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SEARCHING FOR CFC's AND HCFC's ALTERNATIVES.
Part I: A REFRIGERANT DESIGN STRATEGY USING GROUP CONTRIBUTION METHODS

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Abstract

It is now well established that the chlorofluorocarbons (CFC's), the hydrochlorofluorocarbons (HCFC's) and other chlororinated hydrocarbons which are compounds mostly used as refrigerants, are causing more damages than benefits to the environment and particularly to the ozone layer. Therefore one can see how important it is to search for substitutes to these compounds with desirable combination of physical properties to meet the needs of specific applications but, ultimately, with no harms to the environment.

In this paper, although the bases of a computer-aided design of refrigerants (CADR) method being developed are outlined, the main purpose still remains the demonstration of the great ability and importance of group contribution methods in the development of such techniques, particularly for predicting vapour-liquid equilibria and other thermodynamic properties like the enthalpy or entropy of generated systems, by the use of models like the UNIFAC.

***Key words**: CFC's, Refrigerants, Vapour-liquid Equilibria, Group contribution, UNIFAC*

Résumé

Il a été prouvé que les chlorofluorocarbonés (CFC), les hydrochlorofluorocarbonés (HCFC), qui sont utilisés en tant que réfrigérants, ont plus d'inconvénients que d'avantages pour l'environnement et surtout pour la couche d'ozone. Pour cette raison, il es impératif de rechercher des substituts pour ces fluides, mais ayant les mêmes propriétés physiques et spécificités de leur application, sans pour autant avoir des répercussions sur l'environnement.

Dans cette article, les bases d'une méthode de conception assistée par ordinateur des réfrigérants (CADR) sera développée. L'idée principale est de démontrer la grande utilité des méthodes de contribution de groupes dans le développement de ces différentes techniques, particulièrement pour la prédiction de l'équilibre liquide-vapeur et autres propriétés thermodynamiques, telles que l'enthalpie ou l'entropie par l'utilisation des modèles comme l'UNIFAC.

***Mots clés**: CFC, Réfrigérants, Equilibre liquide-vapeur, contribution de groupes, UNIFAC.*

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ملخص

من المعروف و الثابت حاليا، أن الغازات و التي يطلق عليها أسم CRC هي من أهم الغازات التي تسبب أخطارا كبيرة على المحيط، و خاصة طبقة الأزون. من هذا المنطلق أخذت الأبحاث في الوقت الراهن في هذا المجال أهمية كبرى، و هذا لإيجاد غازات بديلة لـ CFC. إن الغازات التي تصدر من مختلف الوسائل يجب معرفة خصائصها بدقة لتفادي الإضرار بالمحيط.

اعتمدنا في هذا المقال، على طريقة أطلقنا عليها أسم (CADR) و تعتمد أصلا على مساهمة المجموعات خصوصا، لمعرفة التوازن (سائل-غاز) و مميزات ترموديناميكية أخرى، مستعملين في هذا نموذج UNIFAC.

***الكلمات المفتاحية**: غازات التبريد، التوازن سائل-غاز، مساهمة المجموعات، UNIFAC.*

The design of new chemicals such as solvents, drugs, pesticides, refrigerants etc., with desirable combination of physical properties to meet the needs of specific applications is still not based on well established rules despite the efforts made in the understanding of intermolecular interactions. The main reason for this is due to the difficulties in establishing the relationship between the properties of a compound and its molecular structure. Therefore, and in general, any computer-aided molecular design method is mainly the inverse process of property prediction or estimation by group contribution methods *i.e.* given a set of desirable properties, it is aimed at finding a combination of structural groups and hence a molecular structure satisfying the preset requirements.

For the assessment of the molecular design outcome, thermodynamic and particularly group contribution models are needed to give directly a quantitative measure of performance related to molecular structure.

DESCRIPTION OF THE REFRIGERANTS DESIGN METHOD

The proposed method relies on the ideas described in [1, 2] for the design of solvents for liquid-liquid extraction and is based on the group contribution approach for predictions /computations of the specified physical properties and its main steps are as follows:

a) Selection of groups

This is the most crucial step since the groups which will form the molecules of the candidate compounds to be considered is mainly guided by the nature of the chemicals contained in the mixture of interest *e.g.* polar, non polar, with hydrogen bonding etc. as well as their reactivity. The main strategy is always to examine how is the interaction of the groups with the physical chemical properties. For instance if hydrogen bonding is to be avoided, groups presenting this character such as OH, COOH etc. are discarded.

b) Definition of the desired properties

A priori, the desired properties according to the problem should be defined in a very clear manner. For instance as far as the search for refrigerants substitutes is concerned the important thermodynamic and transport properties which should be most considered are: boiling point, critical properties, latent heat, vapour and liquid heat capacities, enthalpies, entropies, isobaric or isothermal vapour-liquid phases equilibria, viscosity, thermal conductivity etc.. It should be noted that in the case of mixtures design, only pure component properties are needed, which is an important advantage, and the reliability of the design methodology clearly depends upon the limitations of the methods of prediction of the required properties.

c) Combination of the pre-selected groups

This step is concerned with the combination of the pre-selected groups according to preset combinatorial rules and the generation of chemically feasible molecular structures. In this part, even with a limited number of groups an important number of chemical structures can be generated and to reduce the design problem to a tractable size other constraints may be included *e.g.* molecular weight, boiling or melting points ranges etc.

d) Assessment of the molecular structures

In this final stage the retained molecular structures are classified according to the values of the predicted thermodynamic properties. All the structures not satisfying the preset limits are discarded. Efforts should be made to quantify the properties preferably using group contribution methods. However, the properties can be of different types and are mainly physical, chemical or environmental beside other economical factors. In this part of the work only the thermodynamic criteria is considered. Also for systems where not all the necessary interaction parameters are available, the method devised by Meniai *et al.* [3] can be extended to the case of refrigerant design.

The steps of the proposed refrigerant design strategy are best shown by the simple flow diagram of figure 1.

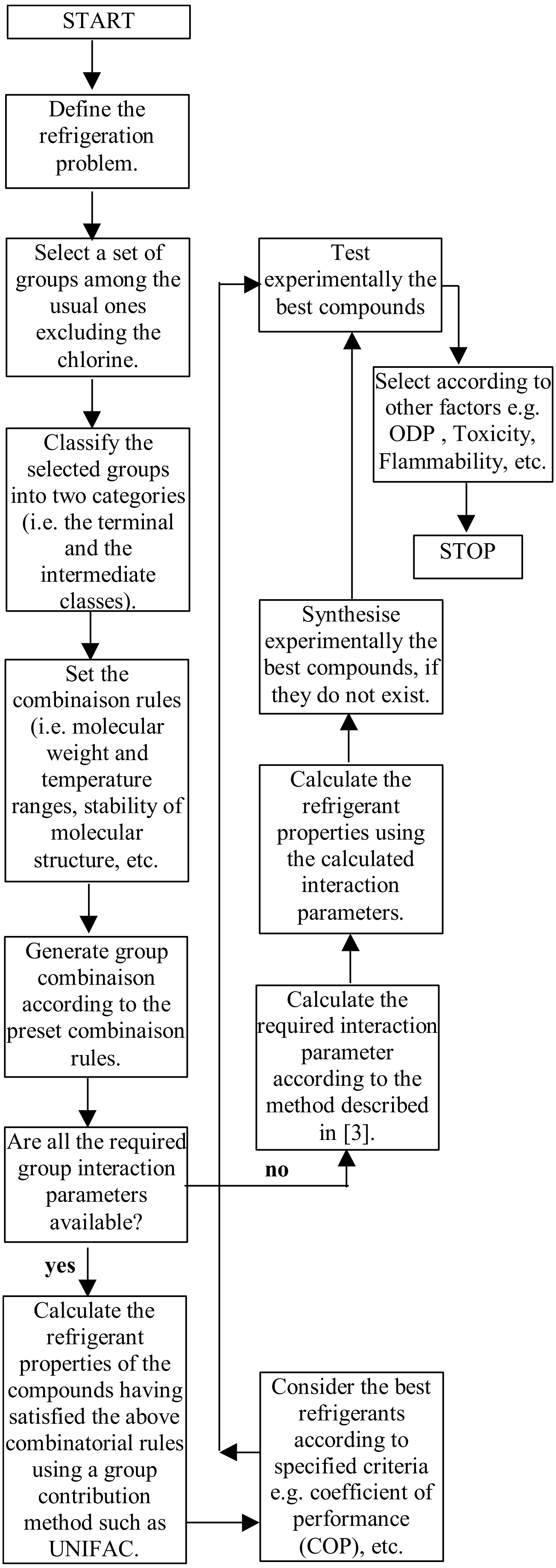

Figure 1: A flow diagram of the design method.

A REFRIGERANT DESIGN EXAMPLE

The method discussed above is tested with a simple example of refrigerants design. Five groups only are chosen (avoiding the chlorine) as the building blocks of the possible refrigerants candidates and are the following: CH_3, CH_2, CH, C and F.

This choice is arbitrary and has been mainly guided by the availability of the interaction parameters between these groups which are also frequently met beside others in the CFC's compounds. CH_3 and F groups characterised by one free valency only, are classified as terminators since they can be used to terminate molecular structures. CH_2, CH and C are the intermediate groups and are used to form the main 'skeleton' of the molecule.

For sake of simplicity only intermediate structures of a maximum of two groups are considered and these are: CH_2, H_2C-CH, CH, H_2C-C, C, HC-C. These structures are terminated with the F or CH_3 groups.

Compound	P1	P2	P3	P4	P5
(CH3) (CH2) (F)	244.49	391.43	47.24	165.50	0.19
(F) (CH2) (F)	220.94	355.22	50.73	127.50	0.20
(CH3) (CH) (F) (CH3)	266.93	420.60	42.00	215.50	0.21
(CH3) (CH) (F) (F)	243.38	385.05	44.92	177.50	0.22
(F) (CH) (F) (F)	219.83	349.22	48.16	139.50	0.23
(CH_3) (C) (F) (CH_3) (CH_3)	287.02	449.60	37.73	266.50	0.19
(CH_3) (C) (F) (F) (CH_3)	263.47	414.36	40.21	228.50	0.20
(CH_3) (C) (F) (F) (F)	239.92	378.85	42.94	190.50	0.21
(F) (C) (F) (F) (F)	216.37	343.06	45.96	152.50	0.22
(CH_3) (CH_2) (CH) (CH_3) (F)	289.81	445.57	37.23	271.50	0.25
(CH_3) (CH_2) (CH) (F) (F)	266.26	410.92	39.66	233.50	0.26
(F) (CH_2) (CH) (F) (F)	242.71	376.01	42.61	242.50	0.24
(CH_3) (CH) (C) (F) (CH_3)	285.18	445.37	42.61	242.50	0.24
(F) (CH) (C) (F) (CH_3)	261.63	410.21	45.59	204.50	0.25
(F) (CH) (C) (F) (F)	238.08	374.78	48.90	166.50	0.26
(CH_3) (CH_2) (C) (F) (CH_3) (CH_3)	309.90	473.86	33.65	322.50	0.24
(CH_3) (CH_2) (C) (F) (F) (CH_3)	286.35	439.48	35.73	284.50	0.24
(CH_3) (CH_2) (C) (F) (F) (F)	262.80	404.86	38.01	246.50	0.25
(F) (CH_2) (C) (F) (F) (F)	239.25	369.98	40.52	208.50	0.26
(CH_3) (CH_2) (C) (F) (CH_3) (CH_3)(CH_3)	333.48	501.34	28.78	387.50	0.24
(CH_2) (CH_2) (C) (F) (F) (CH_3) (CH_3)	309.93	467.59	30.42	349.50	0.25
(CH_3) (CH_2) (C) (F) (F) (F) (CH_3)	286.38	433.60	32.21	311.50	0.26
(CH_3) (CH_2) (C) (F) (F) (F) (F)	262.83	399.39	34.16	273.50	0.26
(F) (CH_2) (C) (F) (F) (F) (F)	239.28	364.93	36.29	235.50	0.27

P1= boiling temperature (K) ; P2= critical temperature (K);

Table 1: Resulting compounds and their physical properties.

Table 1 shows the compounds obtained after elimination of the combinations not having at least one fluorine atom. Some of them (compound 4 and 19) have already shown interesting thermodynamic properties as reported in [4] as well as a zero Ozone Depletion Potential value (ODP) [5]. Physical properties like boiling point, critical properties and acentric factor (and the list can be extended) have also been computed as shown in Table 1, using appropriate group contribution methods described in [6] and these may be used to predict vapour-liquid equilibria as described in the following paragraph. Also most of the predicted values for the different properties for known generated compounds are in a very good agreement with the ones reported in [7]. This makes a quite powerful tool to explore different systems in a systematic manner.

Alternatively, binary mixtures between the generated refrigerants candidates and for other compounds such as hydrocarbons, as suggested in [4], are also worth Considering since pure fluids may have favourable properties when mixed together, but the main problem is to find the optimal proportions to be used in the mixture. Trying every single possibility is a very long, difficult and tedious process and therefore predictive methods can also be essential for this kind of problem of interest i.e. design of refrigerants mixtures.

Clearly for mixtures, the computation of the vapour-liquid phase equilibria is important for the cycle calculation and basically it is required to know the fugacity and activity coefficients in the vapour and liquid phases, respectively. The former is calculated by means of an equation of state (Virial equation in this work) and the latter is derived from a very flexible model known as the UNIFAC. Since this kind of calculations has been extensively discussed in the literature and need not be reported in this paper, it is perhaps useful to describe the UNIFAC model which is fundamentally based on the idea of using existing phase equilibria data for systems for which experimental data is not available or difficult to obtain. It can also be adapted to calculate important refrigerant thermodynamic properties like the molar enthalpy of the liquid h^L and others, as shown in the following section. As an example of vapour/liquid equilibria calculation, we consider the case of fixing the temperature and liquid mole fraction as the independent variables and calculating the corresponding pressure and vapour mole fraction for a binary system. This is based on the resolution of the following system of equations:

$$Py_1\varphi_1(P,y_1) = \gamma_1(T,x_1)x_1 f_1^{\circ L*}(T)exp\left(\frac{Pv_1^{\circ l}}{RT}\right) \tag{1a}$$

$$Py_2\varphi_2(P,y_2) = \gamma_2(T,x_2)x_2 f_2^{\circ L*}(T)exp\left(\frac{Pv_2^{\circ l}}{RT}\right) \tag{1b}$$

where φ_1 and φ_2 are the fugacity coefficients of component 1 and 2 in the vapour phase, y_1 and y_2 are the vapour mole fractions of component 1 and 2, x_1 and x_2 are the liquid mole fractions of component 1 and 2, $v_1^{\circ l}$ and $v_2^{\circ l}$ are the molar volumes at saturation of components 1 and 2 (cm^3/mol), γ_1 and γ_2 are the activity coefficients of component 1 and 2, R is the universal gas constant (82.05 atm cm^3/ K), T temperature of the system (K), P the pressure (atm), f_1^{oL*} and f_2^{oL*} are the fugacities of component 1 and 2, at zero pressure (atm).

φ_1 and φ_2 are calculated as described in thermodynamic standard textbooks as [6], and γ_1 and γ_2 are derived using the UNIFAC model [6] which is described in the following paragraph.

In this model, the activity coefficient is the sum of a combinatorial and a residual part, the first one taking into account the form and geometrical factors whereas the second, is particularly, dealing with the interactions between the different groups. Therefore the activity coefficient γ_i for a constituent i is expressed as follows:

$$ln\,\gamma_i = ln\,\gamma_i^C + ln\,\gamma_i^R \tag{2}$$

where the combinatorial part is given as:

$$ln\gamma_i^C = ln\left(\frac{\phi_i}{x_i}\right) + \frac{1}{2} Z q_i\, ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \tag{3}$$

where j represents every constituent in the mixture; θ_i the molecular surface area fraction of component i in the mixture; ϕ_i is the molecular volume fraction of component i in the mixture; Z is the co-ordination number usually assumed equal to 10 and the other parameters are given by:

$$l_i = \frac{Z}{2}(r_i - q) - (r_i - 1),\ \phi_i = \frac{r_i x_i}{\sum\limits_j r_j x_j},\ \theta_i = \frac{q_i x_i}{\sum\limits_j q_j x_j},$$

$$r_i = \sum_k \nu_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k \nu_k^{(i)} Q_k$$

q_i and r_i are the Van der Waals surface area and volume of molecule i, respectively, $\nu_k^{(i)}$ is the number of groups of type k in molecule i, R_k and Q_k are the group volume and surface parameters as defined in [6].

The residual part is given by the following expression:

$$ln\,\gamma_i^R = \sum_k \nu_k^{(i)}\left[ln\,\Gamma_k - ln\,\Gamma_k^{(i)}\right] \tag{4}$$

with:

$$ln\,\Gamma_k = Q_k\left[1 - ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{mk}}{\sum\limits_n \theta_n \Psi_{nm}}\right],$$

$$\Psi_{mn} = exp\left(\frac{-a_{mn}}{T}\right),\ \theta_m = \frac{Q_m X_m}{\sum\limits_n Q_n X_n},\ X_m = \frac{\sum\limits_j \nu_m^{(j)} x_j}{\sum\limits_j \sum\limits_n \nu_n^{(j)} x_j}$$

where Γ_k and $\Gamma_k^{(i)}$ are, respectively, the residual activity coefficients of group k in the mixture and in a referential solution containing only molecules of type i which represent every constituent in the mixture, m, n or k denote every group in the mixture. γ is the component activity coefficient, a_{mn} is the interaction parameter between group m and n and $ln\Gamma_k^{(i)}$ is easily calculated by setting all mole fractions, but for i, equal to zero.

The molar enthalpies h^L and h^v of the liquid and vapour phases, respectively are expressed as follows:

$$h^v = \sum_{i=1}^{n} y_i \bar{h}_i^{v} = \sum_i y_i h_i^* + \left(B^M - T\frac{dB^M}{dT}\right)\frac{P}{K} \tag{5}$$

$$h^L = \sum_i x_i \bar{h}_i^{L} = \sum_i x_i h_i^* + h^E + \sum_i x_i\left[-\frac{T}{K}\left(B_{ii} + \frac{RT}{P} - v_i^{\circ L}\right)\frac{dP_i^S}{dT}\right.$$
$$\left. + \left(B_{ii} - T\frac{dB_{ii}}{dT}\right)\frac{P_i^S}{K} + \left(v_i^{\circ L} - T\frac{dv_i^{\circ L}}{dT}\right)\frac{P - P_i^S}{K}\right] \tag{6}$$

where:

$\bar{h}_i^{L}$ and $\bar{h}_i^{V}$ are the partial molar enthalpies in the liquid and vapour phases, respectively, (cal/mol), h^E the excess enthalpy (cal/mol), B^M and B_{ii} (cm^3/mol) are the second Virial coefficients for the mixture and the pure components calculated from the critical properties as reported in [2], K is a conversion factor equal to 41.3 if P is expressed in (atm.), the B's in (cm^3/mol) and the h's in (cal/mol), Ps saturated pressure (atm.) and $v_i^{\circ L}$ is the liquid molar volume (cm^3/mol).

Further from thermodynamic, one can write:

$$g^E = RT\sum_k x_i\, ln\,\gamma_i \quad \text{and} \quad s^E = -\frac{\partial g^E}{\partial T} \tag{7}$$

$$h^E = g^E - T\frac{\partial g^E}{\partial T} = RT\sum_k x_i\, ln\gamma$$
$$- RT\left(\sum_i x_i\, ln\,\gamma_i + T\sum_i x_i \frac{\partial\, ln\,\gamma_i}{\partial T}\right) \tag{8}$$

with:

$$\frac{\partial\, ln\,\gamma_i}{\partial T} = \sum_k \nu_k^{(i)}\left(\frac{\partial\, ln\,\Gamma_k}{\partial T} - \frac{\partial\, ln\,\Gamma_k^{(i)}}{\partial T}\right) \tag{9}$$

$$\frac{\partial\, ln\,\Gamma_k}{\partial T} = Q_k\left[\frac{\sum\limits_m \theta_m \Psi_k a_{mk} / T^2}{\sum\limits_m \theta_m \Psi_{mk}} - \right.$$
$$\left.\sum_m \frac{\left(\theta_m \Psi_{km} a_{km} / T^2\right)\left(\sum\limits_n \theta_n \Psi_{nm}\right) - \left(\theta_m \Psi_{km}\right)\left(\sum\limits_n \theta_n \Psi_{nm} a_{nm} / T^2\right)}{\left(\sum\limits_n \theta_n \Psi_{nm}\right)^2}\right]. \tag{10}$$

$\frac{\partial\, ln\,\Gamma_k^{(i)}}{\partial T}$ is calculated similarly as $\Gamma_k^{(i)}$.

As an illustration and for a sake of comparison with the results obtained in [4], isothermal vapour liquid equilibria calculations have been performed for binary mixtures of

X (1)	0.008	0.082	0.121	0.172	0.197	0.246	0.457	0.584	0.694	0.759	0.854
Y (1)	0.024	0.017	0.210	0.250	0.265	0.289	0.365	0.414	0.473	0.523	0.629
P (atm)	6.568	7.354	7.578	7.756	7.811	7.876	7.813	7.547	7.115	6.730	5.950
h^L (kJ/kg)	786.9	796.7	801.9	808.6	811.9	818.2	846.0	862.7	877.1	885.7	898.1
h^V (kJ/kg)	865.2	1009.7	1052.9	1089.2	1101.1	1117.0	1126.4	1097.6	1043.9	994.0	890.2

Table 2: Isothermal vapour-liquid equilibria and molar enthalpy of the liquid (h^L) and vapour (h^V) for HFC134a (1)/ propane (2) system at 283.15°K, derived from Eqn.1.

propane and some of the generated compounds, particularly for compound 19 (HFC134a) for which experimental values have also been reported [4]. The results as shown in figure 2a are very encouraging and demonstrate clearly the suitability of group contribution methods for the design of refrigerant substitutes. The two sets of values are in a good agreement and they can easily be used to detect the possible formation of azeotropes which is desirable for certain applications [8]. Figures 2b and 2c give further illustrations for two other binary mixtures of still propane and one of generated compounds shown in table 1 (($(CH_3)(CH_2)(C)(F)(F)(F)$ and $(CH_3)(C)(F)(CH_3)(CH_3)$). The equilibrium results are showing the usual shapes usually encountered.

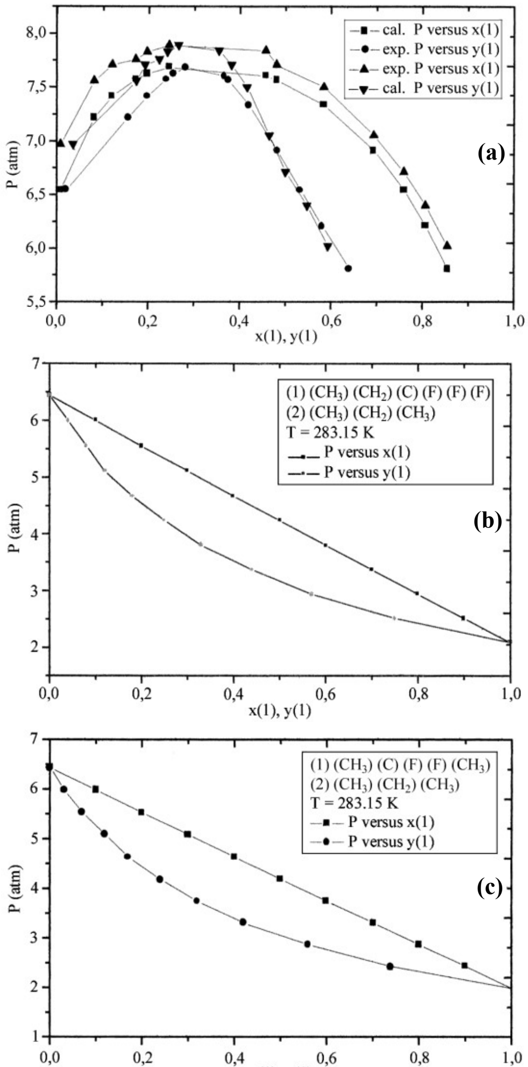

Figure 2: Vapour/Liquid phase equilibria for refrigerants/propane system.

Table 2 presents the calculated molar enthalpy of the liquid $\left(h^L\right)$ and vapour $\left(h^V\right)$ phases a fact which demonstrates clearly the suitability of group contribution methods for the design of refrigerant substitutes since, for example, all terms in equations (5) and (6) can be derived by means of such methods. For instance, the results obtained for the excess enthalpy by this method have been compared with experimental values available in the literature for the R10/R150 system, as shown in figure 3 and where it can be seen that the agreement is excellent, demonstrating once more the capability of this technique of group contribution which enables the exploration of different combination for the design of new refrigerant.

Reporting all the results would be very exhaustive but all possible cases can be examined at will.

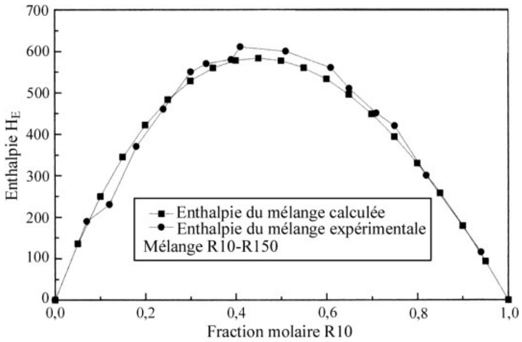

Figure 3: Comparison of calculated and experimental excess enthalpies.

CONCLUSION

In conclusion, this work can be seen as attempt to put forward a method to solve the problem of the nature of the CFC's and their interaction towards the environment. In any case it should be regarded as the preliminary stage of a more elaborate model where others factors beside thermodynamics are will be included.

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