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Retention of halocarbons on a hexafluoropropylene epoxide-modified graphitized carbon black

II. Ethane-based compounds[☆]

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Abstract

The retention characteristics of 18 ethane-based chlorofluorocarbon, bromochlorofluorocarbon and fluorocarbon fluids have been studied as a function of temperature on a stationary phase consisting of a 5% (mass/mass) coating of a low-molecular-mass polymer of hexafluoropropylene epoxide on a graphitized carbon black adsorbent. Measurements were made at -20 , 0 , 20 and 40°C for hexafluoroethane (R-116), pentafluoroethane (R-125), 1,1,2,2-tetrafluoroethane (R-134), 1,1,1,2-tetrafluoroethane (R-134a), 1,1,2-trifluoroethane (R-143), 1,1,2-trifluoroethane (R-143a), 1,1-difluoroethane (R-152a), and fluoroethane (R161). Measurements were made at 40 , 60 , 80 and 100°C for 1,2-dichlorotetrafluoroethane (R-114), 1,1-dichlorotetrafluoroethane (R-114a), chloropentafluoroethane (R-115), 2,2-dichloro-1,1,1-trifluoroethane (R-123), 2-chloro-1,1,1-trifluoroethane (R-133a), 1,1-dichloro-1-fluoroethane (R-141b), 1-chloro-1,1-difluoroethane (R-142b), and 1-chloroethane (R-160). Measurements were performed at 60 , 80 , 100 and 120°C for 1-bromo-2-chlorotetrafluoroethane (R-114B1). 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 retention of tetrafluoroethane and hexafluoroethane. 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 for use as refriger-

ants, blowing and foaming agents, and propellants. These new materials are needed to replace the fully halogenated materials that are thought to contribute to atmospheric ozone depletion, and which will be phased out of production by law. The research that comprises 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

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is the chemical analysis of new fluids that are tested [3–6].

Gas chromatography is one of the major chemical analysis methods that is applied to the study of alternative refrigerants for several important reasons, not the least of which are simplicity and economics of operation [7,8]. It is used both as a qualitative identification tool and for quantitative analysis of impurities that are known to be present in a sample [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. This information would facilitate the identification of unknown or unfamiliar peaks that appear on a chromatogram obtained from, for example, the analysis of a field sample of a new refrigerant fluid. Moreover, these data would facilitate optimization of chromatographic separations by allowing us to predict the response of elution times and separation factors to controllable instrumental parameters. 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 these goals.

In an earlier paper, we discussed in detail the pitfalls and necessary caution that one must use in the application of such retention data [10]. In that paper, we also presented measurements for several methane-based fluids. In this paper, we present temperature-dependent measurements of the net retention volume, corrected to a column temperature of 0°C, of 18 ethane-based fluids that are commonly encountered in alternative refrigerant research and testing. The fluids we have studied are all gaseous at room temperature and pressure. To facilitate the data analysis and comparison, one measurement (at 40°C) is also provided for ethane (R-150). A listing of all the fluids studied is provided in the left-hand column of Table 1, along with the accepted code numbers. An explanation of the numbering system for these compounds has been provided elsewhere [10,11]. 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 and hexafluoroethane. 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], and only a brief review will be presented here. If the volumetric carrier gas flow-rate (at the column exit) is measured and multiplied by the retention time, the retention volume, V_R , is obtained. The adjusted retention volume, V'_R , is the retention volume corrected for the void volume (or mobile phase holdup) of the column. It is obtained by simply subtracting the retention volume of an unretained solute (V_M) such as air:

$$V'_R = V_R - V_M \quad (1)$$

The net retention volume, V_N^0 , is obtained by applying the Martin–James compressibility factor, j , to account for the pressure drop across the column [7]:

$$V_N^0 = jV'_R \quad (2)$$

The specific retention volume, V_g^0 , in units of volume per unit mass of stationary phase, corrects the net retention volume for the amount of stationary phase, and the column temperature is adjusted to 0°C:

$$V_g^0 = 273.15 \cdot \frac{V_N^0}{W_s T_{col}} \quad (3)$$

where T_{col} is the column temperature and W_s is the mass of stationary phase in the column. This value is a characteristic for a particular solute on a particular stationary phase in a particular

Table 1
Net retention volumes, V_N^0 , and their logarithms, of the fluids measured in this study

Name	V_N^0 (ml)	$\log V_N^0$															
		-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)
Hexafluoroethane (R-116)	176.9 ± 1.37 0.76%	82.4 ± 0.82 0.99%	43.2 ± 0.49 1.13%	24.6 ± 0.36 1.48%						2.25	1.92	1.64	1.39				
Pentafluoroethane (R-125)	407.3 ± 5.93 0.96%	172.8 ± 1.74 1.00%	83.5 ± 0.73 0.88%	43.4 ± 0.85 1.90%						2.61	2.24	1.92	1.64				
1,1,2,2-Tetrafluoroethane (R-134)	517.8 ± 4.37 0.84%	216.2 ± 2.69 1.2%	104.3 ± 0.91 0.87%	53.8 ± 0.45 0.84%						2.71	2.34	2.02	1.73				
1,1,1,2-Tetrafluoroethane (R-134a)	481.4 ± 5.43 1.13%	202.5 ± 1.39 0.69	98.0 ± 0.85 0.87%	48.7 ± 0.88 1.80%						2.68	2.31	1.99	1.69				
1,1,2-Trifluoroethane (R-143)	633.1 ± 3.48 0.55%	257.8 ± 3.77 1.46%	121.8 ± 1.09 0.89%	61.1 ± 0.51 0.84%						2.80	2.41	2.09	1.79				
1,1,1-Trifluoroethane (R-143a)	315.7 ± 3.43 1.09%	141.8 ± 1.96 1.38%	70.9 ± 0.60 0.85%	37.5 ± 0.56 1.48%						2.50	2.15	1.85	1.57				
1,1-Difluoroethane (R-152a)	412.8 ± 4.52 1.09%	176.8 ± 2.42 1.36%	88.2 ± 0.76 0.86%	46.4 ± 0.53 1.14%						2.62	2.25	1.95	1.67				
Fluoroethane (R-161)	336.0 ± 3.17 0.94%	146.2 ± 2.01 1.35%	75.2 ± 0.65 0.86%	40.0 ± 0.34 0.86%						2.53	2.17	1.88	1.60				
1,2-Dichlorotetrafluoroethane (R-114)	652.3 ± 10.70 1.60%	302.8 ± 2.78 0.92%	161.3 ± 1.04 0.65%	89.0 ± 1.42 1.60%						2.81	2.48	2.21	1.95				
1,1-Dichlorotetrafluoroethane (R-114a)	682.5 ± 7.10 1.04%	319.0 ± 2.65 0.83%	169.4 ± 1.19 0.70%	93.2 ± 1.59 1.70%						2.83	2.50	2.23	1.97				
Chloropentafluoroethane (R-115)	145.2 ± 0.96 0.66%	73.5 ± 0.82 1.12%	41.9 ± 0.66 1.58%	25.9 ± 0.15 0.58%						2.16	1.87	1.62	1.41				
2,2-Dichloro-1,1,1-trifluoroethane (R-123)	1413.6 ± 44.3 3.15%	613.7 ± 4.95 0.81%	308.1 ± 1.94 0.66%	162.8 ± 2.62 1.61%						3.15	2.79	2.49	2.21				
2-Chloro-1,1,1,2-tetrafluoroethane (R-124)	274.7 ± 1.55 0.56%	128.5 ± 0.94 0.74%	71.8 ± 0.47 0.65%	42.2 ± 0.24 0.58%						2.44	2.11	1.86	1.63				
2-Chloro-1,1,1-trifluoroethane (R-133a)	304.5 ± 4.90 1.60%	144.9 ± 1.08 0.75%	80.0 ± 0.47 0.58%	47.1 ± 0.26 0.55%						2.48	2.16	1.90	1.67				
1,1-Dichloro-1-fluoroethane (R-141b)	918.3 ± 9.71 1.06%	462.5 ± 3.47 0.81%	224.1 ± 1.39 0.62%	124.3 ± 1.99 1.60%						2.96	2.63	2.35	2.09				
1-Chloro-1,1-difluoroethane (R-142b)	210.1 ± 2.71 1.29%	103.2 ± 0.76 0.73%	59.6 ± 0.38 0.64%	35.8 ± 0.20 0.56%						2.32	2.01	1.78	1.55				
1-Chloroethane (R-160)	238.9 ± 2.01 0.84%	126.1 ± 1.40 1.11%	71.3 ± 1.10 1.54%	42.2 ± 0.27 0.65%						2.38	2.10	1.85	1.63				
1-Bromo-2-chlorotetrafluoroethane (R-114B1)		631.3 ± 7.75 1.22%	314.5 ± 1.92 0.61%	167.0 ± 2.69 1.61%	97.4 ± 0.94 0.97%					2.80	2.50	2.22	1.99				

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

carrier gas, and is instrument independent. This is a quantity that may be compared from instrument to instrument, and laboratory to laboratory with a high level of confidence provided the stationary phase used is a single, pure compound. If the mass of stationary phase is not known, or is not meaningful, it is still of value to correct the net retention volume to a column temperature to 0°C (represented by V_N^0) by simply not including the term for W_s (setting it equal to unity). In the present study, the stationary phase is a solid sorbent modified with a liquid coating. Since the retention in this case is not caused exclusively by either adsorption or absorption processes, we will use the net retention volume, V_N^0 , corrected to 0°C (that is, V_g^0 , with $W_s = 1$).

It is also extremely valuable to calculate a relative retention, $r_{a/b}$:

$$r_{a/b} = \frac{V_g^b}{V_g^a} = \frac{V_N^b}{V_N^a} \quad (4)$$

where the alphabetic superscripts refer to the retention volumes of solutes a and b, solute a serving as the reference. The relative retention is dependent only on the column temperature and the type of stationary phase. For reasons of operational simplicity, this parameter is usually one of the best to use for qualitative analysis [7,9]. When measurements are performed carefully, the relative retention varies only with column temperature and stationary phase, and thus forms a reasonable basis for qualitative identification.

To extend the applicability of relative retention data, it is possible to account for temperature by plotting $\ln r_{a/b}$ against $1/T$, where T is the thermodynamic temperature. Such plots are nearly linear (especially in gas-liquid chromatography), and allow comparisons at many column temperatures. The plots can become very non-linear when measured with unmodified solid sorbents as the stationary phase, depending upon the detailed characteristics of the adsorption isotherms. The use of a surface modifier (as was done in the present study) on a solid phase will often increase the linearity of the plots, and shorten retention times.

Although it is not generally considered good practice to extrapolate the plot beyond the temperature range for which experimental data are available, we have found with this class of compounds that extrapolation to temperatures 50°C higher than that used in the correlation can provide acceptable predictions. Naturally, interpolation within the region covered by the experimental data provides very good predictions of both the relative retentions and the net retention volumes. These data can even provide the basis for scaling isothermal analyses to temperature-programmed analyses.

3. Experimental

The measurements presented in this paper 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], 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 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 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 weight 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 (corrected for water vapor pressure) was measured with an electronic soap-bubble flow meter. 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 (see [12]). 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% (mass/mass) coating of a low-molecular-mass polymer of hexafluoropropylene epoxide modifier on a 60–80 mesh (177–250 μm) graphitized carbon black [13]. 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 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 (5 air, 5 fluid, 5 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. 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 on four isotherms for each fluid, approximately equally divided between two temperature ranges, -20 to 40°C and 40 to 100°C . One fluid, 1-bromo-1-chlorotetrafluoroethane (R-114B1), was measured between 60 and 120°C . The samples were

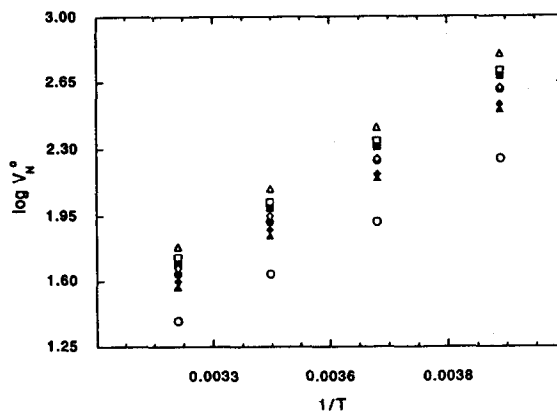


Fig. 1. Plot of the logarithm of the net retention volume, $\log V_N^0$, against $1/T$, for each fluid measured between -20 and 40°C . \circ = R-116; \bullet = R-125; \square = R-134; \blacksquare = R-134a; \triangle = R-143; \blacktriangle = R-143a; \diamond = R-152a; \blacklozenge = R-161.

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 uncertainties are the result of an error propagation performed with the standard deviations

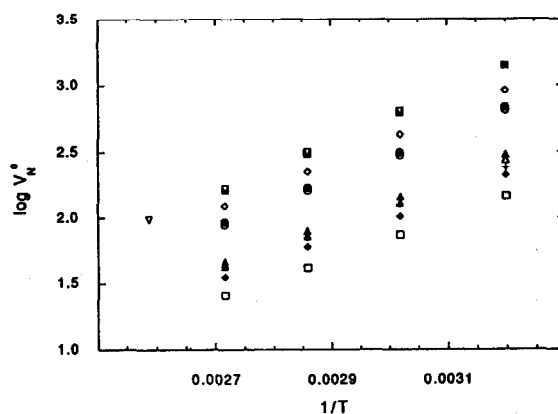


Fig. 2. Plot of the logarithm of the net retention volume, $\log V_N^0$, against $1/T$, for each fluid measured between 40 and 120°C . \circ = R-114; \bullet = R-114a; \square = R-115; \blacksquare = R-123; \triangle = R-124; \blacktriangle = R-133a; \diamond = R-141b; \blacklozenge = R-142b; $+$ = R-160; ∇ = R-114B1.

Table 2

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

Compound	Model	m	b	r	Temperature range (°C)
R-116	L	1138.5	-2.25	0.99999	-20 to 40
R-125	L	1280.89	-2.45	0.99999	-20 to 40
R-134	L	1297.06	-2.41	0.99997	-20 to 40
R-134a	L	1306.11	-2.47	0.99986	-20 to 40
R-143	L	1332.40	-2.46	0.99997	-20 to 40
R-143a	L	1224.56	-2.33	0.99988	-20 to 40
R-152a	L	1244.01	-2.30	0.99989	-20 to 40
R-161	L	1220.87	-2.29	0.99986	-20 to 40
R-114	L	1675.55	-2.54	0.99989	40 to 100
R-114a	L	1676.43	-2.52	0.99993	40 to 100
R-115	P	2.43	6.932	0.99989	40 to 100
R-123	L	1821.42	-2.67	0.99990	40 to 100
R-124	P	2.28	6.088	0.99982	40 to 100
R-133a	P	2.26	6.033	0.99993	40 to 100
R-141b	L	1688.50	-2.43	0.99994	40 to 100
R-142b	P	2.29	6.084	0.99973	40 to 100
R-160	L	1466.95	-2.30	0.99998	40 to 100
R-114B1	L	1773.22	-2.52	0.99994	60 to 120

Note that for R-115, R-124, R-133a and R-142b the coefficients are for the power (P) model rather than the simple linear (L) model.

obtained from replicate measurements of each experimental parameter. The errors were found to be uncorrelated (as determined by examination of Spearman's ρ and Kendall's τ ; see [14]), and the deviations were found to fit a normal distribution and were therefore treated as being entirely random. In addition to the uncertainty,

the relative standard deviation is provided. The precision of the measurements is generally between 0.5 and 1.5%, with the average precision of all the measurements being 1.04%. This figure compares very well with the precision of typical retention parameters (generally between 1 and 2%) obtained in other physicochemical gas chro-

Table 3

Relative retentions, $r_{a/b}$, and their logarithms, of the more volatile fluids measured in this study, with respect to tetrafluoromethane, R-14

Compound	$r_{a/b}$				$\log r_{a/b}$			
	-20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	-20°C (253.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)
R-116	9.72	8.32	6.65	6.15	0.99	0.92	0.82	0.79
R-125	22.14	17.45	12.85	10.85	1.35	1.24	1.11	1.04
R-134	28.14	21.84	16.05	13.45	1.45	1.34	1.21	1.13
R-134a	26.16	20.45	15.08	12.18	1.42	1.31	1.18	1.09
R-143	34.41	26.04	18.74	15.28	1.54	1.42	1.27	1.18
R-143a	17.16	14.32	10.91	9.38	1.23	1.16	1.04	0.97
R-152a	22.43	17.86	13.57	11.60	1.35	1.25	1.13	1.06
R-161	18.37	14.97	11.57	10.00	1.26	1.18	1.06	1.00

Table 4
Relative retentions, $\tau_{r/b}$, and their logarithms, of all of the fluids measured in this study, with respect to hexafluoromethane, R-116

Compound	$\log \tau_{r/b}$															
	-20.0°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)
R-125	2.28	2.10	1.93	1.76					0.36	0.32	0.29	0.25				
R-134	2.89	2.62	2.41	2.19					0.46	0.42	0.38	0.34				
R-134a	2.69	2.46	2.27	1.98					0.43	0.39	0.36	0.30				
R-143	3.54	3.13	2.82	2.48					0.55	0.50	0.45	0.40				
R-143a	1.76	1.72	1.64	1.52					0.25	0.24	0.22	0.18				
R-152a	2.31	2.15	2.04	1.89					0.36	0.33	0.31	0.28				
R-161	1.89	1.80	1.74	1.63					0.28	0.25	0.24	0.21				
R-114				26.52	20.47	17.03	13.43					1.42	1.31	1.23	1.14	
R-114a				27.74	21.57	17.89	14.59					1.44	1.33	1.25	1.16	
R-115				5.90	4.97	4.42	4.05					0.77	0.70	0.65	0.61	
R-123				57.46	41.49	32.53	25.48					1.76	1.62	1.51	1.41	
R-124				11.17	8.64	7.58	6.60					1.05	0.94	0.88	0.82	
R-133a				12.38	9.80	8.45	7.37					1.09	0.99	0.93	0.87	
R-141b				37.33	28.84	23.66	19.45					1.57	1.46	1.37	1.29	
R-142b				8.54	6.98	6.29	5.60					0.93	0.84	0.80	0.75	
R-160				8.53	8.53	7.53	6.60					0.99	0.93	0.88	0.82	
R-114B1				9.71	42.68	33.21	26.13	21.99				0.99	1.63	1.52	1.42	1.34

matographic measurements [15]. A plot of $\log V_N^0$ against $1/T$ is provided in Fig. 1 for each fluid that was measured from between -20 and 40°C . A similar plot is provided in Fig. 2 for the fluids measured between 40 and 120°C . These temperature-dependent data were then fit with the best linear model (simple linear, logarithmic, power or exponential) [10]. 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. Most of the measurements are represented very well (within experimental error) with the simple linear model:

$$\log V_N^0 = m/T + b \quad (5)$$

where m is the slope and b is the intercept. For four fluids, the power model was slightly better able to account for all of the structure in the data, and therefore provides a somewhat more accurate representation of the measurements. The form of this model is:

$$\log^2 V_N^0 = m[\log(1/T)] + b \quad (6)$$

To recover the V_N^0 value from this model, one must take the antilogarithm (that is, 10^x) twice.

The relative retentions, $r_{a/b}$, were calculated with tetrafluoromethane (R-14) and hexafluoroethane (R-116) as reference compounds. Tetrafluoromethane was chosen because it is the least retained of all the fluids examined [10], and was used only for the more volatile fluids studied here. These values are provided in Table 3. Relative retentions with respect to hexafluoroethane were calculated for all of the fluids, however, and are provided in Table 4. Plots of $\log r_{a/b}$ against $1/T$ for each reference are provided in Figs. 3 and 4. The expected trend with temperature is observed, and the plot and fits can therefore be used for prediction of the retention behavior on other columns containing the same stationary phase.

In addition to the quantitative relationships and correlations presented above, the retention parameters we have measured appear to fit an important qualitative scheme that is useful in

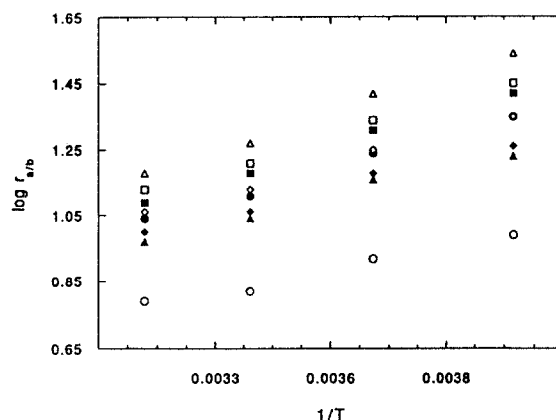


Fig. 3. Plot of the logarithm of the relative retention, $\log r_{a/b}$, with respect to tetrafluoromethane (R-14), against $1/T$, for the fluids measured between -20 and 40°C . \circ = R-116; \bullet = R-125; \square = R-134; \blacksquare = R-134a; \triangle = R-143; \blacktriangle = R-143a; \diamond = R-152a; \blacklozenge = R-161.

understanding the behavior of chlorofluorocarbons and fluorocarbons. One can construct a kind of “periodic chart” or property diagram for these types of compounds [2]. The chart has a triangular format that groups the fluids according to their molecular structures and properties. We present in Fig. 5 such a chart for two-carbon fluids. The top of the chart represents compounds rich in hydrogen (with ethane being the extreme member); the right-hand side represents compounds rich in fluorine (with hexafluoroethane being the extreme member); and the left-hand side represents compounds rich in chlorine (with hexachloroethane being the extreme member). 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 in this study fit this scheme qualitatively, with expected minima in the fluorine-rich section, and expected maxima predicted to occur in the chlorine-rich section. This chart can provide guidance in the design of analyses of (1) compounds not measured in this study, and (2) analyses done with somewhat different modifier concentration on the stationary phase.

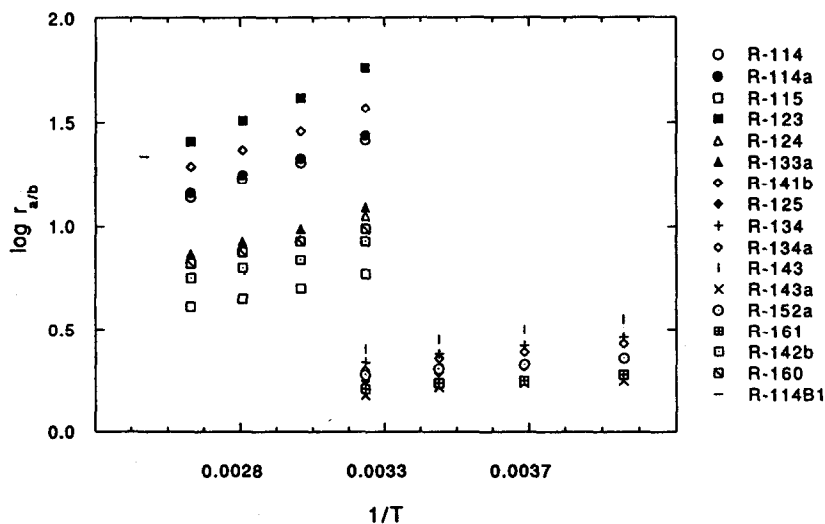


Fig. 4. Plot of the logarithm of the relative retention, $\log r_{a/b}$, with respect to hexafluoromethane (R-116), against $1/T$, for all fluids measured in this study.

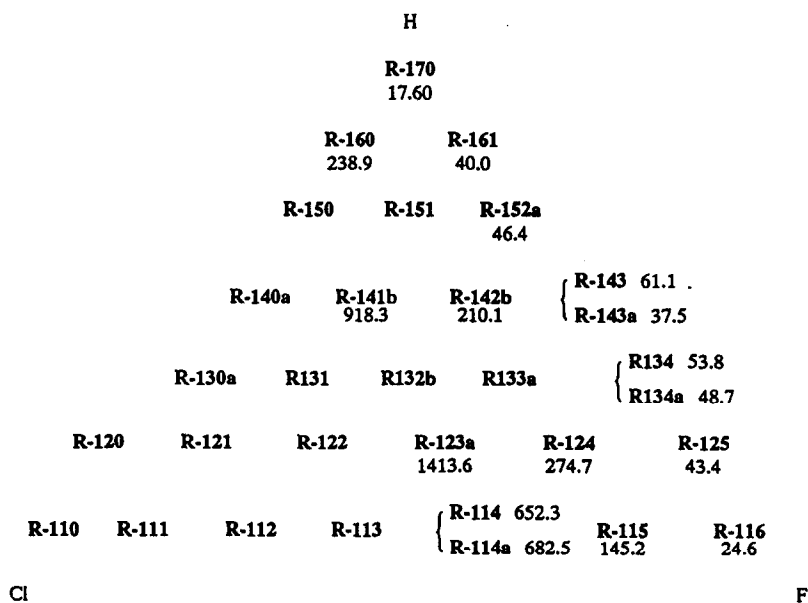


Fig. 5. Triangular diagram that provides a semiquantitative representation of refrigerant properties correlated with molecular structure. In this diagram, we have listed the net retention volumes, V_N^0 , for each of the indicated fluids measured at 40°C (313.15 K).

5. Conclusions

Measurements of the corrected net retention volume and relative retentions of 18 two-carbon 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 most cases, a simple linear relationship accounts for all structure in the data; in a few cases, a power model is slightly better. 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 analytical separation design. In addition, we note that the retention parameters also qualitatively fit the triangular diagram scheme that successfully describes the normal boiling point, flammability, atmospheric lifetime and toxicity of these compounds.

Acknowledgement

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