Bis(isovalerylacetone)ethylenediimine Nickel(II) as Mixed Stationary Phase for Gas Chromatography

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Abstract

Bis(isovalerylacetone)ethylenediimine Nickel (II) (IVA$_2$enNi) was examined as a mixed stationary phase with OV1 on Chromosorb G/NAW 60–80 mesh size for gas chromatography (GC) separation of aromatic hydrocarbons, heteroaromatics, alcohols, aldehydes, ketones, esters, nitro-, and amino compounds. Forty-six compounds were examined, and the GC results were compared with those obtained with 3% OV1 on Chromosorb G/NAW 60–80 mesh size under similar operating conditions. Improved resolutions, peak asymmetry, number of theoretical plates, and Kovats indices were obtained on the mixed stationary phase 3% OV1 + 5% IVA$_2$enNi (w/w) compared to 3% OV1 column. The stability constant (K$_m$), enthalpies (ΔH), entropies (ΔS), and Gibbs free energies (ΔG) of the GC elution on column (2 m x 3 mm i.d.) packed with 3% OV1 + 5% IVA$_2$enNi (w/w) on Chromosorb have been calculated. Donor-acceptor complexation in the gas phase indicated by the negative values of enthalpy (-ΔH) were within 9.4–12.38 Kcal/mol, and Gibbs free energy (-ΔG) ranged from 1.48 to 4.24 Kcal/mol. The retention time transformation on both the phases were calculated. The obtained ratios from the stationary phases 3% OV1 and 3% OV1 + 5% IVA$_2$enNi (w/w) were plotted on the *x*-axis and *y*-axis, respectively. Two-dimensional chromatographic plots for alkanes, aromatics, heteroaromatics, ketones, alcohols, esters, and nitro compounds were obtained with coefficient of determination within 0.4934 and 0.9617, which is indicative of some different kinds of interaction of two stationary phases with the solutes.

Introduction

A sufficiently large number of stationary phases with different polarities are known, but the use of mixed (usually binary) phases allows for extending the analytical possibilities in solving problems on the selective separation of various organic mixtures. It seems interesting to study the chromatographic properties of mixed stationary phases used in gas chromatography (GC) containing metal chelates. They exhibit both selectivity and resolving power for mixtures that are usually separated on stationary phase with difficulty (1–3). Complexation with metal chelates at the phase interface in GC (3) and enantioselective complexation GC (4) has been reviewed. Wasiak and his coworkers reported chemically bonded chelates as selective complexing sorbent for GC (5–7); their relative retention and thermodynamic functions have been calculated. Nickel chelates have also been used in kinetic studies of enantiomerization, enantiomer separation (8,9), and temperature-dependent reversal of elution sequences in complexation GC on chiral phases (10). Copper (II), Nickel (II), and palladium (II) chelates of tetradentate Schiff bases have been examined as stationary phases for GC individually or together with squalane or silicone oils (11–18).

Many efforts have been expanded in the search of selective chromatographic phases (3,4), which allow separations in a single chromatographic run of multiple components of compounds differing in the nature of their functional groups, polarity, and boiling points. The selectivity range in analyses of multiple components can be extended using mixed stationary phases. The thermally stable metal chelate may be capable of various interactions with functional groups of components of mixture (3).

The chromatographic properties of modified stationary phase containing metal chelates depends upon a number of factors including the nature of the metal, distribution of electron density in the complex, and geometry of the complex after its bonding to the support surface or its inclusion into liquid phase (19–21). The major role is played by the geometry of modifying complexes (22,23).

The metal chelates of tetradentate Schiff bases examined as mixed stationary phases are derived from acetylacetone or benzoylacetone with different diamines (11–18). It was considered to examine tetradentate Schiff base derived from isovalerylacetone with diamines, where tetradentate Schiff base formed contained isobutyl groups that were substituted for methyl and its symmetrically formed square planner nickel (II) chelate with longer hydrocarbon chain (24) could better interact with organic compounds for GC separations as mixed GC stationary phase with OV1.

Experimental

The reagent bis(isovalerylacetone)ethylenediimine (H$_2$IVA$_2$en) was prepared as reported (24) by heating together isovalerylacetone with ethylenediamine in 2:1 molar ratio in ethanol.

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β-diketone, isovalerylacetone was prepared by Claisen condensation of methyl isobutylketone with ethyl acetate (25). The nickel (II) and copper (II) chelates were formed by heating together equimolar solution of H_2IVA_2en and nickel (II) acetate or copper (II) acetate in methanol (Figure 1). IR spectra of H_2IVA_2en and its nickel and copper chelates were recorded on a Nicolet AVATAR 330 FT-IR with an attenuated total reflectance (ATR) accessory, smart performer (Thermo Electron, Waltham, MA). A Shimadzu GC-9A with dual flame ionization detector (FID) and glass columns (2 m × 3 mm i.d.) coupled with a Shimadzu CR-6A data processor and computer with CSW 17 (Data Apex) software was used (Kyoto, Japan). The sample injection was by glass liner (10 cm). A 10 g portion of Chromosorb G/NAW 60–80 mesh size (Merck, Darmstadt, Germany) was suspended in chloroform (15 mL), and appropriate amounts of IVA_2enNi or IVA_2enCu and 0.30 g OV1 (BDH, British Drug House, Poole, UK) were added to yield 3%, 5%, and 8% (w/w) of complex dissolved in chloroform (15 mL). The contents were mixed well, and the solvent was removed at reduced pressure in a rotary evaporator (Bucchi, Switzerland). Similarly, 3% OV1 + 5% H_2IVA_2en on Chromosorb was prepared following the same procedure. 3% OV1 (w/w) on Chromosorb was also prepared using the same procedure, but the addition of nickel or copper complex was omitted. The dried materials were packed in clean glass column (2 m × 3 mm i.d.) according to the procedure (26). Each of the columns was conditioned at 140°C for at least 24 h before use. Injections (30–35) of organic com-
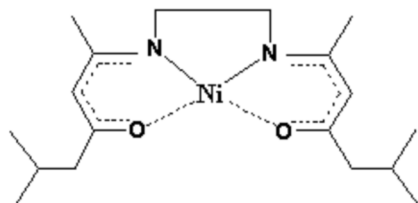
pounds were made on each to deactivate the columns before measuring the analytical responses. Peak identification was based on the retention time of individual compounds and by spiking the mixture in a sequence. The compounds were mixed by equal volumes, and 1 µL of the mixture was eluted at optimized GC conditions for each separation. All chemicals used were of GR-grade (Merck) or puriss-grade (Fluka, Buchs, Switzerland). The retention time transformations (Xa) and two-dimensional chromatographic plots were carried out as described by Steuer et al. (27) and Slonecker et al. (28) by the following equation:

$$Xa = \frac{Rt_i - Rt_o}{Rt_f - Rt_o} \qquad \text{Eq 1.}$$

where Rt_i is the solute retention time, Rt_f is the retention time of the longest eluting component common to both stationary phases (2-nitrotoluene), and Rt_o is the retention time of unretained component (methane).

The Gibbs free energy (-ΔG) at 70, 80, 90, and 100ºC were calculated from the relation:

$$-\Delta G = RT\ln K_m \qquad \text{Eq. 2}$$

where R is the gas constant (1.987 Kcal/mol), T is the absolute temperature, and $\ln K_m$ is the natural log of the stability constant K_m. The enthalpy (-ΔH) was calculated by plotting 1000/T versus $\ln K_m$ and multiplying the slope sensitivity by R. The entropy was calculated by multiplying the intercept by R. The stability constant K_m of the molecular complex between the δ donor molecule and 5% nickel chelate with 3% OV1 was calculated as reported (11). The stability constant K_m of molecule complex between δ-molecule and 5% nickel chelate with 3% OV1 was calculated from the relationship.

$$R' = \frac{t \times t^{ox}}{t^x \times t^o} - 1 = K_m \times m_A \qquad \text{Eq. 3}$$

Figure 1. Structural diagram of nickel(II) chelate of H_2IVA_2en.

where R' is the ratio of the relative retention of the solute on the mixed stationary phase containing 5% nickel chelate and the column with the 3% OV-1, t is the corrected net peak maximum retention time of the δ-donor solute on the column with nickel chelate, t^o is the corrected net peak maximum retention time of the δ-donor on the column with OV1, t^x is the corrected net peak maximum retention time of non-complexing inert reference standard on column with nickel chelate, and t^{ox} is the corrected net peak maximum retention time of non complexing inert reference standard on a column with OV1 (natural gas). The symbol m_A stands for molar concentration. For 5% nickel chelate IVA_2enNi in 3% OV1 on Chromosorb, its value is 0.132 mole/Kg. The stability constant K_m was calculated at temperature 70, 80, 90, and 100ºC on mixed stationary phase containing 5% nickel chelate and 3% OV1 (w/w).
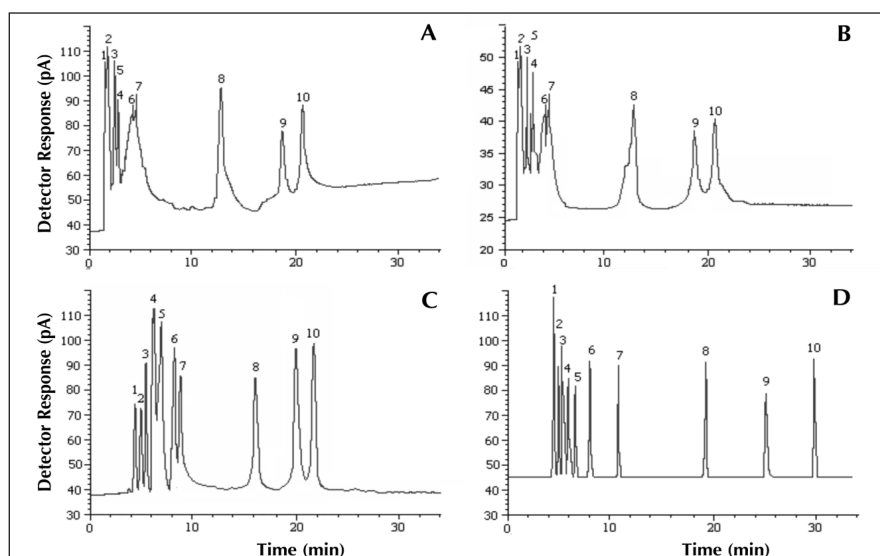

Figure 2. GC separation of mixed alcohols on packed glass columns (2 m × 3 mm i.d.) Chromosorb G/NAW 60–80 mesh size: (A) 3% OV1, (B) 3% OV1 + 5% IVA_2en, (C) 3% OV1 + 5% IVA_2enCu, and (D) 3% OV1 + 5% IVA_2enNi. Peak numbers: 1, Methanol; 2, 2-propanol; 3, 1-propanol; 4, 2-butanol; 5, crotyl alcohol; 6, isoamyl alcohol; 7, 1-pentanol; 8, 1-hexanol; 9, 1-heptanol; and 10, 2-octanol. Conditions: Column temperature 70°C, injection port temp 110°C, detection oven temperature 150ºC, N_2 flow rate 15 mL/min, FID detection.

Table I. Comparative Data of Adjusted Retention Times (t_R'), Kovats Retention Indices (RI), and Retention Time Transformations (Xa) on the Columns 3% OV1 and 3% OV1 + 5% IVA$_2$enNi (w/w)

No	Compound Name	3% OV1 + 5% IV A2enNi			3% OVI		
		t_R' 70°C	RI 70°C	Xa	t_R' 70°C	RI 70°C	Xa
1	Hexane	3.09	600	0.047	1.17	600	0.022
2	Heptane	5.20	700	0.078	2.24	700	0.042
3	Octane	8.47	800	0.127	4.47	800	0.085
4	Nonane	13.69	900	0.206	9.55	900	0.182
5	Decane	23.19	1000	0.349	21.38	1000	0.408
6	Acetonitrile (Cyanomethane)	2.90	588	0.044	0.91	563	0.017
7	Nitromethane	4.23	666	0.064	1.51	632	0.029
8	1,2-Dichloroethane	3.96	652	0.060	1.39	621	0.026
9	2,2-Dimethoxypropane	5.74	729	0.086	2.62	707	0.049
10	2-Nitropropane	7.07	772	0.106	3.68	753	0.070
11	Dioxane	6.14	743	0.092	2.65	709	0.0313
12	Benzene	4.34	671	0.065	1.53	634	0.029
13	Toluene	6.59	758	0.099	3.31	738	0.063
14	o-Xylene	11.76	877	0.177	8.14	861	0.155
15	Mesitylene (1,3,5-trimethyl benzene)	19.13	978	0.288	14.27	937	0.272
16	o-Toluidine (2-Aminotoluene)	45.98	1159	0.692	30.40	1039	0.580
17	2-Nitrotoluene	66.44	1235	1.000	48.96	1104	1.000
18	2-Pyridine Carboxaldehyde	19.93	986	0.300	13.41	928	0.256
19	Pyridine	6.20	745	0.093	2.82	717	0.053
20	2-Picoline (2-Methyl-pyridine)	8.81	818	0.133	4.16	769	0.079
21	4-Picoline (4-Methyl-pyridine)	11.30	869	0.170	6.51	830	0.124
22	2,6-Lutidine	12.49	890	0.188	7.53	850	0.143
23	3-Picoline (3-Methyl-pyridine)	13.32	903	0.200	9.68	884	0.184
24	Aniline	24.45	1029	0.368	17.24	963	0.352
25	Piperidine (Hexahydropyridine)	7.27	778	0.109	3.28	737	0.062
26	Methanol	3.29	614	0.049	0.79	544	0.015
27	2-Propanol	3.71	639	0.045	1.10	589	0.021
28	1-Propanol	4.29	669	0.056	1.76	653	0.033
29	2-Butanol	4.75	690	0.071	2.12	678	0.040
30	Tert-butanol (2-methyl-2-propanol)	3.31	615	0.050	0.88	559	0.016
31	Isoamyl alcohol (3-Methyl-1-butanol)	6.90	767	0.102	3.29	738	0.062
32	1-Pentanol	10.03	844	0.151	4.01	765	0.076
33	1-Hexanol	18.20	968	0.274	11.56	908	0.174
34	1-Heptanol	24.12	1026	0.363	17.59	965	0.335
35	2-Octanol	28.77	1062	0.433	20.45	986	0.390
36	Crotyl alcohol (2-Butenol)	5.39	716	0.081	2.02	672	0.038
37	2-Butanone	2.78	579	0.042	0.54	493	0.010
38	3-Methyl-2-Butanone	4.96	699	0.075	2.16	681	0.041
39	3,3-Dimethyl-2-butanone	5.58	723	0.083	2.81	716	0.053
40	4-Methyl-2-Pentanone	5.71	728	0.086	2.82	717	0.054
41	Mesityl oxide (4-methyl-3-penten-2-one)	7.63	788	0.115	4.69	786	0.089
42	Cyclohexanone	12.03	882	0.181	8.19	861	0.156
43	Benzaldehyde	25.11	1034	0.378	16.26	955	0.245
44	Diethyl Ether	2.69	572	0.040	0.62	512	0.012
45	Propylpropanoate	7.53	785	0.113	4.27	773	0.081
46	Ethyltrifluoroacetate	2.42	560	0.036	0.57	500	0.011

Results and Discussion

The reagent H$_2$IVA$_2$en and its formed nickel and copper chelates were examined on FT-IR, and the spectra obtained agreed with reported values (24). The preparation of mixed stationary phases containing 3%, 5%, and 8% (w/w) metal chelates together with 3% OV1 were examined, but some difficulties were observed in uniformly coating 8% metal chelates on the Chromosorb and some crystals of metal chelates in dried material were detected. 5% gave reproducible results with the ease of preparation of stationary phase and was selected as has been observed earlier (16). The columns only with 5% IVA$_2$enNi or IVA$_2$enCu were not prepared because of poor response observed with similar columns (16). Thermogravimetry of mixed stationary phase containing 5% IVA$_2$enNi and 3% OV1 indicated weight loss from 190ºC and 5% weight loss by 350°C corresponding to metal chelates followed by 3% up to 450°C due to OV1.

Therefore, temperature for conditioning of the column was fixed at 140ºC. Saturated hydrocarbons, aromatic hydrocarbons, heteroaromatics, alcohols, ketones, aldehydes, esters, ethers, nitro-, amino-, and chloro compounds were examined on the columns (a) 3% OV1, (b) 3% OV1 + 5% IVA$_2$en, (c) 3% OV1 + 5% IVA$_2$enCu, and (d) 3% OV1 + 5% IVA$_2$enNi on Chromosorb packed in the columns. The column containing 3% OV1 + 5% IVA$_2$enNi gave better results (Figure 2A–2D), so it was selected. Column (a) containing 3% OV1 was used as a reference. Isothermal elution was carried out for all the compounds (46) investigated. Retention time, capacity factor, peak asymmetry, theoretical plates, and resolution factors (Rs) were calculated on the computer with CSW17 software. Saturated long chain hydrocarbons C$_6$–C$_{10}$ were used onto each of the column, and logarithm of the adjusted retention time was plotted against the carbon number × 100. Linear correlations and coefficient of determination (R^2) were obtained from five calibrators: 0.9994 and $y = 0.0021x – 0.772$ and (2) 0.997 and $y = 0.0032x – 1.844$ for columns 3% OV1 + 5% IVA$_2$enNi and 3% OV1 on Chromosorb, respectively. The curves were used to calculate Kovats retention indices (RI). It was observed that RI values for aromatic hydrocarbons, alcohols, aldehydes, ketones, and heteroaromatics increased on mixed stationary phase of 3% OV1 + 5% IVA$_2$enNi as compared to 3% OV1 (Table I). The alcohols indicated peak tailing on the column with 3% OV1, but some improvement was observed on the mixed stationary phase of 3% OV1 + 5% IVA$_2$enNi. A mixture of ten alcohols

was better separated on the column packed with mixed stationary phase 3% OV1 + 5% IVA$_2$enNi than on the column packed with 3% OV1 on Chromosorb under the same operating conditions (Figure 2A, 2D). The chromatographic elution order of the alcohols was essentially identical on both the columns;

Table II. Values of Stability Constants (lnK$_m$) Against Adjusted Retention Times (tR') on Mixed Stationary Phase*

S/No[†]	lnKm 70°C	lnKm 80°C	lnKm 90°C	lnKm 100°C
1	3.15	2.69	2.35	1.95
2	3.67	3.21	2.88	2.51
3	4.16	3.74	3.38	2.97
4	4.64	4.25	3.91	3.54
5	5.17	4.67	4.37	3.94
6	3.13	2.64	2.29	1.88
7	3.47	3.01	2.64	2.24
8	3.42	2.95	2.55	2.14
9	3.77	3.32	2.94	2.54
10	3.98	3.45	3.09	2.71
11	3.84	3.39	2.98	2.61
12	3.49	3.08	2.65	2.29
13	3.89	3.47	3.02	2.65
14	4.52	4.06	3.58	3.15
15	4.98	4.43	3.98	3.51
16	5.85	5.41	4.95	4.52
17	6.22	5.81	5.39	5.01
18	5.02	4.59	4.15	3.74
19	3.87	3.41	2.97	2.61
20	4.20	3.71	3.32	2.89
21	4.48	3.99	3.48	3.02
22	4.53	4.07	3.66	3.30
23	4.61	4.18	3.74	3.32
24	5.22	4.82	4.28	3.88
25	4.01	3.54	3.12	2.78
26	3.22	2.79	2.35	1.98
27	3.34	2.91	2.44	2.01
28	3.48	3.08	2.61	2.19
29	3.58	3.11	2.72	2.31
30	3.22	2.80	2.35	1.94
31	3.96	3.48	3.07	2.68
32	4.33	3.89	3.45	3.09
33	4.93	4.48	4.08	3.65
34	5.21	4.77	4.31	3.94
35	5.38	4.96	4.47	4.05
36	3.71	3.28	2.85	2.44
37	3.05	2.66	2.24	1.89
38	3.63	3.21	2.78	2.40
39	3.74	3.29	2.88	2.49
40	3.77	3.35	2.92	2.55
41	4.06	3.64	3.22	2.82
42	4.51	4.08	3.62	3.22
43	5.25	4.81	4.37	3.96
44	3.01	2.58	2.08	1.67
45	4.04	3.60	3.21	2.79
46	2.91	2.48	2.06	1.71

* K$_m$ = t_R'/mA (mA = 0.132 mol/Kg). Unit of Km = min. Kg/mol.
† Compound names and numbers are the same as in Table I.

however, modification of stationary phase with nickel (II) chelate increased the column selectivity (14). 3-Methyl-1-butanol and 1-pentanol, which are not separated on 3% OV1, could be completely separated on mixed stationary phase 3% OV1 + 5% IVA$_2$enNi (w/w). The range of Kovats retention indices observed on 3% OV1 increased from 544–986 to 614–1062 on 3% OV1 + 5% IVA$_2$enNi (w/w) as mixed stationary phase. The selectivity of the separation of the alcohol may be due to the electrostatic interactions and capabilities of complexation through donor-acceptor mechanism at the surface of the mixed stationary phase. A 15-component mixture of organic compounds better separated on mixed stationary phase of a 3% OV1 + 5% IVA$_2$enNi (w/w) than on 3% OV1 (Figure 3A–3B). The separations of compounds 4, 5, 6, 11, and 12 were particularly better separated on mixed stationary phase. The order of elution on mixed stationary phase also slightly differed: aniline eluted after decane on 3% OV1 + 5% IVA$_2$enNi (w/w) stationary phase, but aniline eluted before decane on 3% OV1 stationary phase possibly because of the complex formation of aniline with the electron deficit part of the nickel complex. The capacity factor (k') and the number of theoretical plates (N)/column observed on 3% OV1 within 10.68–59.37 k' and 379–1642 N increased to 16.23–118.41 k' and 3517–4712 N on mixed stationary phase of 3% OV1 + 5% IVA$_2$enNi (w/w) under the same conditions. The resolution factor (Rs) between adjacent peaks obtained on 3% OV1 on Chromosorb within 0.53–3.72 Rs increased to 1.17–7.91 Rs on mixed stationary phase of 3% OV1 + 5% IVA$_2$enNi. The better
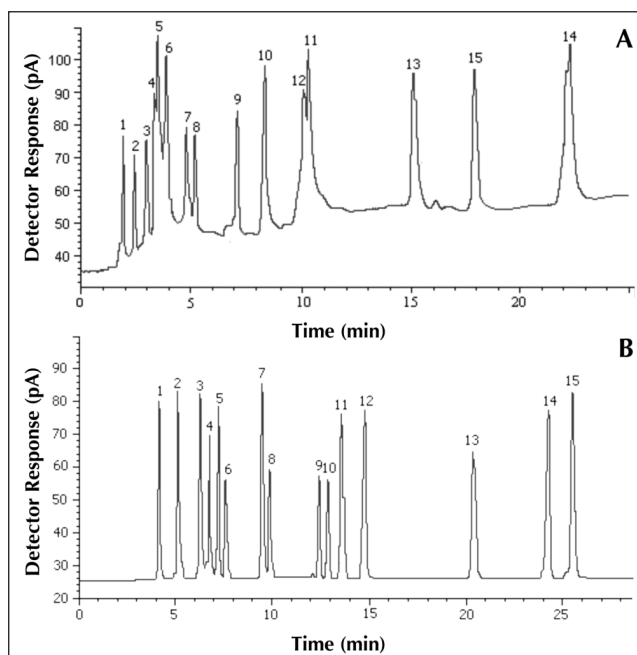

Figure 3. GC separation of mixed alkanes, aromatics and heteroaromatics on packed glass columns (2 m × 3 mm i.d.) Chromosorb G/NAW 60–80 mesh size: (A) 3% OV1 on with theoretical plates (N) = 1, 615; 2, 558; 3, 780; 4, 541; 5, 379; 6, 736; 7, 505; 8, 487; 9, 1082; 10, 1264; 11, 921; 12, 769; 13, 1371; 14, 1642; and 15, 1394. (B) 3% OV1 + 5% IVA$_2$enNi with theoretical plates (N) = 1, 3861; 2, 3922; 3, 3517; 4, 3679; 5, 4557; 6, 4213; 7, 4611; 8, 4401; 9, 4453; 10, 4319; 11, 4533; 12, 4701; 13, 4712; 14, 4482; and 15, 4671. 1, Hexane; 2, 1,2-dichloroethane; 3, heptane; 4, 2,2-dimethoxypropane; 5, pyridine; 6, toluene; 7, octane; 8, 2-picoline; 9, 4-picoline; 10, o-xylene; 11, 2,6-lutidine; 12, nonane; 13, mesitylene; 14, decane; and 15, aniline. Conditions are the same as Figure 2.

separation may be due to intermolecular interaction of the separated compounds on 5% nickel chelate solution with 3% OV1 (w/w) (3). The reproducibility of the separation was checked on the mixed stationary phase in terms of retention time and peak area ($n = 5$). The relative standard deviation (RSD) obtained was within 1.2–1.9% and 2.7–3.2%, respectively. Similarly, a mixture of 21 compounds comprising alkanes, aromatic hydrocarbons, heteroaromatics, alcohols, ketones, esters, and ethers again separated better on mixed stationary phase 3% OV1 + 5% IVA$_2$enNi than 3% OV1 (Figure 4A–4B). The Rs observed within adjacent peaks on 3% OV1 was within 0.48–3.97 Rs but increased to 1.31–8.02 Rs on mixed stationary phase 3% OV1 + 5% IVA$_2$enNi. Repeatability of the separation ($n = 5$) on mixed stationary phase was again checked in terms of retention time and peak area. The RSD was observed within 1.5–2.1% and 1.9–2.8%, respectively.

The adjusted retention times of the given analyte was divided by the adjusted retention time of the most retained analyte (2-nitrotoluene) on both the stationary phases. This ratio was calculated on 3% OV1 and 3% OV1 + 5% IVA$_2$enNi as mixed stationary phase (Table I). The ratios on the mixed stationary phase were plotted on the y-axis and those on 3% OV1 on the x-axis. The plot of all 46 compounds showed R^2 of 0.9617 (Figure 5), which is indicative of some positive correlation between both the columns. However, R^2 of 13 and 22 selected compounds comprising mixtures of aliphatic, aromatic hydrocarbons, heteroaromatics, heterocyclic, alcohols, ketones, and esters with aliphatic, aromatic hydrocarbons, nitrite, nitro, chloro compounds, ethers, heteroaromatics, alcohols, ketones, and esters of indicated values of 0.4934 and 0.5530, respectively (Figure 6A–6B). The results of R^2 lead to suggest some difference in the interaction between the two stationary phases for selective solutes. Stability constant K$_m$, -ΔH, -ΔS, and -ΔG of the complexation reaction of the 5% nickel chelate dispersed with 3% OV1 were calculated for all the 46 compounds investigated including aromatic hydrocarbons, heteroaromatics, alcohols, ketones, ester, and amines. The values of lnK$_m$ are seen to be within 1.71–6.22 (Table II). The plots of 1000/T against lnK$_m$ indicate a linear relationship with R^2 in the range 0.9956–0.9999 (four-point calibration). Heteroaromatics gave values of -ΔH in the range of 10.44–12.43 Kcal/mol as compared to 10.25–12.37 Kcal/mol for aromatic hydrocarbons. The alcohols indicate values of -ΔH in the range of 10.58–11.39 Kcal/mol as compared to 9.07–10.15 Kcal/mol for alkanes. Parallel results are obtained for –ΔS and -ΔG in the range of 17.65–27.33 Kcal/mol and 1.23–4.24 Kcal/mol, respectively (Table III). The values of -ΔG increased in n-alkanes and n-alcohols with an increase in carbon number, which may be due to non-specific interactions on the

Table III. Calculations of Thermodynamic Parameters of Organic Compounds on Mixed Stationary Phase Comtaining 3% OV1 + 5% IVA₂enNi on Chromosorb G/NAW 60–80 mesh size.

S/No	Compound Name	-ΔG 70°C Kcal/mol	-ΔG 80°C Kcal/mol	-ΔG 90°C Kcal/mol	-ΔG 100°C Kcal/mol	-ΔH Kcal/mol	-ΔS Kcal/mol
1	Hexane	2.15	1.88	1.67	1.44	10.02	22.99
2	Heptane	2.50	2.25	2.07	1.86	9.70	21.02
3	Octane	2.84	2.63	2.43	2.20	9.99	20.85
4	Nonane	3.16	2.98	2.82	2.64	9.25	17.76
5	Decane	3.53	3.27	3.15	2.92	10.15	19.37
6	Acetonitrile (Cyanomethane)	2.11	1.85	1.65	1.39	10.43	24.23
7	Nitromethane	2.36	2.11	1.91	1.66	10.33	23.23
8	1,2-Dichloroethane	2.32	2.07	1.87	1.58	10.79	24.66
9	2,2-Dimethoxypropane	2.57	2.32	2.12	1.88	10.18	22.70
10	2-Nitropropane	2.71	2.42	2.22	2.00	10.62	23.12
11	Dioxane	2.62	2.37	2.15	1.93	10.43	22.80
12	Benzene	2.38	2.16	1.91	1.69	10.25	22.94
13	Toluene	2.66	2.43	2.17	1.96	10.61	23.18
14	o-Xylene	3.06	2.84	2.58	2.33	11.67	25.03
15	Mesitylene (1,3,5-trimethyl benzene)	3.39	3.10	2.87	2.60	12.37	26.18
16	o-Toluidine (2-Aminotoluene)	3.91	3.79	3.57	3.35	11.31	21.33
17	2-Nitrotoluene	4.24	4.07	3.88	3.71	10.30	17.65
18	2-Pyridine Carboxaldehyde	3.42	3.22	2.97	2.77	10.88	21.73
19	Pyridine	2.62	2.39	2.14	1.93	10.74	23.64
20	2-Picoline (2-Methyl-pyridine)	2.86	2.60	2.39	2.14	10.99	23.71
21	4-Picoline (4-Methyl-pyridine)	3.01	2.79	2.51	2.23	12.43	27.33
22	2,6-Lutidine	3.10	2.85	2.64	2.44	10.44	21.45
23	3-Picoline (3-Methyl-pyridine)	3.14	2.93	2.69	2.46	10.96	22.76
24	Aniline	3.55	3.38	3.08	2.87	11.59	23.36
25	Piperidine (Hexahydropyridine)	2.73	2.48	2.25	2.06	10.47	22.58
26	Methanol	2.19	1.95	1.67	1.46	10.58	24.45
27	2-Propanol	2.27	2.04	1.76	1.49	11.34	26.38
28	1-Propanol	2.37	2.16	1.88	1.62	11.03	25.19
29	2-Butanol	2.44	2.18	1.96	1.71	10.68	24.05
30	Tert-butanol (2-methyl-2-propanol)	2.19	1.96	1.67	1.43	10.91	25.37
31	Isoamyl alcohol (3-Methyl-1-butanol)	2.70	2.44	2.21	1.98	10.82	23.69
32	1-Pentanol	2.95	2.72	2.41	2.29	10.59	22.26
33	1-Hexanol	3.36	3.14	2.94	2.70	10.78	21.63
34	1-Heptanol	3.55	3.34	3.11	2.92	10.86	21.32
35	2-Octanol	3.66	3.48	3.22	3.00	11.39	22.47
36	Crotyl alcohol (2-Butenol)	2.52	2.30	2.07	1.80	10.78	24.04
37	2-Butanone	2.47	1.86	1.61	1.40	9.92	22.84
38	3-Methyl-2-Butanone	2.80	2.25	2.00	1.77	10.48	23.32
39	3,3-Dimethyl-2-butanone	2.55	2.30	2.07	1.84	10.58	23.43
40	4-Methyl-2-Pentanone	2.57	2.35	2.10	1.89	10.40	24.04
41	4-Methyl-3-penten-2-one	2.76	2.55	2.32	2.09	10.53	22.60
42	Cyclohexanone	3.07	2.86	2.61	2.38	11.01	23.12
43	Benzaldehyde	3.78	3.37	3.15	2.93	10.96	21.50
44	Diethyl Ether	2.05	1.81	1.50	1.23	11.49	27.49
45	Propylpropanoate	2.75	2.52	2.30	2.06	10.53	22.65
46	Ethyltrifluoroacetate	1.98	1.74	1.48	1.26	10.23	24.05

nickel (II) chelate-loaded support by induced polarizability. The stability constant (lnK_m) reflects the free energy (-ΔG) change of the species involved in the association process (11), and parallel results of lnK_m and -ΔG were observed. The negative change in entropy (-ΔG) is consistent with association equilibrium, as individual vibrational and rotational freedom is lost during association.

Conclusion

The mixed stationary phase of 3% OV1 + 5% IVA$_2$enNi (w/w) on Chromosorb G/NAW 60–80 mesh size gave better resolution for alcohols, ketones, esters, aromatic, and heteroaromatics than 3% OV1 on the same support under the same operating conditions. A two-dimensional plot of retention time transformation on stationary phase 3% OV1 against 3% OV1 + 5% IVA$_2$enNi (w/w) for the selected compounds indicated some difference in interaction between both the stationary phases. Electrostatic interaction and capability via donor-acceptor mechanism are indicated on the surface of mixed stationary phases.
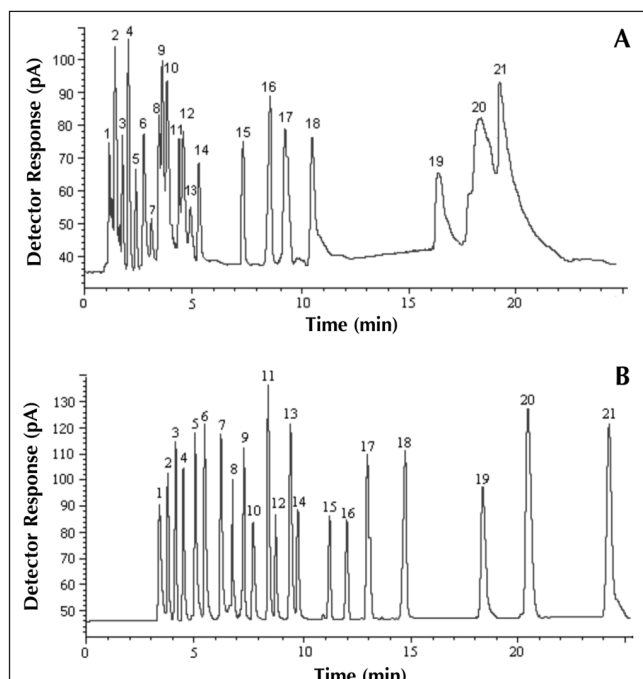
Figure 4. Chromatogram of organic compounds on packed glass columns (2 m × 3 mm i.d.) Chromosorb G/NAW 60–80 mesh size: (A) 3% OV1 with theoretical plates (N) = 1, 257; 2, 651; 3, 429; 4, 813; 5, 278; 6, 546; 7, 176; 8, 459; 9, 423; 10, 531; 11, 387; 12, 506; 13, 140; 14, 578; 15, 743; 16, 923; 17, 1145; 18, 1104; 19, 784; 20, 962; and 21, 1381. (B) 3% OV1 + 5% IVA$_2$enNi with theoretical plates (N) = 1, 998; 2, 2057; 3, 3274; 4, 2978; 5, 4117; 6, 3145; 7, 3396; 8, 3252; 9, 4208; 10, 4112; 11, 2615; 12, 3472; 13, 4365; 14, 3915; 15, 4431; 16, 4148; 17, 3845; 18, 4482; 19, 4321; 20, 4506; and 21, 4241. 1, Ethyltrifluoroacetate; 2, 2-butanone; 3, hexane; 4, 1-propanol; 5, benzene; 6, 2-butanol; 7, heptane; 8, 2,2-dimethoxypropane; 9, pyridine; 10, piperidine; 11, propylpropanoate; 12, 1-pentanol; 13, 2-picoline; 14, octane; 15, 4-picoline; 16, 2,6-lutidine; 17, 3-picoline; 18, nonane; 19, 1-heptanol; 20, 2-octanol; and 21, decane. Conditions: Column temperature 90ºC, injection port temperature 115ºC, detection oven temperature 150ºC, N$_2$ flow rate 15 mL/min, detection FID.
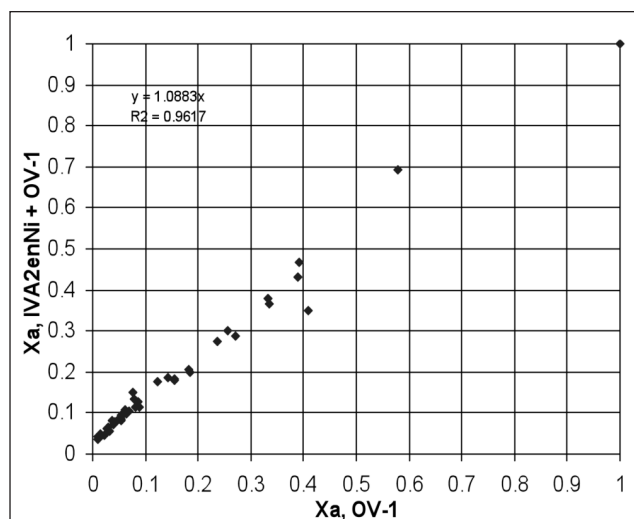

Figure 5. Two-dimensional plot of retention time transformation (Xa) of the organic compounds on stationary phase 3% OV1 versus 3% OV1 + 5% IVA$_2$enNi.
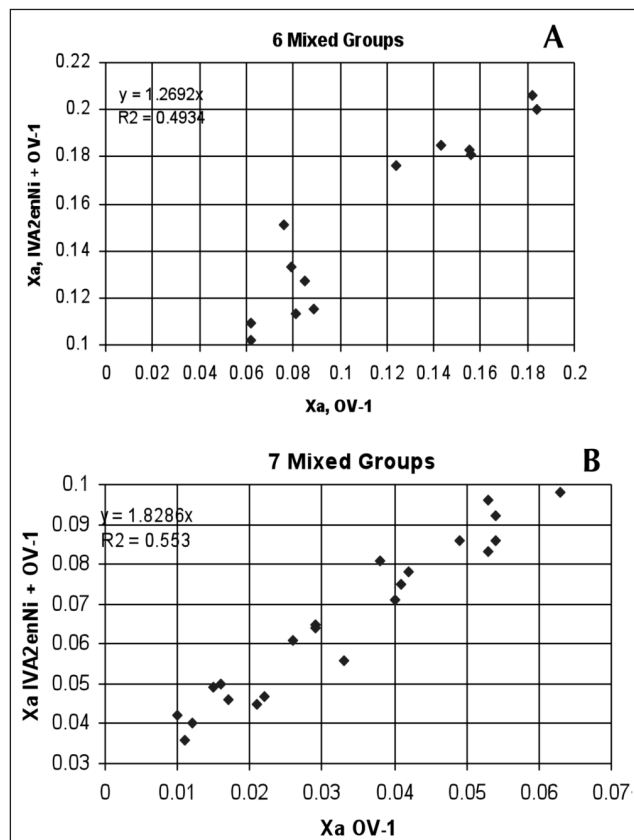

Figure 6. (A) Two-dimensional plot of retention time transformation (Xa) on stationary phase 3% OV1 versus 3% OV1 + 5% IVA2enNi for the compounds: 1, Octane; 2, nonane; 3, o-xylene; 4, 2-picoline; 5, 4-picoline; 6, 2,6-lutidine; 7, 3-picoline; 8, piperidine; 9, isoamyl alcohol; 10, 1-pentanol; 11, mesityl oxide; 12, cyclohexanone; and 13, propylpropanoate. (B) Two-dimensional plot of retention time transformation (Xa) on stationary phase 3% OV1 versus 3% OV1 + 5% IVA2enNi for the compounds: 1, Hexane; 2, heptane; 3, acetonitrile; 4, nitromethane; 5, 1,2-dichloromethane; 6, 2,2-dimethoxypropane; 7, dioxane; 8, benzene; 9, toluene; 10, pyridine; 11, methanol; 12, 2-propanol; 13, 1-propanol; 14, 2-butanol; 15, tert-butanol; 16, crotyl alcohol; 17, 2-butanone; 18, 3-methyl-2-butanone; 19, 3,3-dimethyl-2-butanone; 20, 4-methyl-2-pentanone; 21, diethyl ether; and 22, ethyltrifluoroacetate.

Acknowledgment

References

1. W.J. Kowalski. Application of the solvation parameter model to the characterization of gas chromatographic stationary phases containing tris(3-(trifluoromethyl-hydroxymethylene)camphorato) derivatives of lanthanides. *J. Chromatogr.* **793:** 390–396 (1998).
2. Yu. G. Slizhov and M.A. Gavrilenko. Gas-chromatographic properties of Silochrom with has surface to bush-hammer of nickel dimethylglyoximate and acetylacetonate complex. *J. Anal. Chem. (Transl. of Zh. Analitiche Skoi Khimi)* **56:** 538–541 (2001).
3. Yu. G. Slizhov and M. A. Gavrilenko. Complexation with metal chelates at the phase interface in gas chromatography. *Russian J. Coord. Chem. (Transl. from Koordinatsionnaya khimiya* **28:** 736–752 (2002).
4. V. Schurig. Practice and Theory of Enantioselective Complexation Gas Chromatography. *J. Chromatogr A* **965:** 315–356 (2002).
5. I. Rykowska and W. Wasiak. Comparative Studies of Gas Chromatographic Properties of New Packings with Chemically Bonded Complexes. *J. Chromatogr. Sci.* **39:** 313–320 (2001).
6. W. Wasiak, I. Rykowska, and A. Voelkel. Ketoimino groups as silica surface modifiers. *J. Chromatogr. A* **969:** 133–141 (2002).
7. I. Rykowska and W. Wasiak. Gas chromatography silica packings with chemically bonded complexes of Cu(II) and Cr(III). *Anal. Chim. Acta* **451:** 271–278 (2002).
8. V. Schurig, H. Laderer, D.Wistuba, and A. Mosandi. Enantiomer Separation of n-Alkenyl-3-Acetates and of Alkyl Substituted 1,3-Dioxolanes by Complexation Gas Chromatography. *J. Essent. Off. Res.* **1:** 209–215 (1989).
9. V. Schurig, W. Bürkle, K. Hintzer, and R. Weber. Evaluation of Nickel(II) bis(a-(heptafluorobutanoyl)-terpeneketonates) as Chiral Stationary Phases for the Enantiomer Separation of Alkylsubstituted Cyclic Ethers by Complexation Gas Chromatography. *J. Chromatogr.* **475:** 23–28 (1989).
10. V. Schurig, J. Ossig, and R. Link. Evidence for a temperature dependent reversal of enantioselectivity in complexation gas chromatography on chiral phases. *Angew. Chem.* **101:** 23–29 (1989).
11. J. Maslowska and G. Bazylak. Gas Chromatographic Study of the Axial Ligand Associations of Some Tetradentate Schiff Base Nickel(II) and Copper(II) Chelates. *Pol. J. Chem.* **62:** 331–342 (1988).
12. J. Maslowska and G. Bazylak, Retention of Some Heterocyclic Amines on Mixed Stationary Phases Containing Nickel(II) Schiff Base Chelates. Collect. *Czech: Chem. Comm.* **54:** 1530–1537 (1989).
13. J. Maslowska and G. Bazylak. Tetradentate β-Ketoamine Nickel(II) Complexes As The Electron-Acceptor Stationary Phases In Gas Chromatography. *Zeszyty Naukowe Politechniki Lodzkiej (Technologia I Chemia Spozywcza)* **540:** 37–46 (1990).
14. J. Maslowska and G. Bazylak. Chromatographic Study of Donor-Acceptor Complexes Associations Between Aliphatic Amines Or Alcohols And Tetradentate β-Ketoamine Nickel(II) Chelates. *J. Chromatogr.* **298:** 211–216 (1984).
15. J. Maslowska and G. Bazylak. Nickel(II) Schiff Base Complexes As Stationary Phases In Gas Chromatography. *Acta Universitatis Lodziensis Folia Chim.* **8:** 15–22 (1988).
16. M.Y. Khuhawar, A. Ashfaq Memon, and M.I. Bhanger. Nickel(II) chelates of some tetradentate Schiff bases as stationary phases for gas chromatography. *J. Chromatogr. A* **715:** 366–371 (1995).
17. M.Y. Khuhawar, A. Ashfaq Memon, and M.I. Bhanger. Copper(II) Chelates of Some Tetradentate Schiff Bases as Stationary Phases for Gas Chromatography. *J. Chem. Soc. Pak.* **18:** 276–281 (1996).
18. Abdul J. Laghari, M.Y. Khuhawar, and Zeenat M. Ali. Palladium(II) chelate of tetradentate Schiff base as mixed stationary phase for gas chromatography. *J. Sep. Sci.* **30:** 359–366 (2007).
19. V. Schurig. Resolution of Enantiomers and Isotopic Compositions by Selective Complexation Gas Chromatography on Metal Complexes. *Chromatographia* **13:** 263–270 (1980).
20. V. Schurig. Relative Stability Constants of Olefin-Rhodium(I) vs. Olefin-Rhodium(II) Coordination as Determined by Complexation Gas Chromatography. *Inorg. Chem.* **25:** 945–949 (1986).
21. C.D. Keller and T.F. Bidleman. Collection of airborne polycyclic aromatic hydrocarbons and other organics with a glass fiber filter-polyurethane foam system. *Atmos. Environ.* **8:** 837–845 (1984).
22. Yu. G. Slizhov, M.A Gavrilenko, and A. A. Borbolin. Chromatographic Behavior of Silica Gel Modified with Copper, Nickel, and Europium Chelates. *Zh. Fiz. Khim.* **73:** 1828–1831 (1999).
23. E. Kizza. Determination of acetylacetone and alcohols in titanium chelates. *Anal. Chim. Acta* **281:** 385–389 (1993).
24. L.F. Lindoy, W.E. Moody, and D. Taylor. Mass Spectral and Nuclear Magnetic Resonance (1H and 13C) Study of Metal Complexes of Quadridentate Ligands Derived from 1,2-Diaminoethane and Substituted -Ketones; X-Ray Structure of N,N'-Ethylenebis(5,5-dimethyl-4-oxohexan-2-iminato)nickel(II). *Inorg. Chem.* **16:** 1962–1968 (1977).
25. J.T. Adams and C.R. Hauser. The Acylation of Methyl Ketones with Aliphatic Esters by Means of Sodium Amide. Synthesis of β-Diketones of the Type RCOCH2COR. *J. Am. Chem. Soc.* **66:** 1220–1223 (1945).
26. R.L. Grob, Modern practice of gas chromatography, John Wiley & Sons, NewYork, 1977, p 143.
27. W. Steuer, I. Grant, and F. Erni. Comparison of high-performance liquid chromatography, supercritical fluid chromatography and capillary zone electrophoresis in drug analysis. *J. Chromatogr.* **507:** 125–140 (1990).
28. P. Slonecker, X. Li, T.H. Ridgway, and J.G. Dorsey. Informational Orthogonality of Two-Dimensional Chromatographic Separations. *Anal. Chem.* **68:** 682–689 (1996).