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Influence of Molecular Properties on the Electric Strength of Potential SF6 Substitutes

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Abstract. SF6 gas has been widely used in power industry owing to its excellent insulation performances. However, due to its significant greenhouse effects, many scholars have carried out experimental and theoretical studies to search for the SF6 substitutes. In order to find the promising replacement of the insulation gas SF6, the basic physico-chemical properties and electronegativity of CF-x, HFC and HFO gases, which satisfy the safety and environmental requirements, are calculated based on the density functional theory (DFT). Relative electric strengths of these insulating gases are calculated by solving the Boltzmann equation. The influence of the molecular properties on the electric strength are studied by linear regression analysis. The calculation results show that the correlation coefficients of the molecular mass and electron number relative to the electric strength are 0.678 and 0.692, respectively. Furthermore, the electric strength is increased with higher electronegativity of potential gases and the magnitude of the electric dipole moment and polarizability are related to the electric strength. The correlation coefficient between polarizability and electric strength is 0.647. Considering the potential influential factors on the electric strength, a prediction formula is established through multivariate linear regression. The Pearson's correlation between the calculated value and measured value is 0.948. Therefore, it can be used to predict the electric strength of the potential substituted gases when screening the enormous candidates of SF6.

1. Introduction

Due to the advantages of safety and reliable operation, flexible configuration and simple maintenance, gas-insulation mediums are widely used in high-voltage electric power equipment such as transformers, circuit breakers and switch gears. SF6 gas is an ideal medium[1-2] with high electric strength, good arc extinguishing performance and low boiling point. However, the global warming potential (GWP) of SF6, as one of the six global controlled greenhouse gases, is 23900 times greater than that of CO2. Worse still, SF6 can hardly be decomposed in the atmosphere. Therefore, it is one of the important and urgent

issues in the high voltage field to seek new environmentally friendly gases with the insulation performance similar to or even superior than SF6.

The following requirements should be satisfied for the ideal SF6 substitutes: low boiling point; no ozone consumption, namely that the ozone depletion potential (ODP) is zero; low GWP; stable chemical property; the toxicity level satisfies the permissible exposure limit; the electric strength (ES) is superior than the air[3]. Nowadays, plenty of simulation and experimental research has been done on the electric strength and insulation performance of the potential SF6-alternative gases[4-9], especially the fluorine hydrocarbon gases composed of strong electronegative atoms such as CF3I, c-C4F8 and C3F8[10-14].

However, the research on the specific properties of potential gases through experimental methods will consume plenty of time and efforts, and the alternative gases will be limited to the existing gases. Hence, computational methods were usually used to screen the electrical properties of substituted gases on a large scale. Due to the unclear relation between the molecular structure and the electric strength of the substituted gases, the electric strength is often calculated through Boltzmann equation or Monte Carlo method[10, 15-17]. The collision cross-sections of the gases are needed for the calculation. Due to the limited data source such methods are only applicable to few gases. Besides, the calculation on a large scope of SF6 potential substituted gases is not realistic. The electric strength of SF6 substitutes depends on the level of molecular structure, so research on the relation between molecules properties and electric strength will help to filter the potential gases and select the most promising ones.

The potential substituted gases which are nontoxic, incombustible, non-explosive and with low boiling point are firstly selected from the gases of CF-x (Cabonfluoro-x, x represents the halogen element), HFC (Hydrofluorocabon) and HFO (Hydrofluoroolefin) according to the molecular safety performance and boiling point in the PubChem database. Their basic physico-chemical properties, electronegative parameters and polarization property are calculated based on the density function theory (DFT). The electric strengths of the target gases are calculated according to the electron collision cross-sections. And the dependency of the relative electric strength Er (the ratio of substituted gases electric strength to SF6 gas which is 355 Td) on the molecular mass, electron number, electronegative index, electric dipole moment and electronic polarizability is analyzed by means of multiple linear regression. Then the prediction model of substituted gas electric strength is established based on the result of multiple linear regression.

2. Computational methods

2.1. Estimation of the electronegative index

The density function theory is based on Kohn-Hohenber theorem which can be utilized to calculate the charge distribution and electronic motion. Besides, the density function theory can solve the basic physico-chemical properties of SF6 potential substituted gases accurately and provides the algorithm basis for the analysis and calculation of the electric strength. The B3LYP/6-311G++ (d, p) basis set in Gaussian 09[18] software is used for all calculation in the paper.

The ionization Energy (IE) is a benchmark of how easily a gas molecule loses an electron, and the electronic affinity (EA) measures the attractiveness between nucleus and electrons, that is, the difficulty of binding electrons for a molecular. The gases with high dielectric strength should also have high IE and EA since the free electrons have higher possibility to be attached by the molecules, thus reducing the electron number in the gap[19-20]. The electronegative index En is introduced to assess the molecular electronegativity of the target gas. IE, EA and En are given in equation (1)-(3):

$$IE = E^+ - E \tag{1}$$

$$EA = E - E^- \tag{2}$$

$$E_n = \frac{1}{2}(IE + EA) \tag{3}$$

Where E is the energy of neutral gas molecules; E+ and E- are the energy of the gas molecule with one positive charge and one negative charge, respectively.

2.2. Calculation method of the electric strength

As an inherent feature of insulation gases, the electric strength is the maximum value in a uniform electric field distribution that the gas can withstand without insulation damages. The electric strength of the insulation gas can be calculated by the ionization and attachment coefficients in the gap when the electric breakdown occurs. The effective ionization coefficient is α-η where α is the ionization coefficient and η is the electron attachment coefficient. The discharge turns into a self-consistent state when the following condition is fulfilled according to the Townsend discharge theory:

$$(\alpha - \eta) \cdot d = \ln\left[\frac{\alpha - \eta}{\alpha} \cdot \frac{1}{\gamma} + 1\right] \tag{4}$$

Where d is the gap distance and γ is secondary ionization coefficient. Obviously, the above equation will be satisfied if α-η=0. The function of α-η depends on the gas component, the external electric field and the gas number density. Thus it can be written as:

$$\frac{\alpha - \eta}{N} = f(\frac{E}{N}) \tag{5}$$

Where N is the number density of gas molecules.

The effective ionization coefficient of the target gas is solved by the software BOLSIG[21]. The cross-section data of the electron collision are taken from Plasma Data Exchange Project[21]. It is assumed in the calculation that all particles are in the ground state and the kinetic energy of two electrons is equal upon the collision ionization reaction.

3. Calculation results and discussions

Based on the differences in the atomic composition, carbon chain structure, functional group position and species of substituted gases, their influences on the relative electric strength are discussed in five aspects including the molecular mass, electron number, molecular electronegative index, molecular dipole moment and polarizability.

3.1. Calculation results of the molecular size and electronegativity

The molecules for assessment are selected from the gases of CF-x, HFC and HFO. The results of their molecular mass, electron number, electronegative index and relative electric strength are shown in the Table 1.

Table 1. Molecular size and electronegativity of potential gases

Molecular formula	Molecular mass M_w/(g/mol)	Electron number N_e	Electronegative index E_n/eV	Relative electrical strength E_r
SF_6	146.05	70	8.47	1.000
CH_3F	34.03	18	6.61	0.220
CH_2F_2	52.02	26	6.69	0.300
CHF_3	70.01	34	7.29	0.270
CF_4	88.01	42	8.51	0.594
CF_3Cl	104.46	50	7.13	0.672
CF_2Cl_2	120.91	58	7.23	0.901
CCl_4	153.82	74	6.38	2.030
CF_3I	195.91	86	6.49	1.217
C_2H_4	28.054	16	4.75	0.242
C_2F_4	100.02	48	5.57	0.600
C_2H_6	30.07	18	5.41	0.163
$C_2H_4F_2$	66.05	34	5.55	0.700[22]
C_2F_6	138.01	66	6.93	0.775
C_3H_6	42.08	24	4.42	0.227
C_3H_8	44.10	26	5.10	0.851
C_3F_8	188.02	90	7.40	1.000
$C_2H_3F_3$	84.04	42	7.43	1.620
C_2F_3Cl	116.47	56	5.20	0.690[22]
$C_3H_2F_4$	114.04	56	5.30	0.800[22]
C_3F_6	150.03	72	5.57	1.080

The electronegative indexes of the gases are increased to different degrees when the hydrogen atoms in the compound are substituted by the halogen atoms with strong electronegativity. The electronegative indexes of CH3F, CH2F2, CHF3 and CF4 are increased with the number of F atom in Table 1. The relative electric strength of CH3F, CH2F2 and CF4 also shows a rising trend. Though there is a positive correlation between the electronegative index and the relative electric strength of the substituted gases, more parameters such as the molecular size are needed to accurately predict the electronegative index.

The molecular size can be described by the molecular mass and electron number. The collision cross-section will be greater if the constituent atoms are larger and the number of electron cloud energy levels increases. Table 1 shows that the larger molecules have higher relative electric strength. The relative electric strengths of CF3Cl, CF2Cl2 and CCl4 are gradually increased and they are higher than that of CF4. The electronegativity of Cl atom is slightly lower than that of F atom, while the mass of Cl atom is greater. Hence the electronegative indexes of all molecules are gradually reduced when F atoms are replaced by Cl atom. It also leads to an increasing tendency of the relative electric strength. Besides, I atom is larger than Cl atom, so the relative electric strength of CF3I (1.217) is also higher than that of CF3Cl (0.672).

The correlation of molecular mass, electron number, molecular electronegative index and the relative electric strength of substituted gases can be investigated by SPSS software. The SPSS calculation results of correlation coefficients with relative electrical strength and significance (Sig.) of regression coefficients are shown in Table 2. The molecular mass and electron number contribute more on the evaluation of relative electric strength, while the electronegative index is not that significant in the regression analysis (Sig.>0.05).

Table 2. Pearson correlation of the electric strength with molecular size or electronegativity

Variable	Correlation coefficients with relative electrical strength	Sig.
Relative electrical strength E_r	1.000	-
Molecular mass M_w	0.678	0.000
Electronic number N_e	0.692	0.000
Electronegativity index E_n	0.278	0.110

3.2. Calculation results of the molecular polarization degree
The influence of molecular polarization on the relative electric strength of the substituted gases are studied. The molecular polarization considers the electric dipole moment and polarization degree. The calculation results are shown in Table 3.

Table 3. Polarization characteristics of potential gases

Molecular formula	Structural formula	Electric dipole moment μ/Debye	Polarization degree α/(C·m²/V)	Relative electrical strength E_r
SF_6	F6S	0.00	4.60	1.000
CH_3F	CH3F	2.09	2.47	0.220
CH_2F_2	CH2F2	2.16	2.56	0.300
CHF_3	CHF3	1.78	2.69	0.270
CF_4	CF4	0.00	2.77	0.594
CF_3Cl	CClF3	0.52	4.49	0.672
CF_2Cl_2	CCl2F2	0.55	6.35	0.901
CCl_4	CCl4	0.00	10.27	2.030
CF_3I	CF3I	2.07	4.50	1.217
C_2H_4	CH2=CH2	0.00	4.23	0.242
C_2F_4	CF2=CF2	0.00	4.38	0.600
C_2H_6	CH3CH3	0.00	4.47	0.163
$C_2H_4F_2$	F2CHCH3	2.52	4.56	0.700[22]
C_2F_6	CF3CF3	0.00	4.90	0.775
C_3H_6	CH3CHCH2	0.42	6.41	0.227
C_3H_8	CH3CH2CH3	0.09	6.56	0.851
C_3F_8	CF3CF2CF3	0.15	6.99	1.000
$C_2H_3F_3$	CH3CF3	2.57	4.59	1.620
C_2F_3Cl	F2C=CFCl	0.60	6.20	0.690[22]
$C_3H_2F_4$	H2CCFCF3	2.48	6.42	0.800[22]
C_3F_6	CF3CF=CF2	1.13	6.51	1.080

The electric dipole moment and polarization degree of the gases are associated with the position of each atom in molecules. Even if the constituent atoms of two molecules are exactly the same, the molecular structure is changed with different atom position and atomic sequence. The molecular polarization degree varies with the electron clouds formed by the attraction of the nuclear to electrons. Molecules can be classified into polar and non-polar molecules according to their electric dipole moment. The electric dipole moment induced by the external electric field is greater if the polarization degree is larger for the non-polar molecules, and the permanent electric dipole moment will arise in polar molecules. The contributions of electric dipole moment and polarization degree to the relative electric strength are evaluated by the same method. The results are shown in Table 4.

Table 4. Pearson correlation of molecular polarization degree and relative electric strength

Variable	Correlation with relative electrical strength	Sig.
Relative electrical strength E_r	1.000	-
Electric dipole moment μ	0.030	0.448
Polarization degree α	0.647	0.001

According to Table 4, the correlation between the molecular electric dipole moment and the relative electric strength is fairly low (Pearson's R=0.030), and the electric dipole moment of the non-polar molecules is always zero. Therefore, the electric dipole moment cannot be used to evaluate the relative electric strength alone. But the smaller significance (Sig.<0.01) suggests that the molecular polarization degree is more suitable to indicate the relative electric strength.

C2H4, C2F4 and C2H6 are non-polar molecules and their electric dipole moment is zero. It can be seen from Table 3 that they have similar polarization degrees, but the relative electric strength of C2F4 (0.600) is much higher than those of C2H4 (0.242) and of C2H6 (0.163). Meanwhile, the relative electric strength of gas molecules mainly depends on the electronegativity of constituent atoms and molecular size. The C2F3Cl molecule has almost the same molecular mass, electron number and molecular electronegative index as the C3H2F4 molecule in Table 1, while the electric dipole moment of C3H2F4 (2.477) is higher than that of C2F3Cl (0.5973) in Table 3, which leads to their different relative electric strengths. So the influence of the molecular properties including molecular mass, electron number, electronegative index, electric dipole moment and polarization degree on the relative electric strength needs to be considered.

4. Prediction of the electric strength of gases

4.1. Multiple linear regression analysis of the electric strength
According to the discussions in Section 2, the relative electric strengths of SF6-alternative gases can be evaluated by means of predictor variables including molecular size, electronegativity and polarization degree. The equation of multiple linear regression is established:

$$f = p_0 + p_1 x_{mw} p_2 x_{ne} + p_3 x_{En} + p_4 x_\mu + p_5 x_\alpha \tag{6}$$

where xmw, xne, xEn, xμ and xα are the value of molecular mass Mw, electron number Ne, electronegative index En, electric dipole moment μ and polarization degree α, respectively; p0, p1, p2, p3, p4 and p5 are fitting coefficients and f is the relative electric strength.

The group of coefficients (p0, p1, p2, p3, p4, p5) are estimated to be (-1.846, 0.028, -0.062, 0.218, 0.139, 0.258) by SPSS regression analysis. The correlation coefficient R2 is 0.80 while Sig. is zero. The prediction formula of the electric field strength is expressed in (7).

$$f = -1.846 + 0.028 x_{mw} - 0.062 x_{ne} + 0.218 x_{En} + 0.139 x_\mu + 0.258 x_\alpha \tag{7}$$
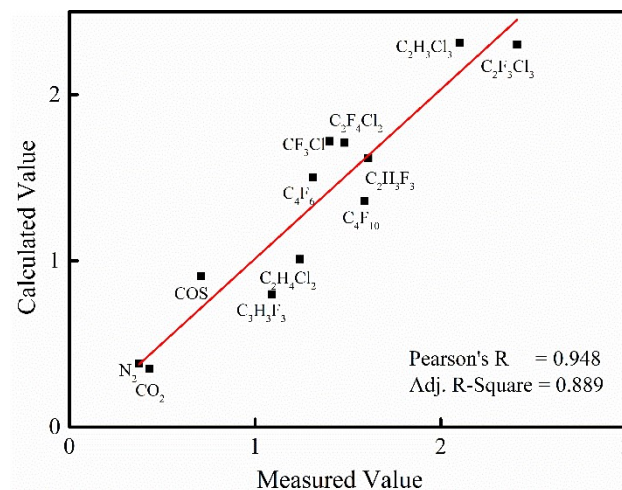
4.2. Calculation of the electric strength of the target gases
The molecular mass, electron number, electronegative index, electric dipole moment and polarization degree of 12 potential substituted gases are calculated based on the density function theory and the results are shown in Table 5.

Table 5. Calculation of physical and chemical properties of typical alternative gas

Molecular formula	x_{mw}	x_{ne}	x_{En}	x_{μ}	x_{α}
N_2	96.07	48	5.97	2.72	6.35
CO_2	44.02	22	8.62	0.00	2.48
COS	60.08	30	6.43	0.78	4.73
$CClF_3$	137.37	66	5.93	0.46	8.25
$C_2H_3F_3$	84.05	42	7.77	2.72	6.35
$C_2H_3Cl_3$	133.41	66	6.32	1.84	10.27
$C_2H_4Cl_2$	98.97	50	6.05	2.09	8.25
$C_2F_3Cl_3$	187.39	90	5.82	0.86	12.4
$C_2F_4Cl_2$	170.93	82	6.09	0.62	8.54
$C_3H_3F_3$	96.07	48	5.97	2.43	6.14
C_4F_6	162.06	78	5.08	0.00	9.08
C_4F_{10}	238.05	114	6.86	0.00	9.09

The data in Table 5 are the input of Equation (8) and the relative electric strength of substituted gases can be obtained according to the prediction model in Section 3.1. The fitting curve of the calculated value and measured value[22-23] is shown in Figure 1. The calculated value of the relative electrical strength is in good agreement with the measured value, and the Pearson's R is 0.948.

Figure 1. Comparison of the calculated and measured value on relative electric strength

5. Conclusion

In the paper the basic physico-chemical properties of the potential SF6 substitutes are calculated based on the density function theory and the relative electric strengths of all substituted gases are solved by Boltzmann Equation. The influence of the molecular mass, electron number, electronegative index, electric dipole moment and polarization degree on the electric strength of insulation gases are discussed in detail. The methods provide a theoretical reference for the rapid screening of SF6 potential substituted gases and for proposal of new gases that meet the requirements for substitution.

Although the electric strength of the substituted gases can be reflected by the electric dipole moment and electronegative index of the constituent atoms to certain degrees, their correlation with relative electrical strength is poor. Therefore they can not be used as the only variable to evaluate the relative electric strength of substituted gases.

The significance of evaluating the relative electric strength of substituted gases with the molecular mass, electronic number and molecular polarization degree is better. The correlation between these three predictor variables of substituted gases and the relative electric strength are 0.678, 0.692 and 0.647 respectively and the Sig. is lower than 0.01.

The prediction model of the relative electric strength is established by multiple linear regression. The regression coefficient R2 of model is 0.80. The Pearson's R between the calculated relative electrical strength of the 12 potential substitute gases by this model and measured values in literature is 0.948. Through the theoretical calculation of the physico-chemical properties of target molecules, the preliminary prediction of the electrical strength of potential substitute gases can be realized.

Acknowledgements

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