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Retention of halocarbons on a hexafluoropropylene-epoxide modified graphitized carbon black Part 5: heavier ethane- and ethene-based compounds

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Abstract

The retention characteristics of thirteen heavier ethane-based and eight ethene-based halocarbon fluids related to alternative refrigerant research have been studied as a function of temperature on a stationary phase consisting of a 5% (by mass) coating of a low molecular mass polymer of hexafluoropropylene epoxide on a graphitized carbon black adsorbent. Measurements were performed at 0, 20, 40, and 60°C for R-152, and at 20, 40, 60, and 80°C for R-124. Measurements were performed at 40, 60, 80, and 100°C for R-123a, R-152, and R-1151-1, and at 60, 80, 100 and 120 for R-132b and R-1130a, R-1121 (cis), and R-1121 (trans). Measurements were performed at 80, 100, 120 and 140°C for R-113, R-123B1, R-141, R-1130 (cis), and R-1130 (trans). Measurements were performed at 100, 120, 140, and 160°C for R-113a, R-121, R-122, R-131, R-131a, R-1110, R-1111, and R-1120. Relative retentions 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 relative retention data were fitted to linear models for the purpose of predicting retention behavior of these compounds to facilitate chromatographic analysis.

Keywords: Relative retention; Refrigerants, alternative; Halocarbons

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 propellants [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 are applied to the study of alternative refrigerants for several important reasons, not the least of which are simplicity and economics of operation [7-9]. A knowledge of the retention characteristics of important fluids on the more useful stationary phases is a valuable tool 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

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relative retentions, $r_{a/b}$, provide the simplest avenue to achieve these goals.

In earlier papers, we presented measurements for eight methane-based, eighteen ethane-based, eleven ethene-based, and twenty five propane-based fluids [10-13]. In this paper, we present temperature-dependent measurements of the relative retentions, $r_{a/b}$. of thirteen heavier ethane-based fluids and eight heavier ethene-based fluids that are commonly encountered in alternative refrigerant research and testing. The fluids we have studied are listed in the left-hand columns of Table 1 and Table 2, along with the accepted code numbers [10,13]. Note that the standard code numbering system does not specifically address brominated and iodinated fluids. A commonly used extension of the standard is applied here. In the case of iodinated fluids, we have further modified the numbering system by including a dash between the I and the iodine number designator that follows, since 'I' and 'I' are easily confused. The measurements were made on the packed-column stationary phase that has proven to be very useful for refrigerant analysis: a 5% coating (mass/mass) of a low molecular mass polymer of hexafluoropropylene epoxide on a graphitized carbon black [10]. The relative retentions were calculated with respect to tetrafluoromethane (R-14) and hexafluoroethane (R-116). In addition to the discussion of qualitative trends in the data, fits to linear models are presented for the logarithms of 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 ±0.01°C. Injection was done via syringe into a flash vaporization inlet (maintained at 175°C). and the samples were always introduced at infinite dilution. The carrier gas line to the injector was modified to allow the column head pressure to be measured with a 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 NIST dead weight pressure balance. The column carrier gas flow-rate (corrected for water vapor pressure) was measured with an electronic soapbubble flow meter. Retention times were measured by a commercial integrator. A Rangue-Hilsch vortex tube was used to provide cooling in the column oven for the subambient temperature measurements [14]. Thermal conductivity detection (TCD) was used with a carrier gas of research grade helium. The TCD was maintained at 125°C for all measurements.

The stationary phase was a commercially prepared packing material consisting of a 5% (by mass) coating of a low molecular mass polymer of hexafluoropropylene epoxide modifier on a 60-80 mesh graphitized carbon black [15]. Some representative properties of this modifier and the column preparation procedure were presented earlier [10].

For each retention measurement, five fluid injections were performed at each column temperature. The corrected retention time was simply obtained by subtracting the air retention time (as a measure of the void volume or gas holdup volume, $t_{\rm m}$) from the retention time of the fluid. At the start of each series of injections, the requisite temperatures (column, flowmeter, and barometer) and pressures (column head and column exit) were recorded. The dispersion in these replicate measurements furnished the uncertainties used for the error propagation that provided the overall experimental uncertainties. These uncertainties are reported with a coverage factor k=2 (two standard deviations, 2σ). The column head pressure was maintained to produce a constant flow-

rate for the measurements. A typical uniformity was 137.9±0.3 kPa (approximately 20 p.s.i.g.). Initially, measurements were performed at multiple pressures to verify consistency in the operation of the chromatograph. The carrier gas flow-rate at the column exit was maintained at 45±0.5 ml/min. Measurements were performed at four temperatures for each fluid. The only exception to this was tetrachloroethene, R-1110, for which only three isotherms are presented. Measurements below 120°C were impossible because of very long retention times which resulted in peak distortion, and because measurements above 160°C would cause excessive stationary phase bleed. The temperatures were chosen to provide adequate retention to minimize extra-column effects. The samples were all obtained from commercial sources in the highest available purity, and were used without further purification.

4. Results and discussion

The relative retentions, $r_{a/b}$, for each fluid with respect to R-14 and R-116 are presented in Table 1 and Table 2, respectively. The reported expanded uncertainties (with a coverage factor k=2) are the result of an uncertainty 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), and the deviations were found to fit a normal distribution and were therefore treated as being entirely random [16]. In addition to the uncertainty, the coefficient of variation in percent is provided. The uncertainty in the measurements is generally between 0.2 and 1.3%, with the average precision of all the measurements of these compounds being 0.7%. This figure compares very well with the precision of typical retention parameters (generally between 1 and 2%) obtained in other physicochemical gas chromatographic measurements [17]. For two of the measurements, relatively large uncertainties were obtained (3.28 and 3.23%, respectively) for R-1120, 1,1,2-trichloroethylene at 100°C. and R-1121 (cis), cis-1,2-dichloro-1-fluoroethene, at 60°C. These fluids are adsorbed very strongly to the unmodified sites on the graphitized carbon black, and

very poor chromatographic peak shapes are obtained unless very high column temperatures are employed. The high uncertainty is thus caused by the inability to adequately measure the retention time of the peak.

A plot of $\log(r_{a/b})$ against (1/T) for each fluid referenced to R-14 is provided in Fig. 1a and Fig. 1b. Similar plots are provided for the fluids referenced to R-116 in Fig. 2a and Fig. 2b. The expected trend of $r_{a/b}$ with reciprocal temperature is observed for each fluid. There is no evidence of any decomposition at the temperatures for which measurements were performed. It is clear from these plots that good separation is achieved for most of the heavier ethane and ethene compounds on this particular stationary phase. In a few cases, however, close elution of a few fluid pairs (R-131a, R-122; R-113a, R-123B1; R-123a, R-115I-1) is observed at the higher temperatures.

The temperature-dependent relative retention data were then fitted with the best linear model (simple linear, logarithmic, power, or exponential). The results of these fits are provided in Table 3 for retentions relative to tetrafluoromethane (R-14), and Table 4 for retentions relative to hexafluoroethane (R-116). Included with each fluid are the coefficients, the Pearson correlation coefficient (r) of the fit, and the temperature range over which the fit was taken.

Many of the measured data obtained for the ethane- and ethene-based fluids are represented very well (within experimental uncertainty) with the simple linear model:

$$\log(r_{a/b}) = m/T + b \tag{1}$$

where m is the slope and b is the intercept. Several were better represented by a logarithmic model:

$$\log(r_{a/b}) = m[\log(1/T)] + b, \tag{2}$$

an exponential model:

$$\log^2(r_{a/b}) = m/T + b, \tag{3}$$

or a power model:

$$\log^{2}(r_{a/b}) = m[\log(1/T)] + b. \tag{4}$$

The choice of model was based strictly on precision of fit and statistical significance of the

Table i Relative retentions, r., and their logarithms, of heavier ethanes and ethenes measured in this study, with respect to tetrafluoromethane, R-14

Name	\$ e/b				log (r.,)		!	
	28°C	4PC	60°C	3.65	20°C	46°C		C
2-Chloro-1, J. J. 2-tetraftuoroethane,	81.1±0.78	58.4±0.19	(333.13 K) 45.1±0.16	35.9±0.08	(N CI 767)	(313.15 K) 1.77	(333.15 K)	(353,15 K)
R-124	0.96%	0.32%	0.36%	0.23%	•	:		3
	40°C	J.09	2, 0 %	100°C	40°C	J.09	B0°C	100°C
	(313.15 K)	(333.15 K)	(353.15 K)	(373.15 K)	(313.15 K)	(333,15 K)	(353.15 K)	(373.15 K)
1,2-Dichloro-1,1,2-trifluoroethane,	275.8±0.62	186.8±0.49	133.5±1.37	98.8±0.32	2:44	2.27	2.13	2.00
R-123a	0.22%	0.26%	1.02%	0.32%				
1,2-Difluoroethane, R-152	16.9±0.18	14.2±0.27	12.6 ± 0.10	10.8±0.09	1.23	1.15	1.10	1.03
	%90°I	1.88%	0.80%	0.82%				
Iodopentafluoroethane, R-1151-1	249.3±0.78	175.1 ± 0.66	127.2 ± 1.08	96.8±0.83	2.40	2.24	2.11	66.1
	0.31%	0.38%	0.85%	0.86%				
	2,09	90, €	100°C	120°C	60°C	X 0.C	160°C	120°C
	(333.15 K)	(353.15 K)	(373.15 K)	(393 IS K)	(333.15 K)	(353.15 K)	(373.15 K)	(393.15 K)
1,2-Dichloro-1,1-difluoroethane,	236.2±1.33	162.6 ± 0.47	118.2 ± 0.48	89.4 ± 0.20	2.37	2.21	2.07	56.1
R-132b	0.57%	0.29%	0.41%	0.23%				
	8 % .C	100°C	120°C	140°C	BO.C	J.001	120°C	14lF.C
	(353.15 K)	(373.15 K)	(393.15 K)	(413.15 K)	(353.15 K)	(373.15 K)	(393.15 K)	(413.15 K)
1,1,2-Trichlorotrifluoroethane, R-113	275.7±0.52	197.8±0.53	146.5±0.30	113.4 ± 0.60	2.44	2.30	2.17	2.0 8
	%61:0	0.27%	0.20%	0.53%				
2-Bromo-2-chloro-1,1,1- Trifluoroethane, R-123B1	301.6±1.27 0.42%	208.6±1.12 0.54%	152.8±0.61 0.40%	116.1±0.41 0.35%	2.48	2.32	2.18	2.07
1,2-Dichloro-I-fluoroethane,	223,0±1.06	155.9 ±0.76	115.3±1.09	88.4 ± 1.17	2.35	2.19	2.06	1.95
K-141	0.48%	0.49%	0.95%	1.33%				
	3. 991	120°C	140°C	160°C	100°C	120°C	146°C	.).(P9).
	(373.15 K)	(393.15 K)	(413.15 K)	(433.15 K)	(373,15 K)	(393.15 K)	(413.15 K)	(433.15 K)
1, i, i - Trichiorotrifluoroethane, R-113a	216.2±2.31 1.07%	158.2±0.38 0.24%	0.34%	94.3 ±0.42	2.3 4	2.30	2.08	2
1,1,2,2-Tetrachlorofluoroethane,	1284.5±6.82	810.5±6.42	546.7 ±6.37	379.5 - 1.39	3.11	2.91	2.74	2.58
R-121	0.53%	0.79%	1.17%	0.37%				
1,2,2-Trichloro-1,1-difluoreethane,	374.1 ± 4.86 1 20%.	259.9±0.81	190,9±0.81	141.9 : 0.43	1.57	245	2.38	2.15
W-122	J., rr. 74		2, 44.70					

1,1,2-Trichloro-2-fluoroethane, R-131	519.1±8.03 1.55%	349.3±1.85 0.53%	250.0±1.40 0.56%	186.0±0.75 0.40%	2.72	2.54	2.40	2.27
1,1,2-Trichkoro-1-fluoroethane, R-131a	393.5±5.69 1.45%	271.8±1.13 0.42%	200.6±0.99 0.50%	149.2±0.61 0.41%	2.60	2.43	2.30	2.17
	60°C (333.15 K)	80°C (353.15 K)	160°C (373.15 K)	126°C (393.15 K)	60°C (333.15 K)	MPC (353.15 K)	100°C (373.15 K)	120°C (393.15 K)
cis-1,2-Dichloro-1-fluoroethene, R-1121c	257.8±5.59 2.17%	170.4±0.88 0.52%	121.9±0.72 0.59%	89.6±0.22 0.25%	2.41	2.23	2.09	1.95
trans-1,2-Dichloro-1-fluoroethene, R-1121t	328.6±10.63 3.23%	214.0±1.65 0.77%	149.4±1.18 0.79%	107.3±0.35 0.33%	2.52	2.33	2.17	2.03
I,I-Dichloroethene, R-H30a	183.3±0.55 0.30%	126.5±0.76 0.60%	91.1±0.52 0.58%	71.3±0.60 0.84%	2.26	2.10	96'1	1.85
	80°C (353.15 K)	100°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	80°C (353.15 K)	100°C (373.15 K)	120°C; (393.15 K)	140°C (413.15 K)
cis-1,2-Dichloroethene, R-1130c	229.9±4.77 2.08%	155.7±2.84 1.82%	112.1±1.46 1.02%	84.9±0.36 0.42%	2.36	2.19	2.05	1.93
trans-1,2-Dichloroethene, R-11301	184.4±2.98 1.62%	127.8±2.10 1.64%	94.7±0.87 0.91%	74.1±0.29 0.39%	2.27	2.11	1.98	1.87
	160°C	120°C	140°C	160°C	100°C	120°C	140°C	160°C
Tetrachloroethene, R-1110	(4 000)	1594.6±14.78 0.93%	989.9±8.12 0.82%	650.1±8.69 1.34%		3.20	3.00	2.81
Trichlorofluoroethene, R-1111	581.3±8.74 1.50%	376.5±4.06 1.08%	256.1±0.91 0.36%	182.6±0.81 0.45%	2.76	2.58	2.41	2.26
1,1,2-Trichloroethene, R-1120	633.9±20.76 3.28%	403.2±5.62. 1.40%	278.5±1.23 0.44%	196.9±0.67 0.34%	2.80	2.61	2.45	2.29

Table 2
Relative retentions, r., and their logarithms, of heavier ethanes and ethenes measured in this study, with respect to hexafluoricethane. R-116

Name	,				log (res)			
1,2-Difluoroethane, R-152	6°C (273.15 K) 3.3±0.06 1.76%	28°C (293.15 K) 3.0±0.05 1.54%	40°C (313.15 K) 2.8±0.02 0.76%	60°C (333.15 K) 2.7±0.02 0.56%	0°C (273.15 K) 0.52	28°C (293.15 K) 0.48	40°C (313.15 K) 0.44	60°C (333.15 K) 0.43
2-Chloro-1,1,1,2-tetrafluoroethane, R-124	20°C (293.15 K) 11.8±0.11 0.96%	46°C (313.15 K) 9.7±0.03 0.32%	60°C. (333.15 K) 8.5±0.03 0.36%	80°C (353.15 K) 7.5±0.02 0.23%	20°C (293.15 K) 1.07	40°C (313.15 K) 0.99	60°C (333.15 K) 0.93	80°C (353.15 K) 0.88
	40°C (3)3.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	40°C (313.15 K)	60°C (333.15 K)	80°C (353,15 K)	100°C (373.15 K)
1,2-Dichloro-1,1,2-trifluoroethane, R-123a	46.0±0.10 0.22%	35.2±0.09 0.26%	28.1±0.29 1.02%	22.9±0.07 0.32%	1.66	1.55	1.45	130
lodopentafluoroethane, R-1151-1	41.6±0.13 0.31%	33.0±0.12 0.38%	26.8±0.23 0.85%	22.4±0.19 0.86%	1.62	1.52	1.43	1.35
1,2-Dichloro-1,1-difluoroethane, R-132b	64°C (333.15 K) 44.6±0.25 0.57%	80°C (353.15 K) 34.2±0.10 0.29%	100°C (373.15 K) 27.4±0.11 0.41%	120°C (393.15 K) 22.6±0.05 0.23%	60°C (333.15 K) 1.65	80°C (353.15 K) 1.53	106°C (373.15 K) 1.44	120°C (393.15 K) 1.35
	88°C (353,15 K)	190°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	80°C (353.15 K)	100°C	120°C	140°C
1,1,2-Trichlorotrifluoroethane, R-113	58.0±0.11 0.19%	45.8±0.12 0.27%	37.0±0.08 0.20%	31.0±0.16 0.53%	1.76	99.	1.57	61.1
2-Bramo-2-chloro-1,1,1- trifluoraethane, R-123B1	63.4±0.27 0.42%	48.4±0.26 0.54%	38.6±0.16 0.40%	31.8±0.11 0.35%	98:1	F.68	65'1	F.50
1,2-Dichlero-1-fluoroethane, R-141	46.9±0.22 0.48%	36.1±0.18 0.49%	29.2±0.28 0.95%	24.2±0.32 1.33%	1.67	1.56	1.47	1.38

331±0111 277±012 1.70 1.60 1.52 0.34% 0.45% 11.5±04 2.47 2.31 2.18 1.17% 0.45% 1.94 1.82 1.72 0.42% 0.40% 1.94 1.82 1.72 0.56% 0.40% 0.40% 1.95 1.84 0.56% 0.40% 0.40% 1.95 1.84 0.56% 0.40% 0.40% 1.96 1.84 1.74 0.56% 0.40% 0.40% 1.99 1.84 1.74 0.56% 0.40% 0.40% 1.99 1.84 1.74 0.56% 0.40% 1.79 1.65 1.45 0.56% 0.40% 1.79 1.65 1.45 0.56% 0.33% 1.79 1.65 1.45 0.79% 0.33% 1.79 1.65 1.54 0.79% 0.33% 1.79 1.65 1.54 0.79% 0.33% 1.79 1.65 1.54 0.79% 0.33% 1.79 1.65 1.54 0.70% 0.42% 1.59 1.47 1.38 1.45 0.91% 0.39% 1.59 1.47 1.38 0.91% 0.39% 1.59 1.47 1.38 0.91% 0.39% 1.79 1.70 1.98 1.85 1.40 0.44% 0.34% 1.71 1.70 1.70 1.70 1.70 1.70 1.70 1.70		100°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	160°C (433.15 K)	160°C (373.15 K)	120°C	140°C	J.4991
1.17% 149.6±1.74 111.5±0.44 2.47 2.31 2.18 1.17% 0.37% 0.37% 1.94 1.82 1.72 0.42% 0.31% 0.31% 1.94 1.82 1.72 0.42% 0.31% 0.31% 1.94 1.82 1.72 0.42% 0.31% 0.31% 1.94 1.84 1.74 0.50% 0.40% 0.40% 1.96 1.84 1.74 0.50% 0.41% 0.41% 0.41% 0.41% 1.35 1.45 1.00°C 120°C 60°C 80°C 100°C 1.00°C 120°C 60°C 80°C 1.45 0.59% 0.25% 1.59 1.55 1.45 0.59% 0.25% 1.79 1.65 1.45 0.59% 0.25% 1.79 1.65 1.45 1.00°C 140°C 140°C 140°C 1.00°C 140°C 140°C 140°C 1.00°C 120°C 140°C 140°C 1.00°C 120°C 140°C 140°C 1.00°C 120°C 140°C 140°C 1.00°C 1.345 1.34 1.35 1.34 1.00°C 1.00°C 1.00°C 1.00°C 1.00°C 1.00°C 1.00°C 1.00°C 1.00°C 1.00°C 1.00	50.1±0.54 1.07%		40.0±0.10 0.24%	33.1±0.11 0.34%	27.7±0.12	1.70	1.00	L.52	(N 61.65)
0.21 \$2.2 ± 0.22 41.7 ± 0.13 1.94 1.82 1.72 0.42% 0.31% 0.31% 1.99 1.84 1.84 0.42% 0.31% 0.31% 1.96 1.84 1.74 0.56% 0.40% 0.41% 1.96 1.84 1.74 0.50% 0.41% 0.41% 1.96 1.84 1.74 1.00°C 1.20°C 60°C 80°C 100°C 5.K) (373.15 K) (333.15 K) (333.15 K) (373.15 K) 0.50% 0.25% 0.25% 1.45 1.45 0.50% 0.25% 0.33% 1.54 1.43 1.3 0.19 0.25% 0.33% 1.54 1.43 1.3 0.10 0.25% 0.33% 1.54 1.43 1.3 0.10 0.25% 0.33% 1.54 1.43 1.3 0.10 0.21 0.33% 0.333.15 K) (333.15 K) (333.15 K) (333.15 K) 1.00	297.7±1.58 0.53%		205.0±1.62 0.79%	149.6±1.74 1.17%	111.5±0.41 0.37%		2.31	2. 81.	2.05
0.47 68.4±0.38 54.7±0.22 2.08 1.95 1.95 1.84 0.56% 0.40% 0.40% 0.40% 0.40% 0.40% 0.40% 0.40% 0.40% 0.41% 0.51% 0.41% 0.41% 0.50% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.41% 0.42% 0.25% 0.25% 0.25% 0.25% 0.33% 0.25% 0.33% 0.33% 0.58% 0.33% 0.33% 0.58% 0.33% 0.43% 0.43% 0.43% 0.43% 0.43% 0.43% 0.44% 0	86.7±1.13 1.30%		65.7±0.21 0.31%	52.2±0.22 0.42%	41.7±0.13 0.31%	1.94	1.82	1.72	297
9.29 54.9±0.27 43.8±0.18 1.96 1.84 1.74 0.50% 0.41% 0.50% 1.84 1.74 100°C 120°C 60°C 80°C 100°C 3.19 28.3±0.17 22.7±0.06 1.69 1.55 1.45 0.19 28.3±0.17 22.7±0.06 1.69 1.55 1.45 0.19 0.25% 1.79 1.65 1.54 0.15 27.1±0.09 1.79 1.65 1.54 0.15 21.1±0.12 18.0±0.15 1.54 1.43 1.33 0.16 21.1±0.12 18.0±0.15 1.54 1.43 1.33 0.58% 0.84% 1.54 1.43 1.33 0.58% 0.44% (413.15 K) (333.15 K) (393.15 K) 1.02% 1.40°C 1.68 1.56 1.47 1.38 1.02% 0.91% 0.39.6 1.59 1.47 1.38 1.02% 0.91% 0.39.6 0.39.6 1.34 </td <td>120.3±1.86 1.55%</td> <td></td> <td>88.3±0.47 0.53%</td> <td>68.4±0.38 0.56%</td> <td>54.7±0.22 0.40%</td> <td>2.08</td> <td>1.95</td> <td>7.7</td> <td>1.74</td>	120.3±1.86 1.55%		88.3±0.47 0.53%	68.4±0.38 0.56%	54.7±0.22 0.40%	2.08	1.95	7.7	1.74
8 (373.15 K) 120°C 66°C 80°C 100°C 5.19 28.3±6.17 22.7±6.06 1.69 1.55 1.45 5.19 28.3±6.17 22.7±6.06 1.69 1.55 1.45 5.39% 0.25% 1.69 1.55 1.45 1.45 5.35 34.6±6.27 27.1±6.09 1.79 1.65 1.54 6.79% 0.33% 1.79 1.65 1.54 6.79% 0.33% 1.79 1.65 1.54 6.16 21.1±0.12 18.0±0.15 1.54 1.43 1.33 6.58% 0.34% 0.34% 1.54 1.43 1.33 6.58% 0.34% 0.353.15 K) 0.35.15 K) 0.39.315 K) 1.45 7.66 28.3±0.29 23.2±0.10 1.68 1.56 1.45 1.49 24.0±0.22 20.3±0.08 1.59 1.47 1.38 1.49 0.91% 0.39% 0.39% 0.39% 0.413.15 K) 1.40	91.2±1.32 1.45%		68.7±0.29 0.42%	54.9±0.27 0.50%	43.8±0.18 0.41%	1.96	1.84	1.74	<u> </u>
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1.16 2.1.1±0.12 18.0±0.15 1.54 1.43 1.33 0.58% 0.84% 0.84% 1.54 1.43 1.33 120°C 144% 80°C 100°C 120°C 5 K) (393.15 K) (413.15 K) (353.15 K) (373.15 K) (393.15 K) 1.66 28.3±0.29 0.42% 1.56 1.45 1.45 1.07% 0.42% 1.59 1.47 1.38 0.91% 0.93% 1.59 1.47 1.38 0.91% 0.99% 1.59 1.47 1.38 140°C 160°C 100°C 120°C 140°C 1 40°C 160°C 100°C 1.38 1.38 3.74 270.8±2.22 191.1±2.55 2.61 2.43 6.82% 1.34% 27.9±0.20 2.13 1.98 1.85 0.36% 0.45% 2.17 2.01 1.88 0.44% 0.34% 2.17 2.01 1.88	62.0±2.00 3.23%		45.0±0.35 0.77%	34.6±0.27 0.79%	27.1±0.09 0.33%	6£.1	1.65	1.54	1.43
5 K) 120°C 146°C, 80°C 160°C 120°C 5 K) (393.15 K) (413.15 K) (353.15 K) (373.15 K) (393.15 K) 5.66 28.3 ± 0.29 23.2 ± 0.10 1.68 1.56 1.45 1.02% 0.42% 1.59 1.47 1.38 1.49 2.40± 0.22 20.3 ± 0.08 1.59 1.47 1.38 0.91% 0.91% 0.39% 1.59 1.47 1.38 1.49°C 1.60°C 100°C 120°C 140°C 1.40°C 100°C 120°C 140°C 1.40°C 1.34% (373.15 K) (393.15 K) 3.74 270.8±2.22 191.1±2.55 2.61 2.43 0.36% 0.45% 2.13 1.98 1.85 0.36% 0.44% 0.34% 2.17 2.01 1.88	34.4±0.24 0.71%		26.6±0.16 0.60%	21.1±0.12 0.58%	18.0±0.15 0.84%	1.54	1.43	1.33	1.26
5 K) (393.15 K) (413.15 K) (353.15 K) (373.15 K) (393.15 K) 28.3 ± 0.29	80°C		100°C	120°C	148°C.	30°C	100°C	120°C	J-05-1
A49 2.40±0.22 2.40±0.22 2.0.3±0.08 1.59 1.47 1.38 1.31 0.91% 0.39% 1.60°C 140°C 140°C 140°C 160°C 1 40°C 160°C 100°C 120°C 140°C 160°C 160°C 3.74 270.8±2.22 191.1±2.55 2.51 2.43 2.28 0.3 70.1±0.25 53.7±0.24 2.13 1.98 1.85 1.73 0.36% 0.45% 2.13 1.98 1.85 1.73 1.42 76.2±0.34 57.9±0.20 2.17 2.01 1.88 1.76 0.44% 0.34% 0.34% 2.17 2.01 1.88 1.76	(353.15 K) 48.4±1.00 2.08%		(373.15 K) 36.1±0.66 1.82%.	(393.15 K) 28.3±0.29 1.02%	(413.15 K) 23.2±0.10 0.42%	(353.15 K) 1.68	(373.15 K) 1.56	(393.15 K) 1.45	(413.15 K) 1.37
IAIPC 160PC 100PC 120PC 140PC 160PC 3.74 270.8±2.22 191.1±2.55 2.61 2.43 2.28 3.74 270.8±2.22 191.1±2.55 2.61 2.43 2.28 433.15 1.34% 2.61 2.43 2.28 63.2% 1.34% 2.13 1.98 1.85 1.73 63.6% 6.45% 2.17 2.01 1.88 1.76 1.42 76.2±0.34 57.9±0.20 2.17 2.01 1.88 1.76 6.44% 0.44% 0.34% 1.76 2.01 1.88 1.76	38.8±0.63 1.62%		29.6±0.49 1.64%	24.0±0.22 0.91%	20.3±0.08 0.39%	1.59	1.47	88:-1	1.31
0.3 70.1±0.25 53.7±0.24 2.13 1.98 1.85 0.36% 0.36% 0.45% 2.17 2.01 1.88 0.44% 0.34%	100°C (373.15 K)		120°C (393.15 K) 403.2±3.74	140°C (413.15 K) 270.8±2.22	160°C (433.15 K) 191.1±2.55	100°C (373.15 K)	120°C (393.15 K) 2.61	140°C (413.15 K) 2.43	160°C (433.15 K) 2.28
1.42 76.2±0.34 57.9±0.20 2.17 2.01 1.88 0.44% 0.34%	134.7±2.03 1.50%		0.75 % 95.2±1.03 1.18%	0.5¢ % 70.1±0.25 0.36%	53.7±0.24 0.45%	2.13	1.98	1.85	1.73
	146.9±4.81 3.28%		101.9±1.42	76.2±0.34 0.44%	57.9±0.20 0.34%	2.17	2.01	8 % .1	1.76

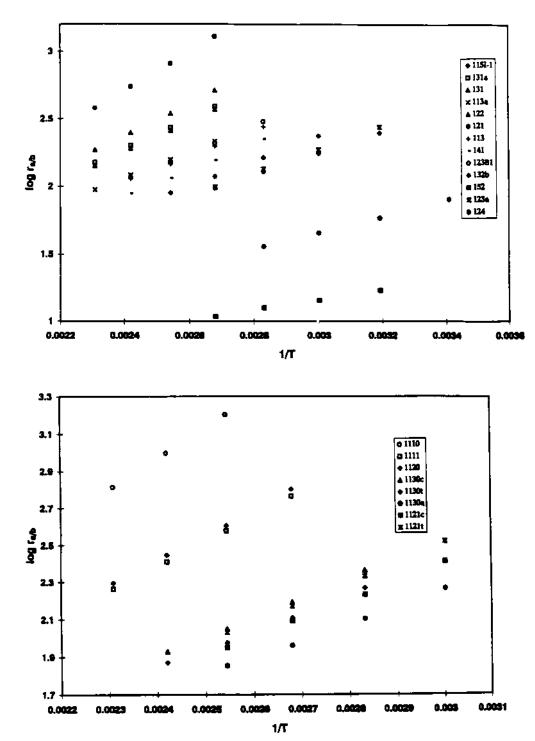


Fig. 1. Plots of the logarithms of the relative retentions (with respect to tetrafluoromethane, R-14), $\log(r_{\star,b})$, against (1/T), where T is the thermodynamic temperature, for each heavier ethane (upper) and heavier ethene (lower) fluid measured.

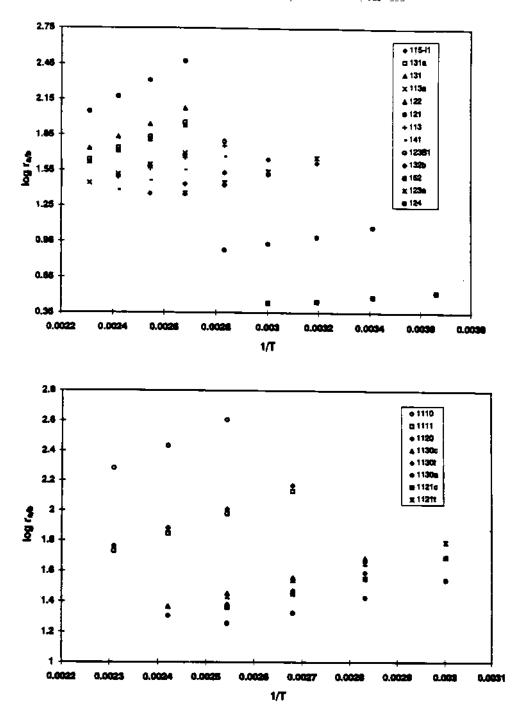


Fig. 2. Plots of the logarithms of the relative retentions (with respect to hexafluoroethane, R-(16), $\log(r_{a,b})$, against (1/T), where T is the thermodynamic temperature, for each heavier ethane (upper) and heavier ethene (lower) fluid measured.

Table 3 Coefficients of the fits of $\log (r_{4,n})$ against (1/T), with the respective correlation coefficients, with tetrafluoromethane (R-14) as the reference (L=linear, P=power, E=exponential, LG=logarithmic)

Name	Model	m	ь	r	Temperature range
2-Chloro-1.1.1.2-tetrafluoroethane, R-124	Е	353.63	0.57	0.99994	
1.2-Dichloro-1.1.2-trifluoroethane, R-123a	P	1.56	1869.91	0.99997	40−100°C
1.2-Difluoroethane, R-152	LG	1.09	7.49	0.99872	40-100°C
Iodopentafluoroethane, R-115I-1	P	1.08	1194.74	0.99999	40-100°C
1.2-Dichloro-1,1-difluoroethane, R-132b	E	424.92	0.66	0.99997	60−120°C
1.1.2-Trichlorotrifluoroethane, R-113	P	1.10	1515.79	0.99998	80-140°C
2-Bromo-2-chloro-1.1.1-triffuoroethane, R-123B1	Е	443.66	0.71	0.99988	80-140°C
1.2-Dichloro-1-fluoroethane, R-141	E	454.79	0.65	0.99989	80-140°C
1.1.1-Trichlorotrifluoroethane, R-113a	L	972.26	-0.27	0.99999	100~160°C
1.1.2.2-Tetrachlorofluoroethane, R-121	Ĺ	1431.53	-0.73	0.99999	100-160°C
1.2.2-Trichloro-1.1-diffuoroethane, R-122	Ĺ	1135.32	-0.47	0.99995	100-160°C
1,1,2-Trichloro-2-fluoroethane, R-131	P	1.21	3429.31	0.99997	100-160°C
1.1,2-Trichloro-1-fluoroethane, R-131a	L	1134.14	-0.44	0.99995	100-160°C
cis-1,2-Dichloro-1-fluoroethene, R-1121c	E	457.87	0.61	0.99994	60-120°C
trans-1,2-Dichloro-1-fluoroethene, R-1121t	₽	1.29	4455.54	0.99994	60-120°C
1.1-Dichloroethene, R-1130a	E	437.88	0.61	0.99966	60-120°C
cis-1.2-Dichloroethene, R-1130c	E	492.23	0.59	0.99995	80-140°C
trans-1,2-Dichloroethene, R-1130t	E	467.73	0.60	0.99990	80-140°C
Trichlorofluoroethene, R-1111	L	1360.99	-0.88	0.99996	100-160°C
1.1.2-Trichioroethene, R-1120	P	1.34	7961.49	0.99997	100-160°C
Tetrachloroethene, R-1110	P	1.37	11 365.59	0.99999	120-160°C

Table 4 Coefficients of the fits of $\log(r_{a,b})$ against (1/T), with the respective correlation coefficients, with hexafluoroethane (R-116) as the reference (L=linear, P=power, E=exponential, LG=logarithmic)

Name	Model	m	b	r	Temperature range
1.2-Difluoroethane, R-152	P	1.59	4215.51	0.99988	0-60°C
2-Chloro-1.1.1.2-tetrafluoroethane. R-124	E	341.90	0.33	0.99984	20-80°C
1.2-Dichloro-1.1.2-trifluoroethane, R-123a	P	1.15	1252.98	0.99997	40–100°C
Iodopentafluoroethane, R-115I-1	P	1.04	646.86	0.99994	40-100°C
1.2-Dichloro-1,1-diffuoroethane, R-132b	Ε	428.67	0.46	0.99999	60-120°C
1.1.2-Trichlorotrifluoroethane, R-113	P	1.07	918.25	0.99994	80-140°C
2-Bromo-2-chloro-1.1.1-trifluoroethane, R-123B1	E	441.97	0.52	0.99990	80−140°C
1,2-Dichloro-1-fluoroethane, R-141	£	457.49	0.46	0.99991	80–140°C
1.1.1-Trichlorotrifluoroethane, R-113a	L	693.54	-0.1 6	0.99999	100-160°C
1.1.2.2-Tetrachlorofluoroethane, R-121	L	1152.82	-0.62	0.99999	100−160°C
1,2,2-Trichloro-1,1-difluoroethane, R-122	L	856.61	-0.36	0.99993	100-160°C
1.1.2-Trichioro-2-fluoroethane, R-131	E	485.64	0.57	0.99996	100-160°C
1.1.2-Trichloro-1-fluoroethane, R-131a	L	855.42	-0.33	0.99989	100-160°C
cis-1,2-Dichloro-1-fluoroethene, R-1121c	E	474.53	0.41	0.99993	60−120°C
trans-1.2-Dichloro-1-fluoroethene, R-1121t	P	1.34	4217.31	0.99992	60~120°C
1,1-Dichloroethene, R-1130a	LG	1.53	10.39	0.99779	60-120°C
cis-1,2-Dichloroethene, R-1130c	Ε	509.39	0.40	0.99995	80-140°C
trans-1,2-Dichloroethene, R-1130t	E	476.12	0.41	0.99955	80–140°C
Trichlorofluoroethene, R-1111	L	1081.38	-0.77	0.99996	100–160°C
1.1.2-Trichloroethene, R-1120	P	1.39	8018.84	0.99993	100~160°C
Tetrachloroethene, R-1110	P	1.40	11 430.93	0.99998	120-160°C

fitted parameters. No physical interpretation is assigned to the coefficients beyond the ability to fit (or account for all of the structure in) the measured data.

5. Conclusions

Measurements of the relative retentions (on a very useful stationary phase) of thirteen heavier ethane- and eight heavier ethene-based halocarbon fluids that are relevant to research on alternative refrigerants have been presented. The relative retentions were calculated with respect to tetrafluoromethane (R-14) and hexafluoroethane (R-116). The logarithms of these data were fitted against reciprocal thermodynamic temperature to several linear models. 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. Moreover, these results can also be used in the design of more sophisticated analytical and preparative-scale separations [18].

Acknowledgments

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