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Journal of Chromatography A, 686 (1994) 245–251

JOURNAL OF
CHROMATOGRAPHY A

Retention of halocarbons on a hexafluoropropylene epoxide-modified graphitized carbon black III. Ethene-based compounds[☆]

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First received 4 May 1994; revised manuscript received 5 August 1994

Abstract

The retention characteristics of 11 ethene-based chlorofluorocarbon, bromochlorofluorocarbon and fluorocarbon fluids have been studied as a function of temperature on a stationary phase consisting of a 5% (m/m) coating of a low-molecular-mass polymer of hexafluoropropylene epoxide on a graphitized carbon black adsorbent. Measurements were performed at –20, 0, 20 and 40°C for trifluoroethene (R-1123), 1,1-difluoroethene (R-1132a), and fluoroethene (vinyl fluoride, R-1141). Measurements were performed at 40, 60, 80 and 100°C for 1,1-dichloro-2,2-difluoroethene (R-1112a), chlorotrifluoroethene (R-1113), 2-chloro-1,1-difluoroethene (R-1122), 1-chloro-1-fluoroethene (R-1121a), 2-bromo-1,1-difluoroethene (R-1122B1) and bromoethene (vinyl bromide, R-1140B1). Measurements were performed at 60, 80, 100 and 120°C for *trans*-1,2-dichloro-1,2-difluoroethene (R-1112t) and *cis*-1,2-dichloro-1,2-difluoroethene (R-1112c). Net retention volumes, corrected to a column temperature of 0°C, were calculated from retention time measurements, the logarithms of which were fitted against reciprocal thermodynamic temperature. The relative retentions, also as a function of temperature, were calculated with respect to the retentions of tetrafluoromethane (R-14) and hexafluoroethane (R-116). Qualitative features of the data are examined, and trends are identified. In addition, the data were fitted to linear models for the purpose of predicting retention behavior of these compounds to facilitate chromatographic analysis.

1. Introduction

Many laboratories are engaged in a comprehensive research program geared toward the development of new fluids to be used as refrigerants, blowing and foaming agents, and pro-

pellants. The research that composes this effort includes thermophysical properties measurements and correlation, materials compatibility testing, chemical stability measurement, and cycle suitability studies [1,2]. An important part of all of these research programs is the chemical analysis of new fluids that are tested [3–6]. Gas chromatography is one of the major quantitative and qualitative analysis methods that is applied to the study of alternative refrigerants for several important reasons, not the least of which are

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[☆] Contribution of the United States Government.

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simplicity and economics of operation [7–9]. A knowledge of the retention characteristics of important fluids on the more useful stationary phases is an important component in the design of effective qualitative and quantitative chromatographic analyses. Corrected retention parameters, such as the net retention volume, V_N^0 (corrected to a column temperature of 0°C), and relative retentions, $r_{a/b}$, provide the simplest avenue to achieve the desired goals.

In earlier papers, we presented measurements for 8 methane-based and 18 ethane-based fluids [10,11]. In this paper, we present temperature-dependent measurements of the net retention volume, corrected to a column temperature of 0°C, of 11 ethene-based fluids that are commonly encountered in alternative refrigerant research and testing. The fluids we have studied are listed in the left hand column of Table 1, along with the accepted code numbers [10,12]. The measurements were made on the packed-column stationary phase that has proven to be very useful for refrigerant analysis: a 5% coating of a low-molecular-mass polymer of hexafluoropropylene epoxide on a graphitized carbon black. The relative retentions were then calculated with respect to tetrafluoromethane (for three of the fluids) and hexafluoroethane (for all fluids). In addition to the discussion of qualitative trends in the data, fits to linear models are presented of the logarithms of the net retention volumes and the relative retentions against thermodynamic temperature, thus providing a predictive capability.

2. Theory

A discussion of the basic definitions, theory and application of corrected retention parameters was presented earlier [10].

3. Experimental

The measurements presented here were performed on a commercial gas chromatograph that had been modified to provide high precision

retention data. All of the experimental details were described earlier [10,11], so only a very general description will be provided here. The chromatograph was modified to provide a highly stable column temperature which was measured with a quartz-crystal oscillator thermoprobe (calibrated against a NIST-standard platinum resistance thermometer) that was accurate to within $\pm 0.01^\circ\text{C}$. Injection was done with a six-port sampling valve containing a sample loop of 0.1 ml volume. The valve was pneumatically actuated with pilot valves using helium as the actuation gas to inject very rapidly and thereby minimize the magnitude of the injection pressure pulse. The injection valve and loop were maintained at 50°C for all measurements. The carrier gas line to the injection valve was modified to allow the column head pressure to be measured with a calibrated Bourdon tube gauge. This gauge was calibrated against a dead mass pressure balance traceable to a NIST standard. The column outlet pressure was measured with an electronic barometer that had a resolution of 1.3 Pa (approximately 0.01 Torr). This barometer was also calibrated against a dead mass pressure balance. The column carrier gas flow-rate was measured with an electronic soap-bubble flow meter (corrected for water vapor pressure). Retention times were measured by a commercial integrator. A Ranque–Hilsch vortex tube was used to provide cooling in the column oven for the subambient temperature measurements [13, and references therein]. Thermal conductivity detection (TCD) was used with a carrier gas of research grade helium. The TCD system was maintained at 50°C for all measurements.

The stationary phase was a commercially prepared packing material consisting of a 5% (m/m) coating of a low-molecular-mass polymer of hexafluoropropylene epoxide modifier on a 60–80-mesh (177–250 μm) graphitized carbon black [14]. Some representative properties of this modifier and the column preparation procedure were presented earlier [10].

For each retention time measurement, five fluid injections were performed at each column temperature. Each series of injections was preceded and followed by five measurements of the

Table 1
The net retention volume, V_N^0 , and their logarithms, of the fluids measured in this study

Name	V_N^0 (ml)															
	-20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	120°C (393.15 K)	-20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	120°C (393.15 K)
Trifluoroethene (R-1123)	280.0 ± 3.70 1.3%	127.0 ± 1.50 1.1%	60.7 ± 0.4 0.56%	33.3 ± 0.5 1.5%	1503.5 ± 8.9 0.6%	636.9 ± 5.3 0.8%	310.0 ± 2.8 0.7%	159.8 ± 2.6 1.6%	2.45	2.10	1.78	1.52	2.80	2.49	2.20	
1,1-Difluoroethene (R-1132a)	152.7 ± 1.3 0.8%	73.1 ± 0.9 1.2%	38.6 ± 0.4 0.9%	21.8 ± 0.3 1.4%	228.3 ± 1.6 0.7%	117.3 ± 1.3 1.1%	63.4 ± 0.8 1.3%	37.6 ± 0.3 0.9%	2.18	1.86	1.59	1.34	2.07	1.80	1.58	
Fluoroethene (R-1141)	146.8 ± 1.3 0.8%	71.4 ± 0.6 0.8%	38.8 ± 0.4 0.9%	21.7 ± 0.3 1.5%	1503.5 ± 8.9 0.6%	636.9 ± 5.3 0.8%	310.0 ± 2.8 0.7%	159.8 ± 2.6 1.6%	2.17	1.85	1.59	1.34	2.80	2.49	2.20	
1,1-Dichloro-2,2-difluoroethene (R-1112a)					228.3 ± 1.6 0.7%	117.3 ± 1.3 1.1%	63.4 ± 0.8 1.3%	37.6 ± 0.3 0.9%								
Chlorotrifluoroethene (R-1113)					220.0 ± 2.5 1.1%	116.6 ± 1.5 1.2%	64.3 ± 1.0 1.5%	37.8 ± 0.21 0.5%								
2-Chloro-1,1-difluoroethene (R-1122)					154.8 ± 1.1 0.7%	82.7 ± 0.7 0.8%	48.8 ± 0.7 1.5%	29.3 ± 0.2 0.5%								
1-Chloro-1-fluoroethene (R-1131a)					509.7 ± 5.1 1.0%	246.1 ± 2.0 0.8%	131.8 ± 1.1 0.8%	74.3 ± 0.4 0.5%								
2-Bromo-1,1-difluoroethene (R-1122B1)					375.4 ± 5.3 1.4%	191.0 ± 1.3 0.7%	106.0 ± 0.4 0.4%	62.6 ± 0.5 0.8%								
Bromooethene (R-1140B1)					698.7 ± 6.3 0.9%	339.8 ± 2.7 0.8%	172.7 ± 2.9 1.6%	97.5 ± 0.98 1.0%								
<i>trans</i> -1,2-Dichloro-1,2-difluoroethene (R-1112i)					662.7 ± 6.0 0.9%	324.8 ± 2.3 0.7%	172.7 ± 2.9 1.6%	97.5 ± 0.98 1.0%								
<i>cis</i> -1,2-Dichloro-1,2-difluoroethene (R-1112c)																

The uncertainties cited are propagated from replicate measurements of the experimental parameters.

carrier gas flow rate, and the injection of five aliquots of air. The air was injected separately, before and after the injection of fluid, to measure the void volume of the column without introducing air as an impurity into the fluid containers. The corrected retention time was simply obtained by subtracting the average air retention time. At the start of each of these fifteen injections (five air, five fluid, five air), the requisite temperatures (column, flowmeter, and barometer) and pressures (column head and column exit) were recorded. These replicate measurements furnished the uncertainties used for the error propagation that provided the overall experimental uncertainties that are reported (two standard deviations, 2σ). The column head pressure was maintained uniformly at 137.9 ± 0.3 kPa (approximately 20 p.s.i.g.) for the measurements, although measurements were initially performed at several other pressures to verify consistency in the operation of the chromatograph. The carrier gas flow-rate at the column exit was maintained at 45 ± 0.3 ml/min.

Measurements were performed at four temperatures for each fluid. One fluid, the *cis*- and *trans*-geometric isomer mixture of 1,2-dichloro-1,2-difluoroethene, R-1112c,t, was measured between 60 and 120°C. The samples were all obtained from commercial sources in the highest available purity, and were used without further purification.

4. Results and discussion

The corrected net retention volumes, V_N^0 , for each fluid are presented in Table 1. The reported expanded uncertainties (with a coverage factor $k=2$) are the result of an error propagation performed with the standard deviations obtained from replicate measurements of each experimental parameter. The uncertainties were found to be uncorrelated (as determined by examination of Spearman's ρ and Kendall's τ ; see [15]), and the deviations were found to fit a normal distribution and were therefore treated as being entirely random [15]. In addition to the uncertainty, the coefficient of variation in percent is

provided. The precision of the measurements is generally between 0.5 and 1.5%, with the average precision of all the measurements on these compounds being 0.96%. This figure compares very well with the precision of typical retention parameters (generally between 1 and 2%) obtained in other physicochemical gas chromatographic measurements [16]. A plot of $\log V_N^0$ against $1/T$ for each fluid is provided in Fig. 1. These temperature-dependent data were then fitted with the best linear model (simple linear, logarithmic, power or exponential). The results of these fits are provided in Table 2. Included with each fluid are the coefficients, the Pearson correlation coefficient of the fit, and the temperature range over which the fit was taken [15]. All of the measurements performed on the ethene-based fluids are represented very well (within experimental error) with the simple linear model:

$$\log V_N^0 = m/T + b$$

where m is the slope and b is the intercept.

The relative retentions, $r_{a/b}$, were calculated with tetrafluoromethane (R-14) as the reference compound for the three most volatile fluids, and with hexafluoroethane (R-116) for all fluids.

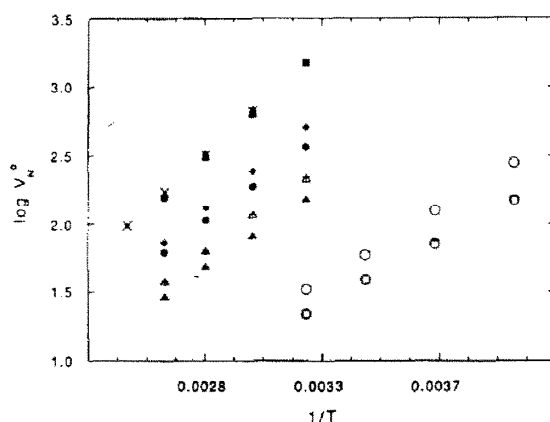


Fig. 1. A plot of the logarithm of the net retention volume, $\log V_N^0$, against $1/T$, for each fluid measured in this study. \circ = R-1123; \bullet (large) = R-1132a; \square = R-1141; \blacksquare = R-1112a; $+$ = R-1113; \triangle = R-1122; \blacktriangle = R-1131a; \blacklozenge (large) = R-1122B1; \bullet (small) = R-1140B1; \blacklozenge (small) = R-1112t; \times = R-1112c.

Table 2
Coefficients of the fits of $\log V_N^0$ against $1/T$, with the respective correlation coefficients

Compound	Model ^a	<i>m</i>	<i>b</i>	<i>r</i>	Temperature range (°C)
R-1123	L	1228.1	-2.40	0.99988	-20 to 40
R-1132a	L	1111.5	-2.21	0.99995	-20 to 40
R-1141	L	1082.6	-2.11	0.99954	-20 to 40
R-1112a	L	1891.0	-2.87	0.99994	40 to 100
R-1113	L	1513.72	-2.48	0.99989	40 to 100
R-1122	L	1485.71	-2.40	0.99991	40 to 100
R-1131a	L	1402.21	-2.29	0.99992	40 to 100
R-1122B1	L	1626.52	-2.49	0.99998	40 to 100
R-1140B1	L	1507.70	-2.24	0.99998	40 to 100
R-1112t	L	1860.82	-2.74	0.99996	60 to 120
R-1112c	L	1808.57	-2.61	0.99999	60 to 120

Note that in each case a simple linear model provided the best representation of the experimental measurements.

^a L = Linear.

These values are provided in Table 3. Plots of $\log r_{a,b}$ against $1/T$ for each reference are provided in Figs. 2 and 3. The expected trend with temperature is observed, and the plots and fits can therefore be used for prediction of the retention behavior on other columns containing the same stationary phase.

It is clear from the retention behavior that some difficulty will be experienced with the separation of many of the ethene-based fluids on the stationary phase used in this study. Despite this packing's great utility in the separation the methane- and ethane-based fluids, and its outstanding chemical and thermal stability, many of the ethene fluids coelute at all temperatures. The coelution is especially pronounced for the following sets: R-1112c, R-1112t, R-1112a; R-1122, R-1113; and R-1141 and R-1132a.

As we have demonstrated in previous papers [10,11], it is possible to construct a kind of "periodic chart" or property diagram for low-molecular-mass halocarbons [2]. The chart has a triangular format that groups the fluids according to their molecular structures and properties. Such charts have been successful in systematizing, in a semiquantitative manner, properties such as normal boiling point, atmospheric lifetime, flammability and toxicity [2]. The retention parameters measured for the methane-

and ethane-based fluids were found to fit this scheme qualitatively, with expected minima in the fluorine-rich section, and expected maxima predicted to occur in the chlorine-rich section. We have found that the correlation with the ethene-based halocarbons that were examined in this study is much less satisfactory. We speculate that the potential of a specific interaction (such as a charge transfer interaction) resulting from the π -bond complicates the retention of the ethene-based halocarbons.

5. Conclusions

Measurements of the corrected net retention volumes and relative retentions of 11 ethene-based halocarbon fluids that are relevant to research on alternative refrigerants have been presented. The logarithms of these data were fitted against reciprocal thermodynamic temperature to several linear models. In all cases, a simple linear relationship accounts for all structure in the data. These derived equations can be used for the prediction of the retention behavior of these fluids on this important stationary phase, and therefore can be used for solute identification and also for the design of analytical and preparative-scale separations. In addition,

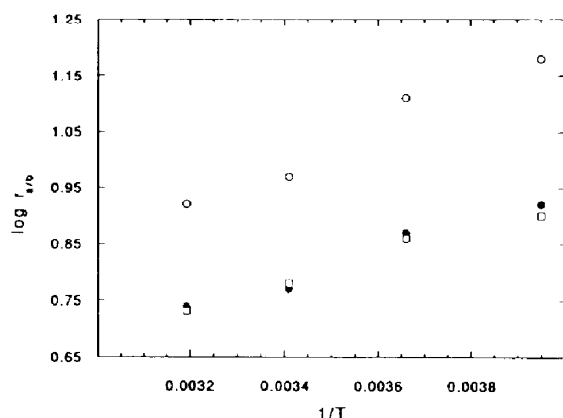


Fig. 2. A plot of the logarithm of the relative retention, $\log r_{a,b}$, with respect to tetrafluoromethane, against $1/T$, for the fluids measured between -20 and 40°C . \circ = R-1123; \bullet = R-1132a; \square = R-1141.

we note that the retention parameters are not qualitatively correlated by the triangular diagram scheme that successfully describes the normal boiling point, flammability, atmospheric lifetime, and toxicity of low molecular mass halocarbons. We had found in previous work that the re-

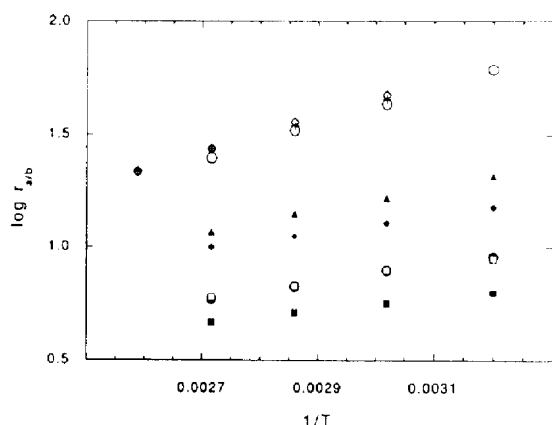


Fig. 3. A plot of the logarithm of the relative retention, $\log r_{a,b}$, with respect to hexafluoromethane, R-116, against $1/T$, for the fluids measured between 40 and 120°C . \circ = R-1112a; \bullet = R-1113; \square = R-1122; \blacksquare = R-1131a; \blacktriangle = R-1122B1; \blacklozenge = R-1140B1; \diamond = R-1112t; $+$ = R-1112c.

tention parameters of methane- and ethane-based halocarbons were qualitatively predicted by this type of property diagram.

Acknowledgements

The financial support of the Colorado Alliance for Science and the United States Environmental Protection Agency, Stratospheric Ozone Protection Branch, is gratefully acknowledged.

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