Retention of halocarbons on a hexafluoropropylene epoxide modified graphitized carbon black
Part 6: Eleven fluoroethers and two iodofluoroalkanes

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Abstract

The retention characteristics of 11 ether-based and 2 iodinated 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, 60, and 80°C for R-E125 and R-E134; at 40, 60, 80, and 100°C for R-E143a, R-CE216, R-E236ea1, R-E245fa1, R-E263fb1, and R13I-1; at 80, 100, 120, and 140°C for R-E235ca2, R-E235da1, R-E347, and R-217I-1; and at 100, 120, 140, and 160°C for R-E280. Measurements were attempted for several other more chlorinated ether-based compounds, but the chromatographic conditions could not be optimized sufficiently to allow standard retention parameters to be measured reliably. 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; Fluoroethers; Iodofluoroalkanes; 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 is 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 relative retentions, $r_{a/b}$, provide the simplest avenue to achieve these goals.

In earlier papers, we presented measurements for 8 methane-based, 30 ethane-based, 19 ethene-based, and 25 propane-based fluids [10–14]. In this paper,

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Table 1

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

Name	$r_{a/b}$ and R.S.D.				$\log r_{a/b}$			
	20°C (293.15 K)	40°C (313.15 K)	60°C (333.15 K)	80°C (353.15 K)	20°C (293.15 K)	40°C (313.15 K)	60°C (333.15 K)	80°C (353.15 K)
Pentafluorodimethyl ether, R-E125	29.0±0.11 0.39%	22.3±0.13 0.58%	18.3±0.07 0.36%	15.4±0.17 1.11%	1.46	1.35	1.26	1.19
Bis(difluoromethyl) ether, R-E134	46.7±1.33 2.85%	35.0±0.10 0.28%	27.2±0.14 0.50%	22.0±0.06 0.29%	1.67	1.54	1.43	1.34

Name	$r_{a/b}$ and R.S.D.				$\log r_{a/b}$			
	40°C (313.15 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)
Methoxy-1,1,1-trifluoroethane, R-E143a	24.7±0.05 0.19%	20.0±0.06 0.31%	16.7±0.09 0.51%	14.4±0.05 0.36%	1.39	1.30	1.22	1.16
Hexafluorooxetane, R-CE216	29.1±0.09 0.31%	23.3±0.18 0.78%	19.5±0.08 0.41%	16.6±0.07 0.46%	1.46	1.37	1.29	1.22
1,2,2,2-Tetrafluoroethyl difluoromethyl ether, R-E236ea1	163.6±2.09 1.28%	113.5±0.64 0.56%	80.1±0.44 0.55%	60.2±0.19 0.31%	2.21	2.06	1.90	1.78
2-(Difluoromethoxy)-1,1,1-trifluoroethane, R-E245fa1	153.8±0.58 0.38%	106.6±0.50 0.47%	77.9±0.44 0.57%	59.1±0.61 1.04%	2.19	2.03	1.89	1.77
2,2,2-Trifluoroethyl methyl ether, R-E263fb1	137.8±0.96 0.69%	95.6±0.71 0.74%	70.8±0.57 0.81%	54.9±0.41 0.74%	2.14	1.99	1.85	1.74
Iodotrifluoromethane, R-13I-1	73.8±1.19 1.61%	56.9±0.42 0.73%	44.7±0.23 0.52%	36.2±0.13 0.36%	1.87	1.76	1.65	1.56

	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)
2-Chloro-1,1,2-trifluoroethyl difluoromethyl ether, R-E235ca2	249.4±2.12 0.86%	173.5±1.65 0.95%	126.7±1.16 0.92%	96.0±0.52 0.54%	2.40	2.24	2.10	1.98
1-Chloro-2,2,2-trifluoroethyl difluoromethyl ether, R-E235da1	307.2±1.39 0.45%	202.3+0.43 0.22%	144.7±0.76 0.53%	106.6±0.40 0.38%	2.49	2.31	2.16	2.03
Fluoromethyl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ether, R-E347	358.9±2.98 0.83%	230.5±0.51 0.22%	157.4±0.75 0.48%	112.9±0.50 0.44%	2.56	2.36	2.20	2.05
1-Iodoheptafluoropropane, R-217I-1	433.4±1.83 0.42%	290.7±1.67 0.57%	209.7±1.39 0.67%	155.3±0.55 0.35%	2.64	2.46	2.32	2.19

	100°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	160°C (433.15 K)	100°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	160°C (433.15 K)
2-Chloroethyl methyl ether, R-E280	264.9±2.66 1.00%	187.1±0.88 0.47%	139.1±0.75 0.54%	104.9+0.45 0.43%	2.42	2.27	2.14	2.02

Table 2

Relative retentions, $r_{a/b}$, and their logarithms, of fluoroethers and iodofluoroalkanes measured in this study, with respect to hexafluoroethane, R-116

Name	$r_{a/b}$ and R.S.D.				$\log r_{a/b}$			
	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	60°C (333.15 K)	0°C (273.15 K)	20°C (293.15 K)	40°C (313.15 K)	60°C (333.15 K)
Pentafluorodimethyl ether, R-E125	4.9±0.02 0.32%	4.2±0.01 0.32%	3.7±0.02 0.53%	3.4±0.02 0.45%	0.69	0.62	0.57	0.54
Bis(difluoromethyl) ether, R-E134	8.1±0.03 0.42%	6.7±0.07 1.06%	5.7±0.07 1.19%	5.1±0.03 0.61%	0.91	0.83	0.76	0.71

Name	$r_{a/b}$ and R.S.D.				$\log r_{a/b}$			
	40°C (313.15 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)
Methoxy-1,1,1-trifluoroethane, R-E143a	4.1±0.01 0.19%	3.8±0.01 0.31%	3.5±0.02 0.51%	3.3±0.01 0.36%	0.61	0.58	0.55	0.52
Hexafluorooxetane, R-CE216	5.0±0.02 0.31%	4.3±0.03 0.78%	3.9±0.02 0.41%	3.4±0.02 0.46%	0.70	0.64	0.59	0.54
1,2,2,2-Tetrafluoroethyl difluoromethyl ether, R-E236ea1	27.3±0.35 1.28%	21.4±0.12 0.56%	16.8±0.93 0.55%	13.9±0.04 0.31%	1.44	1.33	1.23	1.14
2-(Difluoromethoxy)-1,1,1-trifluoroethane, R-E245fa1	25.7±0.10 0.38%	20.1±0.09 0.47%	16.4±0.09 0.57%	13.7±0.14 1.04%	1.41	1.30	1.21	1.14
2,2,2-Trifluoroethyl methyl ether, R-E263fb1	23.0±0.16 0.69%	18.2±0.13 0.74%	14.9±0.12 0.81%	12.7±0.09 0.74%	1.36	1.26	1.17	1.11
Iodotrifluoromethane, R-13I-1	12.3±0.20 1.61%	10.7±0.08 0.73%	9.4±0.05 0.52%	8.4±0.03 0.36%	1.09	1.03	0.97	0.92

	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)
2-Chloro-1,1,2-trifluoroethyl difluoromethyl ether, R-E235ca	52.5±0.45 0.86%	40.2±0.38 0.95%	32.0±0.29 0.92%	26.3±0.14 0.54%	1.72	1.60	1.51	1.42
1-Chloro-2,2,2-trifluoroethyl difluoromethyl ether, R-E235da1	64.6±0.29 0.45%	46.9±0.10 0.22%	36.6±0.19 0.53%	29.2±0.11 0.38%	1.81	1.67	1.56	1.47
Fluoromethyl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ether, R-E347	75.5±0.63 0.83%	53.4±0.12 0.22%	39.8±0.19 0.48%	30.9±0.14 0.44%	1.88	1.73	1.60	1.49
1-Iodoheptafluoropropane, R-217I-1	91.1±0.38 0.42%	67.4±0.39 0.57%	53.0±0.35 0.67%	42.5±0.15 0.35%	1.96	1.83	1.72	1.63

	100°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	160°C (433.15 K)	100°C (373.15 K)	120°C (393.15 K)	140°C (413.15 K)	160°C (433.15 K)
2-Chloroethyl methyl ether, R-E280	61.4±0.62 1.00%	47.3±0.22 0.47%	38.1±0.21 0.54%	30.8±0.13 0.43%	1.79	1.68	1.58	1.49

we present temperature-dependent measurements of the relative retentions, $r_{a/b}$, of 11 ether-based fluids and 2 iodinated fluids that are commonly encountered in alternative refrigerant research and testing. These fluids are among the least common alternative refrigerants, and it is expected that they will find use in specialized machinery such as shipboard chillers, rather than as generally applicable working fluids. The fluids we have studied are listed in the left-hand columns of Table 1 and Table 2, along with their accepted code numbers. A detailed explanation of this standard system of nomenclature is provided elsewhere [10,19]. Note that the standard code numbering system does not specifically address ethers 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 "1" are easily confused, especially in print.

The measurements were made on the packed-column stationary phase that has proved 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. This capability allows the relative retention to be calculated for any temperature within the range of operability of the stationary phase (0 to 180°C).

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, including instrumental conditions and necessary instrumental modifications [10–14]. The flash vaporization inlet was maintained at 175°C for these measurements to ensure complete and rapid sample vaporization. The thermal conductivity detector cell was maintained at 125°C to minimize fluid decomposition. 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 (passing articles between 177 and 250 μm) graphitized carbon black [15]. Some representative properties of this modifier and the column preparation procedure were presented earlier [10]. The purpose of the modifier is to deactivate the highest energy sites on the surface of the adsorbent. We have found that the use of unmodified graphitized carbon black results in distorted chromatographic peaks and unacceptably long retention times. The modifier chosen in this work is stable toward attack by acid gases commonly encountered when analyzing these kinds of fluids. Other common modifiers, such as polyethylene glycols, heavy hydrocarbons, phthalates, etc., degrade rapidly in the presence of such materials.

For each retention measurement, five fluid injections were performed at each column temperature. The corrected retention time was obtained simply by subtracting the air retention time (as a measure of the void volume or gas holdup volume, t_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, or 2σ). The column head pressure was maintained to produce a constant flow-rate for the measurements. Measurements were performed at four temperatures for each fluid. The temperatures were chosen to provide adequate retention, and 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. We chose these compounds as reference materials because they are readily available, of low toxicity, and are convenient to handle as gases. Two standards are presented in order to provide additional flexibility to the user, especially when R-14 is found to elute too quickly to provide sufficiently precise retention times. 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 statistics), 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 R.S.D. (%) is provided. The uncertainty in the measurements is generally between 0.2 and 1.6%, with the average precision of all the measurements of these compounds being 0.6%. 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]. In one case, a relatively larger uncertainty (2.85%) was found for E-134 [bis(difluoromethyl) ether] for the relative retention with respect to R-14 at 20°C. We ascribe this to chromatographic peak distortion at the relatively low temperature, producing a relatively long retention time. Moreover, moderate tailing was noted for this fluid at this temperature. These factors lead to difficulty in determining the peak apex, and therefore the elution time.

A plot of $\log r_{a/b}$ against $1/T$ for each fluid referenced to R-14 and R-116 is provided in Fig. 1 and Fig. 2, respectively. 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 ether and iodinated compounds on this particular stationary phase. In one case, however, close elution of R-E245fa1 and R-E236ea1 at temperatures in excess of approximately 70°C may pose analytical difficulties. At temperatures below this value, there is no difficulty with the separation.

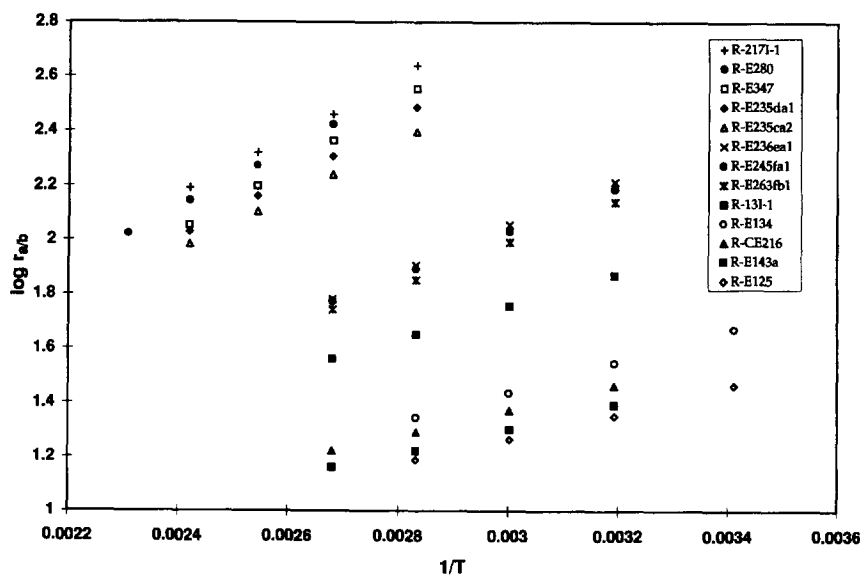Very poor peak shape and therefore very poor

Fig. 1. Plot of the logarithms of the relative retentions, $\log r_{a/b}$, with respect to tetrafluoromethane, R-14, against $1/T$, where T is the thermodynamic temperature, for each fluid measured.
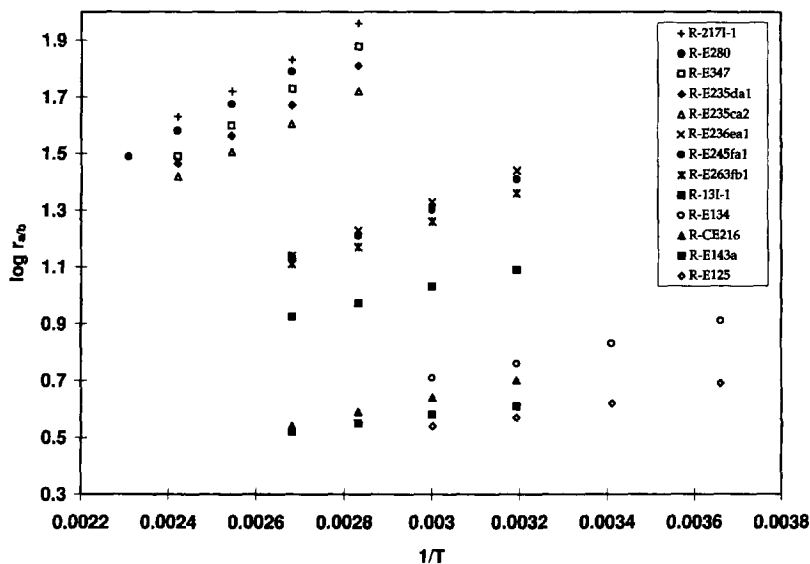
Fig. 2. Plot of the logarithms of the relative retentions, $\log r_{a/b}$, with respect to hexafluoroethane, R-116, against $1/T$, where T is the thermodynamic temperature, for each fluid measured.

chromatographic conditions are obtained on this stationary phase for many ethers that contain a relatively large number of chlorine atoms. The fluids listed in Table 3 produced very distorted peaks, and therefore standard retention measurements could not be made. We ascribe the chromatographic difficulties to several factors. First, specific interactions resulting from adsorption and polarization are probably established between the fluid and the graphitized carbon black. This behavior is evidenced by the pronounced tailing of these peaks, in addition to other distortions. We have found this behavior to be the case for many highly chlorinated fluids measured on this stationary phase. The graphitized carbon black, although modified with the hexafluoropropylene epoxide fluid, is known to strongly interact with highly polarizable

Table 3
Measurements on the following compounds were attempted, but could not be completed because of severe chromatographic distortions, as explained in the text

Code number	Name
R-E123b	Dichlorofluoromethyl difluoromethyl ether
R-E150a	α,α-Dichloromethyl methyl ether
R-E160	Chloromethyl methyl ether
R-E270b	2,2-Dichloroethyl methyl ether
R-E280a	Chloromethyl ethyl ether

species such as the highly chlorinated fluids [18]. We also suspect that fluid decomposition (leading to the formation of acid gases such as hydrogen chloride) will contribute to peak distortion, especially at the elevated temperatures that are required to elute these compounds and to minimize adsorptive interactions. Acid gases will cause acute but (usually) reversible thermal conductivity detector (TCD) aberrations. It is possible to use nickel alloy elements (in the TCD) that are more resistant to attack by chlorinated materials, but this advantage is accompanied by a loss in sensitivity that is experienced with these wires. We have also observed that the adsorptive interactions of some of the fluids we have considered in this work [10–14] are highly exothermic. For fluids that are prone to this type of interaction, the heat generated locally upon adsorption on unmodified stationary phase sites will contribute to fluid decomposition. Attempts to resolve this problem with alternate stationary phases are ongoing. Moreover, any acid gas that is generated in the column may facilitate the cleavage of the ether molecule at the oxygen linkage.

We have not noticed these chromatographic difficulties with the iodinated fluids that we have studied. The iodinated compounds that are of interest in alternative refrigerant work are heavily fluorinated

Table 4
Coefficients of the fits of $\log r_{a/b}$ 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	b	r	Temperature range
Pentafluorodimethyl ether, R-E125	E	357.94	0.43	0.99993	20–80°C
Bis(difluoromethyl) ether, R-E134	P	1.17	1305.00	0.99992	20–80°C
Methoxy-1,1,1-trifluoroethane, R-E143a	E	358.66	0.44	0.99999	40–100°C
Hexafluorooxetane, R-CE216	E	353.11	0.47	0.99992	40–100°C
1,2,2,2-Tetrafluoroethyl difluoromethyl ether, R-E236ea1	L	856.45	−0.52	0.99992	40–100°C
2-(Difluoromethoxy)-1,1,1-trifluoroethane, R-E245fa1	P	1.21	2254.62	0.99998	40–100°C
2,2,2-Trifluoroethyl methyl ether, R-E263fb1	E	405.57	0.59	0.99993	40–100°C
Iodotrifluoromethane, R-13I-1	L	606.90	−0.07	0.99997	40–100°C
2-Chloro-1,1,2-trifluoroethyl difluoromethyl ether, R-E235ca2	P	1.21	2901.21	0.99991	80–140°C
1-Chloro-2,2,2-trifluoroethyl difluoromethyl ether, R-E235da1	E	494.26	0.61	0.99979	80–140°C
Fluoromethyl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ether, R-E347	P	1.39	9087.51	0.99994	80–140°C
1-Iodoheptafluoropropane, R-217I-1	E	448.43	0.74	0.99971	80–140°C
2-Chloroethyl methyl ether, R-E280	L	1085.04	−0.48	0.99998	100–160°C

(as are R-13I-1 and R-217I-1), and therefore have relatively high vapor pressures. High temperatures are not needed to elute these materials, thus the potential for decomposition, and the resulting chromatographic difficulties, is slight.

The temperature-dependent relative retention data were then fitted with the best linear model (simple linear, exponential, logarithmic, power). The results of these fits are provided in Table 4 for retentions relative to tetrafluoromethane (R-14), and Table 5 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. The forms of the models are:

the linear model,

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

the exponential model,

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

the power model:

$$\log^2 r_{a/b} = m \log(1/T) + b, \tag{3}$$

and the logarithmic model:

$$\log r_{a/b} = m \log(1/T) + b, \tag{4}$$

where m and b are fitted coefficients. The choice of

Table 5
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
Pentafluorodimethyl ether, R-E125	P	1.76	13836.22	0.99997	0–60°C
Bis(difluoromethyl) ether, R-E134	Lg	1.27	8.08	0.99997	0–60°C
Methoxy-1,1,1-trifluoroethane, R-E143a	E	311.89	0.23	0.99905	40–100°C
Hexafluorooxetane, R-CE216	L	314.60	−0.31	0.99959	40–100°C
1,2,2,2-Tetrafluoroethyl difluoromethyl ether, R-E236ea1	L	576.54	−0.40	0.99979	40–100°C
2-(Difluoromethoxy)-1,1,1-trifluoroethane, R-E245fa1	E	419.84	0.37	0.99991	40–100°C
2,2,2-Trifluoroethyl methyl ether, R-E263fb1	E	411.22	0.37	0.99995	40–100°C
Iodotrifluoromethane, R-13I-1	P	0.95	258.03	0.99994	40–100°C
2-Chloro-1,1,2-trifluoroethyl difluoromethyl ether, R-E235ca2	P	1.22	2256.68	0.99986	80–140°C
1-Chloro-2,2,2-trifluoroethyl difluoromethyl ether, R-E235da1	E	511.75	0.42	0.99974	80–140°C
Fluoromethyl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl ether, R-E347	P	1.47	10722.31	0.99992	80–140°C
1-Iodoheptafluoropropane, R-217I-1	E	449.00	0.55	0.99997	80–140°C
2-Chloroethyl methyl ether, R-E280	L	806.33	−0.37	0.99997	100–160°C

model was based strictly on goodness of fit and statistical significance of the 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. In many cases, the predictions resulting from two or more models were very close, sometimes within $<0.5\%$ of the measured values. In these cases, we have chosen to present the model that shows the highest statistical significance of the coefficients.

5. Conclusions

Measurements of the relative retentions (on a very useful stationary phase) of 11 ether-based and 2 iodinated 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 [19].

The measurements indicate that good separations are possible with this phase with few exceptions. A number of highly chlorinated ether-based fluids pose serious chromatographic problems with this phase, however.

Acknowledgments

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