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APPLICATION OF COUPLED THERMAL ANALYSIS TECHNIQUES TO THERMODYNAMIC STUDIES OF WATER INTERACTIONS WITH A COMPRESSIBLE IONIC POLYMER MATRIX

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ABSTRACT

The swelling of a compressible matrix (perfluorosulfonated membrane "Nafion") was studied using different thermal analysis techniques coupled with thermogravimetry. Free swelling isotherms, molar heats of interaction, isochore swelling isotherms, swelling pressure, changes of external volume, D.S.C. peaks gave informations on the thermodynamic state of water in the membrane which were confirmed by spectroscopic measurements like NMR, ESR, Mössbauer.

From all data it appears clearly that water molecules are distributed in small droplets around the sulfonate dipoles. The interaction energies are small and show at high water contents the contribution of endothermic terms due to compression of the matrix. The swelling pressures are important (300 to 600 bars). The water content is lower in isochore experiments and it diminishes at low temperatures. So,during cooling of a 20°C saturated sample there is a demixion process with phase separation of excess water. The DSC peaks must be interpreted in terms of desorption-sorption in thermal cycling and not in terms of porometry.

Such a behaviour cannot be explained with classical sorption model. Recently new thermodynamic models of elastic matrices have been developped; the simplest has only two parameters describing the matrix: its dielectric constant and its shear modulus. With the aid of all experimental data, this model will be discussed for a complex system like Nafion.

INTRODUCTION

The gravimetric measurement of sorption isotherms is an effective means to investigate the diffusion of a solvent in a polymer matrix (ref. 1-3). In some cases, equations developed for the description of the adsorption of gases on solid surfaces (e.g. BET) may be used to describe the isotherm, replacing the geometric area by the concentration of sorption sites. In some other cases, sorption may be described as quasi-homogeneous dissolution (Flory equation).

A premise of isotherm equations is the weak interaction of adsorbate molecules in a liquid-like phase, with somewhat stronger bond to the solid surface and even stronger bond to a few singular sites. In many polymers this condition may not be fulfilled. For example clustering of the solvent may occur (ref. 4-6). Furthermore, the polymers cannot be described as inert phases (ref. 7-13); the matrix may change in shape and even in chemical structure. If some of the sites are hydrophilic and others hydrophobic, addition of strong polar liquids like water may result in phase separation. Most polymers are compressible, and the energy of deformation in large swelling may be important.

Mathematical tools to describe such processes are insufficient until now. Obviously, more functions than isotherms have to be measured, which are related directly to phenomena like interaction energies, swelling pressure and volume effects as a function of the uptake of liquid. Thus, different thermal analysis techniques had been coupled in the following investigation, and the results are compared with those of spectroscopic measurements.

EXPERIMENTAL EQUIPMENT

1. Coupled Thermoanalytic Techniques

Isotherm analysis coupled with gravimetric investigations was carried out in an apparatus which could be evacuated down to 10^{-4} Pa. In this apparatus the following measurements were possible:

Microcalorimetry and Thermogravimetry

To determine the molar energy of interaction during sorption an MTB 10-8 SETARAM type microbalance with a sensitivity of 1 µg was used simultaneously with a microcalorimeter of 5 mV/W sensitivity, which corresponds to 210 mm^2/J for 100 µV full-scale deflection and 1 mm/min paper speed. Increasing the pressure in small steps between $P/P_0 = 0$ and 1, the molar energy $\Delta Q/\Delta m$ was calculated which, in this open symmetrical system, equals the isosteric heat (ref. 14-15). In this way it was possible to trace the energy profile of sorption with an accuracy of 10 % (the average power during an increment of pressure had to be above 1 mW, which corresponds to an energy of 3.6 J/h).

Swelling Pressure

To measure the swelling pressure at constant volume, a cell developed by Didier (ref. 16, was used, in which the sample was enclosed between the bottom of the cell and a porous plate adjustable by means of a piston. Vapours and liquids were introduced through a central boring. The pressure was determined from the deformation of a metal foil used as the bottom of the cell (the relative volume extension of the sample due to deformation of the foil had to be below 10^{-3}).

Isochores

Sorption isochores were measured gravimetrically, using a B-60 type SETARAM balance equipped with a closed cell of 50 g mass as described above (ref. 17).

Dimensional Changes

The dimensional changes by free swelling was measured using two different devices:

- film samples were enclosed between a porous plate and a plexiglass sheet under a comparator which measured the variation of thickness
- film-shaped samples (45 x 4 mm) were enclosed in a frame, one end being mobile. The length variation was measured using an induction sensor with 0.3 % precision. Films immersed in a liquid were investigated in this way (ref. 18). We intend to suspend this device from a balance to measure simultaneously the mass gain.

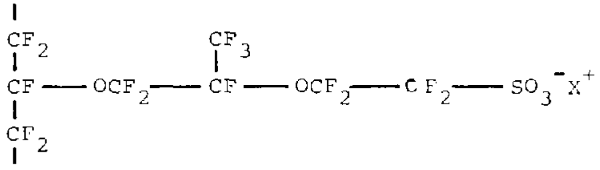
2. Low-temperature Calorimetry

Phase transitions are influenced by interaction forces with the solid. They can be determined in two ways:

- Determination of that part of the liquid which is not subject of phase transition due to binding forces. However phase transition may also be impeded by cluster formation (ref. 19) or by limited mobility in the matrix (ref. 20).
- Determination of the pore size distribution. In fact, taking in account the influence of interphases curvature on melting temperature depression, the thermal effects of phase transitions can be related directly to pore diameter (ref. 21) and to amount of freezing water in pores.

SYSTEM UNDER INVESTIGATION

We investigated the interaction of water with a perfluorinated ionomere membrane "Nafion 1200" (Dupont). Its molecular structure consists in a tetrafluorethylene chain with small branches (2 nm) and a sulphonic group at the end, supplemented by various metallic cations X^+



$$\begin{array}{l} | \\ CF_2 \\ | \\ CF - OCF_2 - \overset{\displaystyle CF_3}{\overset{|}{CF}} - OCF_2 - CF_2 - SO_3^- X^+ \\ | \\ CF_2 \\ | \end{array}$$

The ionic character of Nafion causes high intermolecular Coulomb forces which, again, causes phase separation into an ionic hydrophilic phase and a hydrophobic polymer phase. Ionomers can be used for electrodialysis, ion exchange and separation in electrolytic cells, e.g. in fuel cells and water electrolysers. On account of selectivity, ion conductivity and thermal stability, Nafion has gained industrial importance and, therefore, was the subject of thorough investigations. The microstructure indicates presence of a distinct ionic hydrophilic phase containing most of the ions and their accompanying water molecules in very small droplets (ref. 22-30).

It was, therefore, possible to apply the thermal methods described to determine the thermodynamic characteristics of such water droplets around an ion in a compressible matrix.

RESULTS

- Water isotherms at 20°C, for room temperature dried samples, depend critically on the nature of the cation (Fig. 1): The water uptake varies between 8.5 and 12.5 % but the total sorbed water is more important (between 10 and 15 % corresponding to 7.5 and 10 water molecules per ionic exchange site) because, after RT drying, a residue is always observed which can be removed only between 80 and 220°C.

- The sample volume extension between $^{P}/P_{O}$ = 0.4 and 1 calculated from thickness or length changes corresponds nearly to the water sorbed volume calculated from gravimetric data.

TABLE 1

Nature of cation	H^{+}	Fe^{+++}
Sample volume extension %	17 ± 1	13 ± 1
Water sorbed volume %	16.5 ± 1	12 ± 1

- The constant volume isotherms at 20°C, measured for different initial water contents, are lower than the free swelling isotherms (Fig. 2). The relative difference in amount of sorbed water for saturated pressure ($\frac{\Delta m}{m_o}$) are function of the cations.

TABLE 2

Nature of cation	H^{+}	Na^{+}	Cu^{++}	Fe^{+++}
$\frac{\Delta m}{m_o}$ %	19	29	32	44

- The swelling pressure measured in the liquid phase is important and varies with the cation. For a relative volume change of 0.3 % it ranges between 300 bars for acid Nafion to more than 700 bars for ferric Nafion.

- Energy measurements reveal two interaction regions (Fig. 3), the first one is below a relative pressure of 0.6 with water

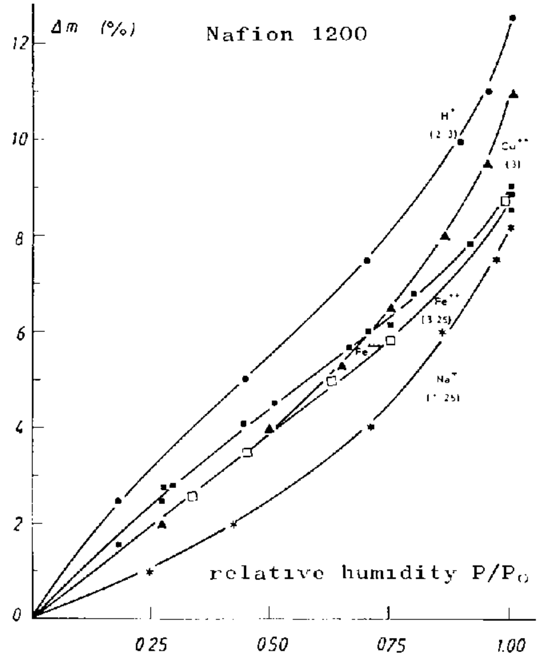


Fig. 1. Water sorption isotherms at 20°C for different cationi forms. (The initial water contents after R.T. drying are noted on the curves.)

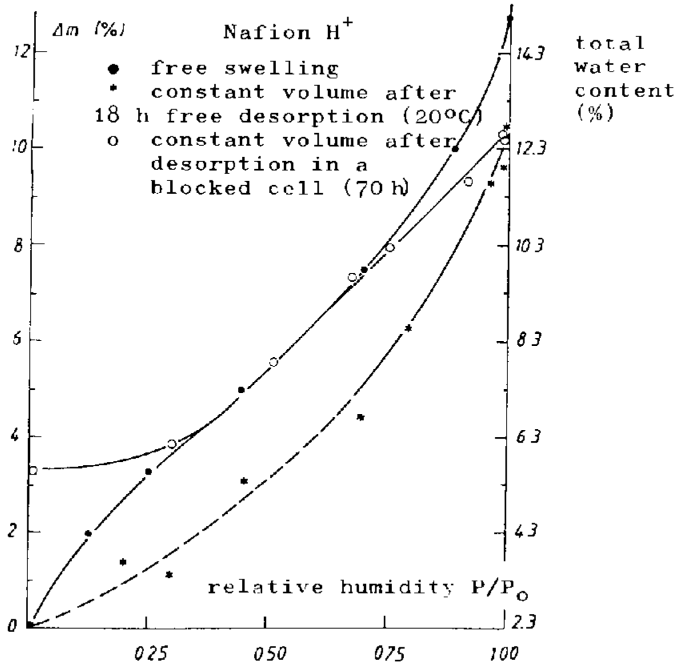


Fig. 2. Comparison of free and isochore swelling isotherms.

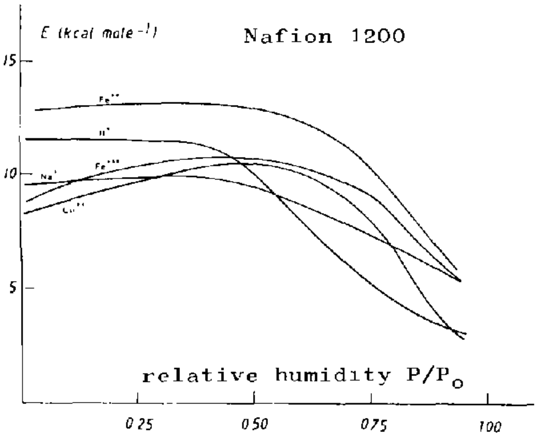


Fig. 3. Molar heat of sorption versus relative humidity for different cationic forms

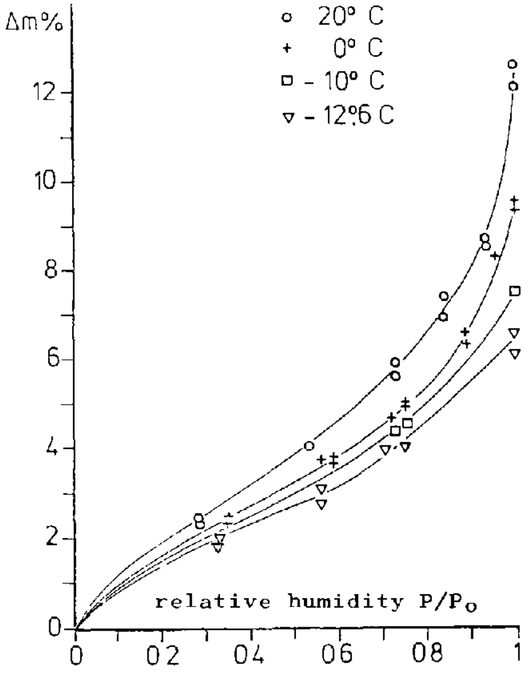


Fig. 4. Sorption isotherms of acid form at low temperatures

adsorption up to 7 % corresponding to 5 moles/SO_3^-. Depending on the cation, the interaction energy of the vapour between -9 and -13 kcal/mol is close to the energy of liquefaction. Thus, it can be concluded that the interaction energy of liquid water with the Nafion is only about ± 1 to 2 kcal/mol, i.e. much lower than the energies of hydration of free cations (ref. 31-34). The first five water molecules are sorbed around the $SO_3^-X^+$ sulphonate (associated dipoles in dry state (ref. 35)). Above the relative pressure of 0.6, the interaction energy decreases down to -5 kcal/mol, i.e. far below the energy of liquefaction. We conclude that swelling is opposed by endothermic effects including the mechanical resistance of the matrix.

Using different spectroscopic methods, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), Mössbauer, it was possible to verify the existence of 2 hydratation regimes and the location on the first 5 water molecules on ion exchange sites (ref. 30, 31, 36).

- In the temperature range from 20 to -13°C, thermogravimetric isotherm investigations result in decreasing amounts of sorbate at the saturation point (Fig. 4). The energy profile does not show the decreasing part. During cooling, no DSC peak is apparent for samples with a water content below 8 %. In the other cases, water in excess of 8 % is separated and freezes as bulk water outside

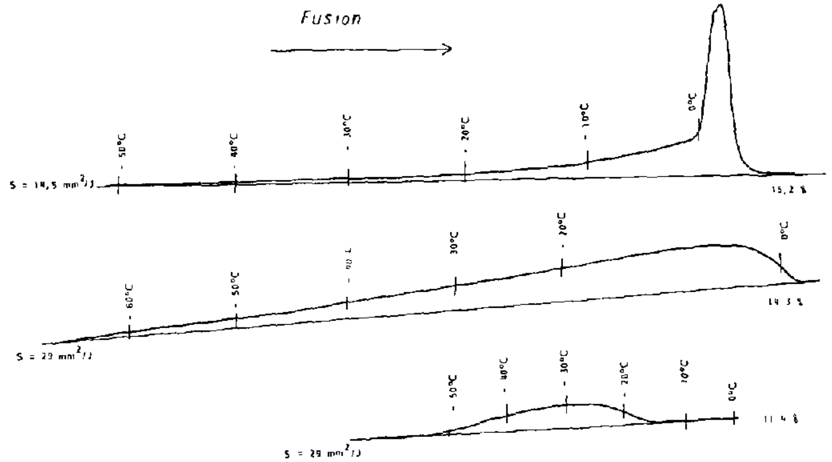


Fig. 5. D.S.C. endothermic peaks with low heating rate (8.8 K/h). The water contents are 15.2 % with an excess of free water (upper curve), 14.2 % (middle curve, 11.4 % (bottom curve). Samples have been first cooled at 6 K/h.

or in holes inside the sample: quantitative analysis of the DSC peaks (Fig. 5) during thermal cycling can be performed according to the freezing of separated water in large holes, using at each temperature below $0^{o}C$ the melting enthalpy of bulk water (column 3, table 3). The results according to the freezing of water in small preexisting pores are less in agreement (column 4, table 3) and this process does not take in account the decreasing of sorption capacity at low temperatures (ref. 36).

TABLE 3

Total water content %	Theoretical freezing water %	Calculated freezing water % in separation process	Calculated freezing water % in small preexisting pores
15.2	7.2	7.7	11.4
14.3	6.3	6.0	8.2
11.4	3.4	2.6	4.4

NMR measurements confirm the first process: a systematic decrease in amplitude of the mobile protons band versus time is observed, showing a decrease in the total number of these protons (ref. 36, 37). The fraction of water which does not show transition phases (8%) retains down to 190 K a mobility which is nearer to that of supercooled water than that of ice; this results from the band width. Another evidence of the sorption-desorption process is obtained from EPR measurements (ref. 38).

DISCUSSION AND CONCLUSIONS

Regarding the various results of all the measuring methods applied, we may describe the hydration of Nafion as follows:

- Swelling presents a limit to the adsorbed amount at saturation pressure, the value of which depends on the nature of the cation. With decreasing temperature, the mass adsorbed decreases as a result of water separation.
- At constant volume, swelling pressures between 300 and 700 bar, depending on the cation, are observed.

- The interaction energy is weak. Water molecules are first bound by the sulphonate dipoles, modifying the degree of association under hydration. For further hydration an endothermic reaction weakens the mechanical strength of the matrix.
- The mobility of the water in Nafion is high. At temperatures down to 170 K, a fraction of mobile supercooled water can always be observed.

To describe the Nafion/water system, thermodynamic models of elastic matrices must be considered. Different attempts have been made (ref. 39, 40). Recently, Kimoto (ref. 41) set importance to mechanical parameters to explain the water sorption and the Donnan equilibrium in chlorine-alcali cells for different ionic membranes. From a pure thermodynamic point of view, Dreyfus (ref. 42) developed a model to describe the swelling of a matrix containing dispersed hydrophilic sites, using only two parameters: the dielectric constant **ε'** and the shear modulus μ . The relevant isotherm equation is:

$$k\ T \ln p/p_o = \frac{4\ \mu\ v_o}{3} \ln \emptyset - \frac{e^2}{6\ r_o\ \varepsilon'}\ \emptyset^{-4/3}$$

where $\emptyset$ is the total equivalent number of moles of water per site during sorption, V_c and r_o are the volume and the radius of the site, respectively. In a first approximation, Dreyfus (ref. 42) was able to calculate the water uptake at saturation pressure, the shapes of the isotherm and the energy profile, and also the possibility of water separation at low temperature. The other results (swelling pressure, free volume extension, isochore curves) are at present being analysed in terms of this model (ref. 43).

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