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Review

Dielectric properties of liquid refrigerants: Facts and trends☆

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ABSTRACT

In this paper we analyse the situation for the dielectric properties of the refrigerants, from the experimental and theoretical point of view, based on more than one decade of research of our group. Examples of the predictive power of simple models will illustrate the existing tools for electrical permittivity and dipole moment prediction and correlation. The relation of Báron and Buep was analysed and extended to include the effects of pressure variation. Analogies between the Vedam equation and rough hard-sphere theory of transport properties were encountered and discussed.

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Propriétés diélectriques des frigorigènes liquides : données et tendances

1. Introduction

The replacement of CFCs and HCFCs by hydro-fluorohydrocarbons (HFC's), is now fully established, needing values of the thermophysical properties of these compounds, chosen with regard to their values of the ozone depletion potential and global warming potential. In spite of the tremendous effort developed to determine new property data, establish equations of state and correlation/predictive schemes, there are still some fields that can still be object of research.

Alternative refrigerants have been extensively studied in our laboratory, both experimentally and theoretically. Table 1 shows the fluids studied, their origin, purity, and ranges of

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Nomenclature

A, B coefficients of Vedam Eq. (1)
A' coefficient of modified Vedam Eq. (3)
C translation-rotational coupling factor
g_K Kirkwood parameter
g_{KF} Kirkwood–Frölich parameter
n refractive index of the liquid
N_A Avogadro's Number
P_M molar polarizability
T absolute temperature
T_c critical temperature
V molar volume
V_0 volume of close-packing for hard spheres
y_i molar fraction
ε_r electrical permittivity or dielectric constant

$\varepsilon_{r,\infty}$ high-frequency relative permittivity
Σ Eulerian deformation or strain
Δ Vedam model parameter defined by Eq. (1)
η viscosity of the liquid
$\eta^{(0)}$ viscosity of low density (dilute gas) fluid
η^* dimensionless viscosity quantity, defined by Eq. (12)
η_{RHS} viscosity of the rough hard-sphere fluid
μ dipole moment of the molecule in the gas phase
μ_L dipole moment of the molecule in the liquid phase
μ_{mix} pseudo-dipole moment in the gas phase of a mixture
ρ_0 reference density of the liquid
$\rho^{sat}(T)$ saturation density at a temperature T
σ hard-sphere diameter

measurement. The most comprehensive studies involved the measurement of the electrical permittivity as a function of temperature and pressure, in the liquid phase, for the conditions normally used in the refrigeration industry, and for Class B (transitional replacements) and Class A (chlorine free) refrigerants. The available theories of Vedam and Kirkwood have been applied to correlate the data and obtain the apparent dipole moment of the liquid and were reviewed recently (Santos et al., 2006). The density functional theory (DFT) was used to model the liquid state and obtain a theoretically based value of the same dipole moments (Costa Cabral et al., 2001). One of the limitations of all these approaches is the need for refractive index data (which are often not available), for the liquid, as a function of density and

Table 1 – Fluids studied, origin, purity, ranges of measurement.

Fluids/mixture	Origin/purity	Temperature range/K	Pressure range/MPa	Reference
HCFC-123	Solvay fluor und derivative, Germany/99.8%	204.04–312.91	0.21–15.13	(Barão, 1995) (Barão et al., 1997a,b) (Barão et al., 1998)
HCFC-141b	Solvay fluor und derivative, Germany/99.8%	202.25–298.25	0.10–15.14	(Barão et al., 1997a,b)
HCFC-142b	Solvay fluor und derivative, Germany/99.9%	206.62–303.75	0.32–18.23	(Barão et al., 1996)
HFC-32	ICI, UK/99.8%	208.42–303.48	2.00–16.10	(Nieto de Castro et al., 1995)
HFC-152a	Solvay fluor und derivative, Germany/99.9%	207.08–297.84	0.50–17.93	(Barão, 1995) (Barão et al., 1998)
HFC-143a	Elf Atochem (France)/99.5%	218.25–294.11	2.00–15.00	(Gurova et al., 2009)
HCFC-134a	Solvay fluor und derivative, Germany/99.8%	298.15–323.15 (g) 205.59–308.16 (l)	0.1245–1.2486 (g) 0.64–16.51 (l)	(Barão, 1995)
HFC-125	Elf Atochem (France)/>99.5%	214.32–303.72	2.00–16.00	(Pereira et al., 2001)
HFC-245fa	Honeywell fluorochemical, Italy/99.9%	218.53–302.84	1.00–16.00	(Gurova et al., 1994)
HFC-227ea	Ausimont, Italy/99.9%	223.15–302.00	1.00–16.00	(Ribeiro et al., 2007)
HFC-236ea	Lancaster Inc, USA/99%	223.15–302.00	1.00–16.00	(Ribeiro et al., 2007)
HFC-365mfc	Solvay fluor und derivative, Germany/>99.5%	223.15–302.00	1.00–16.00	(Ribeiro et al., 2007)
R-404A	Solvay fluor und derivative, Germany/>99.5%	217.65–303.15	2.00–16.00	(Brito et al., 2000b)
R-407C	Solvay fluor und derivative, Germany/>99.5%	220.15–303.15	2.00–16.00	(Brito et al., 2000b)
R-408A	Solvay fluor und derivative, Germany/>99.5%	233.00–303.00	1.00–16.00	(Ribeiro et al., 2008)
R-409A	Solvay fluor und derivative, Germany/>99.5%	233.00–303.00	1.00–16.00	(Ribeiro et al., 2008)
R-410A	Solvay fluor und derivative, Germany/>99.5%	217.15–303.65	2.00–16.00	(Brito et al., 2000a)
R-507	Solvay fluor und derivative, Germany/>99.5%	219.15–303.15	2.00–16.00	(Brito et al., 2000b)

(g) – gaseous state; (l)- liquid state.

temperature. The more rigorous model of Kirkwood–Frölich was applied recently to HFC-236ea (Ribeiro et al., 2007) and HFC-143a (Gurova et al., 2009) and the results showed that the dipole moment in the liquid state is in fact about 30% lower that that obtained by Kirkwood theory, but in excellent agreement with DFT calculations previously performed (Costa Cabral et al., 2001; Ribeiro et al., 2007).

Similar data obtained by other authors are very scarce, and it is mostly restricted to dipole moments in the gas phase, easily obtainable form REFPROP (Lemmon et al., 2002), and some electrical permittivity and refractive index data (Pitschmann and Straub, 2002). Therefore it is very important to use the best available data with molecular theories to develop correlation/prediction schemes, both for electrical permittivity and dipole moments, for pure fluids, and if possible, for the near azeotropic blends, like R-410A [R32/125 (50/50) mass percent] (Brito et al., 2000a), R-404A [R125/R143a/R134a (44/52/4) mass percent], R-407C [R32/R125/R134a (23/25/52) mass percent] and R-507 [R125/R143a (50/50) mass percent] (Brito et al., 2000b), R-408A [R125/R143a/R22 (7/46/47) mass percent] and R-409A [R22/R124/R142b (60/25/15) mass percent] (Nieto de Castro and Ribeiro, 2008). We present in this paper the first effort to systematize all the existing information and to analyse the predictive/estimation power of some of the correlations and theories applied. Details of the theories applied by the authors can be obtained from previous publications (Barão et al., 1997a,b; Costa Cabral et al., 2001; Santos et al., 2006; Ribeiro et al., 2007).

2. Models, results and discussion

The relative permittivity ε_r is defined as the ratio between the permittivity of the fluid, ε, and the permittivity of vacuum, ε_0. Traditionally it was designated by dielectric constant. Experimentally it can be calculated at a given pressure P and temperature T from the ratio between the capacitance of a cell filled with the fluid and the capacitance of the same cell under vacuum, at the same temperature (Barão et al., 1997a,b).

2.1. Vedam formalism

The Vedam formalism is based on the work of Vedam and Chen (1982), Vedam (1983) and Diguet (1986). According to this theory, the variation of the relative permittivity with pressure is a function of the deformation of the volume, showing a non-linear behavior in the case of liquids. This non-linearity can be reduced when the difference between the square root of the electric permittivity of the liquid at a given density $\varepsilon_r^{1/2}(\rho)$, and its value at a reference density $\varepsilon_r^{1/2}(\rho_0)$, usually chosen to be the saturation density at the same temperature $\rho_0 = \rho^{sat}(T)$, Δ, defined by Eq. (1) is analysed as a function of the Eulerian deformation or strain, Σ, defined by Eq. (2). For all the refrigerants studied it is possible to verify that Σ provides a linear relation for Δ independently of the type of molecules that compose the fluid.

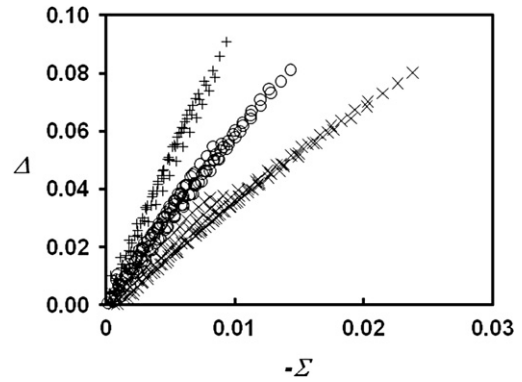$$\Delta = \varepsilon_r^{1/2}(\rho) - \varepsilon_r^{1/2}(\rho_0) = A\sum + B \qquad (1)$$

Fig. 1 – The function Delta (Δ) as a function of the Eulerian Strain (Σ) for three refrigerants for pressures up to 16 MPa. × - HFC-227ea (223–303 K); ○ - HFC-236ea (223–303 K); + - HFC-365mfc (263–303 K) (adapted from Ribeiro et al., 2007).

$$\Sigma = \frac{1}{2}\left[1 - \left(\frac{\rho}{\rho_0}\right)^{2/3}\right] \qquad (2)$$

As an example, Fig. 1 shows the results obtained for HFC-227ea, HFC-236ea and HFC-365mfc, from 223 to 303 K and pressures up to 16 MPa for HFC-227ea and HFC-236ea, and HFC-365mfc at temperatures from 263 K to 303 K up to 16 MPa (Ribeiro et al., 2007). The results are the same for all the refrigerants so far studied, when the density data are very accurate, namely the value of the scaling factor ρ_0 can be well defined. The coefficients A and B are temperature dependent, but because B is very small, we can considerer it zero and simplify the Eq. (2) to:

$$\Delta = A'(T)\sum \qquad (3)$$

This equation can be used to calculate the electrical permittivity of the refrigerants at the temperatures for which data exists. This is shown in Fig. 2 for HFC-125 (Pereira et al., 2001), which plots the deviations between the experimental
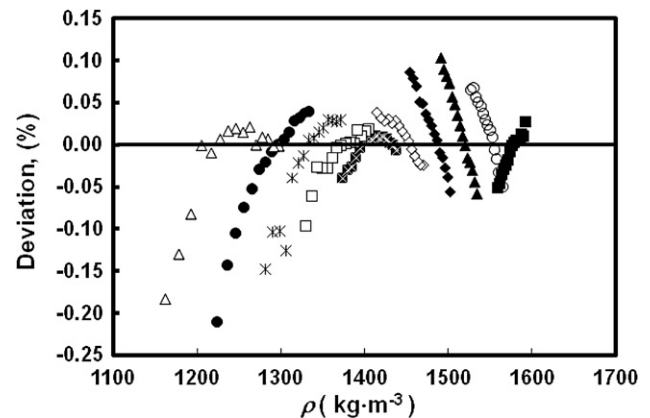

Fig. 2 – Deviations of calculated relative permittivity values from experimental data [$100(\varepsilon_{VR} - \varepsilon_{exp})/\varepsilon_{exp}$] for HFC-125, according to the modified Vedam relation, Eq. (3), (Pereira et al., 2001). ■ 217.65 K; ○ 223.65 K; ▲ 233.15 K; ◆ 243.15 K; 253.15 K; ■ 263.16; □ 273.15 K; ✳ 283.15 K; ● 293.15 K; △ 303.15 K.

data of electrical permittivity and estimated values, calculated according to this method. As can be seen the differences are smaller than 0.25%, an excellent capability, as most of the published data for this property have uncertainties greater than 0.5%. The small systematic curvature is caused by assuming $B = 0$, but we gain in the fact that only one parameter is needed. If we correlate the values of A' as a function of T, we can use this equation to interpolate in temperature, with a minor increase in the maximum and average deviations. However this fact can also be used as a predictive tool, a fact here reported for the first time. If we represent the logarithm of the ratio between $A'(T)$ and its value at the reduced temperature of 0.7, the same used by Pitzer (1939) to define the reference point for the definition of the acentric factor, for all the refrigerants studied, we obtain, a universal function:

$$\ln\left(\frac{A'(T)}{A'(0.7T_c)}\right) = a_1 + a_2\left(\frac{T}{T_c}\right) \qquad (4)$$

where $a_1 = 1.147036511$ and $a_1 = -1.659219867$, with a standard deviation of 0.045. Fig. 3 shows the representation obtained, together with the individual data points for nine refrigerants studied. The universal behavior is clear, and once known the value of $A'(0.7T_c)A$, ρ_0 and $\varepsilon_r(\rho_0)$ determined for a refrigerant, we can calculate the electrical permittivity of any of these refrigerants for temperatures outside the range measured, using Eqs.(1–4). Table 2 shows the values necessary to use for this prediction of the electrical permittivity of the refrigerants, and the valid temperature ranges. Values of ρ_0 can be obtained from REFPROP (Lemmon et al., 2002). As ε_r (ρ,T) the electrical permittivity can be expressed as a function o temperature and pressure through the dielectric equation of state expressed in the general form

$$\varepsilon_r(\rho, T) = b_0 + \frac{b_1}{T} + b_2\rho + \frac{b_3\rho}{T} \qquad (5)$$

the values of $\varepsilon_r(\rho_0)$ can be calculated from the equations ε_r (ρ,T) shown in Table 3 for the refrigerants studied.

Table 2 – Constants for the modified Vedam equation for the refrigerants studied.

Refrigerant	T_c/K	-A'(0.7T_c)	Temperature range/K
HFC-32	351.26	9.1448	208.42–303.48
HFC-152a	386.41	7.8950	207.08–297.84
HFC-143a	345.86	7.2622	218.25–294.11
HFC-134a	374.21	7.1220	205.59–308.16
HFC-125	339.17	5.6129	214.32–303.72
HFC-245fa	427.20	6.5784	218.53–302.84
HFC-236ea	412.44	5.7717	223.15–303.15
HFC-227ea	374.80	3.9024	223.15–303.15
HFC-365mfc	187.70	8.1093	263.15–303.15

2.2. Kirkwood and Kirkwood–Frölich formalisms

The Kirkwood formalism (Kirkwood, 1939) was the first molecular theory for the liquid state, and it could relate the electrical permittivity with density and temperature. This formalism agrees well with the experimental results, providing numerical values of polarizability, and dipole moment of the molecule through the Kirkwood parameter g_K, equal to square of the ratio between the apparent dipole moment in the liquid phase and that of the gaseous phase (no rotation hindrance), a measure of the rotational hindrance in the liquid state. This model was extensively applied to all the refrigerants that we have measured[1] (Santos et al., 2006; Ribeiro et al., 2007; Gurova et al., 2009) and to mixtures of fixed composition (Brito et al., 2000a,b; Nieto de Castro and Ribeiro, 2008). The values obtained showed, that in fact, the dipole moments obtained were greater that those found in the gaseous phase, and that g_K could really explain the rotational mobility of the individual molecules inside the "cage" of nearest neighbors. As a main conclusion we can state that 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 (Santos et al., 2006). Molecules like 1,1,1,2-tetrafluoroethane, HFC-134a, and 1,1-difluoroethane, HFC-152a, have restricted rotation in the liquid state, caused by hydrogen bonding. This was already proved for HFC-134a and HFC-143a (Costa Cabral et al., 2001). For HFC-134a, the distances between the active fluorine and hydrogen atoms in the different dimers vary between 0.253 and 0.295 nm, while for HFC-143a, the distances between the active fluorine and hydrogen atoms in the different dimers vary between 0.251 nm and 0.294 nm, values well known in hydrogen bonds in other compounds.

From all the systems studied it was concluded that this theory was just a first approximation, and that more reliable values for the dipole moments in the liquid phase should be obtained from the application of Frölich theory (1958). In fact, in the liquid phase the molecules are close to each other, so the orientation polarization of a molecule is influenced by the surrounding dielectric. Onsager (1936) has given a more careful treatment of the continuum approach. In his model, a point dipole is placed in the centre of a cavity of relative permittivity $\varepsilon_{r,\infty}$, and the effect of the surrounding dielectric
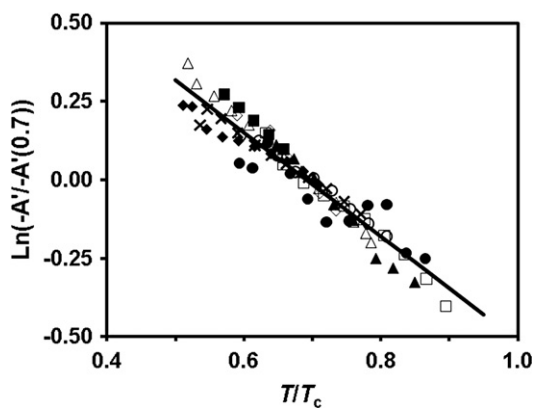

Fig. 3 – Universal correlation for modified Vedam equation parameter, A'. ● - HFC-32; □ - HFC-125; △ - HFC-134a; ▲ - HFC-143a; × - HFC-152a; ○ - HFC-227ea; - HFC-236ea; ◆ - HFC-245fa; ■ - HFC-365mfc. The line corresponds to Eq. (4).

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[1] For each particular fluid the reference can be found in Table 1.

Table 3 – Dielectric equation of state data (Eq. (5)).				
Refrigerant	b_0	b_1/K	$10^{-2}b_2/kg^{-1}\cdot m^3$	$b_3/K\cdot m^3\cdot kg^{-1}$
HFC-32	-2.403 ± 0.7899	700.53 ± 302.73	3.086 ± 0.0005	6.611 ± 0.206
HFC-152a	15.90 ± 0.2000	6842.1 ± 87.100	-1.45 ± 0.0002	10.79 ± 0.068
HFC-143a	11.811 ± 0.6740	-3928 ± 2100	-1.02 ± 0.165	6.4656 ± 0.0006
HFC-134a	12.50 ± 0.3000	4723.2 ± 111.90	-1.17 ± 0.0002	7.197 ± 0.078
HFC-125	-6.364 ± 0.0310	3314 ± 7.800	8.91 ± 0.309	-15.426 ± 0.784
HFC-245fa	-3.345 ± 0.0370	2980 ± 9.510	3.618 ± 0.387	-4.5909 ± 0.984
HFC-236ea	-3.747 ± 0.0420	2652.2 ± 10.852	26.72 ± 4.393	-1.9026 ± 1.137
HFC-227ea	-2.831 ± 0.0125	2028.9 ± 3.2303	4.049 ± 0.1310	-6.6918 ± 0.338
HFC-365mfc	-13.14 ± 0.0790	7370.8 ± 22.287	6.572 ± 0.8373	-8.6918 ± 2.357

is measured by the dielectric response of the polarization charges induced on the wall of the cavity, resulting:

$$\frac{(\varepsilon_r - \varepsilon_{r,\infty})(2\varepsilon_r - \varepsilon_{r,\infty})}{\varepsilon_r(\varepsilon_{r,\infty} + 2)^2}\left(\frac{M}{\rho}\right) = \frac{N_0 g\mu^2}{9\varepsilon_0 k_B T} \tag{6}$$

The high-frequency relative permittivity ε_r, ∞ is commonly calculated from the Maxwell relation $\varepsilon_r, \infty = n^2$, where n is the refractive index of the liquid at temperature T. Eq. (6) is then transformed in the Kirkwood–Frölich Eq. (7), where KFF is the Kirkwood–Frölich Function:

$$\text{KFF} = \frac{(\varepsilon_r - n^2)(2\varepsilon_r + n^2)}{\varepsilon_r(n^2 + 2)^2}\left(\frac{M}{\rho}\right) = \frac{N_0 g_{KF}\mu^2}{9\varepsilon_0 k_B T} \tag{7}$$

This equation can be used to predict the dipole moment in the liquid phase, $\mu_L^2 = \mu^2 g_{KF}$, yielding a value of the Kirkwood–Frölich parameter g_{KF} if the dipole moment in the gaseous phase is available and the refractive index is known as a function of temperature. This formalism was applied to all the refrigerants of Class C (HFC's) and will be reported soon (Nieto de Castro and Ribeiro, 2010). Table 4 shows the values obtained for the pure HFC's studied, while Fig. 4 represents μ_L as a function of μ. As reported previously with the Kirkwood theory (Nieto de Castro and Ribeiro, 2008) two lines are sketched in the plot. The dotted 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 hindered or 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 Pople (1951) for liquid water assuming a structure consisting of a water molecule hydrogen bonded to four neighbours, 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 conclusions are, however, different from those found with the Kirkwood model. Here, only HFC-236ea has hindered rotation in the liquid state, while all the other refrigerants have partial hindered rotation, and therefore a greater mobility. This result complements the discussion reported recently for HFC-143a (Ribeiro et al., 2007), where it has been shown that the SCIPCM model,[2] with B3PW91/D95V(d,p) level, developed by Costa Cabral et al. (2001), generated a value for the dipole moment in the liquid phase of 2.75 D, in excellent agreement with the Kirkwood–Frölich model (2.53 D), and much smaller than the Kirkwood value (3.34 D). Similar results were obtained for the other C2 and C3 refrigerants, and are also presented in Table 4. The deviation found for HFC-32 has been explained by the importance of clustering (2–8 molecules) (Costa Cabral et al., 2001).

This analysis shows that the Kirkwood model is limited, namely because there is the possibility of formation of dimers or n-molecule clusters in the liquid state, not accounted for in this theory, and especially present in HFC-32. We therefore recommend the use of the Kirkwood–Frölich model whenever the refractive index in the liquid state is known.

The dipole moments for the refrigerants that we have measured liquid state dielectric properties in the follow the order in the gaseous state:

236ea < 227ea < 245fa < 125 < 32 < 134a < 152a
< 143a < 365mfc.

For those already processed using the Kirkwood–Frölich model (presented in Table 4) the order for the gaseous phase is the following:

236ea < 227ea < 245fa < 125 < 32 < 134a < 152a < 143a

while for the liquid phase it is:,

227ea < 125 < 245fa < 236ea < 143a < 152a < 134a < 32.

Table 4 – Dipole moments and Kirkwood–Frölich parameter.				
Refrigerant	μ/D	μ_I/D	g_{KF}	μ_{SCIPCM}/D
HFC-32	1.978	2.89	2.14	2.35
HFC-152a	2.262	2.82	1.56	2.77
HFC-143a	2.340	2.53	1.17	2.75
HFC-134a	2.058	2.83	1.90	2.65
HFC-125	1.563	1.99	1.62	1.94
HFC-236ea	1.129	2.07	3.35	–
HFC-227ea	1.456	1.90	1.71	1.98
HFC-245fa	1.549	2.06	1.77	–

$1D = 3.333564 \times 10^{-30}$ cm.

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[2] SCIPM means Self Consistent Isodensity Polarized Continuum Model (Foresman et al., 1996). B3PW91/D95V(d,p) level is the combination chosen for the molecular orbital functions used in the interaction energies calculations. See Costa Cabral et al. (2001).
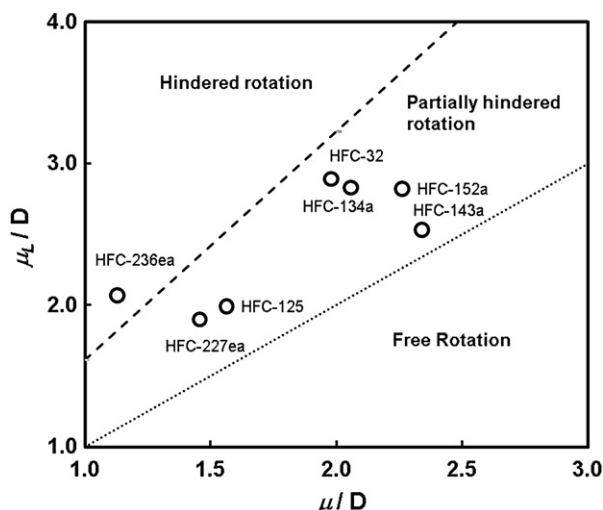
Fig. 4 – Plot of μ_L as a function of μ for the HFC's studied. The broken line represents the value $g = 2.6$, and the dotted line, the value $g = 1$.

The Kirkwood–Frölich parameter, g_{KF}, shows the following trend:

143a < 152a < 125 < 227ea < 245fa < 134a < 32 < 236ea.

We are now in the position to say that the molecules of HFC-143a have the highest mobility in the liquid state, and although hydrogen bonding between dimers has been detected (Costa Cabral et al., 2001), it seems that it does not restrict its rotational mobility. The strong dipole of HFC-32 and the possibility of generating clusters in the liquid state turn its molecule very static, from the rotational mobility point of view. It will be interesting to perform self-diffusion measurements in these compounds to explore these speculations.

Predicting the values of dipole moments in the gaseous phase is now possible using the vector group contribution methods, and all the programs used for molecular structure generation and description yield dipole moments as the result of the analysis, so we do not intend to propose any predictive scheme. However, for the liquid state, the situation is completely different, as it is not possible to generate dipole moments without performing theoretical calculations as described (Costa Cabral et al., 2001). The normal use of the dipole moment (or polar strength) in property estimation schemes (Poling et al., 2001) raises the expectation that it should be possible to predict the dipole moments of these and related molecules, from other molecular properties. However, the attempts made so far by the authors have not generated any sensible scheme and therefore were abandoned. It is gratifying that we have the Kirkwood–Frölich formalism, and therefore reasonable values for the dipole moments of these refrigerants, which are the most significant pure fluids used in the refrigeration industries.

The application of the previous formalisms to refrigerant mixtures can be based on the following assumptions:

a) Availability of permittivity and EOS data for mixtures, like the near azeotropic blends, R-410A (Brito et al., 2000a), R-

404A, R-407C and R-507 (Brito et al., 2000b), R-408A and R-409A (Ribeiro et al., 2008). In this case it is immediately possible to use the Kirkwood formalism and obtain the apparent dipole moments in the liquid phase. Any considerations about the Kirkwood parameter need the value of the dipole moment of the mixture in the gas phase, a datum that is not usually available, even if we assume just for a fixed composition. The dipole moment in the gas phase (and the polarizability) can be calculated from the pure component values and mixing rules, which were obtained by the authors recently (Ribeiro et al., 2008), by using the definition of molar polarizability, P_M, for a pure polar gas, based on the theory of Debye (Hilczer and Malecki, 1986). The application of the Debye equation to mixtures in the gaseous state is theoretically possible, especially for dilute gas mixtures, for which we have the individual components dipole moments. As molecules in a perfect gas mixture do not interact, the molar polarization of this reference mixture with N components of molar fraction y_i can be assumed to be additive. As demonstrated in the work by Ribeiro et al. (2008), the quadratic value of the pseudo-dipole moment in the gas phase mixture, μ_{mix}, is given by:

$$\mu_{mix}^2 = \sum_{i=1}^{N} y_i \mu_i^2 \tag{8}$$

and the Kirkwood factor is given by:

$$g_{mix} = \frac{\left(\mu_{mix}^*\right)^2}{\mu_{mix}^2} \tag{9}$$

Problems are encountered in the implementation, since dielectric data for some components of the mixtures in commercial use are not available (e.g., HCFC22 and HCFC124), but can be made for some mixtures (Gurova et al., 2009).

b) If data on refractive indices are available, the Kirkwood–Frölich formalism can be applied, with the same limitations as those found for the Kirkwood formalism.

2.3. The Barón and Buep (B&B) Equation

Several attempts to correlate the electrical permittivity of polar liquids with other thermophysical properties have been made in the past, and we will not discuss them all here. Some are based on the theoretical models (Mopsik, 1969) or are purely empirical (Báron et al., 1977). A recent review of these equations became available recently (Marshall, 2008). From these papers, one extremely useful idea developed by Báron and Buep (1997) deserves our attention, because it can be transformed to a universal behavior for refrigerants. These authors have shown that the inverse of the electrical permittivity is a linear function of fluidity (1/η), η being the viscosity of the liquid, for water and other associated liquids. Its equation is:

$$\frac{1}{\varepsilon_r} = \frac{C}{\eta} + D \tag{10}$$

Báron and Buep (1997) have used only atmospheric pressure data, but their equation can be extended to accommodate the
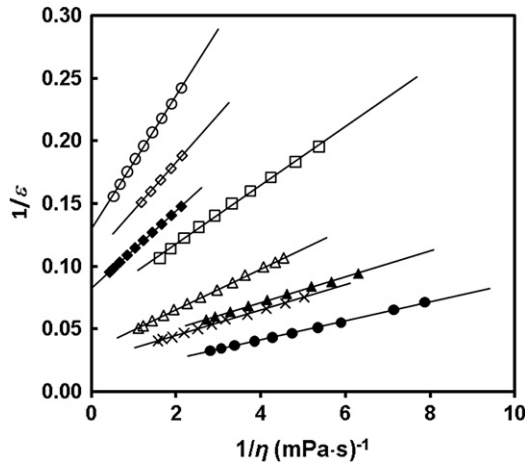
Fig. 5 – Báron and Buep model (Eq. (10)) for all the refrigerants studied, at 15 MPa. ● - HFC-32; □ - HFC-125; △ - HFC-134a; ▲ - HFC-143a; × - HFC-152a; ○ - HFC-227ea; - HFC-236ea; ◆ - HFC-245fa; ■ - HFC-365mfc. **Solid lines represent the fit of Eq. (10).**

pressure variation. Eq. (10) was applied to HFC-32, HFC-125, HFC-134a, HFC-143, HFC-152a, HFC-245fa, HFC-236ea and HFC-227ea, and the results are displayed in Fig. 5 at a fixed pressure (15 MPa) and in Fig. 6 for HFC-134a for three pressure levels, 2, 5 and 15 MPa. Data for viscosity were taken, for the sake of consistency, from REFPROP (Lemmon et al., 2002). As we can see, the model is applicable to all refrigerants studied, for fixed pressure and in the case of HFC-134a it is shown the application as a function of pressure, the slope C being a linear function of pressure. We can conclude that the equation describes a universal behavior. Moreover, from Fig. 5 it is clear that all the straight lines (drawn as trendlines) converge to a fixed value of around -2.5 ± 0.5 in the fluidity axes, a fact that can be explored in a near future in developing
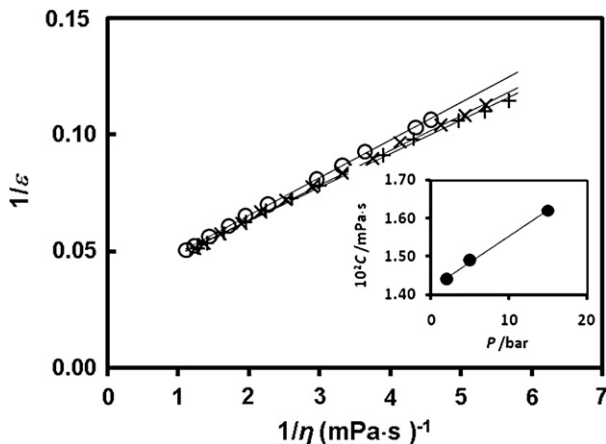

Fig. 6 – Báron and Buep model (Eq. (10)) for HFC-134a, for three pressure levels. + - 2 MPa; × - 5 MPa; ○ - 15 MPa. **The small variation of C with temperature can be seen in the insert.**

Table 5 – Coeficients for the Báron and Buep equation.

Refrigerant	C_0	C_1/MPa^{-1}	D	Temperature range/K
HFC-32	0.0068	$5 \cdot 10^{-5}$	0.0111	208.42–303.48
HFC-152a	0.0089	$8 \cdot 10^{-5}$	0.0248	207.08–297.84
HFC-143a	0.0089	$1 \cdot 10^{-4}$	0.0299	218.25–294.11
HFC-134a	0.0142	$1 \cdot 10^{-4}$	0.0330	205.59–308.16
HFC-125	0.0187	$3 \cdot 10^{-4}$	0.0235	214.32–303.72
HFC-245fa	0.0284	$2 \cdot 10^{-4}$	0.0822	218.53–302.84
HFC-236ea	0.0339	$4 \cdot 10^{-4}$	0.1022	223.15–303.15
HFC-227ea	0.0514	$1 \cdot 10^{-4}$	0.1293	223.15–303.15

Corresponding States Principle (CSP) correlations. Eq. (10) can then be written:

$$\frac{1}{\varepsilon_r} = \frac{C(P)}{\eta} + D = \frac{C_0 + C_1 P}{\eta} + D \tag{11}$$

Table 5 shows the values of C and D for all the refrigerants studied. The success of this equation can be explained with the help of the traditional applications of rough hard-sphere theories to the properties of the liquid state, namely viscosity (Dymond and Assael, 1996). Looking more carefully to the Vedam equation and to the definition of the Eulerian strain, there is a variation of $\varepsilon_r^{1/2}$ with a ratio of the density to the value of the density at a reference temperature, raised to the power 2/3. In the heuristic extensions of the van der Walls model (or rough hard-sphere theories), a dimensionless viscosity quantity η^* is defined as:

$$\eta* = \frac{\eta}{\eta^{(0)}} \left(\frac{V}{V_0}\right)^{2/3} = F_\eta\left(\frac{V}{V_0}\right) \tag{12}$$

where $\eta^{(0)}$ the viscosity of low density (dilute gas) fluid, V the molar volume and V_0 the volume of close-packing for hard spheres, (given by $N_A \, \sigma^3/2^{1/2}$, σ being the diameter of the sphere). In applying this theory to current liquids, the close packed volume is obtained empirically, and it is a function of temperature, and the viscosity of the rough hard sphere is given by:

$$\eta \approx \eta_{RHS} \approx C \cdot \eta_{SHS} = R_\eta F_\eta\left(\frac{V}{V_0}\right) \tag{13}$$

The factor C was introduced by Chandler (1975) as the translation-rotational coupling factor, and the theory assumes it is a constant for each fluid, independent of density and temperature, but greater or equal to one. Taking into account Eqs. (1–3) and (13), we can conclude that the foundations of the Vedam equations are exactly the same, whereby the reference density, also a function of temperature, can play the role that $V_0 (T)$ plays in the rough hard-sphere theory. We will pursue this line, trying to transform Báron and Buep relation in a sound theoretically based estimation scheme for the electrical permittivity of the polar liquids, including refrigerants.

3. Conclusions

The understanding of the influence of molecular structure in the dielectric properties of liquid refrigerants is now

proceeding smoothly, and we can now state that rigorous measurements, together with a good equation of state, and theoretical formalisms can be used to calculate dipole moments in the liquid state. However the possibility of developing universal behaviors and/or corresponding states approaches to calculate the electrical permittivity of these polar liquids is still at is infancy. The authors have in this paper developed, based on their experimental measurements on the electrical permittivity of one, two and three carbon HFC's, predictive techniques based on the modified Vedam equation, applied the Kirkwood–Frölich formalism to obtain dipole moments in the liquid state and studied the generalization of the Báron and Buep equation that relates this property with viscosity to all the HFC's studied. The modified Vedam equation, with the universal relationship developed can be used to estimate the values of the electrical permittivity at any temperature and pressure in the liquid range, for $0.5 < T/T_c < 0.9$, and up to 20 MPa. The dipole moments obtained with the Kirkwood–Frölich formalism can be used to interpret the intermolecular forces between polar liquids and contribute to the understanding of the rotation mobility and the possibility of hydrogen bond formation between hydrogen and fluorine atoms. Finally, the Báron and Buep empirical equation was demonstrated to be universal for the refrigerants in the T, P diagram. This relation between the reciprocal of the electrical permittivity and the fluidity is a powerful tool to estimate permittivity from viscosity data, usually more available in the literature to end users. The authors hope to study the universal behavior of this equation, namely its relation with the rough hard spheres approach to the transport properties of liquids, to establish more accurate (and theoretically sound) property estimation schemes. Studies of this type will also open the understanding of new refrigerants, namely those composed by HFC's and ionic liquids, now thought to be a good alternative to classic mixtures in absorption refrigeration.

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