Journal of Chromatography, 288 (1984) 95–103
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 304

CHROMATOGRAPHIC SEPARATION OF HYDROCARBON GASES ON ZEOLITES WITH THE USE OF CARBON DIOXIDE AS CARRIER GAS

T. G. ANDRONIKASHVILI*
Institute of Physical and Organic Chemistry, Academy of Sciences of the Georgian SSR, Tbilisi (U.S.S.R.)
V. G. BEREZKIN
Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow (U.S.S.R.)
and
L. Ya. LAPERASHVILI and N. A. NADIRADZE
Institute of Physical and Organic Chemistry, Academy of Sciences of the Georgian SSR, Tbilisi (U.S.S.R.)

SUMMARY

In gas chromatography on zeolites "active" carrier gases such as water vapour and carbon dioxide are rarely used because they are adsorbed on zeolites selectively and strongly. It is shown here that the use of carbon dioxide as the carrier gas allows the complete separation of model mixtures of hydrocarbon gases on zeolites at a lower column temperature and faster than with the use of conventional inert carrier gases such as nitrogen or helium.

It was found that mixtures of C_1–C_4 hydrocarbon gases can be separated on zeolites of type Y in the sodium, cadmium and silver forms at column temperatures of 25–100°C. The specificity of the effect of silver and cadmium cations in zeolites on the separation of these mixtures is different to that with the use of helium or nitrogen as the carrier gas. Calculation of the heats of adsorption and the change in the entropy of adsorption (ΔS) of hydrocarbon gases in their chromatography on zeolites showed that they are considerably dependent on the nature of the carrier gas used.

INTRODUCTION

Usually in gas chromatography on zeolites inert gases such as helium, hydrogen and nitrogen are used as carrier gases, as they are poorly adsorbed[1,2]. "Active" carrier gases such as water vapour or carbon dioxide are rarely used because they are selectively and strongly adsorbed on zeolites, decreasing their adsorptive and separating ability.

Zeolites are highly active sorbents with good molecular-sieving properties and are mainly used for the chromatographic separation of gaseous mixtures. Active centres of the zeolite cations and hydroxide ions are positioned at various sites in the zeolite framework and interact with the sorbate molecules to various extents. The molecules of the carrier gas occupy only some of the active centres of the zeolite in the elution process and therefore the adsorbent does not lose its separating properties completely.

0021-9673/84/$03.00

On the other hand, as early as 1957[3] it was established that the nature of the carrier gas considerably affects the specific retention volumes of the individual components of mixtures of light gases in their separation on a column filled with activated carbon, and leads to a decrease in the specific retention volumes, almost halving it in some instances.

The use of carbon dioxide as a carrier gas in the separation of hydrocarbon gas mixtures results in faster and more complete separations on silica gel than when hydrogen or helium is used[4]. It was assumed[4] that the carbon dioxide deactivates the silica gel and in part plays the role of a displacer.

The possibility of using active carrier gases such as ethylene, ethane and carbon dioxide for the separation of mixtures of high-boiling hydrocarbons on zeolites of the X and Y type has been demonstrated[5], but a comparatively high pressure at the inlet of the chromatographic column was necessary.

The aim of this work was the investigation of the effect of carbon dioxide as the carrier gas on the separation of hydrocarbon gas mixtures on zeolites such as NaY, CdY and AgY, where the nature of the cation, especially with cadmium and silver, has a much stronger effect on the amplification of the intermolecular interactions between the molecules of the adsorbates and the adsorbent[6].

EXPERIMENTAL

Investigations were carried out on LXM-8MD chromatograph with a 0.5 m × 4 mm I.D. column. Cadmium and silver forms of zeolites were prepared from the initial sodium form of type Y zeolite, by multiple treatment with 0.1 *N* cadmium(II) chloride and silver nitrate solutions. Specimens with 80% cadmium and silver cation substitution were obtained. Granules of size 0.5–1.0 mm were prepared from the zeolite powder without adding a binder. Thermal activation of the zeolites was performed in the column by heating at 400°C for 4 h. The column temperature (isothermal) was varied over the range 20–200°C. A thermal conductivity detector was used. The flow-rate of the carrier gas was constant at 50 ml/min. Nitrogen and helium were used as carrier gases for the sake of comparison.

A mixture of C_1–C_4 hydrocarbon gases was used as a model mixture. To establish the effect of the nature of the carrier gas on the separation of this model mixture, the specific retention volumes of separate compounds (V_g), selectivity coefficients of binary mixtures (K_c), uniformity criteria ($\bar{\Delta}$) and fast-action coefficients of multi-component mixtures (λ), characterizing the selectivity of zeolites, and the heights equivalent to a theoretical plate, which show the effectiveness of the chromatographic column[7], were determined. To define the character of the adsorptive interactions, physico-chemical characteristics such as heats of adsorption (Q) and entropy change (ΔS) were calculated[8].

RESULTS AND DISCUSSION

The results indicate that the nature of the carrier gas strongly affects the separation of the model mixtures. With the use of carbon dioxide on NaY zeolite a six-component mixture of hydrocarbon gases can be separated completely at a column temperature of 20°C, whereas the usual carrier gases such as hydrogen and

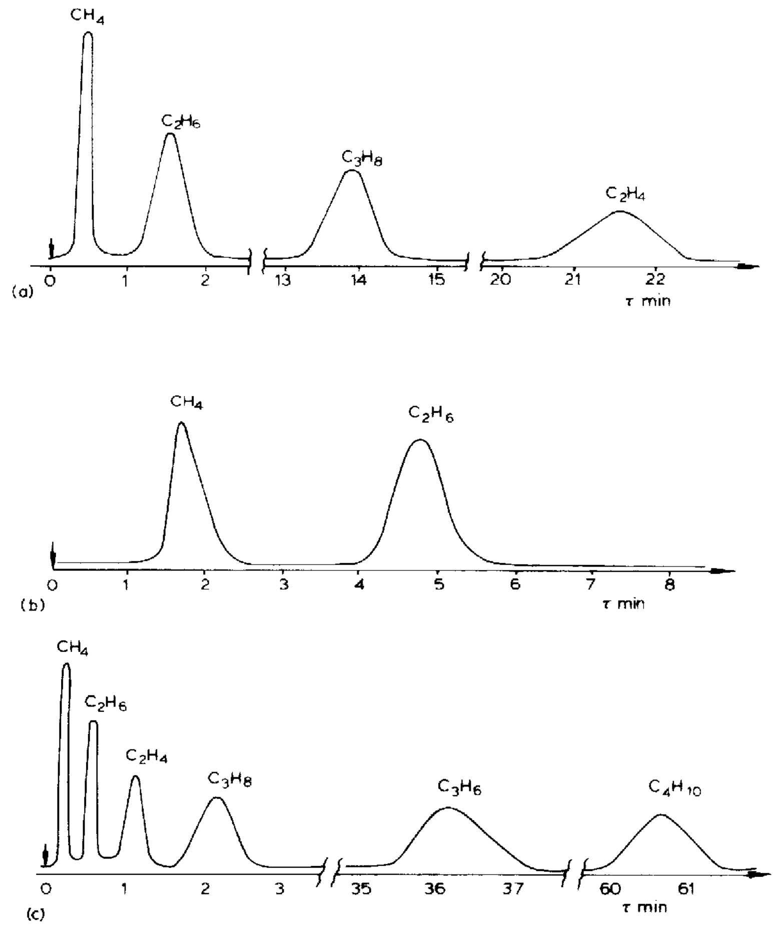

Fig. 1. Chromatogram showing the separation of C_1–C_4 hydrocarbon gases. Adsorbent NaY; column temperature, 20°C; carrier gas, (a) helium, (b) nitrogen and (c) carbon dioxide.

helium are not able to separate this mixture (Fig. 1). Note that the use of carbon dioxide as the carrier gas on this form of zeolite, unlike helium or nitrogen[1], does not result in a temperature inversion of the elution sequence propane–ethylene and butane–propylene, *i.e.*, an unsaturated compound is eluted after the corresponding saturated compound with same number of carbon atoms in the molecule at any column temperature. It can be seen from Table I that on columns filled with NaY zeolite and also with CdY and AgY zeolite, with carbondioxide as the carrier gas there is a considerable decrease in the specific retention volumes of the hydrocarbon gases, especially at low column temperatures, at which there is adsorption of carbon dioxide on the zeolites, screening of cations and partial deactivation of the adsorbent.

It follows from Table I, however, independent of the nature of the carrier gas, that the role of the cation of the zeolite in the intermolecular interaction is to increase the specific retention volumes for almost in all the compounds studied in the order $Na^+ < Cd^{2+} < Ag^+$.

TABLE I

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE SPECIFIC RETENTION VOLUMES (V_g) OF C_1–C_4 HYDROCARBON GASES IN CHROMATOGRAPHY ON NaY, CdY AND AgY ZEOLITES

Column temperature (°C)	Hydrocarbon	Carrier gas								
		He			N_2			CO_2		
		NaY	CdY	AgY	NaY	CdY	AgY	NaY	CdY	AgY
20	Methane	3.91	8.35	14.19	3.48	7.59	13.20	2.46	3.96	6.60
	Ethane	26.91	52.8	186.45	24.55	51.81	185.50	11.61	29.7	72.6
	Ethylene	301.3	–	–	–	–	–	46.47	–	–
	Propane	195.5	495	–	–	494.0	–	79.24	233.69	891.0
	Propylene	–	–	–	–	–	–	502.2	–	–
	Butane	–	–	–	–	–	–	944.14	–	–
140	Methane	1.60	1.68	2.16	1.58	1.20	1.68	1.11	1.18	1.68
	Ethane	4.32	4.32	10.56	4.12	4.08	10.08	2.38	3.84	9.12
	Ethylene	12.96	81.20	–	11.40	86.60	–	5.07	57.60	–
	Propane	17.92	17.52	73.2	15.52	18.00	79.2	8.24	16.80	54.48
	Propylene	81.60	–	–	66.69	–	–	29.46	–	–
	Butane	68.48	89.12	522.72	62.57	85.20	446.4	37.69	68.40	374.4

TABLE II

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE SELECTIVITY COEFFICIENTS (K_c) OF SEPARATE BINARY MIXTURES IN THEIR CHROMATOGRAPHY ON NaY, CdY AND AgY ZEOLITES

Column temperature (°C)	*Binary mixture*	*Carrier gas*								
		He			N_2			CO_2		
		NaY	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*
20	Methane–ethane	0.75	0.71	0.86	0.79	0.74	0.87	0.65	0.70	0.83
	Ethane–propane	0.76	0.81	–	–	0.81	–	0.74	0.77	0.85
	Propane–butane	–	–	–	–	–	–	0.84	–	–
	Ethane–ethylene	–	–	–	–	–	–	0.63	–	–
	Propane–propylene	–	–	–	–	–	–	0.73	–	–
140	Methane–ethane	0.46	0.54	0.68	0.45	0.55	0.77	0.36	0.52	0.66
	Ethane–propane	0.61	0.62	0.75	0.59	0.63	0.77	0.51	0.59	0.71
	Propane–butane	0.59	0.64	0.78	0.60	0.65	0.80	0.54	0.60	0.74
	Ethane–ethylene	0.50	0.89	–	0.47	0.91	–	0.36	0.87	–
	Propane–propylene	0.64	–	–	0.62	–	–	0.59	–	–

TABLE III

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE UNIFORMITY CRITERIA ($\bar{\Delta}$) AND FAST-ACTION COEFFICIENT (λ) IN THE CHROMATOGRAPHIC SEPARATION OF A MIXTURE OF SATURATED C_1–C_4 HYDROCARBONS ON NaY, CdY AND AgY ZEOLITES

Column temperature: 140°C.

Carrier gas	$\bar{\Delta}$			λ *(sec^{-1})*		
	NaY	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*
He	0.260	0.281	0.101	$2.6 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$
N_2	0.259	0.298	0.041	$1.1 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
CO_2	0.598	0.322	0.134	$7.2 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$	$3.2 \cdot 10^{-3}$

The decrease in the specific retention volumes of individual substances of a mixture when carbon dioxide is used as the carrier gas allows the separation of the model mixture on any of the cation-exchange forms of the zeolite and a corresponding decrease in the analysis time at an average column temperature 60–80°C lower than that with the usual inert carrier gases such as helium and nitrogen. It is also noteworthy that the chromatograms have more symmetrical peaks.

As Table II shows, the selectivity coefficients of separate binary mixtures, which in our case reflect the effect of the nature of the of cation zeolite on the completeness of separation, increase, as expected[6], in the order $Na^+ < Cd^{2+} < Ag^+$. However, the nature of the carrier gas also has an effect. With carbon dioxide, the selectivity coefficients of the individual hydrocarbon pairs are decreased. This is probably connected with the partial screening of cations of the zeolite. With an increase in the column temperature the difference in the selectivity coefficients is reduced to some extent, as adsorption of carbon dioxide on the active centres of the zeolite is decreased. The nature of the carrier gas affects the uniformity criteria ($\bar{\Delta}$) of the separation of multi-component mixture and the fast-action coefficient (λ), which actually characterize the completeness of separation of the model mixture. As shown in Table III, the most complete separation of the four-component mixture occurs when carbon dioxide is used as the carrier gas. Obviously, carbon dioxide is not only a carrier but also a displacer, resulting in the formation of symmetrical peaks with only a small spread.

The effectiveness of the chromatographic column was defined by the height equivalent to a theoretical plate, calculation of which was performed on the basis of the chromatograms. Table IV shows that the most effective columns are those in which carbon dioxide was used as the carrier gas. This is connected with the fact that, independent of the cation-exchange form of the zeolite, more symmetrical and narrower peaks are obtained than with helium or nitrogen. The height equivalent to a theoretical plate for the zeolites with carbon dioxide as the carrier gas is almost by an order of magnitude lower.

Calculations of the heats of adsorption of hydrocarbon gases (Table V) show that carbon dioxide weakens to some extent the strength of the interaction between adsorbate molecules and the adsorbent, although in this instance an increase in the

TABLE IV

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE HEIGHTS EQUIVALENT TO A THEORETICAL PLATE (mm) OF C_1–C_4 HYDROCARBON GASES ON NaY, CdY AND AgY ADSORBENTS

Column temperature (°C)	*Hydrocarbon*	*Carrier gas*								
		He			N_2			CO_2		
		NaY	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*
20	Methane	6.25	5.77	0.74	6.03	2.25	0.36	2.25	1.00	0.06
	Ethane	1.00	1.67	0.28	1.00	0.48	0.45	0.77	0.14	0.15
	Propane	0.50	1.47	–	–	0.30	–	0.29	0.08	0.07
	Ethylene	0.65	–	–	–	–	–	0.28	–	–
140	Methane	2.58	3.01	3.01	2.62	3.01	4.01	1.06	0.36	0.56
	Ethane	2.22	2.25	1.00	2.24	0.74	2.25	0.56	0.56	0.85
	Propane	0.66	0.56	0.46	0.76	1.27	1.05	0.41	0.49	0.43
	Butene	0.42	0.38	0.33	0.38	1.86	2.06	0.31	0.73	0.16
	Ethylene	0.69	0.53	–	2.25	3.84	–	0.56	0.34	–
	Propylene	0.51	–	–	0.66	–	–	0.31	–	–

TABLE V

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE HEATS OF ADSORPTION (kcal/mole) OF C_1–C_4 HYDROCARBON GASES ON NaY, CdY AND AgY ADSORBENTS

Temperature measuring range: 140–160°C.

Hydrocarbon	*Carrier gas*								
	He			*N_2*			*CO_2*		
	NaY	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*
Methane	3.91	7.44	8.52	3.96	7.72	7.95	3.05	6.74	6.7
Ethane	5.66	8.82	8.85	5.86	8.59	8.16	4.71	6.99	7.29
Propane	6.18	8.94	9.22	6.73	9.00	9.84	5.91	7.36	7.40
Butane	8.70	9.39	11.24	8.85	10.13	10.69	8.00	8.81	7.68
Ethylene	8.10	20.43	–	8.17	18.28	–	7.20	15.42	–
Propylene	14.71	–	–	15.16	–	–	12.30	–	–

heats of adsorption is observed, depending on the nature of the cation of the zeolite, in the order $Na^+ < Cd^{2+} < Ag^+$.

The change in the entropy of the gas during chromatography indicates indirectly the freedom of motion of the adsorbate molecule in the zeolite pores. The large is the entropy change, the greater is the restriction of motion of the substances being chromatographed. It follows from Table VI that the restriction of motion increases depending on the nature of the cation in the order $Na^+ < Cd^{2+} < Ag^+$. The use of carbon dioxide as the carrier gas, however, results to a decrease in the entropy change and, consequently, in more free motion of adsorbate molecules.

In conclusion, the use of carbon dioxide as the carrier gas improves the separating ability of zeolites without complete suppression of the effect of the nature of cation on the separation of mixtures and widens the range of the use of zeolites in gas chromatography.

TABLE VI

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE CHANGE IN ENTROPY OF ADSORPTION (ΔS *kcal/mole · °K*) OF C_1–C_4 HYDROCARBON GASES ON NaY, CdY AND AgY ZEOLITES

Column temperature: 140°C.

Hydrocarbon	*Carrier gas*								
	He			*N_2*			*CO_2*		
	NaY	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*	*NaY*	*CdY*	*AgY*
Methane	0.94	1.05	1.54	0.91	0.38	1.03	0.21	0.34	1.05
Ethane	2.91	2.91	3.23	2.81	2.80	4.59	1.73	2.68	2.99
Propane	5.72	5.69	8.52	6.55	5.74	8.68	4.19	5.60	7.93
Butane	8.38	8.91	12.42	8.21	8.83	12.11	5.75	8.38	11.75
Ethylene	5.09	8.75	–	4.38	8.87	–	3.23	8.06	–
Propylene	8.75	–	–	8.35	–	–	6.72	–	–

REFERENCES

1 T. G. Andronikashvili, *Zh. Vses. Khim. Ova.*, No. 1 (1983) 96.
2 A. Dyer, *Separ. Sci. Technol.*, 13 (1978) 501.
3 S. A. Green and M. E. Roy, *Anal. Chem.*, 28 (1957) 252.
4 D. A. Vyakhirev and A. I. Bruk, *Zh. Fiz. Khim.*, 33 (1959) 1309.
5 P. Briom, T. P. Boyd and T. W. Leevelyn, *U.K. Pat.*, 1,350,580, 1974.
6 G. V. Tsitsishvili and T. G. Andronikashvili, *J. Chromatogr.*, 58 (1971) 39.
7 M. S. Vigdergauz, *Rascheti v Gasovoi Khromatographii*, Khimiya, Moscow, 1978, p. 30.
8 M. A. Khan, *Lab. Pract.*, 11 (1962) 195.