Dual cohesive energy densities of perfluorosulphonic acid (Nafion) membrane

Richard S. Yeo

Department of Energy and Environment, Brookhaven National Laboratory, Upton, New York 11973, USA

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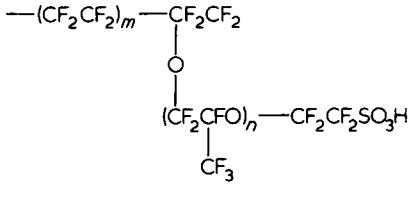
The cohesive energy density of Nafion has been determined experimentally from swelling measurements using the method of Britow and Watson. The results show that there are two distinct swelling envelopes corresponding to dual cohesive energy densities: one is ascribed to the organic part of the membrane, whereas the other is tentatively attributed to the ion clusters in the material. In addition, the cohesive energy density of Nafion, calculated from both Small's and Hayes' methods, are in agreement with experimental results.

INTRODUCTION

Nafion[1] is a copolymer of tetrafluoroethylene and a vinyl sulphonic acid, which can be represented by the following structure:



The copolymers of commercial interest fall within the limits of $m = 5-12$ and n is usually equal to 1.

Nafion, one of the ion-containing polymers[2], has been studied extensively in recent years because of its industrial importance[3]. The bulk of the evidence coming from stress relaxation[4], small-angle X-ray diffraction[4,5], electron microscopy[6], and infra-red spectroscopy[7] measurements, suggests that the ions in Nafion are clustered. An attempt was made to elucidate the structure of the clusters using Mössbauer spectroscopy[8]. The results revealed that the 4*s* electron distribution of counterion, Fe^{3+}, is partly distorted. This ion clustering not only affects a wide range of physical properties of the polymer[4], but is also closely related to the electrochemical performance of the polymer as an ion-selective membrane[5].

Although many ion-exchange membranes have been extensively used as separators in electrochemical systems both with aqueous and non-aqueous electrolytes[9–13], application of Nafion has been limited so far to those systems with aqueous media, such as chloroalkali cells[14], water electrolysers[15], hydrogen–halogen cells[16–18], and zinc–bromine batteries[19]. It has been reported that Nafion membranes swell more in many organic solvents than in water and result in increased conductivities[3,20]. This is in contrast to ion exchange membranes based on sulphonated crosslinked polystyrene.

Recent studies[21,22] on the properties of Nafion in non-aqueous solvents reveal that the solvent strongly affects the ionic transport processes in the membrane. In light of this, it is of considerable interest to explore the interactions between solvents and Nafion membranes as well as the relationship to the supermolecular structure of the membranes.

In this study, the swelling behaviour of Nafion in various solvents and the solubility parameter, the square root of cohesive energy density (*CED*) of Nafion were determined experimentally. In addition, the solubility parameter was also calculated with both Small's[23] and Hayes'[24] formulae. The former was related to the structural formula, whereas the latter was based on the structural formula together with the glass transition temperature of the polymer.

EXPERIMENTAL

The membranes, 0.25 mm thick and having equivalent weights (*EW*) of 1100 and 1200, were kindly supplied by du Pont. The membranes were used as received. A wide range of strong hydrogen bonding solvents were used and are listed in *Table 1*.

The equilibrium swelling values for Nafions were obtained by immersing rectangular pieces of ~0.5 g in the desired solvent at 25°C for more than 3 days. The samples were then surface dried and weighed in closed vessels. The degree of swelling of Nafion can be expressed by the volume fraction of solvent uptake, v_1, which was calculated from the densities of the solvents and the polymer (2.1 g cm^{-3}). The density of the polymer was determined from the measured dimensions of the weighed membrane.

RESULTS

Swelling in pure solvents

The solvent uptake by Nafion together with the solubility parameters and molal volumes of the solvents used are listed in *Table 1*. The solvent uptake for Nafion of 1200 *EW*, is plotted against solvent solubility parameter, δ_1, in *Figure 1*. Two distinct swelling envelopes are observed, a strong peak at about 9.5 Hb (Hildebrand) along with a broad peak spans

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Table 1 Solubility parameters and molal volumes of solvents and solvent uptake by Nafion

Solvent	δ (cal cm^{-3})$^{1/2}$	V_1 cm^3 mol^{-1}	% Increase in weight 1100[a]	1200[a]
Triethyl amine	7.4	139.4	22	24
Diethyl amine	8.0	103.2	21	40
2-Ethyl hexanol	9.5	158.0	–	77[b]
n-Amyl alcohol	10.9	109.0	73	59
Cyclohexanol	11.4	106.0	–	64[b]
n-Butanol	11.4	91.5	74	65[b]
2-Propanol	11.5	76.8	58	50[b]
1-Propanol	11.9	75.2	55	40
Ethanol	12.7	58.5	50	32
Methanol	14.5	40.7	54	37
Ethylene glycol	14.6	55.8	66	44
Glycerol	16.5	73.3	56	40
Formamide	19.2	39.8	56	37
Water	23.4	18.0	21	17[b]

a Equivalent weight
b Ref 3

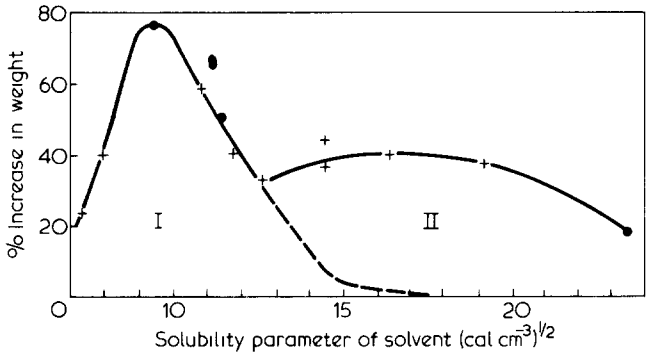

Figure 1 Solvent uptake vs. solubility parameters of solvents. +, present study; ○, after ref 3

from 12.8 to 23.4 Hb. They are denoted as envelope I and II, respectively. The dashed curve is calculated from the method to be described later.

Swelling behaviour of polymer is generally expressed in terms of χ by the modified Flory–Rehner equation[25,26]:

$$\ln(1-\nu_2)+\nu_2+\chi\nu_2^2=\frac{2V_1C}{RT}\left(\nu_2^{1/2}-\frac{1}{2}\nu_2\right) \quad (1)$$

with $C = RT\rho/2M_c$ (ref 27) where ρ and M_c are the density and EW of the polymer, respectively. V_1 is the molal volume of the solvents. The χ parameters recorded in *Table 2* were calculated from equation (1). The volume fractions, ν_2, of polymer in the swollen state are also included in *Table 2*.

Using the procedure of Britow and Watson[28], δ_2 is related to χ by the following equation:

$$\frac{\delta_1^2}{RT}-\frac{\chi}{V_1}=\left(\frac{2\delta_2}{RT}\right)\delta_1-\frac{\delta_2^2}{RT}-\frac{\beta}{V_1} \quad (2)$$

where β is a constant (0.1–0.4).

The value of δ_2 can be obtained from the slope and intercept of the straight lines by plotting the left-hand side of equation (2) against δ_1. *Figure 2* shows such a plot for Nafion of 1200 *EW*. It is clear that the data fit well into two straight lines. denoted as lines A and B, which correspond to envelopes I and II of *Figure 1*.

From the slopes of lines A and B, δ_2 are calculated as 9.68 and 17.27 Hb, respectively, whereas from the intercept of the lines, δ_2 are 9.61 and 17.37 Hb, respectively. Similarly, for Nafion of 1100 *EW*, δ_2 are 10.08 and 16.71 Hb, calculated from the slopes and 10.04 and 16.86 Hb calculated from the intercepts.

The dashed line in *Figure 2* represents the extrapolation of line A. For polymers with a single value of δ_2, one would expect only a single straight line in the range of δ_1 (7.4 to 23.5 Hb) studied. This broken line produces the broken curve in *Figure 1* by back calculation with the above-mentioned procedure.

It is evident that Nafion, in contrast to many other polymers, exhibits two solubility parameter values.

Swelling in mixed solvents

The solvent uptake by Nafion in many solvent/water mixtures was reported previously[3]. The data on diglyme/water, cellusolve/water and isopropanol/water are plotted against δ_{mix} as shown in *Figure 3*. The values of the solubility parameter of the mixed solvent were calculated using the following expression:

$$\delta_{mix}=\nu_a\delta_a+\nu_b\delta_b \quad (3)$$

Table 2 Volume fraction of swollen polymer (ν_2) and interaction parameter (χ) for Nafion of 1200 *EW*

Solvent	ν_2	χ
Triethyl amine	0.585	0.525
Diethyl amine	0.453	0.340
2-Ethyl hexanol	0.339	–0.334
n-Amyl alcohol	0.393	0.156
Cyclohexanol	0.416	0.237
n-Butanol	0.371	0.180
2-Propanol	0.427	0.389
1-Propanol	0.487	0.509
Ethanol	0.537	0.643
Methanol	0.503	0.646
Ethylene glycol	0.543	0.660
Glycerol	0.599	0.708
Formamide	0.590	0.770
Water	0.736	1.071

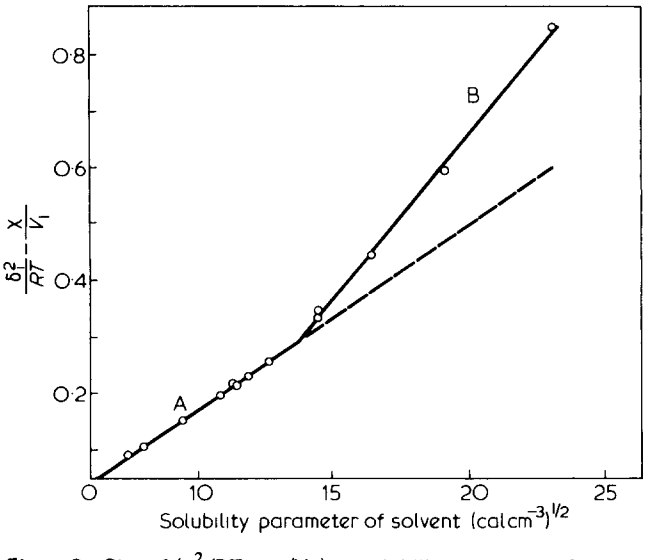

Figure 2 Plot of $(\delta_1^2/RT - \chi/V_1)$ vs. solubility parameter of solvents

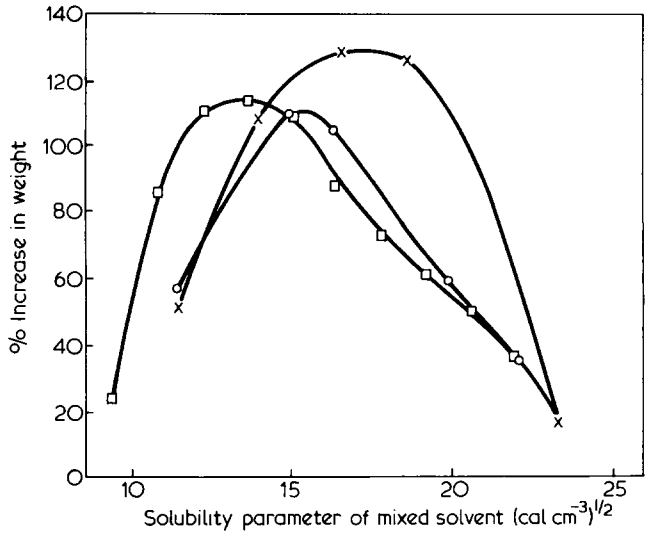

Figure 3 Solvent uptake vs. solubility parameter of mixed solvent. x, Isopropanol/water; ○, cellosolve/water; □, diglyme/water

where δ_a, δ_b and v_a, v_b are the solubility parameter and the volume fraction of the components of the mixed solvents.

The maximum of the swelling envelopes appears at δ_1 = 16 ~ 17 Hb, similar to that of envelope II for the case of pure solvent, except that the magnitude of swelling envelopes for mixed solvent is larger than that for pure solvent.

Calculation of δ_2 from Small's method

The δ_2 can be estimated based upon the structural formula of the compound by using Small's formula:

$$\delta_2 = \rho \sum_i G_i/M \qquad (4)$$

where G is the molar-attraction constant, ρ and M are the density and molecular weight of the polymer, respectively. It is assumed that the contributions of the individual atoms or groups to the overall value of the solubility parameter of the molecule are additive.

Since the G value for the SO_3H group is not available, the δ_1 for trifluoromethane sulphonic acid, CF_3SO_3H (a molecule with chemical structure resembling that of Nafion) is calculated.

Using a boiling point of 162°C and a density of 1.696 g cm^{-3}, the calculated δ_1 value for CF_3SO_3H is 10.9 Hb by the method described elsewhere[29]. It follows that the G_{SO_3H} is equal to 690 cal$^{1/2}$ (cm^3)$^{1/2}$ using Small's method.

Taking 2.1 g cm^{-3} for the density of Nafion, the calculated δ_2 value is 7.6 Hb for EW = 1100 and 7.2 Hb for EW = 1500.

Calculation of δ_2 from glass transition temperature

An empirial equation relating cohesive energy density, glass transition temperature, T_g, and polymer structure was established by Hayes[24]:

$$CED = \frac{n}{V_1}(0.5\,RT_g - 25) \qquad (5)$$

where V_1 is the molal volume, R is the gas constant, and n is a number analogous to the degrees of freedom in the expression of kinetic energy. Using the rules given by Hayes, n is estimated to be 192 for Nafion of 1200 EW. T_g for the Nafion precursor, Nafion-H and Nafion-C_s are 10°C [30], 110°C [4] and 212°C [4], respectively. The corresponding δ_2 values are calculated to be 9.28, 10.93 and 12.39 Hb.

DISCUSSION

The presence of two solubility parameter values in Nafion is unique. This feature has never been found for any other material whose solubility parameter has been reported[29]. The value of δ_2 (line A) is similar to that of many organic compounds and polymers, thus it is likely that the solvents, with δ_1 in the range of envelope I, will strongly interact with the organic backbone and perhaps with the long side chain of the polymer. The interaction only causes the membrane to swell fully without losing its integrity and dissolving in the solvents. However, there is no crosslinking in Nafion. It is suggested that the polymer is held together by the crystallinity of the polymers or van der Waals forces or both. A small amount of crystallinity was found to be present in the polymer[5], especially the non-ionizing resins, and the crystallinity decreases with decreasing EW. Polymers with EW below 1000 become too weak for use in the swollen form and they may be soluble.

The reason for the presence of the swelling envelope II is still unknown. Since the value of δ_2 (line B) is close enough to that of H_2SO_4 [31] (a pure ionic compound after solvation), it may be attributed to the regions other than the organic part of the membrane, perhaps the ion clusters of the polymer.

Although the relationship between δ_2 and EW of Nafion was not studied in detail, some observations can be made. The separation of the two δ_2 values is smaller for the lower EW samples. It appears that as the EW decreases further, the two δ_2 values will likely merge into one and finally reach a value close to that of CF_3SO_3H, a low carbon compound resembling Nafion. As mentioned above, samples of EW below 1000 may be soluble.

The swelling of Nafion in mixed solvents, with δ_1 in the range of envelope II, strongly supports the existence of the second δ_2 value. Moreover, the swelling of Nafion in mixed solvents is larger than in pure solvents (envelope II). The reason remains unknown at present.

The δ_2 value calculated by Small's method is less than the corresponding value obtained experimentally. However, the experimental determination involved strong hydrogen bonding solvents whereas Small's method assumes no hydrogen bonding. In general, the δ_2 values of polymers decrease with a decrease in the hydrogen bonding capability of the solvents used in the determination.

The incorporation of ions into organic polymers affects the properties of the materials profoundly. The glass transition temperature increases appreciably, and accordingly the δ_2 value will increase. The δ_2 for Nafion precursor, a non-ionic material, is similar to δ_2 (line A) of Nafion-H whereas the δ_2 for Nafion-C_s is close to that of δ_2 (line B) of Nafion-H. The above observation again is consistent with the tentative assignment of δ_2 (line A) to the organic part of the polymer and δ_2 (line B) to the ion cluster.

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