ELSEVIER

Retention of halocarbons on a hexafluoropropylene epoxide-modified graphitized carbon black
IV. Propane-based compounds

Thomas J. Bruno*, Kelly H. Wertz, Michael Caciari[1]

Thermophysics Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, CO 80303, USA

Abstract

The retention characteristics of 25 propane-based bromofluorocarbon, chlorocarbon, chlorofluorocarbon, 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 0, 20, 40 and 60°C for R-245ca and R-245cb. Measurements were performed at 20, 40, 60 and 80°C for R-227ca, R-227ea, R-236ea, R-236fa, R-245fa, and R-263fb. Measurements were performed at 40, 60, 80 and 100°C for R-217ba, R-254cb and R-1243b, and at 60, 80, 100 and 120°C for R-280da and R-217caB1. Measurements were performed at 80, 100, 120 and 140°C for R-215aa, R-216ba, R-253fb, R-262da, and R-270aa. Measurements were performed at 100, 120 140 and 160°C for R-215ba, R-225ca, R-225cb, R-243db, R-270da, R-270fa, and R-270fb. 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.

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. This research includes the measurements and correlation of thermophysical prop-

erties, testing of the compatibility of the materials, measurement of the chemical stability, and studies on their suitability for recycling [1,2]. An important part of these research programs is the chemical analysis of the new developed fluids [3–6]. For several reasons gas chromatography is one of the major quantitative and qualitative analysis methods that is applied to the study of alternative refrigerants, not the least of which are its simplicity and economics of operation [7–9]. Knowledge of the retention characteristics of important fluids on the more useful stationary

---

* Corresponding author.
[1] Permanent address: Fort Lupton High School, Fort Lupton, CO, USA.

phases is a valuable tool in the design of effective qualitative and quantitative chromatographic analyses. Determination of the corrected retention parameters, such as the net retention volume, V_N^0 (corrected to a column temperature of 0°C), and relative retentions, $r_{a/b}$, provides the simplest route to achieve these goals.

In previous papers, we presented measurements for 8 methane-based, 18 ethane-based, and 11 ethene-based fluids [10–12]. In this paper, we present measurements on the temperature dependence of the relative retentions, $r_{a/b}$, of 25 propane-based fluids that are commonly encountered in alternative refrigerant research and testing. The studied fluids are listed in the left-hand columns of Tables 1 and 2, along with the accepted code numbers [10,13]. 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 hexafluoro-propylene epoxide on a graphitized carbon black [10]. The relative retentions were calculated with respect to tetrafluoromethane (R-14) and hexa-fluoroethane (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 maintain a high-ly 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. Details of the instrumental modifications were presented earlier [10]. Injection was done via a syringe, and the samples were always introduced at infinite dilution. 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 weight 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 [14]. Thermal conductivity detection (TCD) was used with research-grade helium as carrier gas. The TCD was maintained at 125°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 [15]. Some representative properties of this modifier and the column preparation procedure were presented earlier [10].

For each retention measurement, five 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 hold up volume). At the start of each series of injections, 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 re-

Table 1
Relative retentions, $r_{a/b}$, and their logarithms, of all of the fluids measured in this study, with respect to tetrafluoromethane, R-14

Name	$r_{a/b}$				$\log(r_{a/b})$			
	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)
1,1,2,3,3-Pentafluoropropane (R-245ca)	112.0 ± 1.09 0.97%	75.6 ± 0.44 0.58%	54.8 ± 0.18 0.32%	42.7 ± 0.12 0.28%	2.05	1.88	1.74	1.63
1,1,1,2,2-Pentafluoropropane (R-245cb)	63.9 ± 0.36 0.57%	46.4 ± 0.23 0.50%	35.2 ± 0.18 0.51%	28.9 ± 0.06 0.19%	1.81	1.67	1.55	1.46
	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)
1,1,1,2,2,3,3-Heptafluoropropane (R-227ca)	58.9 ± 0.18 0.31%	43.5 ± 0.32 0.73%	34.4 ± 0.16 0.46%	27.6 ± 0.14 0.50%	1.77	1.64	1.54	1.44
1,1,1,2,3,3,3-Heptafluoropropane (R-227ea)	94.2 ± 0.27 0.29%	65.6 ± 0.76 1.16%	48.6 ± 0.29 0.60%	37.3 ± 0.16 0.44%	1.97	1.82	1.69	1.57
1,1,1,2,3,3-Hexafluoropropane (R-236ea)	100.8 ± 0.85 0.84%	71.8 ± 0.39 0.55%	53.0 ± 0.45 0.85%	41.0 ± 0.23 0.55%	2.00	1.86	1.72	1.61
1,1,1,3,3,3-Hexafluoropropane (R-236fa)	110.6 ± 0.93 0.84%	74.9 ± 0.27 0.36%	55.4 ± 0.24 0.43%	42.7 ± 0.16 0.38%	2.04	1.88	1.74	1.63
1,1,1,3,3-Pentafluoropropane (R-245fa)	110.7 ± 0.97 0.88%	76.1 ± 0.19 0.25%	56.3 ± 0.24 0.51%	43.4 ± 0.23 0.53%	2.04	1.88	1.75	1.64
1,1,1-Trifluoropropane (R-263fb)	60.1 ± 00.34 0.57%	45.4 ± 0.12 0.26%	36.2 ± 0.22 0.62%	29.6 ± 0.35 1.17%	1.78	1.66	1.56	1.47
	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)
2-Chloroheptafluoropropane (R-217ba)	111.3 ± 0.33 0.30%	83.2 ± 0.25 0.30%	63.5 ± 0.24 0.46%	50.7 ± 0.15 0.30%	2.05	1.92	1.80	1.71
3,3,3-Trifluoropropene (R-1243)	38.1 ± 0.53 1.4%	29.6 ± 0.24 0.8%	24.0 ± 0.36 1.50%	19.8 ± 0.16 0.8%	1.58	1.47	1.38	1.30
	60°C (333.15 K)	80°C (353.15K)	100°C (373.15 K)	120°C (393.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	120°C (393.15 K)
2-Chloropropane (R-280da)	131.5 ± 0.77 0.59%	99.4 ± 0.40 0.40%	76.4 ± 0.31 0.24%	61.1 ± 0.22 0.36%	2.12	2.00	1.88	1.79
n-Heptafluoropropyl bromide (R-217caB1)	217.3 ± 1.30 0.60%	151.4 ± 1.06 0.70	106.9 ± 1.71 1.6%	82.0 ± 0.82 1.0%	2.34	2.18	2.03	1.91
	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)
1,2,2-Trichloropentafluoropropane (R-215aa)	778.0 ± 5.91 0.76%	506.7 ± 2.22 0.44%	347.7 ± 1.82 0.47%	251.1 ± 2.26 0.90%	2.89	2.71	2.54	2.40
1,2-Dichlorohexafluoropropane (R-216ba)	239.8 ± 2.01 0.84%	169.6 ± 0.51 0.30%	126.0 ± 1.36 1.08%	97.4 ± 0.30 0.31%	2.38	2.23	2.10	1.99
3-Chloro-1,1,1-trifluoropropane (R-253fb)	191.1 ± 0.50 0.26%	135.4 ± 0.79 0.58%	99.9 ± 0.33 0.33%	77.8 ± 0.42 0.54%	2.28	2.13	2.00	1.89
2-Chloro-1,3-difluoropropane (R-262da)	172.7 ± 0.71 0.41%	126.8 ± 1.27 1.00%	95.5 ± 0.33 0.35%	76.2 ± 0.36 0.47%	2.24	2.10	1.98	1.88
2,2-Dichloropropane (R-270aa)	288.9 ± 1.27 0.44%	206.8 ± 0.66 0.32%	155.9 ± 0.41 0.26%	120.5 ± 0.59 0.49%	2.46	2.32	2.19	2.08
1,1,2,2-Tetrafluoropropane, R-254cb	38.0 ± 0.14 0.36%	30.5 ± 0.06 0.21%	25.4 ± 0.10 0.41%	21.8 ± 0.06 0.28%	1.58	1.48	1.41	1.34

Table 1. *Continued*

Name	$r_{a/b}$				$\log(r_{a/b})$			
	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)
1,2,3-Trichloropentafluoropropane (R-215ba)	555.5 ± 6.06 1.09%	382.4 ± 4.47 1.17%	270.6 ± 2.22 0.82%	198.2 ± 0.69 0.35%	2.75	2.58	2.43	2.30
3,3-Dichloro-1,1,1,2,2-pentafluoropropane (R-225ca)	309.6 ± 0.62 0.20%	217.0 ± 1.26 0.60%	160.7 ± 0.41 0.26%	121.9 ± 0.69 0.57%	2.49	2.34	2.21	2.09
1,3-Dichloro-1,1,2,2,3-pentafluoropropane (R-225cb)	305.3 ± 4.30 1.41%	210.3 ± 1.20 0.57%	156.6 ± 1.13 0.72%	118.0 ± 0.55 0.47%	2.49	2.32	2.20	2.07
2,3-Dichloro-1,1,1-trifluoropropane (R-243db)	438.5 ± 1.75 0.40%	302.6 ± 0.91 0.30%	217.4 ± 0.57 0.26%	158.1 ± 0.38 0.24%	2.64	2.48	2.34	2.20
1,2-Dichloropropane (R-270da)	377.6 ± 1.47 0.39%	279.1 ± 1.45 0.52%	197.6 ± 0.83 0.42%	148.6 ± 0.91 0.61%	2.58	2.45	2.30	2.17
1,3-Dichloropropane (R-270ta)	497.8 ± 2.64 0.53%	348.2 ± 3.87 1.11%	253.8 ± 2.33 0.92%	185.5 ± 0.48 0.26%	2.70	2.54	2.40	2.27
1,1-Dichloropropane (R270fb)	377.6 ± 2.76 0.73%	265.9 ± 1.25 0.47%	194.5 ± 0.70 0.36%	147.5 ± 0.74 0.50%	2.58	2.43	2.29	2.17

ported (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. The temperatures were chosen to provide adequate retention to minimize extra-column effects. All samples were 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 Tables 1 and 2, respectively. 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), 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 precision of the measurements is generally between 0.5 and 1.5%, with the average precision of all the measurements on these compounds being 0.6%. This figure compares very well with the precision of typical retention parameters (generally between 1 and 2%) obtained in other physicochemical gas chromatographic measurements [16]. A plot of $\log(r_{a/b})$ against $1/T$ for each fluid referenced to R-14 is provided in Fig. 1a,b. Similar plots are provided for the fluids referenced to R-116 in Fig. 2a,b.

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 at which measurements were performed. It is clear from these plots that good separation is achieved for most of the propane-based compounds on this particular stationary phase. In a few cases, coelution of fluids is observed at the higher temperatures, however.

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 Tables 3 and 4. Included with each fluid are the

Table 2
Relative retentions, $r_{a,b}$, and their logarithms, of all of the fluids measured in this study, with respect to hexafluoroethane, R-116

Name	$r_{a,b}$				$\log(r_{a,b})$			
	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)
1,1,2,3,3-Pentafluoropropane (R-245ca)	13.9 ± 0.13 0.97%	11.0 ± 0.06 0.58%	9.2 ± 0.03 0.32%	8.1 ± 0.02 0.28%	1.14	1.04	0.96	0.91
1,1,1,2,2-Pentafluoropropane (R-245cb)	7.9 ± 0.05 0.57%	6.7 ± 0.04 0.50%	5.9 ± 0.03 0.51%	5.5 ± 0.01 0.19%	0.90	0.77	0.77	0.74
	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)
1,1,1,2,2,3,3-Heptafluoropropane (R-227ca)	8.6 ± 0.03 0.31%	7.3 ± 0.05 0.73%	6.5 ± 0.03 0.46%	5.8 ± 0.03 0.50%	0.93	0.86	0.81	0.76
1,1,1,2,3,3,3-Heptafluoropropane (R-227ea)	13.7 ± 0.04 0.29%	10.9 ± 0.13 1.16%	9.2 ± 0.06 0.60%	7.8 ± 0.03 0.44%	1.14	1.04	0.96	0.89
1,1,1,2,3,3-Hexafluoropropane (R-236ea)	14.6 ± 0.17 0.84%	12.0 ± 0.07 0.55%	10.0 ± 0.09 0.85%	8.6 ± 0.05 0.55%	1.17	1.08	1.00	0.94
1,1,1,3,3,3-Hexafluoropropane (R-236fa)	16.1 ± 0.14 0.84%	12.5 ± 0.05 0.36%	10.4 ± 0.04 0.43%	9.0 ± 0.03 0.38%	1.21	1.10	1.02	0.95
1,1,1,3,3-Pentafluoropropane (R-245fa)	16.1 ± 0.14 0.88%	12.7 ± 0.03 0.25%	10.6 ± 0.05 0.51%	9.1 ± 0.05 0.53%	1.21	1.10	1.03	0.96
1,1,1-Trifluoropropane (R-263fb)	8.7 ± 0.05 0.57%	7.6 ± 0.02 0.26%	6.8 ± 0.04 0.62%	6.2 ± 0.04 0.62%	0.94	0.88	0.83	0.70
	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)
2-Chloroheptafluoro-propane (R-217ba)	18.6 ± 0.06 0.30%	15.7 ± 0.05 0.30%	13.4 ± 0.06 0.46%	11.7 ± 0.04 0.30%	1.27	1.20	1.13	1.07
3,3,3-Trifluoropropene (R-1243)	6.3 ± 0.09 1.40%	5.6 ± 0.04 0.80%	5.1 ± 0.08 0.70%	4.6 ± 0.04 0.80%	0.80	0.75	0.70	0.66
	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	120°C (393.15 K)	60°C (333.15 K)	80°C (353.15 K)	100°C (373.15 K)	120°C (393.15 K)
2-Chloropropane (R-280da)	24.8 ± 0.15 0.60%	20.9 ± 0.08 0.40%	17.7 ± 0.04 0.24%	15.5 ± 0.06 0.36%	1.40	1.32	1.25	1.19
n-Heptafluoropropyl bromide (R-217caB1)	41.0 ± 0.25 0.60%	31.8 ± 0.22 0.70%	24.9 ± 0.40 1.60%	20.8 ± 0.21 1.000%	1.61	1.50	1.40	1.32
	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)
1,2,2-Trichloropentafluoropropane (R-215aa)	163.6 ± 1.24 0.76%	117.4 ± 0.52 0.44%	87.9 ± 0.41 0.47%	68.7 ± 0.62 0.90%	2.21	2.07	1.94	1.84
1,2-Dichlorohexafluoropropane (R-216ba)	50.4 ± 0.42 0.84%	39.2 ± 0.12 0.30%	31.9 ± 0.34 1.08%	26.7 ± 0.08 0.31%	1.70	1.59	1.50	1.43
3-Chloro-1,1,1-trifluoropropane (R-253fb)	40.2 ± 0.10 0.26%	31.4 ± 0.18 0.58%	25.3 ± 0.08 0.33%	21.3 ± 0.13 0.59%	1.60	1.50	1.40	1.33
2-Chloro-1,3-difluoropropane (R-262da)	36.3 ± 0.15 0.41%	29.4 ± 0.29 1.00%	24.1 ± 0.08 0.35%	20.9 ± 0.10 0.47%	1.56	1.47	1.38	1.32
2,2-Dichloropropane (R-270aa)	60.8 ± 0.27 0.44%	47.9 ± 0.15 0.32%	39.4 ± 0.10 0.26%	33.0 ± 0.16 0.49%	1.78	1.68	1.60	1.52
1,1,2,2-Tetrafluoropropane, R-254cb	6.5 ± 0.02 0.36%	5.7 ± 0.01 0.21%	5.0 ± 0.02 0.41%	4.5 ± 0.01 0.28%	0.81	0.75	0.70	0.65

Table 2. *Continued.*

Name	$r_{a,b}$				$\log(r_{a,b})$			
	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)
1,2,3-Trichloropentafluoropropane (R-215ba)	128.7 ± 1.40 1.09%	96.7 ± 1.17 1.17%	74.0 ± 0.61 0.82%	58.2 ± 0.20 0.35%	2.11	1.99	1.87	1.77
3,3-Dichloro-1,1,1,2,2-pentafluoropropane (R-225ca)	71.8 ± 0.14 0.20%	54.9 ± 0.33 0.60%	44.0 ± 0.11 0.26%	35.8 ± 0.20 0.57%	1.86	1.74	1.64	1.55
1,3-Dichloro-1,1,2,2,3-pentafluoropropane (R-225cb)	70.7 ± 1.00 1.41%	53.2 ± 0.30 0.57%	42.8 ± 0.31 0.72%	34.7 ± 0.16 0.47%	1.85	1.73	1.63	1.54
2,3-Dichloro-1,1,1-trifluoropropane (R-243db)	101.6 ± 0.41 0.40%	76.5 ± 0.23 0.30%	59.5 ± 0.15 0.26%	46.5 ± 0.11 0.24%	2.01	1.88	1.77	1.67
1,2-Dichloropropane (R-270da)	87.5 ± 0.34 0.39%	70.6 ± 0.37 0.52%	54.1 ± 0.23 0.42%	43.7 ± 0.27 0.61%	1.94	1.85	1.73	1.64
1,3-Dichloropropane (R-270fa)	115.4 ± 0.61 0.53%	88.0 ± 0.97 1.11%	69.4 ± 0.64 0.92%	54.5 ± 0.14 0.26%	2.06	1.95	1.84	1.74
1,1-Dichloropropane (R-270fb)	87.5 ± 0.64 0.73%	67.2 ± 0.32 0.47%	53.2 ± 0.19 0.36%	43.4 ± 0.22 0.50%	1.94	1.83	1.73	1.64

Table 3
Coefficients of the fits of $\log(r_{a,b})$ against $1/T$, with the respective correlation coefficients, with tetrafluoromethane (R-14) as the reference

Name	Model	m	b	r	Temperature range (°C)
1,1,1,2,2,3,3-Heptafluoropropane (R-227ca)	P	1.10	898.82	0.99976	20–80
1,1,1,2,3,3,3-Heptafluoropropane (R-227ea)	P	1.22	2035.09	0.99997	20–80
1,1,1,2,3,3-Hexafluoropropane (R-236ea)	L	676.21	−0.30	0.99996	20–80
1,1,1,3,3,3-Hexafluoropropane (R-236fa)	E	389.63	0.54	0.99999	20–80
1,1,2,3,3-Pentafluoropropane (R-245ca)	E	346.43	0.58	0.99997	0–60
1,1,1,2,2-Pentafluoropropane (R-245cb)	E	322.24	0.55	0.99982	0–60
1,1,1,3,3-Pentafluoropropane (R-245fa)	E	382.37	0.56	0.99996	20–80
1,1,2,2-Tetrafluoropropane, R-254cb	E	325.61	0.56	0.99999	40–100°C
1,1,1-Trifluoropropane (R-263fb)	E	326.24	0.59	0.99997	20–80
2-Chloroheptafluoropropane (R-217ba)	P	1.05	853.99	0.99996	40–100
3,3,3-Trifluoropropene (R-1243)	E	381.19	0.47	0.99992	40–100
n-Heptafluoropropyl bromide (R-217caB1)	E	444.44	0.62	0.99968	60–120
2-Chloropropane (R-280da)	L	727.58	−0.06	0.99987	60–120
1,2,2-Trichloropentafluoropropane (R-215aa)	P	1.19	3059.12	0.99995	80–140
1,2-Dichlorohexafluoropropane (R-216ba)	E	436.34	0.69	0.99994	80–140
3-Chloro-1,1,1-trifluoropropane (R-253fb)	E	457.49	0.63	0.99998	80–140
2-Chloro-1,3-difluoropropane (R-262da)	E	422.27	0.68	0.99996	80–140
2,2-Dichloropropane (R-270aa)	P	1.07	1274.28	0.99980	80–140
1,2,3-Trichloropentafluoropropane (R-215ba)	LG	3.03	20.67	0.99992	100–160
3,3-Dichloro-1,1,1,2,2-pentafluoropropane (R-225ca)	P	1.19	2918.06	0.99999	100–160
1,3-Dichloro-1,1,2,2,3-pentafluoropropane (R-225cb)	P	1.22	3380.21	0.99991	100–160
2,3-Dichloro-1,1,1-trifluoropropane (R-243db)	LG	2.98	20.30	0.99999	100–160
1,2-Dichloropropane (R-270da)	LG	2.76	18.93	0.99899	100–160
1,3-Dichloropropane (R-270fa)	LG	2.88	19.78	0.99999	100–160
1,1-Dichloropropane (R-270fb)	L	1105.50	−0.38	0.99997	100–160

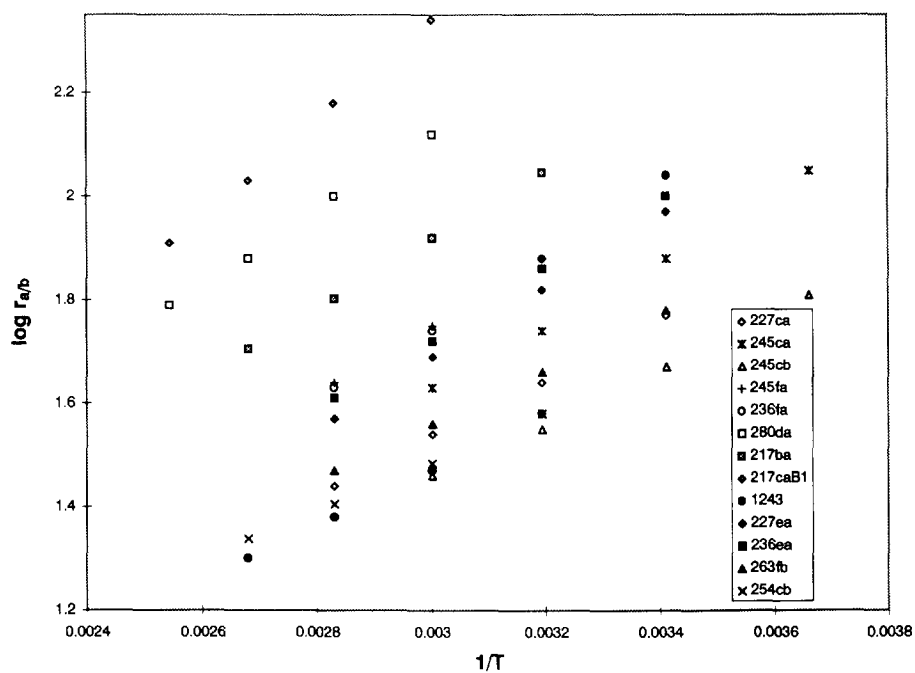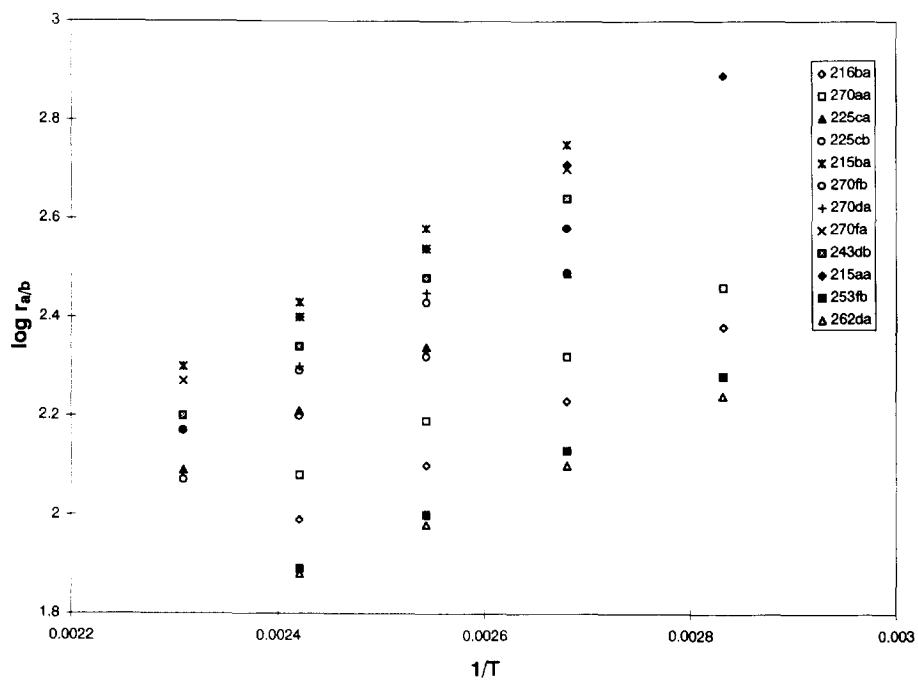L = linear, P = power, E = exponential, LG = logarithmic.

Fig. 1. Plots of the logarithms of the relative retentions (with respect to tetrafluoromethane, R-14) $\log(r_{a/b})$ against $1/T$, for each fluid measured.

coefficients, the Pearson correlation coefficient of the fit, and the temperature range over which the fit was taken.

Many of the measured data obtained for the propane-based fluids are represented very well (within experimental error) 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 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.

5. Conclusions

Measurements of the relative retentions (on a very useful stationary phase) of 25 propane-based halocarbon fluids that are relevant to research on alternative refrigerants have been presented. The logarithms of these data were fitted against the reciprocal thermodynamic tem-

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

Name	Model	m	b	r	Temperature range (°C)
1,1,1,2,2,3,3-Heptafluoropropane (R-227ca)	E	338.95	0.29	0.99934	20–80
1,1,1,2,3,3,3-Heptafluoropropane (R-227ea)	E	411.97	0.28	0.99990	20–80
1,1,1,2,3,3-Hexafluoropropane (R-236ea)	P	1.18	971.79	0.99994	20–80
1,1,1,3,3,3-Hexafluoropropane (R-236fa)	E	404.73	0.30	0.99968	20–80
1,1,2,3,3-Pentafluoropropane (R-245ca)	P	1.44	3794.79	0.99974	0–60
1,1,1,2,2-Pentafluoropropane (R-245cb)	E	398.31	0.22	0.99998	0–60
1,1,1,3,3-Pentafluoropropane (R-245fa)	E	392.34	0.32	0.99991	20–80
1,1,2,2-Tetrafluoropropane, R-254cb	L	316.43	−0.19	0.99993	40–100°C
1,1,1-Trifluoropropane (R-263fb)	E	289.86	0.35	0.99980	20–80
2-Chloroheptafluoropropane (R-217ba)	L	393.10	0.02	0.99975	40–100
3,3,3-Trifluoropropene (R-1243)	L	276.40	−0.08	0.99976	40–100
n-Heptafluoropropyl bromide (R-217caB1)	E	434.39	0.44	0.99981	60–120
2-Chloropropane (R-280da)	L	451.08	0.04	0.99975	60–120
1,2,2-Trichloropentafluoropropane (R-215aa)	E	454.35	0.61	0.99993	80–140
1,2-Dichlorohexafluoropropane (R-216ba)	E	431.65	0.50	0.99995	80–140
3-Chloro-1,1,1-trifluoropropane (R-253fb)	E	461.44	0.43	0.99998	80–140
2-Chloro-1,3-difluoropropane (R-262da)	E	411.13	0.49	0.99991	80–140
2,2-Dichloropropane (R-270aa)	E	390.81	0.59	0.99974	80–140
1,2,3-Trichloropentafluoropropane (R-215ba)	LG	2.33	15.91	0.99992	100–160
3,3-Dichloro-1,1,1,2,2-pentafluoropropane (R-225ca)	P	1.19	2175.65	0.99998	100–160
1,3-Dichloro-1,1,2,2,3-pentafluoropropane (R-225cb)	P	1.23	2651.06	0.99978	100–160
2,3-Dichloro-1,1,1-trifluoropropane (R-243db)	LG	2.29	15.55	0.99999	100–160
1,2-Dichloropropane (R-270da)	LG	2.07	14.18	0.99814	100–160
1,3-Dichloropropane (R-270fa)	LG	2.18	14.98	0.99994	100–160
1,1-Dichloropropane (R-270fb)	L	826.79	−0.27	0.99996	100–160

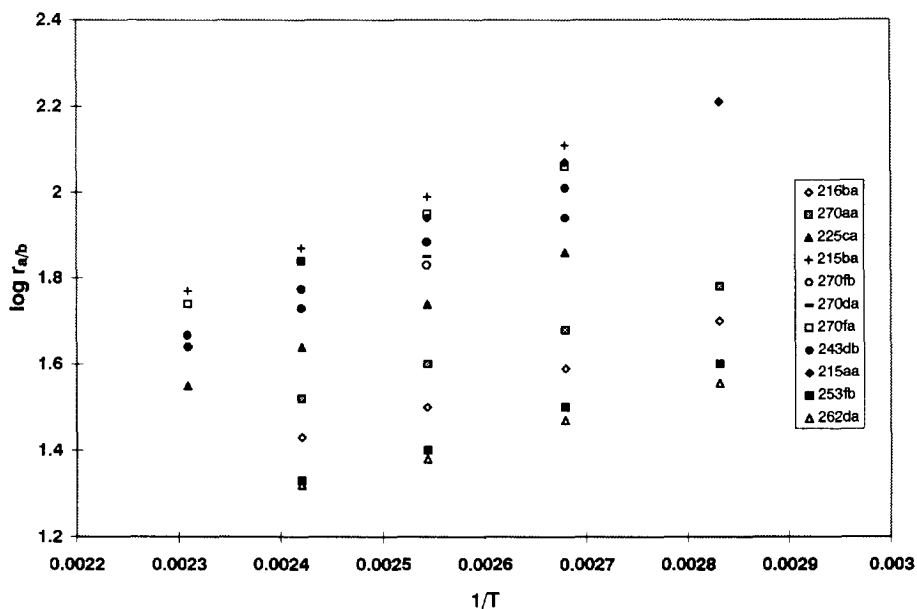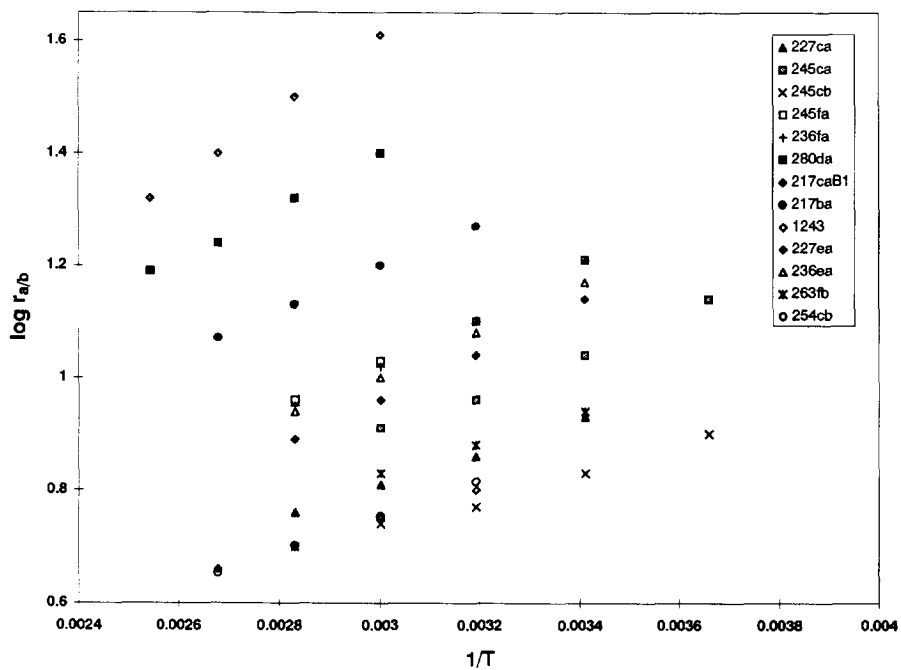L = linear. P = power. E = exponential, LG = logarithmic.

Fig. 2. Plots of the logarithms of the relative retentions (with respect to hexafluoromethane, R-116) log ($r_{a/b}$) against $1/T$, for each fluid measured.

perature 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 and also for the design of analytical and preparative-scale separations.

Acknowledgements

References

[1] E.J. Lizardos, Maint. Technol., 6 (1993) 17–19.
[2] M.O. McLinden and D.A. Didion, ASHRAE J., 29 (1987) 32–42.
[3] T.J. Bruno, Spectroscopic Library for Alternative Refrigerant Analysis, National Institute of Standards and Technology (U.S.), Special Publication 794, 1990, p. 192.
[4] T.J. Bruno, Strategy of Chemical Analysis of Alternative Refrigerants, National Institute of Standards and Technology (U.S.), Technical Note 1340, 1990, p. 104.
[5] T.J. Bruno, ASHRAE Trans., 98 (1992) 204–208.
[6] T.J. Bruno, ASHRAE Trans., 98 (1992) 210–215.
[7] R.L. Grob (Editor), Modern Practice of Gas Chromatography, John Wiley & Sons, New York, 2nd ed., 1985.
[8] T.J. Bruno, Chromatographic and Electrophoretic Methods, Prentice-Hall, Englewood Cliffs, NJ, 1991.
[9] J.E. Willett, Gas Chromatography, (Analytical Chemistry by Open Learning), John Wiley & Sons, Chichester, 1987.
[10] T.J. Bruno and M. Caciari, J. Chromatogr. A, 672 (1994) 149–158.
[11] T.J. Bruno and M. Caciari, J. Chromatogr. A, 679 (1994) 123–132.
[12] T.J. Bruno and M. Caciari, J. Chromatogr. A, 686 (1995) 245.
[13] T.J. Bruno (Editor), CRC Handbook for the Analysis and Identification of Alternative Refrigerants, CRC Press, Boca Raton, FL, 1994.
[14] T.J. Bruno, Anal. Chem., 58 (1986) 1596.
[15] J.L. Glajch and W.G. Schindel, LC · GC, 4 (1986) 574–580.
[16] J.D. Gibbons and S. Chakraborti (Editors), Nonparametric Statistical Inference, Marcel Dekker, New York, NY, 1992.
[17] T.J. Bruno and D.E. Martire, J. Phys. Chem., 87 (1986) 2430–2436.