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GAS-SOLID CHROMATOGRAPHY ON CATION-EXCHANGE RESINS

DARC TOPOLOGICAL ANALYSIS OF THE BEHAVIOR OF ALKENES ON NICKEL IONS*

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SUMMARY

Retention indices of 44 alkenes in gas-solid chromatography were determined on the Ni^{2+} form of a cation-exchange resin and on the corresponding unsulfonated copolymer matrix. The Ni^{2+} form was prepared from a sulfonated Porapak Q ethylvinylbenzene-divinylbenzene copolymer. DARC topological analysis (DTA) was applied to the Kováts retention indices determined at 175°C. DTA helps to delineate the evolution of specific π bond- Ni^{2+} ion interactions with progressive variations of the structural effects of the alkenes.

INTRODUCTION

Gas-solid chromatography (GSC) on metal-containing surfaces is of continuing interest, particularly for the analysis of unsaturated hydrocarbons^{1,2}. Such analyses are selective because of specific interactions due to the possibility of formation of charge-transfer complexes³. Attention has also been drawn to the specific interactions between olefins and cations in gas-liquid chromatography when solutions of different salts or metal complexes are used⁴. The high selectivity of stationary phases containing silver nitrate, particularly efficient for the separation of internal olefinic isomers, is well known⁵. Different complexes of rhodium have also been used^{6,7}. However, GSC has the advantage of enabling one to work at relatively high temperatures, which significantly reduces the time of analysis. References to the use of

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metal-containing packings in GSC are numerous. Different cationic forms of zeolites¹ and ion-exchange resins⁶ have been used for the separation of various types of organic compounds.

The recent development of data processing methods applicable to chromatography, including topological analysis of structural effects^{9,10} and factor analysis of trends¹¹, has led to better quantification of these specific interactions¹²⁻¹⁴. Such information is useful both for improving the rapid analysis of hydrocarbons and for a physico-chemical understanding of catalysis. Indeed, similarities between chromatographic and catalytic parameters, such as the type of support and its effects on adsorbates, are evident. The reactivity of alkenes in catalysis and their chromatographic adsorption on metal-ion-containing surfaces is governed by the strength of the specific interaction between the carbon-carbon double bond and the cation. This interaction is dependent on the nature of the cation, its environment and the structural environment of the carbon-carbon double bond. An example of this dependence is found in the work of Jacobson and Pittman¹⁵, who used polystyrene-divinylbenzene resin anchored nickel complexes for selective oligomerizations and hydrogenations. McMunn *et al.*¹⁶ studied the influence of the environment of the catalyst sites on the selectivity for various nickel and platinum forms as homogeneous and heterogeneous catalysts. Steric control of the alkyl group can also govern the selectivity in metathesis^{17,18}. Furthermore, complementary information dealing with the possibilities of approach of alkene molecules at the surface of a catalyst can be deduced from their non-specific adsorption in GSC on graphitized carbon black¹⁹.

Within the framework of our study of GSC on cation-exchange resins^{8,20} we have recently reported on trends in the selectivity of various hydrocarbons with the help of correspondence factor analysis (CFA)¹¹. The role played by the cross-linked ethylvinylbenzene-divinylbenzene copolymer matrix and the relative chromatographic specificities of different cations (H^+ , K^+ , Tl^+ , Na^+ , Ag^+ , Ni^{2+} , Zn^{2+} , Cd^{2+}) have been delineated¹¹. We have now undertaken a more precise study of molecular structural effects on specific interactions of a homogeneous series of alkenes with selected cations using the principle of DARC topological analysis (DTA) based on the concepts of the DARC topological system (DARC is an abbreviation for description, acquisition, retrieval and computer-aided design²¹⁻²⁴). In this paper we present the first results, dealing with the specificity of the nickel form of the cation-exchange resin.

EXPERIMENTAL

Apparatus

All chromatographic work was carried out using a Varian Model 200 chromatograph with flame-ionization detectors (Varian Instruments, Palo Alto, CA, U.S.A.). The instrument was modified slightly to accommodate a calibrated thermometer in the oven.

Glass columns (10 cm \times 6 mm O.D.) were used. The packing material was held in the column by silanized glass-wool plugs at the ends.

Ultra-high-purity nitrogen (AGL Welding Supply, Clifton, NJ, U.S.A.) was used as the carrier gas. All measurements were performed at 175°C and with a carrier gas flow-rate of 40 ml/min.

Packings

The preparation of lightly sulfonated resins was described previously¹¹. The sulfonated resin (0.85 mequiv./g H⁺) was converted into the nickel form by passing a measured volume of 0.1 M nickel nitrate solution through a glass column filled with dried resin. The converted resin was washed with water and then dried to 80°C in a vacuum oven for 4 h.

The metal content of the resin was determined by atomic-absorption spectrophotometry on acid-digested samples. The particular resin used in this study contained 1.8% of nickel. The unsulfonated form of the resin (UnS) consisted of Porapak Q (80–100 mesh), obtained from Waters Assoc. (Milford, MA, U.S.A.).

Reagents and chemicals

All test compounds were of the highest purity commercially available and were used as received (mainly from Aldrich, Milwaukee, WI, U.S.A., Tridom/Fluka, Hauppauge, NY, U.S.A., and Pfaltz and Bauer, Stamford, CT, U.S.A.). About 50 μ l of compound were placed in an air-filled 30-ml butyl-rubber-stoppered bottle (Pierce Hypo-Vial, Pierce Chemical Co., Rockford, IL, U.S.A.). After mixing the contents of the bottle, 10–15- μ l samples of the vapor were withdrawn in a disposable hypodermic syringe fitted with a 25-gauge needle and injected into the instrument.

Retention data

Retention times were determined by measurement of distances on the recorder chart tracings, after verifying that the chart speed control was accurate and precise. Kováts retention indices were calculated using the customary method with the normal hydrocarbons as reference compounds. The precision of the Kováts retention indices reported was ± 3 units based on duplicate injections carried out in random sequence.

Data processing

Factor analysis of Kováts retention indices and other numerical techniques chiefly stress stationary phase behavior. In order to understand fully the interaction between the solutes and the stationary phase with respect to the behavior of the individual solute-carbon atoms, a topological analysis was carried out on a large set of solutes.

Correlation between structure and chromatographic retention were set up by the DARC/PELCO (perturbation of an environment limited concentric and ordered) procedure developed by Dubois and co-workers^{21–24}. The principles of this procedure have been described previously with respect to their applications in chromatography⁹, which were developed for analytical^{9,10,25–27} or physico-chemical purposes^{12–14}. This procedure has been applied in other fields such as pharmacology^{28–32} and spectroscopy^{33–35}. Only salient features will be mentioned here.

Fig. 1 shows the derivation for a set of eight alkenes from ethene, with the carbon-carbon double bond taken as the focus. Each of the alkenes is associated with a graph, with the topological sites of the molecule (the skeletal carbon atoms) corresponding to the nodes of the graph. Superposition of the graphs gives a composite trace characteristic of this set of compounds. Fig. 2a gives the trace for the set of 44 alkenes used in this study (they are listed in Table I). Each site in this

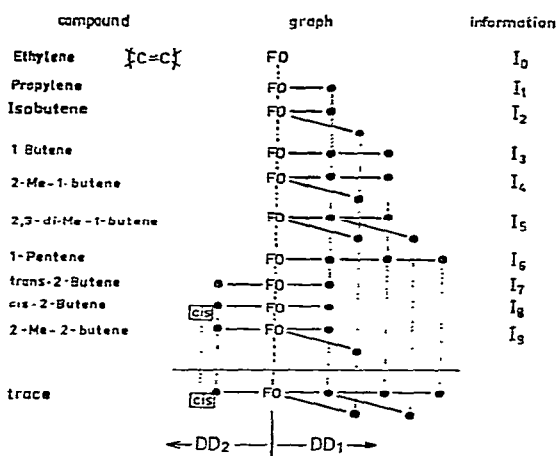


Fig. 1. Principle of superposition of the elementary graphs of some alkenes to give the characteristic trace of the population studied.

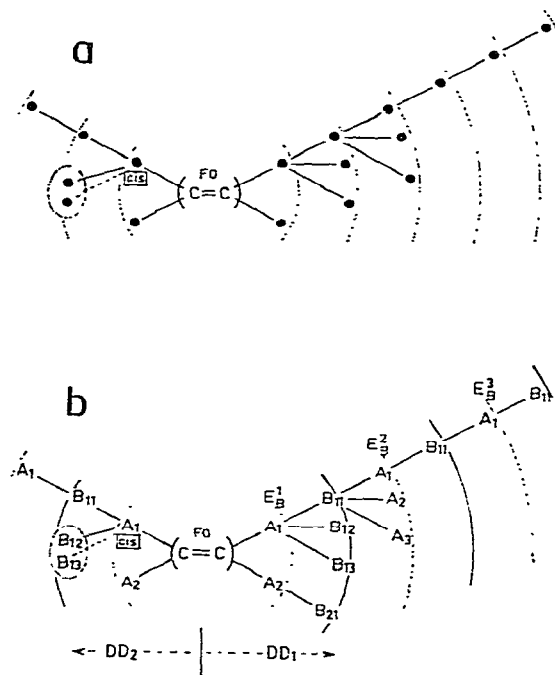


Fig. 2. (a) Characteristic trace of the population of 44 alkenes listed in Table I; (b) topological site ordering of the molecular environment by the ELCO concept for the superposition of the elementary graphs.

trace is specified unequivocally in the environment by a linear labelling order A_i or B_{ij} (Fig. 2b).

The influence of each site is interpreted as a perturbation term (P). For example, the term A_2 in the first environment E_B^1 is formally equivalent to the differ-

TABLE I

TOPOLOGICAL ANALYSIS OF BEHAVIOR OF ALKENES ON THE UNSULFONATED SUPPORT AND ON THE NICKEL FORM OF THE CATION-EXCHANGE RESIN





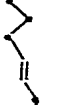


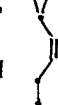









Experimental (1) and (3) and calculated Kováts retention indices at 175°C and Kováts retention index increments (ΔI).

No.	Compound	Graph	Unsulphonated support			Ni ²⁺ form of resin			ΔI (3)-(1)	B.p. (°C)
			Exptl. (1)	Calc. (2)	Diff. (1)-(2)	Exptl. (3)	Calc. (4)	Diff. (3)-(4)		
1	Ethylene		200	200	0	212	212	0	12	-103.7
2	Propylene		304	306	-2	380	414	-34	76	-47.7
3	1-Butene		404	399	5	493	497	-4	3	6.3
4	trans-2-Butene		410	409	1	486	501	-15	3	0.9
5	cis-2-Butene		418	412	6	499	502	-3	11	3.7
6	Isobutene		398	402	-4	537	508	29	-4	6.9
7	2-Methyl-1-butene		493	495	-2	622	592	30	8	31.2
8	2-Methyl-2-butene		507	506	1	622	595	27	16	38.6
9	1-Pentene		493	495	-2	582	585	-3	-1	30.0
10	trans-2-Pentene		502	502	0	574	584	-10	-5	36.4
11	cis-2-Pentene		507	505	2	579	586	-7	-5	36.9
12	2,3-Dimethyl-1-butene		577	570	7	650	674	-24	0	55.6
13	3,3-Dimethyl-1-butene		550	559	-9	658	632	26	14	41.2

(Continued on p. 120)

TABLE I (continued)

No.	Compound	Graph	Unsulphonated support		Ni ²⁺ form of resin		Calc. (5)	Diff. (5)-(3)	ΔI (3)-(1)	B.p. (°C)
			Exptl. (1)	Calc. (2)	Diff. (1)-(2)	Exptl. (3)				
14	2-Ethyl-1-butene		593	593	0	678	667	11	85	64.7
15	2-Methyl-1-pentene		590	591	-1	675	679	-4	85	62.1
16	3-Methyl-1-pentene		574	570	4	674	667	7	100	54.2
17	4-Methyl-1-pentene		573	574	-1	673	650	22	100	53.9
18	2-Methyl-2-pentene		596	598	-2	681	684	-3	85	67.3
19	3-Methyl-trans-2-pentene		601	599	2	679	678	1	78	70.4
20	3-Methyl-cis-2-pentene		601	601	0	679	680	-1	78	67.7
21	4-Methyl-trans-2-pentene		573	577	-4	676	667	9	103	58.6
22	4-Methyl-cis-2-pentene		573	580	-7	676	668	8	103	56.4
23	1-Hexene		590	595	-5	673	678	-5	83	63.5
24	trans-2-Hexene		602	598	4	675	672	3	73	67.9
25	cis-2-Hexene		602	601	1	675	673	2	73	68.9
26	trans-3-Hexene		593	595	-2	671	673	-2	78	67.1
27	2,4-Dimethyl-1-pentene		664	670	-6	716	745	-29	52	81.6

28	2,3,3-Trimethyl-1-butene		661	655	6	699	726	-27	699	0	38	77.9
29	2,3-Dimethyl-2-pentene		697	697	0	723	723	0	723	0	26	97.4
30	4-Methyl-1-hexene		680	673	7	750	744	6	757	-7	70	86.7
31	1-Heptene		692	690	2	767	769	-2	766	1	75	93.6
32	<i>trans</i> -2-Heptene		692	698	-6	760	765	-5	764	-4	68	97.9
33	<i>trans</i> -3-Heptene		693	691	2	762	761	1	759	3	69	95.7
34	<i>cis</i> -3-Heptene		693	694	-1	762	762	0	763	-1	69	95.8
35	3-Ethyl-2-pentene		695	696	-1	742	754	-12	746	-4	47	96.0
36	4,4-Dimethyl- <i>cis</i> -2-pentene		665	662	3	720	719	1	734	-14	55	80.4
37	2-Methyl- <i>cis</i> -3-heptene		767	767	0	850	850	0	850	0	83	112.0
38	1-Octene		796	796	0	861	861	0	861	0	65	121.3
39	<i>trans</i> -2-Octene		794	794	0	857	857	0	855	1	63	124.9
40	<i>cis</i> -2-Octene		794	796	-2	857	857	0	860	-3	63	125.6
41	<i>trans</i> -3-Octene		794	791	3	857	854	3	851	6	63	123.3
42	2-Ethyl-1-hexene		789	788	1	849	848	1	841	8	60	120
43	2,4,4-Trimethyl-1-pentene		750	750	0	790	790	1	790	0	40	101.5
44	2,4,4-Trimethyl-2-pentene		747	747	0	791	791	1	791	0	44	104.9

ence in behaviors of isobutene and propylene. As this site also appears in other compounds (I_4 , I_5 and I_9 in Fig. 1), its perturbation term is estimated by an average value obtained by a multiple regression program that takes into account all the members of a given set of compounds containing this site¹³.

These perturbation terms are the components of a vector $\vec{I}(m)$ that characterizes the information for an experimental population made up of m compounds. This vector is defined by the basic topology-information relationship

$$I(\varepsilon) = \langle \vec{T}(\varepsilon) | \vec{I}(m) \rangle$$

where $I(\varepsilon)$ is the contribution from the environment and $\vec{T}(\varepsilon)$ is the topological vector of the environment. $\vec{T}(\varepsilon) = (X_1, X_2, \dots, X_j, \dots, X_n)$; thus $X_j = 1$ when the j th site of the environment is occupied and $X_j = 0$ when it is not.

The PELCO method consists of calculating the $\vec{I}(m)$ vector and defining thereby a topology information correlation which will be represented as the diagrams in Figs. 3 and 4. Information concerning a compound X can be calculated from information $I(X_0)$ for a reference compound (here ethylene) and can be expressed as $I(X) = I(X_0) + I(\varepsilon)$. Some examples are shown in Fig. 5.

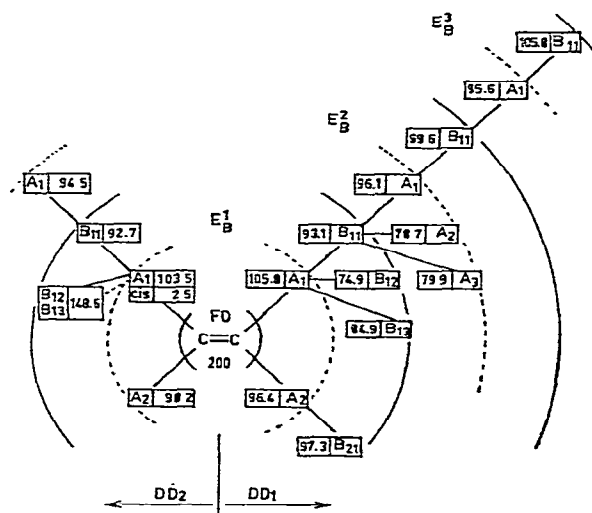


Fig. 3. Topological information diagram for retention on the unsulfonated copolymer matrix.

RESULTS AND DISCUSSION

Retention indices of the alkenes on the unsulfonated support (UnS) and on the nickel form of the cation-exchange resin are given in Table I. Fig. 6 shows a plot of the Kováts retention indices of the alkenes on the unsulfonated ethylvinylbenzene-divinylbenzene copolymer matrix *versus* the boiling point of the compounds. Regular variations are observed for isomeric compound subpopulations defined by carbon atom number.

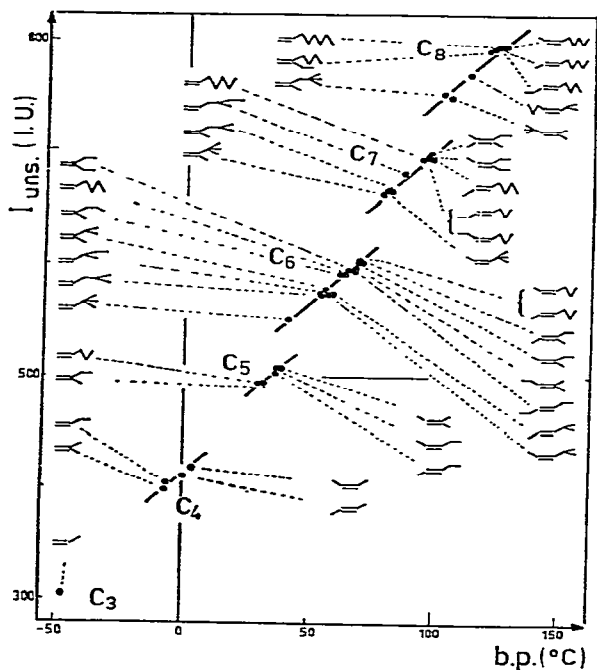


Fig. 6. Retention index of alkenes (I_{uns}) on the unsulfonated copolymer, in index units (I.U.), as a function of boiling point of the alkene. Regular trends are observed for every subpopulation (from C_4 up to C_8).

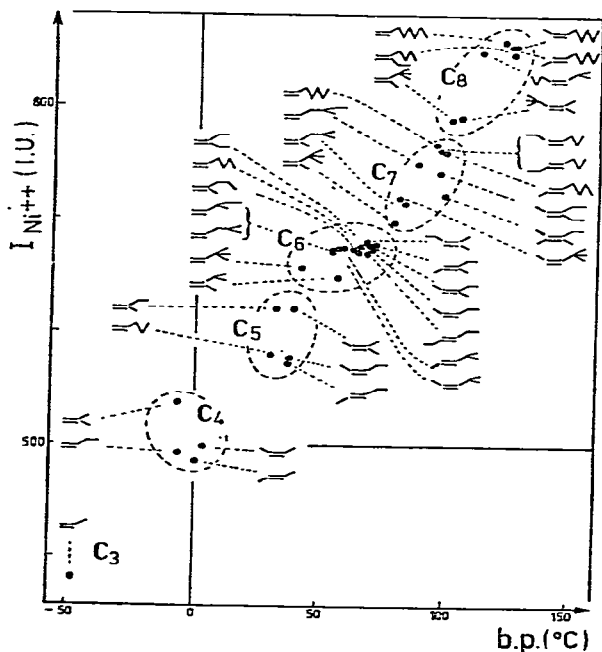


Fig. 7. Retention index of alkenes on the nickel form of the ion exchanger as a function of boiling point of the alkene. The dispersion of the data for each subpopulation suggests, in this instance, a relatively complex law for the structural effects on the adsorption phenomena.

and the *cis*- and *trans*-3-methyl-2-pentenes) decreasing to 25 I.U. on the Ni^{2+} form. For the heptenes the range of Kováts retention indices increases from 40 I.U. on the UnS column to 70 I.U. on the Ni^{2+} form and for the octenes from 50 I.U. on the UnS column to 70 I.U. on the Ni^{2+} form. The increase in Kováts retention index (ΔI) from the UnS to the Ni^{2+} packing is shown in Fig. 8. The ΔI shows the specificity brought by the Ni^{2+} ion at the molecular level. ΔI varies from the unexpectedly low value of 12 I.U. for ethylene up to 139 I.U. for isobutene. Only the previously mentioned geminal 1-alkenes and 2-methyl-2-butene have a ΔI in the range 115–130 I.U. In the range 100–115 I.U. we find some hexene isomers, the crowded 3,3-dimethyl-1-butene, the branched 3-methyl-1-pentene, 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene. In addition to ethylene, the lower ΔI values are observed for tetrasubstituted ethylene, 2,3-dimethyl-2-pentene with $\Delta I = 26$ I.U., and for compounds having steric strain in the vicinity of the carbon-carbon double bond. 2,4,4-Trimethyl-1-pentene ($\Delta I = 40$ I.U.) and 2,4,4-trimethyl-2-pentene ($\Delta I = 44$ I.U.) are two compounds that show this property.

The difficulty in discerning other than gross changes by classical means makes the DTA treatment of this set of data particularly attractive as a method for delineating the structural trends and placing them on a quantitative basis.

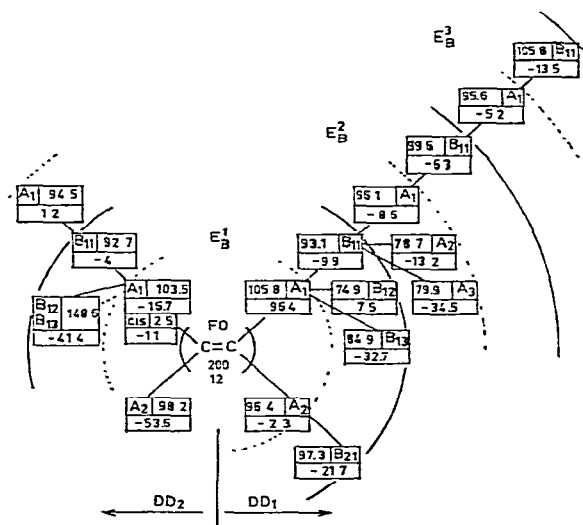


Fig. 8. Extent of specific interactions of alkenes with the nickel form of the ion exchanger. Upper values in each box are retentions on unsulfonated copolymer, lower values are the specific and supplementary contributions due to the nickel form of the ion exchanger.

DTA behavior: unsulfonated support

The DARC topology information diagram (Fig. 3) gives the behavior of alkenes on the unsulfonated matrix and Fig. 5 demonstrates the ease of using the diagram. Every substitution at the ethylenic focus contributes about 100 I.U., and the chain lengthening results in an incremental increase of approximately 100 I.U., as expected. Branching in the first development direction, DD_1 , in such compounds as 3,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene results in a contribution of

about 80 I.U. In addition, no noticeable specificity is observed for *cis*-alkenes relative to the corresponding *trans*-isomers.

The contribution of topological sites is different here to those values observed in gas-liquid chromatography (GLC) for a similar series of alkenes on the non-polar stationary phases Squalane and Apiezon¹³. The contribution of substitution at the ethylenic focus was slightly higher and the contribution from branching was 10–20 I.U. lower for these liquid phases. The topological values for the UnS column are very close to those obtained on a sulfonated packing in the hydrogen form, the data for which will be published in a subsequent paper. This indicates that the sulfonated and unsulfonated forms of the resin retain the compounds in the same manner. The addition of the metal results in the differences in selectivity.

The statistical significance of the topological analysis is high. Differences between the experimental and the calculated retention indices using $I(\epsilon)$ are small (the average deviation is 2.6 I.U., the standard deviation 4.8 I.U.) and this reinforces the validity of using the additivity of the contributions of the topological sites.

DTA behavior: nickel form of the resin

The DTA behavior of the alkenes on the Ni²⁺ form of the sulfonated resin is shown in Fig. 4. There are readily observable differences in topological site contributions between this form and the unsulfonated form of the copolymer, particularly with monosubstitution, tetrasubstitution and branching. The differences in values for the various topological sites between Figs. 3 and 4 are due to the specific interactions of the nickel form of the sulfonated support relative to the unsulfonated matrix. The specific interactions due to the nickel form are given in Fig. 8; these will now be examined in detail.

The carbon-carbon double bond, which is the focus in the DTA treatment, shows a slight specificity (+12 I.U.) relative to the unsulfonated matrix. Monosubstitution on the ethylenic focus given by site A₁, in the first environment E_B¹ of the first development direction, labelled DD₁, which refers to the first direction of development of the graph according to a controlled algorithmic growth²², is very important. This specificity of 96.4 I.U. shows a strong increase in the specific interaction between Ni²⁺ and the carbon-carbon double bond due to the monosubstitution of the sp² carbon atom of the ethylenic focus. This is in agreement with the increase of π net charge of $-0.0133 e$ calculated by CNDO/2 *ab initio* calculations³⁴ for propylene relative to ethylene.

Chain lengthening for 1-alkenes results in a decrease of about 10 I.U. from the preceding specific interaction for every topological site. These negative contributions (−9.9, −8.6, −6.3, −5.2 and −13.5) are in agreement with the influence on retention index of the successive addition of a carbon atom to the chain from 1-butene to 1-octene.

Geminal disubstitution, as exemplified by site A₂ in the DD₁ direction in the E_B¹ region, shows no specific interaction (−2.3 I.U.), except for isobutene, which will be discussed later.

Disubstitution with *trans*-isomers is given by A₁ in E_B¹ of the second development direction DD₂. The specific interaction for a carbon in A₁ is −16.7 I.U. The *cis*-isomer shows no improvement in specificity (−1.1 I.U.). Site A₁ also appears in trisubstituted ethylenes such as 2-methyl-2-butene.

These new parameters take into account deviations due to adsorption phenomena when different groups or, more specifically, when different topological sites are present simultaneously. It can readily be seen that all of these interactions are negative and contribute to a diminution of the relatively strong influence of site A_2 (in E_B^1 of DD_1) introduced by isobutene (147.4 I.U.). As an example, when site A_2 is present together with a *tert.*-butyl group on the same sp^2 carbon, the weights of the interactions between site A_2 and B_{11} , B_{12} and B_{13} (in E_B^1 of DD_1) are -22.7 , -57.9 and -12 I.U., respectively. The sum of these interactions is -92.6 I.U. for the *tert.*-butyl group and helps to explain why a difference of only 41 I.U. is observed between the experimental retention indices of 2,3,3-trimethyl-1-butene and 3,3-dimethyl-1-butene instead of 157 I.U., which is the difference between the experimental values for propylene and isobutene.

The numerical expressions of these interactions are not just a mathematical device; they also have a physico-chemical meaning. They show the decrease of the specific interaction between the carbon-carbon double bond and the Ni^{2+} ion when different sites are present simultaneously. These interactions are in agreement with the Kováts retention index increments, ΔI , which themselves are indicative of the specific interactions, with the Ni^{2+} ion, for the whole molecule. The strong decrease observed in ΔI values for propene, 3,3-dimethyl-1-butene and 2,3,3-trimethyl-1-butene of 139, 108 and 38 I.U., respectively, also shows the influence of the simultaneous presence of a methyl and a *tert.*-butyl group on the same sp^2 carbon. Another example that illustrates this point is the fact that ΔI for 3,3-dimethyl-1-butene is 108 I.U. but only 73 I.U. for the geminal isomer 2,3-dimethyl-1-butene.

Specific interactions; ionization potentials

To evaluate the possibilities of charge transfer between the π bond of alkenes and the empty orbitals of the Ni^{2+} ion, a frontier molecular orbital treatment that would consider the energies and shapes of the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor would be attractive^{35,36}, but difficult owing to the complexity of the studied olefins. Photo-electron spectroscopy has been shown to be a valuable physical method for evaluating substituent effects when reactivity is based on charge-transfer possibilities³⁶.

The specific interactions of the alkenes with the Ni^{2+} ion, expressed as Kováts retention index increments, ΔI , is plotted in Fig. 10 against the olefin ionization potentials (IP) determined elsewhere by photoelectron spectroscopy³⁷. This figure shows that for monosubstituted ethylenes, linear or branched, and for the lower geminal alkenes (isobutene and 2-methyl-1-butene) the degree of specific interaction (ΔI) is closely related to the IP. For 1,2-disubstituted ethylene, trisubstituted ethylene (2-methyl-2-butene), crowded alkenes with a *tert.*-butyl group and tetrasubstituted ethylene (2,3-dimethyl-2-pentene) we can observe successive decreases in ΔI despite the availability of the π electron.

These trends are in good agreement with the DTA results in Fig. 9, in the same way that DTA results dealing with alkenes in GLC have been compared successfully with CNDO/2 *ab initio* calculations¹³.

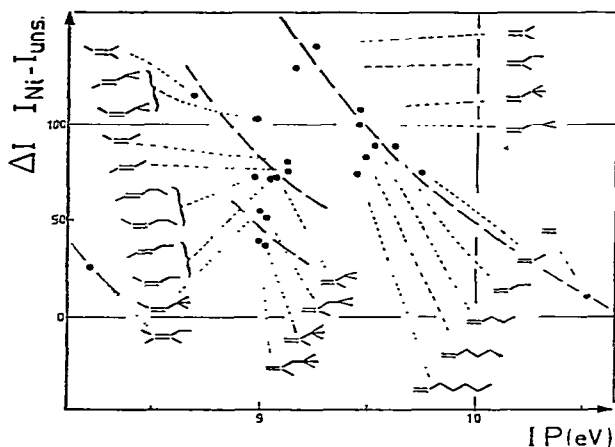


Fig. 10. Specific contribution to retention (ΔI) due to the nickel form of the ion exchanger relative to the unsulfonated copolymer matrix (uns.) as a function of substitution potential of the alkene (IP). Decrease of the specific interaction with degree of substitution, branchings or bulky groups for di-, tri- or tetrasubstituted ethylenes suggest a dominant influence of steric effects.

CONCLUSION

DARC topological analysis of the behavior of alkenes in GSC on the Ni^{2+} form of a cation-exchange resin allows a determination of structural effects on the specificity brought by the Ni^{2+} cation relative to the unsulfonated matrix. Furthermore, DTA can be used to aid in explaining the behavior of molecules at the level of their skeleton carbon atom. The contributions of all the possible groups (*n*-alkyl, isopropyl, *tert.*-butyl, neopentyl, etc.) obtained by progressive substitution of ethylene, taken as the reference compound, are easily deduced from the topology information diagrams. DTA shows clearly the influence of structural effects on the ability of the molecules to form charge-transfer complexes between Ni^{2+} and the olefin. Specific adsorption on Ni^{2+} is related to the overlap of the π bonds and is very sensitive to hindrance due to the degree of substitution or to the substitution of bulky groups. This steric effect counteracts the electronic effect that would favor interaction.

The different spectroscopic methods used in the field of catalysis for the study of adsorbed species are generally limited to very simple molecules. DTA of retention indices, however, offers the possibility of studying any molecule that belongs to a coherent series, with the precision of the DTA results being directly related to the precision of the experimental results^{14,38}. Indeed, as in every mathematical method, our model is partly conventional. The use of topology-information diagrams needs only a minimum of training, which is easily obtained with some examples showing how to calculate retention indices for compounds whose graphs are included in the trace of the population studied. This paper underlines the complementarity between DTA and factor analysis methods, such as correspondence factor analysis (CFA)¹¹, for the physico-chemical exploitation of tables of data and analyses of main trends on structural bases.

Work is under way to study and elucidate the specificities brought about by

the use of other cations (Ag^+ , Zn^{2+} , etc.) that have shown interesting and complementary effects¹¹.

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