

Relative Permittivity and Dipole Moments of Replacement Refrigerant Mixtures (R408A and R409A) in the Liquid State

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This paper provides reliable dielectric property information on two refrigerant mixtures regarded as replacements for chlorodifluoromethane (CAS no. 75-45-6) (HCFC22) and R502 (CHClF₂ + CClF₂CF₃) ($w_1 = 0.49$; $w_2 = 0.51$). Liquid phase relative permittivity measurements are reported for R408A (CHF₂CF₃ + CF₃CH₃ + CHClF₂) ($w_1 = 0.07$; $w_2 = 0.46$; $w_3 = 0.47$) and R409A (CHClF₂ + CHClFCH₃ + CClF₂CH₃) ($w_1 = 0.60$; $w_2 = 0.25$; $w_3 = 0.15$). The measurements were performed by using a direct capacitance method at temperatures from $T = (233 \text{ to } 303) \text{ K}$ under pressures up to 16 MPa. A complete set of tables of experimental data, covering dielectric property needs for most engineering applications, is provided. The data obtained was correlated as a function of density, pressure, and temperature. The apparent dipole moments (μ^*) of R408A and R409A in the liquid state were obtained from the Kirkwood modification of the Onsager equation for the variation to the modified molar polarization with temperature and density. The μ^* value found for R408A was $1.043 \cdot 10^{-29} \text{ C} \cdot \text{m}$ and $1.047 \cdot 10^{-29} \text{ C} \cdot \text{m}$ for R409A. The coefficient of thermal expansion and the coefficient of compressibility in the liquid state were derived from the experimental data, with uncertainties better than 2 % and 0.3 %, respectively.

Introduction

Refrigerants are the working fluids in refrigeration, air-conditioning, and heat pumping systems. They absorb heat from one area, such as an air-conditioned space, and reject it into another, such as outdoors, usually through evaporation and condensation, respectively. These phase changes occur both in absorption and mechanical vapor compression systems, but they do not occur in systems operating on a gas cycle using a fluid such as air. The design of refrigeration equipment depends strongly on the properties of the selected refrigerant. Refrigerant selection involves compromises between conflicting desirable thermodynamic properties. Some parameters such as ozone depletion potential (ODP) and global warming potential (GWP) contribute to the choice of the new hydrofluorocarbons (HFC's).

R408A is a low ODP near azeotropic blend of chlorodifluoromethane (CAS no. 75-45-6) (HCFC22), pentafluoroethane (CAS no. 354-33-6) (HFC125) and 1,1,1-trifluoroethane (CAS no. 420-46-2) (HFC143a). R408A was developed to provide a fast, convenient, and reliable retrofit solution for medium and low temperature refrigeration systems which currently use R502.¹ Common refrigerants used in the past were either single component refrigerants or azeotropic blends that behaved as a single component when used in a refrigeration system. Near azeotropic blends such as R408A will behave almost the same as azeotropes such as R502, for all practical purposes. The temperature glide of R408A is quite small. This glide is usually not noticeable compared to normal temperature changes due to

pressure.² R408A was not developed to use in new equipment but rather in R502 systems.³

R409A is a low ozone depleting blend of HCFC22, 1-chloro-1,2,2,2-tetrafluoroethane (CAS no. 2837-89-0) (HCFC124), and 1-chloro-1,1-difluoroethane (CAS no. 75-68-3) (HCFC142b). Refrigerant R409A is formulated to closely resemble the properties of the refrigerant dichlorodifluoromethane (CAS no. 75-71-8) (CFC12).⁴ R409A is an alternative refrigerant blend for retrofitting CFC12 medium and low temperature refrigeration systems. These systems, which typically contain a hermetic or semihermetic compressor, are used in commercial food storage, vending machines, ice machines, and transport refrigeration. R409A provides a slightly higher capacity than CFC12 and 1,1,1,2-tetrafluoroethane (CAS no. 811-97-2) (HCFC134a) in lower temperature applications.⁵

Recent advances in the understanding of polar interactions in the gas and liquid phases show the extreme importance of these data to the study of the electric properties of polar fluids, giving insight into the molecular theory of liquids and, at the same time, to give some important experimental values which can contribute to the design of machinery used in the air-conditioning and refrigeration industry, namely for electrical insulation.⁶

The relative permittivity (ϵ_r) provides information about the behavior of molecules under an electrical field, and it is dependent on chemical structure and molecular interactions. In addition, these values are important for designing process equipment, with friction or rotating parts, when considering electrical discharges or static electricity.

In our previous studies of refrigerant mixtures, we have measured the ϵ_r of R410A,⁷ an HFC based refrigerant composed of 50/50 wt % of HFC32/HFC125, and the dipole moment of the mixtures R404A, R407C, and R507 in the temperature range $T = (217 \text{ to } 303) \text{ K}$ and pressure range (2 to 16) MPa.⁸ The measurements

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Table 1. Physical Properties and Purity of the Refrigerant Mixtures

chemical name	perfluoroethane + 1,1,1-trifluoroethane + chlorodifluoromethane	chlorodifluoromethane + 1-chloro-1,2,2,2-tetrafluoroethane + 1-chloro-1,1-difluoroethane
ASHRAE nomenclature ²⁰	R408A	R409A
molecular formula	CHF ₂ CF ₃ + CF ₃ CH ₃ + CHClF ₂	CHClF ₂ + CHClFCF ₃ + CClF ₂ CH ₃
composition	HFC125 + HFC143a + HCFC22	HCFC22 + HFC124 + HCFC142b
mass fraction (<i>w</i>)	(0.07 + 0.46 + 0.47)	(0.60 + 0.25 + 0.15)
relative molar mass/g·mol ⁻¹	87.02	97.40
ODP (R11 = 1)	0.026	0.048
GWP ^a (CO ₂ = 1)	3000	1400
bubble temperature/glide point @ 0.1 MPa/K ^b	228.6/0.7	229.6/8.5
estimated water content/mg·kg ⁻¹	< 10	8
purity	> 99.5 %	> 99.5 %
replacing	R502	CFC12
sample provider	Solvay Fluor and Derivative, Germany	Solvay Fluor and Derivative, Germany

^a Integrated Time Horizon = 100 years. ^b Temperature glide: $(T_{\text{dew}} - T_{\text{bubble}})$.

were carried out using a direct capacitance method, for the liquid phase in the temperature and pressure ranges normally used in the air-conditioning and refrigeration industry.⁷

Experimental

The experimental setup is based on a three terminal arrangement, and the ϵ_r was obtained from between the ratio of the capacitances of the cell with the sample, $C(P,T)$, and under vacuum, $C_0(T)$. The instrumentation has been described previously.^{9,10} The $C_0(T)$ was measured prior to filling the cell with the sample using an impedance analyzer (Shlumberger, model 1260) with an accuracy of $\pm 5 \cdot 10^{-4}$ pF. This equipment was calibrated by Laboratório de Metrologia Eléctrica da Companhia Portuguesa Radio Marconi, Lisbon, using standards of capacitance of 1 pF, 10 pF, 100 pF, 1000 pF, 0.01 μ F, 0.1 μ F, and 1 μ F. The technique employed a four terminal connection to the cell in order to compensate for parasitic impedances. The mean value of a 10-dimensional sample taken at a 10 kHz frequency provides the experimental value of ϵ_r , which proved to be properly suited to the working accuracy. The measuring process involving instrumentation is fully automated and operated from a computer graphics user interface, making the data analysis faster and statistically more significant. The temperature of the cell was measured with a platinum resistance thermometer (100 Ω at 273 K), located near the sample. The resistance of the Pt100 thermometer was determined with a four wire measurement, with a 5.5 digital multimeter (Keithley, model 199 DMM), calibrated with three standard resistors at four points, with an uncertainty of 0.01 K. The pressure vessel is immersed in a cylindrical copper vessel cooled by a serpentine connected to a commercial cryostat (Julabo, model FPW90-SC), filled with ethanol, and operative in the temperature range from (183 to 373) K, with an accuracy of 0.1 K. For the measurements of capacitance under pressure, a high-pressure line was used, composed by a liquid-pressure generator (HIP, model 87-6-5) and an air-operated, diaphragm-type compressor (Newport Scientific, model 46-14021-2). The pressure was measured with a pressure transducer from Setra Systems, calibrated with a dead-weight gage (Ruska, Model 2485 Piston Pressure Gage), with an uncertainty of 0.01 MPa, over the pressure range.

The samples of R408A and R409A, with a purity of 99.9% were provided by Solvay Fluor and Derivate, Germany, and used without further purification. Their purity and physical properties can be seen in Table 1. The measurements were performed over the temperature and pressure ranges of (233 to 303) K and (1 to 16) MPa, respectively. The density values (ρ) of these refrigerants were calculated using the REFPROP

database, version 7.¹¹ The uncertainty of the experimental measurements of the mixtures ϵ_r with the present apparatus was found to be better than 0.22 %, for a confidence interval of 95 % (ISO definition, $k = 2$). This value is slightly higher than the uncertainty obtained for pure fluids¹⁰ because there is additional uncertainty caused by composition characterization and possible evaporation during the measurements of the near azeotropic blends, especially at high temperatures.

Results

Dielectric Properties. Tables 2 and 3 present the ϵ_r data as a function of pressure and density for each isotherm, for R408A and R409A, T_n being a nominal temperature.¹⁰ All the experimental points measured at a given temperature T , close to T_n , were adjusted to this temperature using the following relation:

$$\epsilon_r(T_n, P) = \epsilon_r(T, P) + \left(\frac{\partial \epsilon_r}{\partial T} \right)_P (T_n - T) \quad (1)$$

Figures 1 and 2 show the ϵ_r in the temperature range of (233 to 303) K as a function of density for R408A and R409A, respectively. For both mixtures, $(\partial \epsilon_r / \partial P)_T$ and $(\partial \epsilon_r / \partial \rho)_T$ are positive, and $(\partial \epsilon_r / \partial T)_P$ is negative. The experimental data of the ϵ_r values were fitted by a maximum likelihood iterative χ^2 method for a multiparameter and multivariable function in density and temperature (iterations implemented by a Levenberg–Marquardt procedure) according to

$$\epsilon_r(\rho, T) = \frac{a_1}{T/K} + a_2 \rho / \text{kg} \cdot \text{m}^{-3} + \frac{a_3 \rho / \text{kg} \cdot \text{m}^{-3}}{T/K} \quad (2)$$

with a standard deviation of 0.002 % for R408A and 0.007 % for R409A. For industrial needs, the data were also fitted to a function in pressure and temperature according to

$$\epsilon_r(P, T) = b_0 + \frac{b_1}{T/K} + b_2 P / \text{MPa} + \frac{b_3 P / \text{MPa}}{T/K} \quad (3)$$

with a standard deviation of 0.03 % for R408A and 0.23 % for R409A. The coefficients of eqs 2 and 3 with their uncertainties are given in Table 4.

The theory of molecular polarizability developed by Kirkwood after the definition of Onsager's local field^{12,13} can be used to calculate, an apparent dipole moment of the liquid μ^* using

$$\text{KF} = \frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{9\epsilon_r} \left(\frac{M}{\rho} \right) = \frac{N_A}{3} \left(\alpha + \frac{\mu^{*2}}{3k_B T \epsilon_0} \right) \quad (4)$$

where M is the relative molar mass of the fluid, N_A is the Avogadro constant, α is the molecular polarizability of the

Table 2. Relative Permittivity (ϵ_r) of R408A, from $T = (233.15 \text{ to } 303.15) \text{ K}$ and $P = (1 \text{ to } 16) \text{ MPa}$

T K	P MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	$\epsilon_r(T,P)$	$\rho(T_n,P)$ $\text{kg}\cdot\text{m}^{-3}$	$\epsilon_r(T_n,P)$	T K	P MPa	ρ $\text{kg}\cdot\text{m}^{-3}$	$\epsilon_r(T,P)$	$\rho(T_n,P)$ $\text{kg}\cdot\text{m}^{-3}$	$\epsilon_r(T_n,P)$
$T_n/K = 303.15$						$T_n/K = 293.15$					
303.80	16.00	1127	8.0996	1129	8.1357	293.34	16.00	1157	8.6004	1157	8.6117
303.80	15.00	1122	8.0632	1124	8.0996	293.34	15.00	1153	8.5648	1153	8.5762
303.79	14.00	1118	8.0173	1120	8.0533	293.33	14.00	1149	8.5120	1149	8.5228
303.79	13.00	1113	7.9712	1115	8.0075	293.33	13.00	1145	8.4650	1145	8.4759
303.80	12.00	1108	7.9254	1110	7.9625	293.32	12.00	1140	8.4179	1141	8.4283
303.79	11.00	1103	7.8786	1105	7.9153	293.32	11.00	1136	8.3709	1136	8.3814
303.79	10.00	1097	7.8315	1099	7.8685	293.32	10.00	1131	8.3239	1132	8.3344
303.79	9.00	1092	7.7804	1094	7.8175	293.31	9.00	1126	8.2769	1127	8.2868
303.79	8.00	1086	7.7259	1088	7.7633	293.30	8.00	1121	8.2299	1122	8.2392
303.78	7.00	1079	7.6727	1082	7.7097	293.30	7.00	1116	8.1828	1117	8.1923
303.78	6.00	1073	7.6152	1075	7.6524	293.30	6.00	1111	8.1358	1111	8.1453
303.78	5.00	1066	7.5499	1068	7.5874	293.29	5.00	1105	8.0888	1106	8.0977
303.79	4.00	1058	7.4858	1061	7.5241	293.29	4.00	1099	8.0417	1100	8.0507
303.78	3.00	1050	7.4179	1053	7.4559	293.28	3.00	1093	7.9947	1093	8.0031
303.79	2.00	1042	7.3431	1045	7.3819	293.29	2.00	1086	7.9511	1087	7.9602
$T_n/K = 283.15$						$T_n/K = 273.15$					
283.18	16.00	1185	9.2426	1185	9.2445	273.16	16.00	1212	9.8966	1212	9.8972
283.17	15.00	1182	9.2066	1182	9.2079	273.15	15.00	1209	9.864	1209	9.8640
283.18	14.00	1178	9.1695	1178	9.1714	273.15	14.00	1206	9.8327	1206	9.8327
283.17	13.00	1174	9.1193	1174	9.1206	273.15	13.00	1203	9.7866	1203	9.7866
283.17	12.00	1171	9.0759	1171	9.0772	273.15	12.00	1199	9.7451	1199	9.7451
283.17	11.00	1167	9.0325	1167	9.0338	273.15	11.00	1196	9.7037	1196	9.7037
283.17	10.00	1163	8.9891	1163	8.9904	273.13	10.00	1192	9.6623	1192	9.6609
283.17	9.00	1158	8.9456	1158	8.9470	273.12	9.00	1189	9.6209	1189	9.6187
283.17	8.00	1154	8.9022	1154	8.9036	273.14	8.00	1185	9.5794	1185	9.5787
283.17	7.00	1150	8.8588	1150	8.8602	273.14	7.00	1181	9.538	1181	9.5373
283.16	6.00	1145	8.8154	1145	8.8161	273.13	6.00	1177	9.4966	1177	9.4951
283.16	5.00	1140	8.7720	1140	8.7727	273.18	5.00	1173	9.4551	1173	9.4573
283.15	4.00	1135	8.7286	1135	8.7286	273.13	4.00	1169	9.4137	1169	9.4122
283.15	3.00	1130	8.6851	1130	8.6851	273.13	3.00	1164	9.3723	1164	9.3708
283.15	2.00	1125	8.6417	1125	8.6417	273.14	2.00	1160	9.3309	1160	9.3301
283.15	1.00	1119	8.6035	1119	8.6035	273.16	1.00	1155	9.2894	1155	9.2901
$T_n/K = 263.15$						$T_n/K = 253.15$					
263.18	16.00	1239	10.5386	1239	10.5409	253.13	16.00	1265	11.3787	1265	11.3771
263.18	15.00	1182	10.5061	1236	10.5083	253.13	15.00	1262	11.3482	1262	11.3466
263.17	14.00	1233	10.4704	1233	10.4718	253.13	14.00	1260	11.3183	1260	11.3167
263.17	13.00	1230	10.4345	1230	10.4360	253.14	13.00	1257	11.2850	1257	11.2841
263.16	12.00	1227	10.3987	1227	10.3994	253.14	12.00	1254	11.2503	1254	11.2495
263.16	11.00	1224	10.3629	1224	10.3636	253.13	11.00	1252	11.2174	1252	11.2157
263.15	10.00	1221	10.3270	1221	10.3270	253.12	10.00	1249	11.1845	1249	11.1820
263.15	9.00	1218	10.2915	1218	10.2915	253.12	9.00	1246	11.1516	1246	11.1491
263.15	8.00	1215	10.2554	1215	10.2554	253.11	8.00	1243	11.1187	1243	11.1153
263.14	7.00	1211	10.2195	1211	10.2188	253.11	7.00	1240	11.0858	1240	11.0824
263.14	6.00	1208	10.1837	1208	10.1829	253.12	6.00	1237	11.0529	1237	11.0504
263.14	5.00	1204	10.1479	1204	10.1471	253.13	5.00	1234	11.0200	1234	11.0183
263.15	4.00	1201	10.1121	1201	10.1121	253.12	4.00	1231	10.9871	1231	10.9845
263.15	3.00	1197	10.0762	1197	10.0762	253.13	3.00	1228	10.9542	1228	10.9525
263.14	2.00	1193	10.0404	1193	10.0396	253.14	2.00	1224	10.9213	1224	10.9205
263.14	1.00	1189	10.0046	1189	10.0038	253.14	1.00	1221	10.8884	1221	10.8876
$T_n/K = 243.15$						$T_n/K = 233.15$					
243.13	16.00	1290	12.3055	1290	12.3038	233.15	16.00	1316	13.2626	1316	13.2626
243.13	15.00	1288	12.2786	1288	12.2768	233.15	15.00	1313	13.2354	1313	13.2354
243.13	14.00	1286	12.2487	1286	12.2469	233.15	14.00	1311	13.2126	1311	13.2126
243.13	13.00	1283	12.2193	1283	12.2175	233.15	13.00	1309	13.1877	1309	13.1877
243.13	12.00	1281	12.1899	1281	12.1881	233.15	12.00	1307	13.1569	1307	13.1569
243.13	11.00	1279	12.1605	1279	12.1587	233.15	11.00	1305	13.1276	1305	13.1276
243.13	10.00	1276	12.1311	1276	12.1293	233.15	10.00	1303	13.0998	1303	13.0998
243.13	9.00	1274	12.1017	1274	12.0999	233.15	9.00	1300	13.0719	1300	13.0719
243.13	8.00	1271	12.0723	1271	12.0705	233.15	8.00	1298	13.0441	1298	13.0441
243.13	7.00	1268	12.0429	1268	12.0411	233.15	7.00	1296	13.0163	1296	13.0163
243.13	6.00	1266	12.0135	1266	12.0117	233.15	6.00	1293	12.9908	1293	12.9908
243.13	5.00	1263	11.9841	1263	11.9823	233.15	5.00	1291	12.9621	1291	12.9621
243.12	4.00	1260	11.9547	1260	11.9519	233.15	4.00	1288	12.9361	1288	12.9361
243.12	3.00	1257	11.9253	1257	11.9225	233.15	3.00	1286	12.9051	1286	12.9051
243.12	2.00	1254	11.8959	1254	11.8931	233.15	2.00	1283	12.8737	1283	12.8737
243.12	1.00	1251	11.8665	1251	11.8637	233.15	1.00	1281	12.8513	1281	12.8513

molecule, ϵ_0 is the electric permittivity in a vacuum, T is the absolute temperature, k_B is the Boltzmann constant, and ρ is the density. The apparent dipole moment is defined as $\mu^* = g^{1/2}\mu$, where μ is the dipole moment in the ideal gas state and g is the Kirkwood correlation parameter, that measures the restriction to rotation imposed by a cage of molecules surround-

ing a given one. Kirkwood,¹² on the basis of a quasicrystalline model, defined this parameter g as

$$g = \frac{\mu^{*2}}{\mu^2} = 1 + \sum_{i=1}^{\infty} z_i \langle \cos \gamma_i \rangle \quad (5)$$

Table 3. Relative Permittivity (ϵ_r) of R409A, from $T = (243.15 \text{ to } 303.15) \text{ K}$ and $P = (1 \text{ to } 16) \text{ MPa}$

T	P	ρ	$\epsilon_r(T,P)$	$\rho(T_n,P)$	$\epsilon_r(T_n,P)$	T	P	ρ	$\epsilon_r(T,P)$	$\rho(T_n,P)$	$\epsilon_r(T_n,P)$
K	MPa	$\text{kg}\cdot\text{m}^{-3}$		$\text{kg}\cdot\text{m}^{-3}$		K	MPa	$\text{kg}\cdot\text{m}^{-3}$		$\text{kg}\cdot\text{m}^{-3}$	
$T_n/K = 303.15$						$T_n/K = 293.15$					
303.28	16.00	1264	7.1600	1264	7.1689	293.32	16.00	1291	7.6930	1292	7.7054
303.27	15.00	1260	7.1222	1261	7.1304	293.32	15.00	1288	7.6627	1289	7.6751
303.27	14.00	1257	7.0876	1257	7.0958	293.31	14.00	1285	7.6304	1285	7.6421
303.27	13.00	1253	7.0541	1253	7.0623	293.31	13.00	1281	7.5925	1282	7.6042
303.27	12.00	1249	7.0128	1249	7.0210	293.31	12.00	1278	7.5527	1278	7.5644
303.26	11.00	1245	6.9744	1245	6.9819	293.30	11.00	1274	7.5189	1275	7.5298
303.26	10.00	1241	6.9365	1241	6.9440	293.30	10.00	1271	7.4754	1271	7.4863
303.27	9.00	1236	6.8958	1237	6.9039	293.30	9.00	1267	7.4444	1267	7.4553
303.27	8.00	1232	6.8537	1232	6.8619	293.30	8.00	1263	7.4046	1263	7.4156
303.26	7.00	1227	6.8080	1228	6.8155	293.29	7.00	1259	7.3609	1259	7.3711
303.26	6.00	1222	6.7653	1223	6.7728	293.29	6.00	1255	7.3232	1255	7.3334
303.27	5.00	1217	6.7190	1218	6.7271	293.29	5.00	1251	7.2820	1251	7.2922
303.26	4.00	1212	6.6718	1213	6.6793	293.28	4.00	1246	7.2332	1247	7.2426
303.26	3.00	1207	6.6223	1207	6.6298	293.29	3.00	1242	7.1941	1242	7.2043
303.25	2.00	1201	6.5708	1202	6.5775	293.28	2.00	1237	7.1484	1237	7.1579
303.25	1.00	1195	6.5291	1196	6.5359	293.27	1.00	1232	7.1006	1232	7.1093
$T_n/K = 283.15$						$T_n/K = 273.15$					
283.18	16.00	1319	8.2426	1319	8.2450	273.11	16.00	1345	8.8001	1345	8.7967
283.18	15.00	1316	8.2115	1316	8.2138	273.10	15.00	1342	8.7630	1342	8.7588
283.18	14.00	1313	8.1815	1313	8.1839	273.10	14.00	1340	8.7394	1340	8.7352
283.17	13.00	1310	8.1502	1310	8.1517	273.10	13.00	1337	8.7094	1337	8.7052
283.17	12.00	1307	8.1140	1307	8.1156	273.10	12.00	1334	8.6754	1334	8.6711
283.16	11.00	1303	8.0807	1303	8.0815	273.10	11.00	1331	8.6468	1331	8.6426
283.16	10.00	1300	8.0487	1300	8.0495	273.09	10.00	1328	8.6134	1328	8.6084
283.16	9.00	1297	8.0120	1297	8.0128	273.09	9.00	1325	8.5834	1325	8.5783
283.15	8.00	1293	7.9731	1293	7.9731	273.09	8.00	1322	8.5445	1322	8.5395
283.15	7.00	1290	7.9372	1290	7.9372	273.09	7.00	1319	8.5142	1319	8.5092
283.15	6.00	1286	7.8993	1286	7.8993	273.08	6.00	1316	8.4823	1316	8.4764
283.15	5.00	1282	7.8573	1282	7.8573	273.09	5.00	1313	8.4455	1313	8.4405
283.15	4.00	1279	7.8174	1279	7.8174	273.08	4.00	1309	8.4086	1309	8.4028
283.15	3.00	1275	7.7788	1275	7.7788	273.08	3.00	1306	8.3694	1306	8.3636
283.14	2.00	1271	7.7404	1271	7.7396	273.08	2.00	1303	8.3384	1302	8.3325
283.14	1.00	1266	7.6985	1266	7.6977	273.08	1.00	1299	8.2901	1299	8.2843
$T_n/K = 263.15$						$T_n/K = 253.15$					
262.99	16.00	1371	9.4125	1371	9.3980	253.03	16.00	1396	10.2488	1396	10.2370
262.99	15.00	1369	9.3892	1368	9.3747	253.03	15.00	1394	10.2157	1394	10.2040
262.98	14.00	1366	9.3634	1366	9.3480	253.03	14.00	1392	10.1575	1392	10.1458
262.98	13.00	1364	9.3273	1363	9.3119	253.02	13.00	1390	10.1323	1389	10.1196
262.98	12.00	1361	9.3013	1361	9.2859	253.02	12.00	1387	10.1068	1387	10.0941
262.98	11.00	1359	9.2701	1358	9.2547	253.02	11.00	1385	10.0775	1385	10.0648
262.97	10.00	1356	9.2393	1356	9.2230	253.02	10.00	1383	10.0499	1382	10.0372
262.97	9.00	1353	9.2115	1353	9.1952	253.02	9.00	1380	10.0186	1380	10.0059
262.97	8.00	1351	9.1802	1350	9.1639	253.03	8.00	1378	9.9886	1377	9.9769
262.97	7.00	1348	9.1466	1347	9.1304	253.02	7.00	1375	9.9577	1375	9.9450
262.96	6.00	1345	9.1183	1345	9.1012	253.02	6.00	1373	9.9230	1372	9.9103
262.96	5.00	1342	9.0802	1342	9.0630	253.02	5.00	1370	9.8970	1370	9.8843
262.96	4.00	1339	9.0490	1339	9.0319	253.02	4.00	1368	9.8600	1367	9.8474
262.96	3.00	1336	9.0189	1336	9.0017	253.02	3.00	1365	9.8325	1365	9.8199
262.96	2.00	1333	8.9887	1333	8.9716	253.01	2.00	1362	9.7909	1362	9.7773
262.95	1.00	1330	8.9504	1330	8.9324	253.02	1.00	1359	9.7597	1359	9.7471
$T_n/K = 243.15$											
243.22	16.00	1421	11.2524	1421	11.2598						
243.22	15.00	1419	11.2268	1419	11.2342						
243.22	14.00	1417	11.1971	1417	11.2046						
243.22	13.00	1415	11.1590	1415	11.1664						
243.21	12.00	1413	11.1260	1413	11.1324						
243.22	11.00	1410	11.0765	1411	11.0839						
243.21	10.00	1408	11.0394	1408	11.0457						
243.21	9.00	1406	10.9882	1406	10.9945						
243.21	8.00	1404	10.9603	1404	10.9666						
243.21	7.00	1402	10.9205	1402	10.9269						
243.21	6.00	1399	10.8580	1400	10.8643						
243.21	5.00	1397	10.8301	1397	10.8364						
243.21	4.00	1395	10.7959	1395	10.8022						
243.21	3.00	1392	10.7619	1393	10.7682						
243.20	2.00	1390	10.7256	1390	10.7309						
243.20	1.00	1387	10.6922	1388	10.6974						

where z_i is the number of neighbors to the central molecule under consideration in the i th coordination shell, and $\langle \cos \gamma_i \rangle$ is the average cosine angle γ formed by the dipole moments of molecules in the i th shell with the dipole of the central molecule.

The greater the value of g , the greater the orientational order imposed by the neighbors. The value of μ^* can be calculated by a linear regression of the left-hand side of the eq 4 as a function of $1/T$. The experimental values of ϵ_r were used to

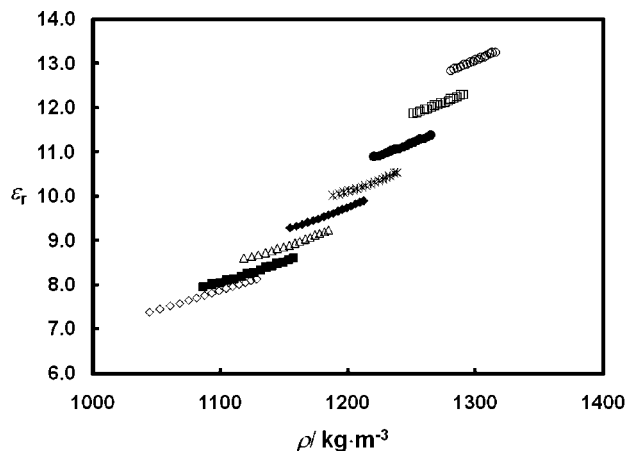


Figure 1. Relative permittivity (ϵ_r) of R408A as a function of density (ρ), at nominal temperatures: \diamond , 303.15 K; \blacksquare , 293.15 K; \triangle , 283.15 K; \blacklozenge , 263.15 K; \bullet , 253.15 K; \square , 243.15 K; \circ , 233.15 K.

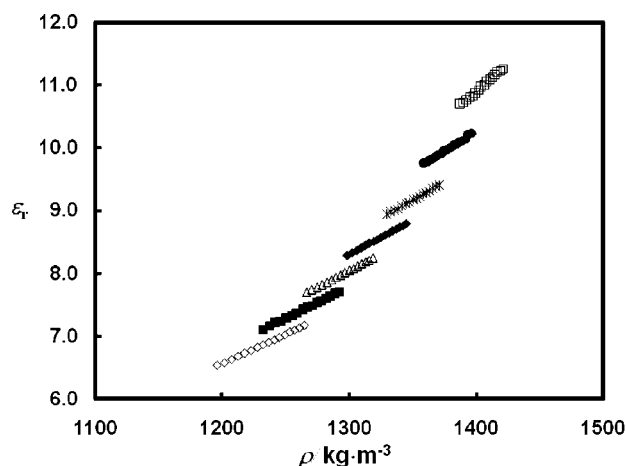


Figure 2. Relative permittivity of (ϵ_r) R409A as a function of density (ρ), at nominal temperatures: \diamond , 303.15 K; \blacksquare , 293.15 K; \triangle , 283.15 K; \blacklozenge , 263.15 K; \bullet , 253.15 K; \square , 243.15 K.

Table 4. Coefficients of the Dielectric Equations of State for Equations 2 and 3

coefficients	R408A	R409A
a_1/K	-5235.6 ± 855.6	-34023.5 ± 2958.5
$10^{-2}a_2/m^3 \cdot kg^{-1}$	-1.336 ± 0.214	-8.8708 ± 0.6558
$a_3/K \cdot m^3 \cdot kg^{-1}$	6.7139 ± 0.6416	27.736 ± 1.998
b_0	-11.375 ± 0.2870	-14.378 ± 1.201
b_1/K	5632.9 ± 75.8	6233.1 ± 318.3
$10^{-2}b_2/MPa^{-1}$	16.548 ± 2.979	0
$b_3/K \cdot MPa^{-1}$	-32.752 ± 7.869	0

calculate the Kirkwood function, and Figure 3 shows its variation with $1/T$ for R408A and R409A. The values of μ^* were found to be $1.043 \cdot 10^{-29}$ C·m for R408A and $1.047 \cdot 10^{-29}$ C·m for R409A.

The relation between the dipole moment of a mixture in the gaseous state and the dipole moment of its components is still not well-understood. The dipole moment of the mixture in the gas phase can be calculated, as a first approximation, by using the definition of molar polarizability, $P_{M,i}$ for a pure polar gas, based on the theory of Debye:¹⁴

$$P_M = \frac{\epsilon_r - 1}{\epsilon_r + 2} \left(\frac{M}{\rho} \right) = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3k_B T} \right) \quad (6)$$

The application of Debye equation to mixtures in the gaseous state is theoretically possible, especially for dilute gases, for

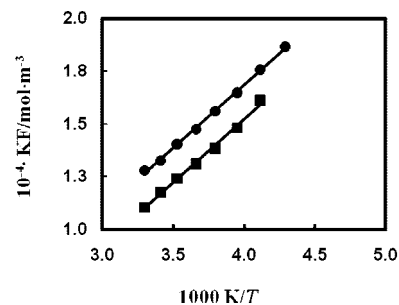


Figure 3. Kirkwood function as a function of $1/T$ for \bullet , R408A, \blacksquare , R409A, and $-$, Kirkwood.

Table 5. Values of the Kirkwood Parameter (g_{mix}) and Dipole Moment in the Gaseous (μ_{mix}) and Liquid Phases (μ^*) for Several Refrigerant Mixtures

fluid	components	$10^{-29}\mu_{mix}^*$	$10^{-30}\mu_{mix}$	g_{mix}
		C·m	C·m	
R404A	HFC125, HFC143a, HFC134a	1.100	6.951	2.506
R407C	HFC32, HFC125, HFC134a	1.144	6.498	3.100
R408A	HFC125, HFC143a, HCFC22	1.043	5.921	3.106
R409A	HCFC22, HCFC124, HCFC142b	1.047	5.257	3.967
R410A	HFC32, HFC125	1.104	6.211	3.159
R507	HFC125, HFC143a	1.088	6.858	2.510

which components we have the individual dipole moments. As the molecules in a perfect gas mixture do not interact, the molar polarization of this reference mixture with i components of molar fraction y_i can be assumed to be additive and given by the following:

$$P_{M,mix} = \sum_i y_i P_{M,i} = \frac{N_A}{3\epsilon_0} \left(\sum_i y_i \alpha_i + \frac{1}{3k_B T} \sum_i y_i \mu_i^2 \right) \quad (7)$$

or

$$P_{M,mix} = \frac{\epsilon_{r,mix} - 1}{\epsilon_{r,mix} + 2} \left(\frac{\bar{M}_{mix}}{\rho_{mix}} \right) = \frac{N_A}{3\epsilon_0} \left(\alpha_{mix} + \frac{\mu_{mix}^2}{3k_B T} \right) \quad (8)$$

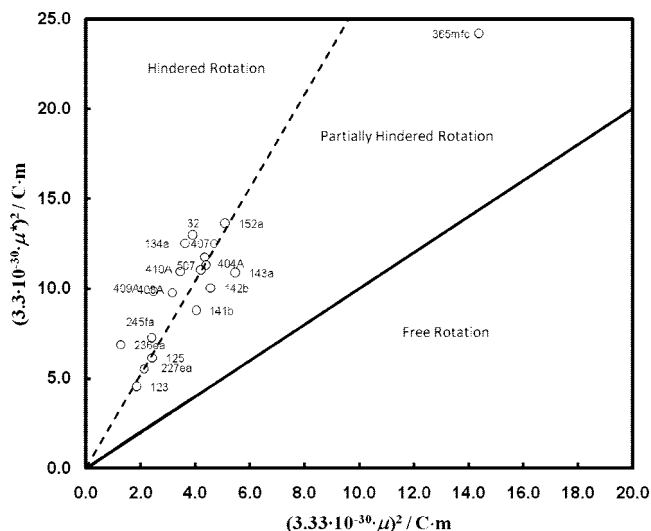


Figure 4. Plot of μ^* as a function of μ for all the refrigerants studied. The broken line represents the value $g = 2.6$,¹⁶ and the solid line, the value $g = 1$.

Table 6. Coefficients of Isothermal Thermal Expansion (α_P) Calculated from Equation 13 for R408A, from $T = (238.15$ to $298.15)$ K and up to $P = 16$ MPa

P MPa	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}
		$T_n/\text{K} = 298.15$	$T_n/\text{K} = 288.15$		$T_n/\text{K} = 278.15$		$T_n/\text{K} = 268.15$	
16.00	1143	0.002397	1171	0.002341	1199	0.002262	1226	0.002170
15.00	1139	0.002449	1168	0.002383	1195	0.002299	1223	0.002203
14.00	1134	0.002504	1164	0.002436	1192	0.002335	1220	0.002235
13.00	1130	0.002563	1160	0.002482	1189	0.002380	1217	0.002270
12.00	1125	0.002622	1156	0.002538	1185	0.002423	1213	0.002304
11.00	1121	0.002693	1152	0.002594	1181	0.002470	1210	0.002342
10.00	1116	0.002768	1147	0.002656	1177	0.002515	1207	0.002385
9.00	1110	0.002847	1143	0.002724	1174	0.002565	1203	0.002430
8.00	1105	0.002933	1138	0.002797	1170	0.002626	1200	0.002470
7.00	1099	0.003036	1133	0.002875	1165	0.002686	1196	0.002516
6.00	1093	0.003145	1128	0.002956	1161	0.002752	1192	0.002569
5.00	1087	0.003266	1123	0.003051	1157	0.002836	1189	0.002611
4.00	1080	0.003402	1117	0.003152	1152	0.002900	1185	0.002685
3.00	1073	0.003563	1112	0.003268	1147	0.002985	1181	0.002747
2.00	1066	0.003750	1106	0.003393	1142	0.003079	1176	0.002810
1.00					1137	0.003187	1172	0.002877
		$T_n/\text{K} = 258.15$	$T_n/\text{K} = 248.15$		$T_n/\text{K} = 238.15$			
16.00	1252	0.002066	1278	0.001997	1303	0.001931		
15.00	1249	0.002093	1275	0.002020	1301	0.001951		
14.00	1247	0.002123	1273	0.002044	1299	0.001971		
13.00	1244	0.002153	1270	0.002067	1296	0.001992		
12.00	1241	0.002186	1268	0.002092	1294	0.002013		
11.00	1238	0.002216	1265	0.002121	1292	0.002036		
10.00	1235	0.002249	1262	0.002150	1289	0.002059		
9.00	1232	0.002284	1260	0.002180	1287	0.002084		
8.00	1229	0.002318	1257	0.002212	1284	0.002109		
7.00	1226	0.002358	1254	0.002244	1282	0.002135		
6.00	1222	0.002402	1251	0.002275	1279	0.002162		
5.00	1219	0.002447	1248	0.002307	1277	0.002191		
4.00	1216	0.002487	1245	0.002344	1274	0.002223		
3.00	1212	0.002539	1242	0.002379	1271	0.002254		
2.00	1209	0.002595	1239	0.002418	1269	0.002286		
1.00	1205	0.002650	1236	0.002460	1266	0.002321		

Table 7. Coefficients of Compressibility (κ_T) Calculated from Equation 14 for R408A from $T = (233.15$ to $303.15)$ K and $P = (2$ to $16)$ MPa

P MPa	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}
		$T_n/\text{K} = 303.15$	$T_n/\text{K} = 293.15$		$T_n/\text{K} = 283.15$		$T_n/\text{K} = 273.15$	
16.00	1126	0.003959	1155	0.003419	1183	0.002966	1211	0.002593
15.00	1122	0.004109	1151	0.003535	1180	0.003051	1208	0.002666
14.00	1117	0.004270	1147	0.003652	1176	0.003154	1204	0.002732
13.00	1112	0.004450	1143	0.003780	1172	0.003241	1201	0.002806
12.00	1107	0.004651	1139	0.003926	1169	0.003354	1198	0.002881
11.00	1102	0.004873	1134	0.004092	1165	0.003469	1194	0.002973
10.00	1097	0.005107	1129	0.004250	1161	0.003585	1191	0.003057
9.00	1091	0.005381	1124	0.004447	1156	0.003727	1187	0.003160
8.00	1085	0.005688	1119	0.004646	1152	0.003863	1183	0.003263
7.00	1078	0.006027	1114	0.004883	1147	0.004027	1179	0.003367
6.00	1072	0.006438	1108	0.005133	1143	0.004201	1175	0.003498
5.00	1065	0.006894	1103	0.005433	1138	0.004386	1171	0.003630
4.00	1057	0.007445	1096	0.005755	1133	0.004609	1167	0.003763
3.00	1049	0.008114	1090	0.006147	1127	0.004843	1162	0.003933
2.00					1122	0.005117	1157	0.004095
		$T_n/\text{K} = 263.15$	$T_n/\text{K} = 253.15$		$T_n/\text{K} = 243.15$		$T_n/\text{K} = 233.15$	
16.00	1238	0.002279	1264	0.002010	1289	0.001784	1315	0.001582
15.00	1235	0.002333	1261	0.002054	1287	0.001810	1312	0.001615
14.00	1232	0.002379	1258	0.002098	1285	0.001853	1310	0.001641
13.00	1229	0.002441	1256	0.002134	1282	0.001880	1308	0.001667
12.00	1226	0.002505	1253	0.002187	1280	0.001922	1306	0.001692
11.00	1223	0.002568	1250	0.002231	1277	0.001957	1304	0.001726
10.00	1219	0.002632	1248	0.002285	1275	0.001993	1301	0.001752
9.00	1216	0.002705	1245	0.002338	1272	0.002036	1299	0.001786
8.00	1213	0.002778	1242	0.002400	1270	0.002079	1297	0.001820
7.00	1209	0.002869	1239	0.002454	1267	0.002123	1294	0.001846
6.00	1206	0.002944	1236	0.002517	1264	0.002175	1292	0.001889
5.00	1202	0.003044	1232	0.002588	1261	0.002220	1290	0.001923
4.00	1199	0.003145	1229	0.002652	1259	0.002272	1287	0.001966
3.00	1195	0.003247	1226	0.002741	1256	0.002333	1284	0.002009
2.00	1191	0.003367	1223	0.002814	1253	0.002387	1282	0.002044

Table 8. Coefficients of Thermal Expansion (α_P) Calculated from Equation 13 for R409A, from $T = (248.15 \text{ to } 298.15) \text{ K}$ and $P = (1 \text{ to } 16) \text{ MPa}$

P MPa	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}	$\bar{\rho}(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	α_P K^{-1}
		$T_n/\text{K} = 298.15$	$T_n/\text{K} = 288.15$		$T_n/\text{K} = 278.15$		$T_n/\text{K} = 268.15$	
16.00	1278	0.002159	1305	0.002028	1332	0.001956	1358	0.001872
15.00	1275	0.002197	1302	0.002057	1329	0.001980	1355	0.001895
14.00	1271	0.002232	1299	0.002089	1326	0.002007	1353	0.001916
13.00	1268	0.002271	1296	0.002120	1323	0.002037	1350	0.001939
12.00	1264	0.002312	1292	0.002154	1320	0.002065	1347	0.001964
11.00	1260	0.002356	1289	0.002190	1317	0.002098	1345	0.001988
10.00	1256	0.002403	1286	0.002227	1314	0.002127	1342	0.002015
9.00	1252	0.002450	1282	0.002267	1311	0.002160	1339	0.002043
8.00	1248	0.002503	1278	0.002307	1308	0.002197	1336	0.002071
7.00	1244	0.002559	1275	0.002354	1304	0.002234	1333	0.002101
6.00	1239	0.002621	1271	0.002400	1301	0.002270	1330	0.002133
5.00	1234	0.002684	1267	0.002452	1298	0.002312	1327	0.002163
4.00	1230	0.002754	1263	0.002508	1294	0.002353	1324	0.002200
3.00	1225	0.002835	1258	0.002564	1290	0.002398	1321	0.002237
2.00	1219	0.002920	1254	0.002626	1286	0.002450	1318	0.002275
1.00	1214	0.003010	1249	0.002696	1283	0.002502	1314	0.002313
		$T_n/\text{K} = 258.15$	$T_n/\text{K} = 248.15$					
16.00	1383	0.001833	1408	0.001799				
15.00	1381	0.001852	1406	0.001815				
14.00	1379	0.001874	1404	0.001832				
13.00	1376	0.001892	1402	0.001853				
12.00	1374	0.001913	1400	0.001869				
11.00	1371	0.001936	1398	0.001889				
10.00	1369	0.001960	1395	0.001907				
9.00	1366	0.001983	1393	0.001927				
8.00	1364	0.002009	1391	0.001947				
7.00	1361	0.002033	1388	0.001970				
6.00	1359	0.002061	1386	0.001993				
5.00	1356	0.002090	1384	0.002016				
4.00	1353	0.002118	1381	0.002040				
3.00	1350	0.002147	1379	0.002066				
2.00	1347	0.002177	1376	0.002091				
1.00	1344	0.002215	1373	0.002116				

Table 9. Coefficients of Compressibility (κ_T) Calculated from Equation 14 for R409A from $T = (243.15 \text{ to } 303.15) \text{ K}$ and up to $P = (2 \text{ to } 16) \text{ MPa}$

P MPa	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}	$\bar{\rho}'(T_n, P)$ $\text{kg}\cdot\text{m}^{-3}$	κ_T MPa^{-1}
		$T_n/\text{K} = 303.15$	$T_n/\text{K} = 293.15$		$T_n/\text{K} = 283.15$		$T_n/\text{K} = 273.15$	
16.00	1263	0.002891	1290	0.002534	1317	0.002239	1344	0.001980
15.00	1259	0.002979	1287	0.002603	1314	0.002298	1341	0.002028
14.00	1255	0.003059	1284	0.002672	1311	0.002341	1338	0.002062
13.00	1251	0.003157	1280	0.002750	1308	0.002400	1335	0.002112
12.00	1247	0.003263	1277	0.002820	1305	0.002460	1333	0.002154
11.00	1243	0.003363	1273	0.002899	1302	0.002520	1330	0.002203
10.00	1239	0.003487	1269	0.002994	1298	0.002588	1327	0.002261
9.00	1234	0.003613	1265	0.003082	1295	0.002656	1324	0.002304
8.00	1230	0.003748	1261	0.003187	1292	0.002733	1321	0.002362
7.00	1225	0.003901	1257	0.003285	1288	0.002811	1318	0.002421
6.00	1220	0.004056	1253	0.003408	1284	0.002889	1314	0.002488
5.00	1215	0.004246	1249	0.003540	1281	0.002991	1311	0.002555
4.00	1210	0.004446	1244	0.003673	1277	0.003078	1308	0.002623
3.00	1205	0.004666	1240	0.003816	1273	0.003190	1304	0.002692
2.00	1199	0.004913	1235	0.003985	1269	0.003303	1301	0.002783
		$T_n/\text{K} = 263.15$	$T_n/\text{K} = 253.15$		$T_n/\text{K} = 243.15$			
16.00	1370	0.001767	1395	0.001570	1420	0.001416		
15.00	1367	0.001799	1393	0.001601	1418	0.001432		
14.00	1365	0.001832	1390	0.001633	1416	0.001448		
13.00	1362	0.001857	1388	0.001650	1414	0.001478		
12.00	1360	0.001905	1386	0.001681	1412	0.001495		
11.00	1357	0.001938	1384	0.001713	1410	0.001518		
10.00	1354	0.001972	1381	0.001745	1407	0.001549		
9.00	1352	0.002020	1379	0.001777	1405	0.001566		
8.00	1349	0.002061	1376	0.001802	1403	0.001597		
7.00	1346	0.002102	1374	0.001849	1401	0.001621		
6.00	1343	0.002159	1371	0.001874	1398	0.001652		
5.00	1340	0.002201	1369	0.001914	1396	0.001676		
4.00	1337	0.002251	1366	0.001962	1394	0.001708		
3.00	1334	0.002308	1363	0.001995	1391	0.001747		
2.00	1331	0.002374	1360	0.002036	1389	0.001771		

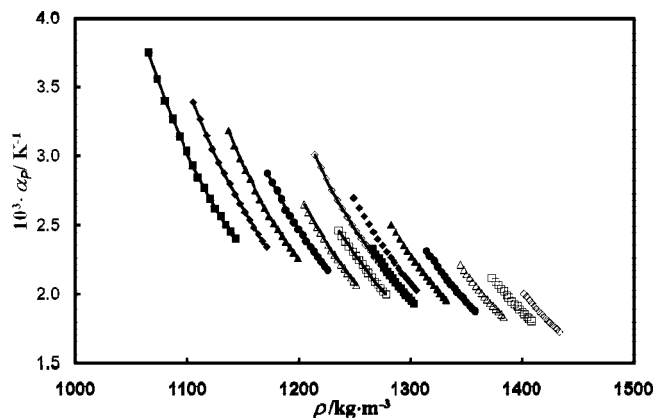


Figure 5. Coefficient of thermal expansion (α_p) for R408A and R409A. For the sake of simplicity, the symbols for each isotherm are the same for different fluids. A solid line is added for R408A. All the symbols without lines added represent the different isotherms for R409A: ■, 298.15 K; ◆, 288.15 K; ▲, 278.15 K; ●, 268.15 K; △, 258.15 K; □, 248.15 K; ◇, 238.15 K.

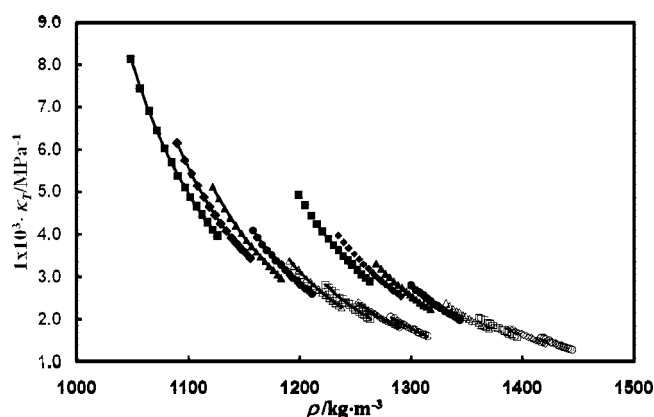


Figure 6. Coefficient of compressibility (κ_T) for R408A and R409A. For the sake of simplicity, the symbols for each isotherm are the same for different fluids. A solid line is added for R408A. All the symbols without lines added represent the different isotherms for R409A: ■, 303.15 K; ◆, 293.15 K; ▲, 283.15 K; ●, 273.15 K; △, 263.15 K; □, 253.15 K; ◇, 243.15 K; ○, 233.15 K.

where the quadratic value of the pseudo-dipole moment of the mixture in the gaseous phase μ_{mix} and the mixture mean polarizability α_{mix} are defined as follows:

$$\mu_{\text{mix}}^2 = \sum_{i=1}^{\infty} y_i \mu_i^2 \quad (9)$$

$$\alpha_{\text{mix}} = \sum_i y_i \alpha_i \quad (10)$$

Using the values of the dipole moments of the different constituents in the gas phase for each mixture,¹¹ we can obtain the values for the gaseous mixture dipole moments presented in Table 5. Equation 5 can then be used to calculate g for each mixture, from the experimental values obtained for μ^* in the liquid state. These are also presented in Table 5.

For all the mixtures studied so far,^{7,8} including the mixtures reported here, the values obtained for μ^* , based on the Kirkwood theory, show the following trend: R408A < R409A < R507 < R404A < R410A < R407C. The values of the pseudo-dipole moment for the gaseous mixtures (μ_{mix}) calculated using eq 9 have a different order: R409A < R408A < R410A < R407C < R507 < R404A. If we assume that

the Kirkwood factor defined by eq 5 can be extended to liquid state mixtures of polar molecules, the value of g_{mix} can be defined as follows:

$$g_{\text{mix}} = \frac{(\mu_{\text{mix}}^*)^2}{\mu_{\text{mix}}} \quad (11)$$

Using eq 11, the values of g_{mix} follow the order: R404A < R507 < R407C < R408A < R410A < R409A.

As mentioned before, the greater the value of g , the bigger the orientational order imposed by the neighbors, decreasing the ability of the molecules to rotate freely in the liquid state. Although it is easier to understand the local order in pure refrigerant liquids, as presented before,^{4,7-10} these results seem to justify that, on average, the molecules of the components in R408A are relatively mobile, while those of R409A are not. Those systems that have HFC143a have more rotational mobility, a fact probably derived from the properties of this compound.^{9,15,16} In addition, R409A has two chlorinated components (HCFC22 and HCFC142b), which make the molecules bigger and, therefore, induce a greater hindered rotation, if the nearest neighbors cage is nearly identically. The possibility of existing preferential interactions between the mixture components, including the possibility of cluster formation, is also a matter that has to be proved by molecular simulation¹⁷ or neutron diffraction studies.¹⁸ This analysis also needs information about the dielectric behavior of HCFC22 and HCFC124, which are not available at the moment.

However, there is some more that can be extracted from comparisons with the behavior of other refrigerants. There is a strong correlation between the apparent dipole moment in Kirkwood theory and the dipole moment of the same compound in the gas phase, given by eq 5. If we represent μ^* as a function of μ , we can obtain the plot of Figure 4. The same can now be registered for the refrigerant mixtures, using eq 11. Two lines are sketched in the plot. The solid line represents the border between free rotation in the liquid state ($g = 1$) and the partially hindered rotation area. The broken line divides the zones for partially hindered rotation and restricted rotation of the molecules in the liquid phase. This line is drawn taking into account a value of $g = 2.6$, the value obtained by Pople¹⁹ for liquid water assuming a structure consisting of a water molecule hydrogen bonded to four neighbors, considered here as a border between partially hindered rotation of a molecule in the cavity formed by contiguous molecules, and the restricted rotation, where several orientations are not possible by specific interactions imposed by the molecules present in the cage wall.

The number of fluorine atoms is significant in this decision (the more fluorine atoms or the bigger the ratio between fluorine and hydrogen atoms in the molecule, the more restricted the rotation in the liquid phase).⁹ Refrigerants like HCFC141b, HCFC142b, HFC143a, and HFC365mfc can have partially hindered rotation,^{9,10,15,16} while HFC245fa, HFC236ea, HFC134a, HFC32, and HFC152a, as well as some mixtures, have restricted rotation in the liquid state due to hydrogen bonding. This was already proven for HFC134a and HFC143a.¹⁵

Derived Thermodynamic Properties. The accuracy of the ε_r data, as well as the approximate linear dependence on T and P or ρ , makes it possible to estimate the isobaric coefficient of thermal expansion α_p and of the isothermal compressibility κ_T . The thermodynamic definitions of these coefficients are the following:

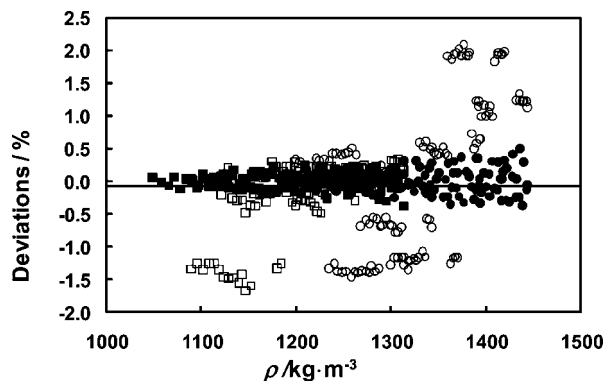


Figure 7. Deviations between the determined coefficients of thermal expansion and compressibility and REFPROP7,¹¹ as a function of density, for R408A and R409A. For the sake of simplicity, different isotherms for the same fluid have the same symbols. R408A (□, α_p ; ■, κ_T); R409A (○, α_p ; ●, κ_T).

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (12)$$

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (13)$$

Using the derivatives of the ϵ_r ($\partial \epsilon_r / \partial P$)_T, ($\partial \epsilon_r / \partial T$)_P, ($\partial \epsilon_r / \partial \rho$)_P, and ($\partial \epsilon_r / \partial \rho$)_T, it can be shown that

$$\alpha_p = -\frac{\left(\frac{\partial \epsilon_r}{\partial T} \right)_P}{\rho \left(\frac{\partial \epsilon_r}{\partial \rho} \right)_P} \quad (14)$$

and

$$\kappa_T = \frac{\left(\frac{\partial \epsilon_r}{\partial P} \right)_T}{\rho \left(\frac{\partial \epsilon_r}{\partial \rho} \right)_T} \quad (15)$$

The values of the coefficients can be calculated from the experimental data in the following way. For α_p , the derivatives of ϵ_r (eq 14) were calculated at each pressure, interpolating the temperature dependence between two consecutive nominal temperatures to obtain ($\partial \epsilon_r / \partial \rho$)_P and the density dependence between the two values $\rho_1(T_{n1}, P)$ and $\rho_2(T_{n2}, P)$ to obtain ($\partial \epsilon_r / \partial T$)_P. The point is then referred to the average density $\bar{\rho} = (\rho_1 + \rho_2) / 2$. In the case of κ_T , the derivatives of the ϵ_r were calculated at each nominal temperature, interpolating the pressure dependence between two consecutive pressures to obtain ($\partial \epsilon_r / \partial P$)_T and the density dependence between the two values $\rho_1'(T_n, P_1)$ and $\rho_2'(T_n, P_2)$ and to obtain ($\partial \epsilon_r / \partial \rho$)_T. The point is then referred to the average density $\bar{\rho}' = (\rho_1' + \rho_2') / 2$.

Equations 14 and 15 constitute the basis for calculating the coefficients α_p and κ_T from ϵ_r experimental data. The use of REFPROP7,¹¹ namely for the values of ($\partial \epsilon_r / \partial \rho$)_P and ($\partial \epsilon_r / \partial \rho$)_T, carries the uncertainty of the database model to our scheme, but unfortunately, there is no experimental density values for these mixtures, that could provide a more stringent comparison. So, the uncertainty of our reported values will be necessarily greater than the model of REFPROP7, as it includes also our global uncertainty in the experimental data points of ϵ_r .

Tables 6 and 8 show the values obtained for R408A and R409A, respectively, as a function of pressure, for different temperatures for α_p , and Tables 7 and 9 show the values obtained for κ_T for R408A and R409A. The values of $\bar{\rho}$ and $\bar{\rho}'$ used are also displayed.

Figures 5 and 6 show the values of α_p and κ_T obtained as a function of density for the different isotherms. Figure 7 shows the deviations between the determined α_p and κ_T values and REFPROP7,¹¹ as a function of density for all isotherms. As explained above, these figures show the uncertainties in the coefficients obtained from the dielectric measurements, as the comparison with the REFPROP7 database as a baseline, eliminates the uncertainty of the database and the error propagation of these values in our calculation. Deviations in the determination of κ_T never exceed 0.5 % (at the higher densities), with an average deviation of ± 0.2 %. The values determined for α_p are somewhat more uncertain, deviations being of the order of ± 2 %, possibly due to the fact that the spacing between the different pressure levels needs to be smaller. Although the comparison is not made with direct experimental data or from an equation of state not based in a CSP analysis, as REFPROP7 for these mixtures is, these results show that the calculation of these coefficients from ϵ_r measurements is rather promising, especially for the κ_T in the liquid state. It can provide an alternative way of obtaining these coefficients, if measurements of this property as a function of density are performed. Application of this scheme to pure fluids such as HFC125 which has a well-developed equation of state (EOS) shows that deviations for α_p are smaller than ± 0.3 %, almost ten times better.

Conclusions

This paper reports ϵ_r measurements for two alternative refrigerant mixtures, at temperatures from $T = (233 \text{ to } 303)$ K under pressures up to 16 MPa, in the liquid phase. The uncertainty of the measurements is estimated to be better than 0.22 % ($k = 2$). The experimental values were correlated as a function of density and temperature, generating two different dielectric equations of state for the two fluids. Kirkwood theory allows a direct determination of the value of the apparent dipole moment (μ^*) in the liquid phase, found to be $1.043 \cdot 10^{-29}$ C·m for R408A and $1.047 \cdot 10^{-29}$ C·m for R409A, as well as the Kirkwood correlation factor (g) found to be 3.11 for R408A and 3.97 for R409A. The values of the dipole moments (μ) in the ideal gaseous phase were calculated from the dipole moments of the components in the mixture, using an extension of the Debye equation for a pure perfect gas to perfect gas mixtures. They were found to be $5.921 \cdot 10^{-30}$ C·m for R408A and $5.257 \cdot 10^{-30}$ C·m for R409A. These results permit a better understanding of rotational mobility of these molecules in the liquid state.

Values of α_p and κ_T were obtained from the ϵ_r measurements, with an estimated uncertainty of 2 % and 0.3 % respectively, a result that supports the possibility of obtaining these coefficients directly from ϵ_r , with an uncertainty comparable to other experimental or calculation methods.

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