

Thermodynamic Study of the Tetradentate Keto-amine Nickel(II) Complexes as Stationary Phase for Gas Chromatography

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Summary: Stability constant (K_m), enthalpies ($-\Delta H$), entropies ($-\Delta S$) and Gibb's free energy ($-\Delta G$) of gas chromatographic (GC) elution of alcohols, aldehydes, ketones, aromatic hydrocarbons, hetroaromatic compounds and analine from stainless steel column (3m x 3 mm id) packed with [1] OV101 3% [2] OV101 3% + bis(acetylacetonone) ethylenediimine nickel(II) (AA_2enNi) 5%, [3] OV101 3% + bis (acetylacetonone) propylene diimine nickel(II) (AA_2pnNi) 5% [4] OV101 3% + bis(acetylacetonone) dl-stilbenediimine nickel(II) ($dl-AA_2S Ni$) 5% [5] and OV101 3% + bis(acetylacetonone) meso-stilbenediimine nickel(II) ($meso-AA_2S Ni$) 5% on Chromosorb G/NAW 60-80 mesh size have been calculated. The donor-acceptor complexation in gas phase is indicated with negative values of enthalpy, entropy and Gibb's free energy.

Introduction

Selective complexation on gas chromatography has been extensively studied. In this process the coordinatively unsaturated metal complexes are added to the stationary phases or are chemically bonded with silica surface to introduce chemical selectivity as an aid to the chemical separation [1-4]. A number of metal chelates have been examined including copper(II) and nickel(II) acetylacetonates [1,3], triphenylphosphine complexes of rhodium (II) and ruthanium(II) [4], nickel(II) bis[3-(trifluoroacetyl) IR-camphorate] in squalene [5], nickel, palladium and platinum complexes of N-dodecylsalicylaldehydes and n-octylglyoximes [6], beryllium, aluminium, nickel and zinc complexes of n-nonyl- β -diketone [7], nickel (II) complexes of dimethylglyoxime and salicylaldehyde [8], metallic phthalocyanines [9] and copper (II) and nickel(II) chelates of tetradentate Schiff base [10-13]. Recently nickel(II) chelates of tetradentate ligands bis (acetylacetonone) ethylenediimine (H_2AA_2en), bis (acetylacetonone) propylenediimine (H_2AA_2pn), bis

(acetylacetonone)dl-stilbenediimine ($dl-H_2AA_2S$) and bis(acetylacetonone) meso-stilbenediimine ($meso-H_2AA_2S$) have been reported as mixed stationary phase with OV101 for the selective separation of alcohol, aldehydes, ketones, aromatic hydrocarbons and hetro-aromatic compounds [14]. In the present work, thermo-dynamical functions of the elution of organic compounds from mixed stationary phase of nickel chelates H_2AA_2en , H_2AA_2pn , $dl-H_2AA_2S$ and $meso-H_2AA_2S$ have been calculated to ascertain the donar-accepter complexation in gas phase.

Results and Discussion

The stability constant K_m of molecular complex between the δ - donar molecular and nickel chelate with OV-101 was calculated from relationship.

$$R' = \frac{t \ t^{OX}}{t^x \ t^o} - 1 = K_m \times m_A$$

where R' is the ratio of the relative retention of the solute on mixed stationary phase containing nickel chelate and the column with OV101, t_i is the corrected net peak maximum retention time of the δ -donor solute on a column with nickel chelate, t_i° is the corrected net peak maximum retention time of the δ -donor solute on a column with OV101, t° is the corrected net peak maximum retention time of non complexing inert reference standard on a column with a nickel chelate and t^{OX} the corrected net peak maximum retention time of non complexing inert reference standard on a column with OV101 (*n*-hexane). m_A is molal concentration of the nickel chelate dl-AA₂SNi in OV101 on the Chromosorb G/NAW is (0.115). K_m was calculated at temperature 70,80 and 90°C from R' and m_A by inserting the retention time of the solute at 70,80 and 90°C on mixed stationary phase containing nickel chelate and OV101.

The Gibbs free energy ($-\Delta G$) at 70°C, 80°C and 90°C were calculated from the relationship.

$$-\Delta G = RT \ln k_m$$

where R = Gas Constant (1.987 k.cal/mol), T = Absolute temperature, $\ln k_m$ is natural log of stability constant K_m . The enthalpy ($-\Delta H$) was calculated by plotting $1000/T$ versus $\ln K_m$ and multiplying slope sensitivity with R . Entropy ($-\Delta S$) was calculated by multiplying intercept with R .

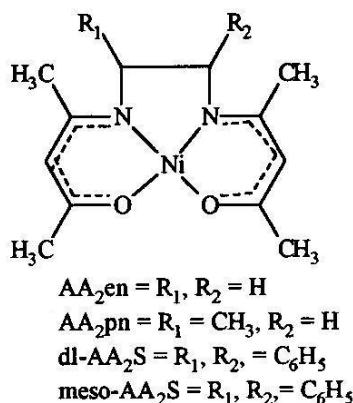


Fig. 1

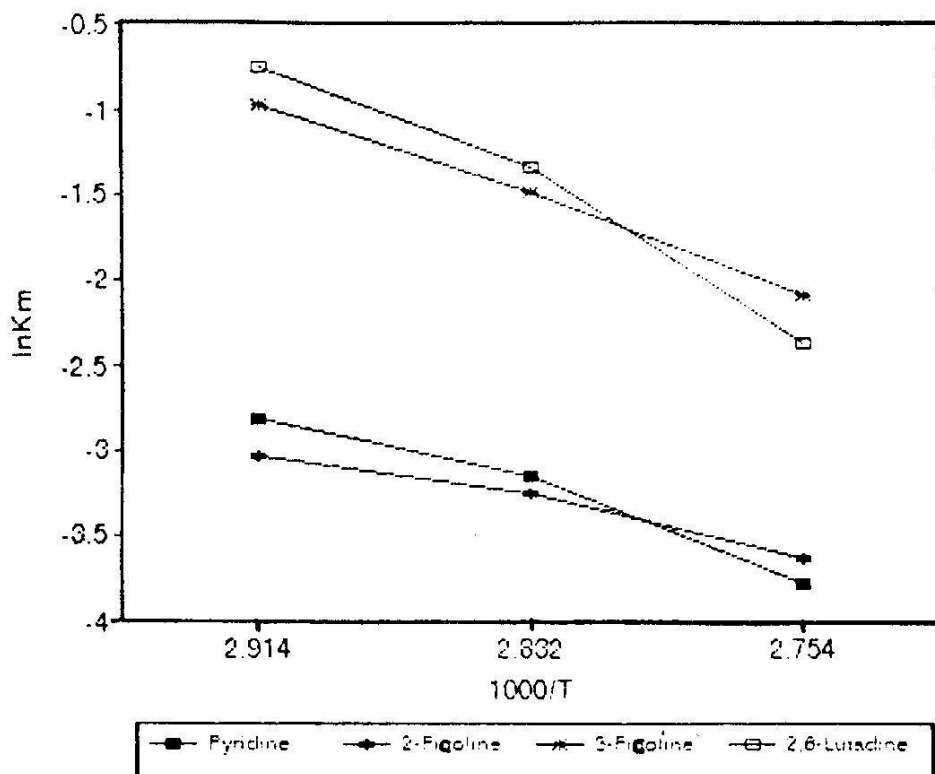
The results obtained are summarized in Table 1-2. The stability constants k_m of heteroaromatics, alcohols, aromatic hydrocarbons, aldehydes, ketones and aniline were calculated at 70, 80 and 90°C. It was observed that when $1000/T$ was plotted against $\ln k_m$ linear relationships were obtained. The coefficient of correlations (r) on mixed stationary phase OV101 3% + dl-AA₂SNi 5% were obtained within 0.9886-0.9999 (Fig. 2). Similarly (r) on mixed stationary phases OV101 3% + AA₂pnNi 5%, OV101 3% + AA₂enNi 5% (Fig. 3) and OV101 3% + meso-AA₂SNi 5% were obtained in the range of 0.8336-0.99986, 0.9894-0.9999 and 0.9889-0.9995 respectively. The results indicate somewhat better

Table-1: Stability constant (k_m) enthalpies $-\Delta H$, (kcal/mole) entropies $-\Delta S$ (cal/mol-k) and free energy $-\Delta G$ (kcal/mole) of the complexation reaction with dl-AA₂SNi dispersed with OV-101.

No.	Solute	dl-AA ₂ SNi				-ΔG			
		70°C	80°C	90°C	-ΔH	-ΔS	70°C	80°C	90°C
1.	Pyridine	0.060	0.042	0.022	12.42	41.70	1.91	2.22	2.75
2.	2-Picoline	0.048	0.038	0.026	7.59	28.12	2.07	2.29	2.63
3.	3-Picoline	0.378	0.225	0.122	14.03	42.78	0.66	1.04	1.51
4.	2,6-dimethyl Lutadine	0.466	0.260	0.093	19.96	59.53	0.52	0.94	1.71
5.	1-Pentanol	2.063	1.975	1.878	1.16	1.95	+0.49	+0.47	+0.45
6.	1-Hexanol	1.893	1.833	1.766	0.89	1.33	+0.43	+0.42	+0.41
7.	1-Heptanol	2.321	2.208	2.086	1.32	2.19	+0.57	+0.55	+0.53
8.	Octanol	1.202	1.154	1.093	1.17	3.06	+0.12	+0.10	+0.07
9.	Toluene	1.991	1.908	1.817	1.13	1.93	+0.47	+0.45	+0.43
10.	o-Xylene	3.013	2.873	2.731	1.21	1.36	+0.75	+0.74	+0.72
11.	m-Xylene	2.970	2.796	2.620	1.55	2.36	+0.74	+0.72	+0.69
12.	p-Xylene	2.906	2.809	2.634	1.53	2.29	+0.73	+0.72	+0.70
13.	Paraldehyde	1.373	1.303	1.220	1.46	3.36	+0.21	+0.18	+0.14
14.	Benzaldehyde	2.465	2.304	2.168	1.54	2.70	+0.61	+0.58	+0.55
15.	MIBK	0.928	0.838	0.771	2.30	6.86	0.05	0.12	0.18
16.	Cyclohexanone	2.671	2.467	2.293	1.88	3.54	+0.67	+0.63	+0.60
17.	Aniline	3.323	3.206	3.067	1.00	0.53	+0.82	+0.81	+0.80

Table-2: Stability constant (k_m) enthalpies $-\Delta H$, (kcal/mole) entropies $-\Delta S$ (cal/mol-k) and free energy $-\Delta G$ (kcal/mole) of the complexation reaction with AA_2enNi dispersed with OV-101.

No.	Solute	k_m			AA_2enNi		$-\Delta G$		
		70°C	80°C	90°C	$-\Delta H$	$-\Delta S$	70°C	80°C	90°C
1.	Pyridine	0.301	0.269	0.234	3.12	11.47	0.81	0.92	1.04
2.	2-Picoline	0.110	0.099	0.084	3.34	14.10	1.50	1.62	2.19
3.	3-Picoline	0.425	0.389	0.351	2.37	8.61	0.58	0.66	0.75
4.	2,6-dimethyl Lutadine	0.20	0.169	0.134	5.03	17.87	1.09	1.28	1.45
5.	1-Pentanol	0.648	0.582	0.517	2.80	9.02	0.29	0.38	0.47
6.	1-Hexanol	0.869	0.860	0.850	0.27	1.07	0.09	0.095	0.11
7.	1-Heptanol	0.886	0.872	0.858	0.39	1.40	0.087	0.09	0.11
8.	Octanol	0.707	0.703	0.696	0.19	1.25	0.23	0.24	0.26
9.	Toluene	1.416	1.355	1.297	1.03	2.34	+0.24	+0.21	+0.18
10.	o-Xylene	1.889	1.853	1.812	0.51	0.23	+0.44	+0.43	+0.42
11.	m-Xylene	1.807	1.773	1.738	0.48	0.20	+0.40	+0.40	+0.39
12.	p-Xylene	1.723	1.709	1.686	0.27	0.29	+0.37	+0.37	+0.37
13.	Paraldehyde	1.629	1.465	1.308	2.72	6.96	+0.33	+0.27	+0.19
14.	Benzaldehyde	1.489	1.460	1.418	0.68	1.18	+0.27	+0.26	+0.25
15.	MIBK	0.790	0.771	0.747	0.67	2.48	0.16	0.18	0.21
16.	Cyclohexanone	0.990	0.982	0.969	0.26	0.79	0.006	0.012	0.022
17.	Aniline	1.807	1.805	1.763	0.64	0.65	+0.42	+0.41	+0.40



linearity with mixed stationary phase containing dl-AA₂SNi and AA₂enNi.

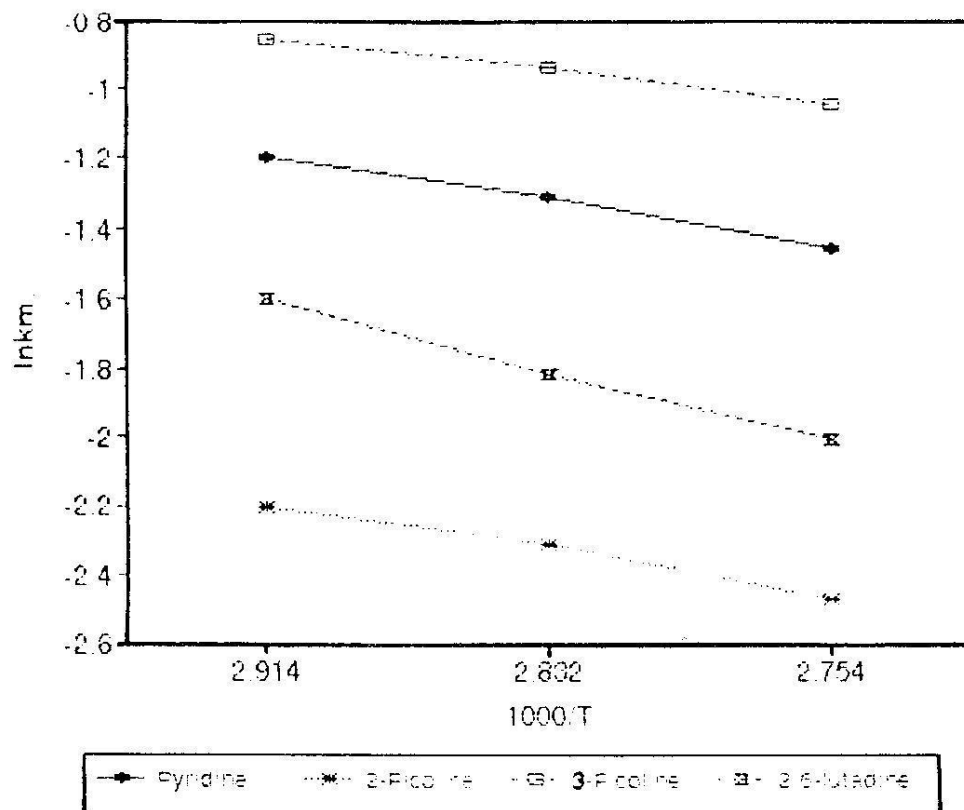
Enthalpy (-ΔH) is the measure of heat of adsorption of the solute on the adsorbent. The values of -ΔH for hetero-aromatics, aromatic hydrocarbons, alcohols, aldehydes, ketones and aniline on mixed stationary phase containing dl-AA₂SNi, are summarized in Table-1 are higher than -ΔH values on mixed stationary phase containing AA₂enNi (Table-2). The value on the average indicate that heteroaromatics have higher -ΔH value, followed by in the sequence, the aromatic hydrocarbons, aldehydes, alcohols, ketones and aniline. Aromatic aldehyde (benzaldehyde) has higher -ΔH value than aliphatic aldehyde (paraaldehyde). However, values of -ΔH are slightly different on the column containing AA₂enNi. The values are higher for heteroaromatic, followed by alcohols, aromatic hydrocarbons, aldehydes, ketones and aniline.

By comparing the -ΔH values on mixed stationary phases containing dl-AA₂SNi, meso-

AA₂SNi, AA₂pnNi and AA₂enNi (Table-3). The values are slightly higher on the stationary phase containing dl-AA₂SNi. Thus, it is observed that β-ketoamines ligand substituted with phenyl groups at the bridge position (Fig. 1) causes higher stability of adduct molecule with aromatic ring with increased in -ΔH values, but column with unsubstituted β-ketoamine AA₂enNi indicated -ΔH values for alcohols higher than aromatic hydrocarbons.

Table-3: Comparative study of Enthalpies -ΔH (kcal/mole) on different GC columns packed in (3m x 3mm i.d) Stainless Steel column on Chromosorb G/NAW 60-80 mesh size.

No.	Name of Compound	-ΔH on col. dl-AA ₂ SNi + OV-101	-ΔH on col. AA ₂ SNi + OV-101	-ΔH on col. AA ₂ enNi + OV-101	-ΔH on col. AA ₂ pnNi + OV-101
1.	Pyridine	12.42	10.37	3.12	4.09
2.	2-Picoline	7.59	6.18	3.34	4.13
3.	Toluene	1.13	0.83	1.03	0.87
4.	o-Xylene	1.21	0.85	0.51	0.61
5.	Benzaldehyde	1.54	1.13	0.68	0.69
6.	Octanol	1.17	0.85	0.19	0.55
7.	MIBK	2.30	1.27	0.69	0.45



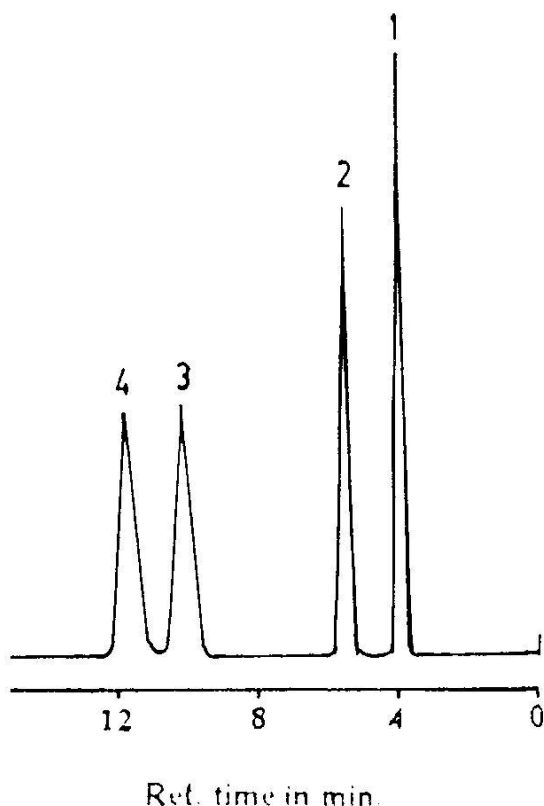


Fig. 4

Finally the chromatogram (Fig. 4) for the separation of aromatic hydrocarbons on mixed stationary phase 3% OV101 + 5% dl-AA₂SNi indicate better peak shape and separation than the stationary phase containing only 3% OV101 and support the utility of the mixed stationary phase for the separation of organic compounds.

Experimental

The reagents H₂AA₂en, H₂AA₂pn, dl-H₂AA₂S and meso-H₂AA₂S and their nickel(II) chelates (Fig. 1) were prepared, as reported [15,16], by heating acetylacetone with the appropriate 1,2-diamine in 2:1 molar ratio in ethanol. An equimolar solution (0.01 M) of nickel(II) acetate and the reagent in methanol was warmed together to obtain nickel(II) chelates.

A Hitachi Model 163 gas chromatograph equipped with a flame ionization detector and a Hitachi Model 056 recorder was used.

An appropriate amount of OV101 (BDH) individually or together with nickel chelate dissolved in chloroform, was added by thoroughly mixing with appropriate amount of Chromosorb G/NAW (60-80 mesh) (Merck) to prepare 3% OV101 or 3% OV101 + 5% nickel chelate on Chromosorb G/NAW. The solvent was removed at reduced pressure on a rotavapor (Buchi). For AA₂cNi and AA₂pnNi ethanol was used as solvent. The dried material were packed in column (3 m x 3 mm i.d.) using the usual procedure. Each of the column was conditioned at 130°C for atleast 24 hr, before use. Ten to fifteen injections of different compounds were made on each columns before measuring the analytical responses.

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