raw water because it comes from a lake, river is rarely suitable for industrial use as it is, fast and reliable method of measuring the ionic content in solutions [5-10].



Structure (1) Preparation of chalcogen ligand H₄L_{Chal}

2. Materials and methods

1. Copper sulfate pentahydrate (bulk and nano).
2. H₄L_{Chal}(ligand) as shown in
3. The solutions' electrical conductivity were estimated by (JENCO, Vision Plus EC3175).

3. Results and Discussion

The conductivity of different bulk CuSO₄ and nano CuSO₄ additions were measured in different percentage of ethanol (10%, 30%, and 50%). Straight lines were obtained for different ethanol percentages having small slope directions. The Λ_0 molar conductances are read by drawing the relation between molar conductances Λ_m and C^{1/2} [10-12].

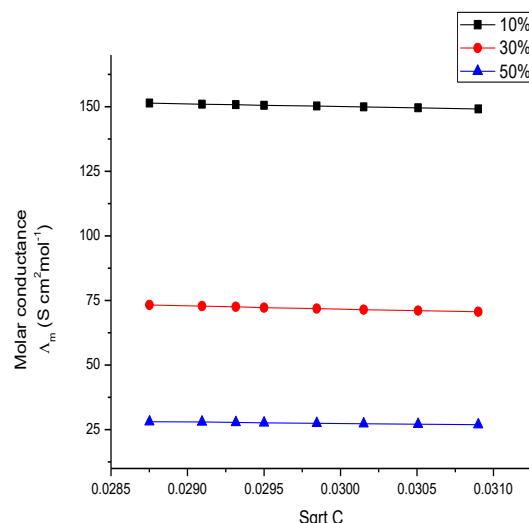


Fig.1. The relation between molar conductance (Λ_m) and C^{1/2} of bulk CuSO₄ in EtOH-H₂O mixture at 298.15K

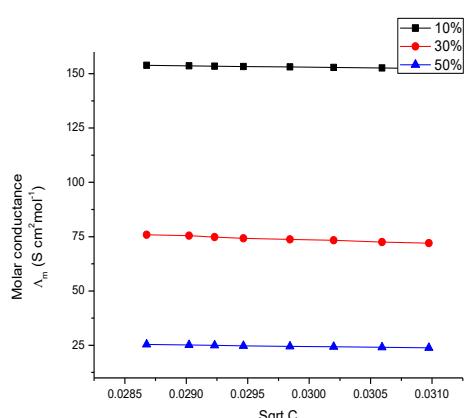


Fig.2.The relation between molar conductance (Λ_m) and $C^{1/2}$ of bulk CuSO₄in EtOH-H₂O mixture at 308.15K.

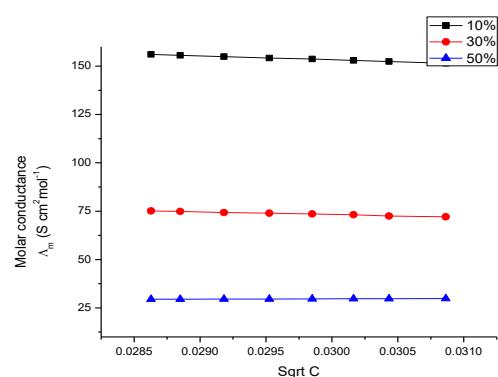


Fig.3.The relation between molar conductance (Λ_m) and $C^{1/2}$ of bulk CuSO₄in EtOH-H₂O mixture at 303.15K

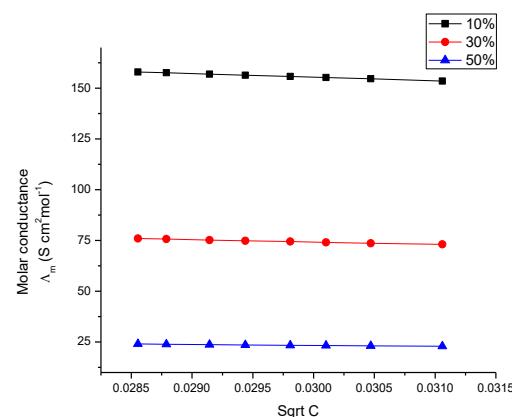


Fig.4.The relation between molar conductance (Λ_m) and $C^{1/2}$ of bulk CuSO₄in EtOH-H₂O mixture at 313.15K

The molar conductances are decreased by more adding ethanol indicating decrease of the mobility of free ions due to association and aggregation of ions.

The association constant K_A increased by increase of EtOH percentage.

The dissociation degree α for CuSO₄. The dissociation constant K_D decreased by the increase of EtOH percentage. Triple ion association constant K_3 is very small. The Gibbs free energies of association ΔG_A and Gibbs free energies of transfer are increased by increase in percentage of EtOH favoring rise in ions-solvent interaction. All conduct metric data for bulk CuSO₄ calculated use Fuoss-Shedlovsky method [4-12] at 303.15K are greater than that at 298.15K due to the increase in the kinetic energy.

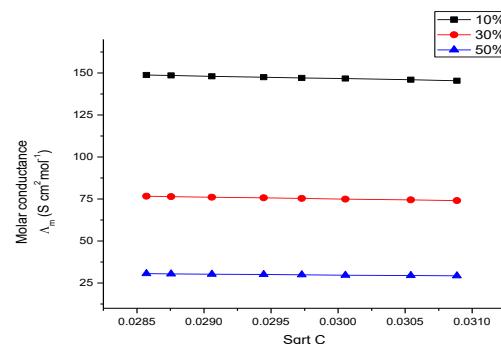


Fig.5.The relation between molar conductance (Λ_m) and $C^{1/2}$ of nano CuSO₄in EtOH-H₂O mixture at 298.15K

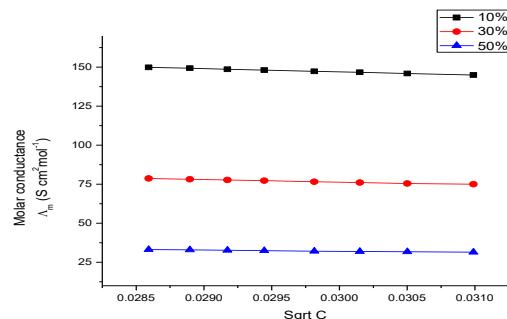


Fig.6.The relation between molar conductance (Λ_m) and $C^{1/2}$ of nano CuSO₄in EtOH-H₂O mixture at 303.15K

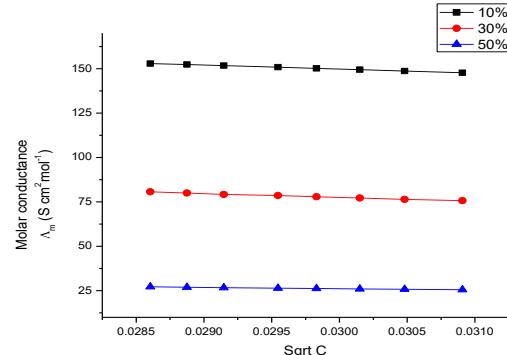


Fig.7.The relation between molar conductance (Λ_m) and $C^{1/2}$ of nano CuSO₄in EtOH-H₂O mixture at 328.15K

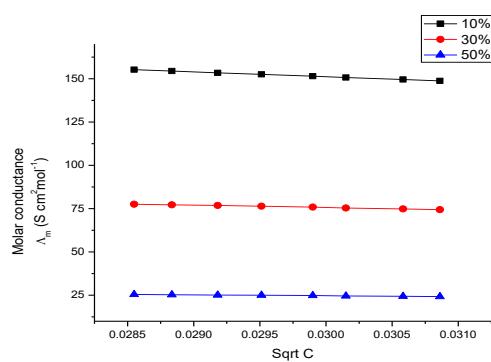


Fig.8. The relation between molar conductance (Λ_m) and $C^{1/2}$ of nanoCuSO₄ in EtOH-H₂O mixture at 313.15K

Table(1) Degree of dissociation (α), dissociation constant (K_D), triple ion association constant (K_3), and Gibbs free energy of association (ΔG_A) for bulk CuSO₄ in mixture of (EtOH-H₂O) at different temperatures

	Vol.% of EtOH	$10^3 K_D$	α	$10^5 K_3$	ΔG_A
	10	0.0032	0.8393	-0.0053	-4.2605
298.15K	30	0.0011	.6864	-0.0091	-6.8827
	50	0.0009	.6607	0.0095	17.3096
	10	0.0013	0.7190	3.0004	16.6461
303.15K	30	0.0009	0.6530	5.0000	-7.6652
	50	0.0606	0.9890	2.0002	-7.0669
	10	.0052	0.8919	8.0003	-3.4659
308.15K	30	0.0006	0.5952	6.0001	-8.8448
	50	0.0005	0.5672	8.0003	-9.3474
	10	0.0016	0.7447	2.0001	-6.8085
313.15K	30	0.0009	0.6648	4.0008	-8.1551
	50	0.0008	0.6518	6.0000	-8.5287

Table (2): Degree of dissociation (α), dissociation constant (K_D), triple ion association constant (K_3) and Gibbs free energy of association (ΔG_A) for nano CuSO₄ in mixture of (EtOH-H₂O) at different temperatures

	Vol.% Of EtOH	$10^3 K_D$	α	$10^5 K_3$	ΔG_A
	10	0.0022	0.7947	-0.0064	15.1363
298.15K	30	0.0011	0.6907	-0.0089	-.8018
	50	0.0008	0.6382	-0.0101	7.5589
	10	0.0012	0.6996	3.0008	-.9581
303.15K	30	0.0007	0.6098	6.0002	-2.2681
	50	0.0007	0.6110	6.0008	-.2511
	10	0.0011	0.6881	4.0000	7.4222
308.15K	30	0.0004	0.5403	8.0005	19.5812
	50	0.0006	0.5747	8.0000	19.0833
	0.0008	0.6424	5.0001	18.4081	0.0008
313.15K	0.0009	0.6465	5.0003	-.3485	0.0009
	0.0008	0.6202	7.0001	8.7364	0.0008

ΔG_A for nano CuSO₄ in mixed EtOH-H₂O is greater than bulk CuSO₄ in same solvents and temperature. Higher values of ΔG_A for nano

CuSO₄ solutions than bulk CuSO₄ at same EtOH-H₂O composition and temperature.

By drawing the relation between $\log K_A$ and $1/T$ giving straight line with slope $(-\Delta H_A/2.303R)$ as shown in Figures 9, 10

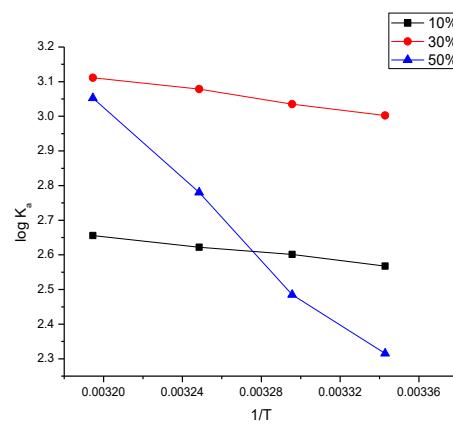


Fig.9. $\log K_A$ against $1/T$ for B-CuSO₄ in EtOH-H₂O mixture

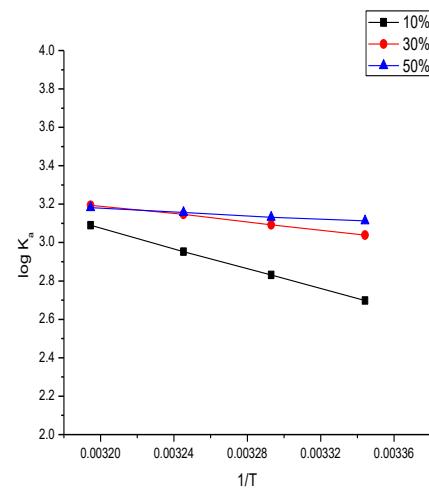


Fig.10. $\log K_A$ against $1/T$ for N-CuSO₄ in EtOH-H₂O mixture

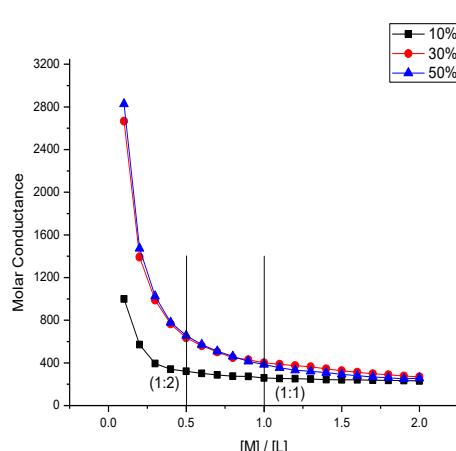


Fig.11. at 298.15K

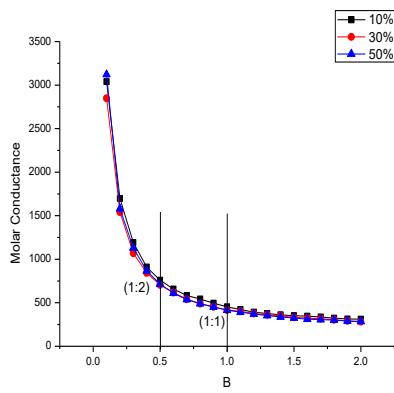


Fig.12. at 303.15K

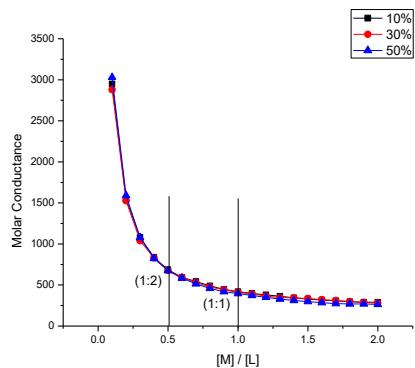


Fig.16. at 303.15K

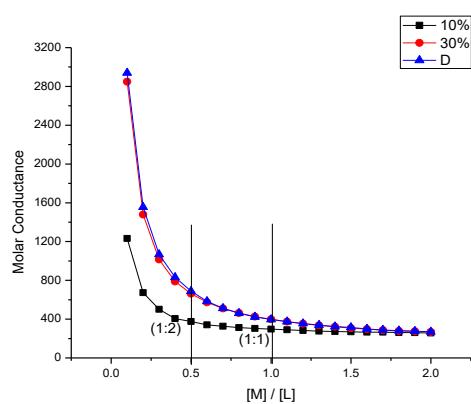


Fig.13. at 308.15K

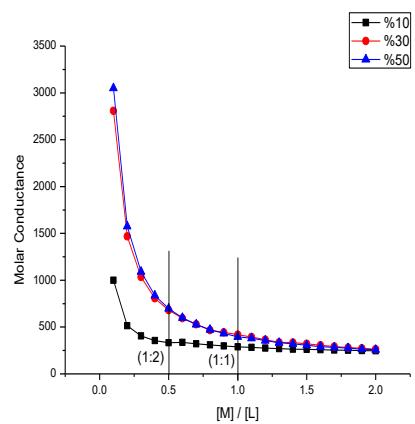


Fig.17. at 308.15K

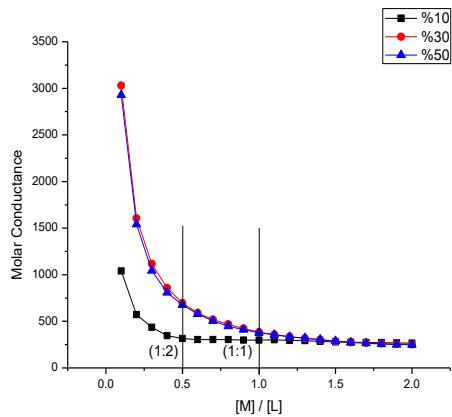


Fig.14. at 313.15K

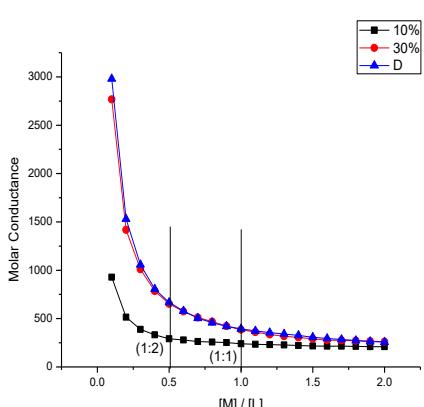


Fig.15. at 298.15K

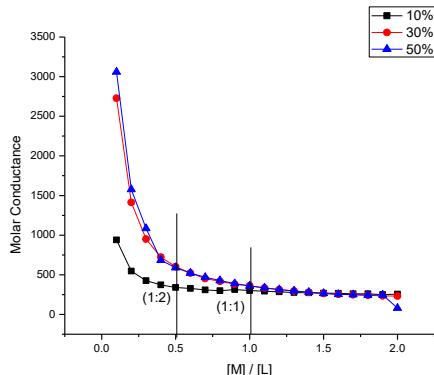


Fig.18 at 313.15K

The relation between (Λ_m) and the $[M]/[L]$ molar ratio of bulk $\text{CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ complexation in $(\text{EtOH}-\text{H}_2\text{O})$ mixed solvents as shown in figures (11-14).

The relation between (Λ_m) and the $[M]/[L]$ molar ratio of nano $\text{CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ complexation in $(\text{EtOH}-\text{H}_2\text{O})$ mixed solvents as shown in figures (15-18)

The plot of $\log K_f$ versus $(1/T)$ at different temperatures for bulk $\text{CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M: L stoichiometric complexes in 10%, 30%, 50% $(\text{EtOH}-\text{H}_2\text{O})$ mixed solvents as shown in figures (19-21)

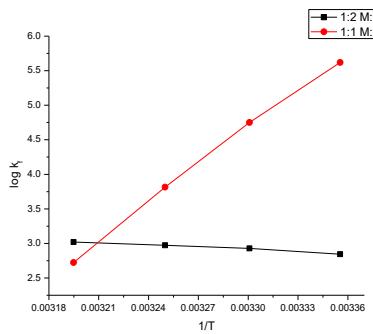


Fig.19. $\log K_f$ versus $(1/T)$ for $B\text{-CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 10% (EtOH–H₂O) mixed solvents

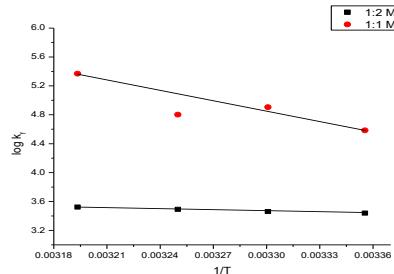


Fig.20. $\log K_f$ versus $(1/T)$ for $B\text{-CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 30% (EtOH–H₂O) mixed solvents

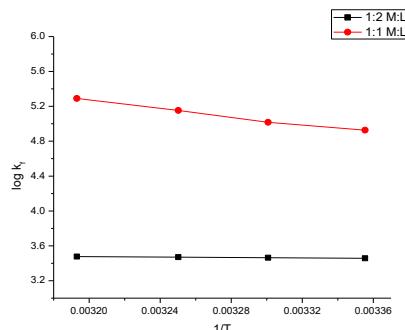


Fig.21. $\log K_f$ versus $(1/T)$ for $B\text{-CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 50% (EtOH–H₂O) mixed solvents

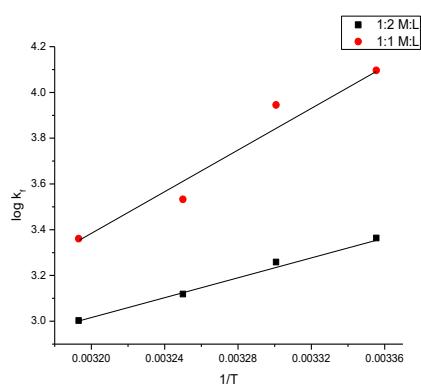


Fig.22. $\log K_f$ versus $(1/T)$ for $N\text{-CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 10% (EtOH–H₂O) mixed solvents

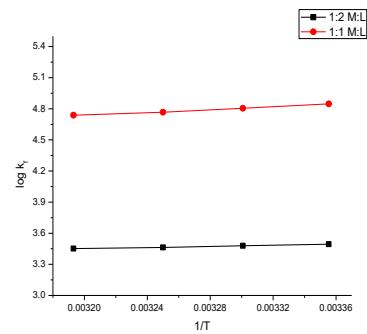


Fig.23. $\log K_f$ versus $(1/T)$ for $N\text{-CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 30% (EtOH–H₂O) mixed solvents

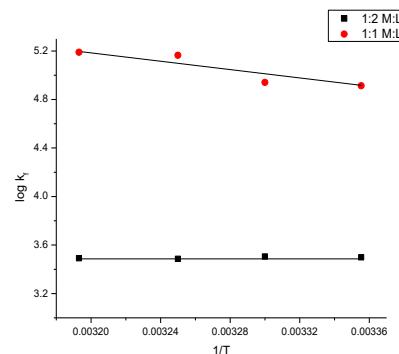


Fig.24. $\log K_f$ versus $(1/T)$ for $N\text{-CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 50% (EtOH–H₂O) mixed solvents

The plot of $\log K_f$ versus $(1/T)$ at different temperatures for nano $\text{CuSO}_4\text{-H}_4\text{L}_{\text{Chal}}$ (1:2) and (1:1) M:L stoichiometric complexes in 10%, 30%, 50% (EtOH–H₂O) mixed solvents as shown in figures(22-24)

1:1 (M/L) complexes are more stable because they have greater thermodynamic parameters than 1:2 (M/L) complexes. Very high positive entropy of complex formation for nano $\text{CuSO}_4 + \text{H}_4\text{L}_{\text{Chal}}$ shows easier formation 1:1 and 1:2 complexes.

Conclusions:

1 Gibbs free energies of association, ΔG_A for nano CuSO_4 in mixed EtOH-H₂O is greater than bulk CuSO_4 in same solvents and temperature,

2-Higher values of ΔG_A for nano CuSO_4 solutions than bulk CuSO_4 at same EtOH-H₂O composition and temperature.

3-High positive entropy of complex formation for nano $\text{CuSO}_4 + \text{H}_4\text{L}_{\text{Chal}}$ indicating easier more complexation than bulk salt.

4. References:

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