Application of the Group Contribution Approach to Nafion Swelling

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ABSTRACT: The anisotropic swelling of Nafion 112 membrane in pure organic liquids was monitored by an optical method. The findings were used as a basis for application of the group contribution method to the relative expansion in equilibrium. From a total of 38 organic liquids under study, 26 were selected as an evaluational set from which the group and structural group contributions were assigned. The remaining 12 compounds were used as the testing set. Value of ±1.5% in relative expansions was determined to be the experimental error. Maximum differences between the experimental and calculated relative expansions in both sets did not exceed the value of ±3%. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1745–1750, 2009

Key words: group contribution method; membranes; structure-property relations; swelling; pure organic liquid

INTRODUCTION

Prediction of the physical and chemical properties of pure substances and mixtures is a serious problem in the chemical process industries. These properties are important for modeling, simulating, and controlling chemical plants. Many researchers are involved in the development of methods for predicting properties of organic, inorganic, and biochemical compounds.

One of the possibilities for prediction is the group contribution method. When the contribution of a part of a molecule (atom, bond, group, etc.) to a particular property is constant regardless of the nature of the rest of the molecule, the property is termed an additive one. Knowing the molecule structure, the additive property may be easily and quickly calculated by summing up of the contributions corresponding to the parts of the molecules (units). The units in new group contribution methods are usually central atoms with their surrounding. Their contributions are obtained by fitting of an adopted mathematical/physical function to a set of experimental data.[1,2]

These estimation methods are therefore essentially empirical. A large variety of group contribution methods have been designed during last centuries, differing in a field of their applicability and in the set of experimental data. They were developed to estimate, e.g., critical properties,[3–9] acentric factor,[10] activity coefficients,[11] vapor pressure,[8,12] liquid viscosity,[6] gas viscosity,[13] heat capacity,[6,14,15] enthalpy of vaporization,[9,16] entropy of vaporization,[16] normal boiling temperature,[6,7,9] liquid thermal conductivity,[17] gas thermal conductivity,[18] gas permeability,[19] diffusion coefficients,[19] liquid density,[20] surface tension.[21]

This article aims to apply the group contribution approach to estimate the swelling of Nafion membrane in various organic liquids. We have chosen Nafion membrane because of its wide and important employment in chemical industry. Nafion is a poly (tetrafluoroethylene) (PTFE) polymer with perfluorovinyl pendant side chains ended by sulfonic acid groups. The PTFE backbone guarantees a great chemical stability in both reducing and oxidizing environments. The sulfonic exchange groups on the side chains have very high acidity.[22,23] Nafion membrane is used in fuel cells, membrane reactors, gas dryers, production of NaOH, electrodialyses, etc.[24–28] In many applications Nafion is immersed in liquid, which significantly affects the membrane properties (viz., swelling and transport properties of permeates).[29–32]

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TABLE I
Characterization of the Compounds Used in this Study

Compound	Formula	Structure
Alcohols		
Methanol	CH_4O	*alc* + CH_3 + OH
Ethanol	C_2H_6O	*alc* + CH_3 + CH_2 + OH
Isopropanol	C_3H_8O	*alc* + 2(CH_3) + CH +OH + *br*
Propanol	C_3H_8O	*alc* + CH_3 + 2(CH_2) + OH
2-Methyl-1-propanol	$C_4H_{10}O$	*alc* + 2(CH_3) + CH_2 + CH + OH + *br*
1-Butanol	$C_4H_{10}O$	*alc* + CH_3 + 3(CH_2) + OH
1-Pentanol	$C_5H_{12}O$	*alc* + CH_3 + 4(CH_2) + OH
3-Methyl-1-butanol	$C_5H_{12}O$	*alc* + 2(CH_3) + 2(CH_2) + CH + OH + *br*
4-Methyl-2-pentanol	$C_6H_{14}O$	*alc* + 3(CH_3) + CH_2 + 2(CH) + OH + *br*
Cyclopentanol	$C_5H_{10}O$	*alc* + 4(CH_2) + CH + OH + *cy*
1-Hexanol	$C_6H_{14}O$	*alc* + CH_3 + 5(CH_2) + OH
cyclohexanol	$C_6H_{12}O$	*alc* + 5(CH_2) + CH + OH + *cy*
2-Methylcyclohexanol	$C_7H_{14}O$	*alc* + CH_3 + 4(CH_2) + 2(CH) + OH + *cy*
1-Octanol	$C_8H_{18}O$	*alc* + CH_3 + 7(CH_2) + OH
1-Decanol	$C_{10}H_{22}O$	*alc* + CH_3 + 9(CH_2) + OH
Ketones		
Acetone	C_3H_6O	*ket* + 2(CH_3) + C=O
Acetylacetone	$C_5H_8O_2$	*ket* + 2(CH_3) + CH_2 + 2(C=O)
2-Butanone	C_4H_8O	*ket* + 2(CH_3) + CH_2 + C=O
2-Pentanone	$C_5H_{10}O$	*ket* + 2(CH_3) + 2(CH_2) + C=O
Cyclopentanone	C_5H_8O	*ket* + 4(CH_2) + C=O + *cy*
Methylisobutylketone	$C_6H_{12}O$	*ket* + 3(CH_3) + CH_2 + CH + C=O + *br*
Cyclohexanone	$C_6H_{10}O$	*ket* + 5(CH_2) + C=O + *cy*
2-Methylcyclohexanone	$C_7H_{12}O$	*ket* + CH_3 + 4(CH_2) + CH + C=O + *cy*
Ethers		
Diethyl ether	$C_4H_{10}O$	*eth* + 2(CH_3) + 2(CH_2) + —O—
1,2-Dimethoxyethane	$C_4H_{10}O_2$	*eth* + 2(CH_3) + 2(CH_2) + 2(—O—)
Diisopropyl ether	$C_6H_{14}O$	*eth* + 4(CH_3) + 2(CH) + —O— + 2(*br*)
Dipropyl ether	$C_6H_{14}O$	*eth* + 2(CH_3) + 4(CH_2) + —O—
Dibutyl ether	$C_8H_{18}O$	*eth* + 2(CH_3) + 6(CH_2) + —O—
Carboxylic acids		
Acetic acid	C_2H_4O	*carb* + CH_3 + OH + C=O
Propionic acid	C_3H_6O	*carb* + CH_3 + CH_2 + OH + C=O
Compounds with two functional groups		
2-Ethoxyethanol	$C_4H_{10}O_2$	½(*alc* + *eth*) + 1(CH_3) + 3(CH_2)+ 1(OH) + 1(—O—)
2-Propoxyethanol	$C_5H_{12}O_2$	½(*alc* + *eth*) + CH_3 + 4(CH_2) + OH + —O—
2-Butoxyethanol	$C_6H_{14}O_2$	½(*alc* + *eth*) + CH_3 + 5(CH_2) + OH + —O—
1-Propoxy-2-propanol	$C_6H_{14}O_2$	½(*alc* + *eth*) + 2(CH_3) + 3(CH_2) + CH + OH + —O—
Esters		
Methyl acetate	$C_3H_6O_2$	*est* + 2(CH_3) + C=O + —O—
Isobutyl acetate	$C_6H_{12}O_2$	*est* + 3(CH_3) + CH_2 + CH + C=O + —O— + *br*
Butyl acetate	$C_6H_{12}O_2$	*est* + 2(CH_3) + 3(CH_2) + C=O + —O—
Hexyl acetate	$C_8H_{16}O_2$	*est* + 2(CH_3) + 5(CH_2) + C=O + —O—

EXPERIMENTAL

The study of swelling represents the monitoring of visual manifestation of the complex of all the processes taking place between the membrane and surrounding liquid. The change in the size of the membrane sample is taken here as a measure of swelling.

Materials

Nafion® 112 membrane, produced by DuPont, USA, was used as received. According to the manufacturer, the membrane Nafion 112 has nominal thickness 51 μm, density 2000 kg m^{-3}, ionic conductivity 8.3 S m^{-1}, and acid capacity 0.89 mequiv g^{-1}.

Table I lists all the chemicals used in experiments, together with their fragmentation to structural units (see computational procedure). The manufacturers of the chemicals are PENTA (for 1-butanol, 1-pentanol, and methylisobutyl ketone) and Sigma-Aldrich (for others). Pro-analysis grade chemicals were used in all experiments.

Experimental setup

All experiments were carried out at 25°C and at atmospheric pressure. A modification of the optical apparatus, described in our previous papers,[33,34] was used to measure the change of two dimensions of a flat membrane sample (in the drawing direction

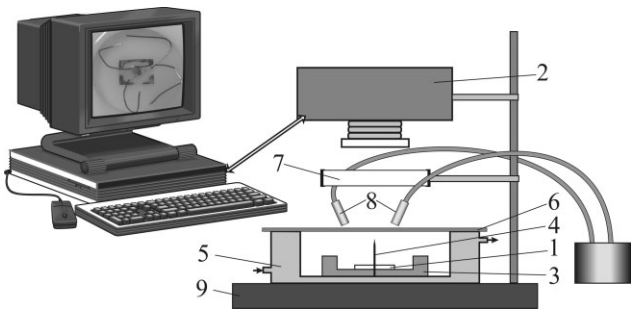

Figure 1 Schema of the experimental setup for monitoring of dimensional changes of flat membranes: 1, membrane sample; 2, digital camera interconnected with a PC; 3, circle Teflon cell; 4, sharp pin; 5, thermostatted vessel; 6, photographic plate; 7, magnifying glass; 8, cold illuminator; and 9, stand with holders.

and in the perpendicular direction) in liquid medium. A cold illuminator was used to light the sample placed in a thermostated vessel, covered with a glass photographic plate to prevent the evaporation of the liquid (Fig. 1). A square membrane sample sides were cut off parallelly with the edges of a sheet supplied by manufacturer. The images of a square 5 × 5 mm fixed on a spike in the circle Teflon cell were taken by a digital camera Olympus Camedia 5050 connected to a computer. The photographs were analyzed by PC using the program QuickPHOTO MICRO.

The relative expansions A_{exp} (for the drawing direction) and/or B_{exp} (for the perpendicular direction) were calculated from the side lengths of the dry membrane sample (a_{10}, a_{20}, b_{10}, b_{20}) and the side lengths of the swelled membrane sample in equilibrium (a_1, a_2, b_1, b_2) (see Fig. 2) according to the eqs. (1) and (2). The experimental error of A_{exp} and/or B_{exp} was ±1.5%.

$$u_{a1} = \frac{a_1 - a_{10}}{a_{10}},\ u_{a2} = \frac{a_2 - a_{20}}{a_{20}},\ u_{b1} = \frac{b_1 - b_{10}}{b_{10}},\ u_{b2} = \frac{b_2 - b_{20}}{b_{20}} \quad (1)$$

$$A_{exp}/\% = \frac{u_{a1} + u_{a2}}{2} \times 100,\ B_{exp}/\% = \frac{u_{b1} + u_{b2}}{2} \times 100 \quad (2)$$

The experimental values of the relative expansions are given in Tables III and IV. It can be seen that relative expansions obtained for the drawing direction are always smaller than those for the perpendicular direction. With respect to the known fact that Nafion shows distinct anisotropy developed as a result of preferential orientation of the chains or crystalline regions in the polymer raising at forming processes (drawing and extrusion),[34–41] it is not surprising that the values of A are smaller than B.

COMPUTATIONAL PROCEDURE

The proposed method utilizes the four kinds of the structural units: constants, C-backbone, functional groups, and molecular geometry.

Constants:

alc for alcohols
ket for ketones
eth for ethers
carb for carboxylic acids
est for esters

C-backbone:

$CH_3...CH_3$—
$CH_2...$—CH_2—
CH...>CH—

Functional groups:

OH...hydroxyl group
C = O...carbonyl group
—O—...ether group

Molecular geometry:

cy...whatever cycle in molecule
br...branching—group

$$CH_3 - \underset{\displaystyle |}{CH} - \\ \quad\ CH_3$$

Chemicals presented in Table I were divided into two groups. The first group comprises chemicals

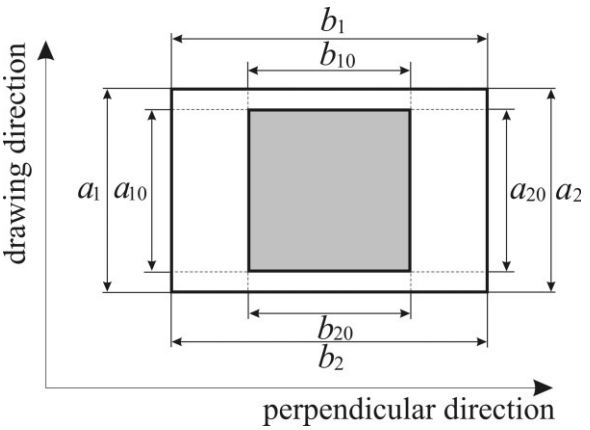

Figure 2 Description of membrane dimensions a_{10}, a_{20}, b_{10}, b_{20} ... side lengths of the dry membrane a_1, a_2, b_1, b_2 ... side lengths of the swelled membrane in equilibrium.

TABLE II
The Contribution Values of the Structural Units for Individual Relative Expansions

Units	Contribution values: To relative expansion *A*	Contribution values: To relative expansion *B*
Constants		
alc	7.9390	24.8597
ket	10.4067	26.7824
eth	−2.1737	−17.8055
carb	−4.7196	2.3642
est	0.1741	−1.2482
C-backbone		
CH_3	0.2264	8.4030
CH_2	0.2896	−0.3956
CH	−3.3998	−11.5341
Functional group		
OH	11.0630	17.3970
C=O	−1.5846	−11.7664
—O—	4.7259	16.1654
molecular geometry		
br	3.0213	1.8247
cy	0.7828	12.7858

used for calculation of the contributions of the structural units (the evaluational set), whereas the compounds included in the second one (called the testing set) were used to test the proposed contribution method.

The contributions of the structural units were determined by minimization functions S_A and/or S_B

$$S_A = \sum_{i=1}^{m} (A_{\text{exp},i} - A_{\text{calc},i})^2 \quad (3)$$

$$S_B = \sum_{i=1}^{m} (B_{\text{exp},i} - B_{\text{calc},i})^2 \quad (4)$$

where i denotes the sequence number of the compound from the evaluational set (see Table III)

$A_{\text{exp},i}$... experimental value of the relative expansion A

$B_{\text{exp},i}$... experimental value of the relative expansion B

$A_{\text{calc},i}$... calculated value of the relative expansion A

$B_{\text{calc},i}$... calculated value of the relative expansion B

m ... number of compounds.

The Microsoft EXCEL Solver was used for the calculating. The results obtained by the group contribution method were compared with experimental data using the following statistical quantities:

An absolute error:

$$\Delta A_i = A_{\text{exp},i} - A_{\text{calc},i}, \ \Delta B_i = B_{\text{exp},i} - B_{\text{calc},i} \quad (5)$$

An average absolute error:

$$\delta A = \frac{\sum_{i=1}^{m} |\Delta A_i|}{m}, \ \delta B = \frac{\sum_{i=1}^{m} |\Delta B_i|}{m} \quad (6)$$

TABLE III
Results for Compounds of the Evaluational Set

i	Compound	$A_{\text{exp},i}$	$A_{\text{calc},i}$	ΔA_i	$B_{\text{exp},i}$	$B_{\text{calc},i}$	ΔB_i
1	Methanol	19.76	19.23	0.53	51.33	50.66	0.67
2	Ethanol	19.94	19.52	0.42	49.79	50.26	−0.47
3	Isopropanol	18.40	19.08	−0.68	49.14	49.35	−0.21
4	Propanol	18.07	19.81	−1.74	51.77	49.87	1.90
5	1-Butanol	21.67	20.10	1.57	50.38	49.47	0.91
6	3-Methyl-1-butanol	19.68	19.66	0.02	46.03	48.56	−2.53
7	Cyclopentanol	18.42	17.54	0.88	41.71	41.93	−0.22
8	Cyclohexanol	15.51	17.83	−2.32	40.81	41.53	−0.72
9	2-Methylcyclohexanol	15.57	14.37	1.20	38.34	38.79	−0.45
10	1-Octanol	19.78	21.26	−1.48	46.95	47.89	−0.94
11	1-Decanol	23.42	21.83	1.59	49.17	47.10	2.07
12	Acetylacetone	7.98	7.98	0.00	19.66	19.66	0.00
13	2-Pentanone	8.92	9.85	−0.93	28.76	31.03	−2.27
14	Cyclopentanone	11.01	10.76	0.25	27.61	26.22	1.39
15	Methylisobutylketone	10.10	9.41	0.69	31.00	30.12	0.88
16	Diethyl ether	3.73	3.58	0.15	16.61	14.37	2.24
17	1,2-Dimethoxyethane	8.31	8.31	0.00	30.54	30.54	0.00
18	Dipropyl ether	3.01	4.16	−1.15	10.64	13.58	−2.94
19	Dibutyl ether	5.75	4.74	1.01	13.50	12.79	0.71
20	Acetic acid	4.84	4.99	−0.15	17.33	16.40	0.93
21	Propionic acid	5.42	5.27	0.15	15.07	16.00	−0.93
22	2-Ethoxyethanol	20.72	19.77	0.95	42.46	44.31	−1.85
23	1-Propoxy-2-propanol	15.64	16.59	−0.95	43.02	41.17	1.85
24	Methyl acetate	4.60	3.77	0.83	19.40	19.96	−0.56
25	Isobutyl acetate	3.87	3.91	−0.04	20.12	18.25	1.87
26	Hexyl acetate	4.42	5.22	−0.80	16.67	17.98	−1.31

TABLE IV
Results for Compounds of the Testing Set

Compound	A_{exp}	A_{pred}	ΔA	B_{exp}	B_{pred}	ΔB
2-Methyl-1-propanol	18.54	19.37	−0.83	49.37	48.96	0.41
4-Methyl-2-pentanol	16.48	16.19	0.29	45.96	45.83	0.13
1-Pentanol	20.14	20.39	−0.25	50.61	49.08	1.53
1-Hexanol	21.61	20.68	0.93	49.68	48.68	1.00
Acetone	10.24	9.27	0.97	33.96	31.82	2.14
2-Butanone	9.67	9.56	0.11	29.17	31.43	−2.26
Cyclohexanone	11.33	11.05	0.28	26.89	25.82	1.07
Methylcyclohexanone	8.64	7.59	1.05	26.07	23.09	2.98
Diisopropyl ether	3.20	2.70	0.50	12.45	12.55	−0.10
2-Propoxyethanol	19.55	20.06	−0.51	45.52	43.91	1.61
2-Butoxyethanol	19.16	20.35	−1.19	45.96	43.51	2.45
Butyl acetate	5.70	4.64	1.06	19.50	18.77	0.73

RESULTS AND DISCUSSION

Our experimental data on the relative expansion, gained with the compounds falling into the evaluational group, served as a database for determination of the structural units values. Calculated values of contributions are given in Table II. To appraise the reliability of performance of the proposed contribution method, the calculated values A_{calc} and B_{calc} for the Nafion swelling were compared with the experimental ones for all the compounds pertaining to the evaluational set; calculated values and the differences between them and the experimental data presents Table III. To appraise the prediction ability of the method, the experimental data on Nafion swelling in the liquids from the testing set (i.e., not used for contributions evaluation) were compared with the values predicted using the above determined contributions. The results, given in Table IV, show that the proposed method leads to good correlation with experimental data.

Considering the contribution values given in Table II, it can be said that the main part of resulting value of the relative expansion consists of constants and the values of the functional groups, whereas the units of C-backbones play the minor role. The maximum difference between the experimental and calculated relative expansion values in the evaluational set was found to be 2.94% [the mean deviations, calculated according to eq. (6), are 0.69% for relative expansion A and 1.19% for relative expansion B, i.e., smaller than the experimental error ±1.5% in A_{exp} and/or B_{exp}]. For the compounds of the testing set the maximum difference had similar value of 2.98%, the mean deviation for relative expansion A is 0.66%, for relative expansion B is 1.37%, again smaller than the experimental error. The results show that the group contribution methods can be applied even to such processes as the swelling of membranes.

CONCLUSIONS

A simple group contribution method allowing the prediction of dimensional changes of Nafion membrane upon its immersion into liquid medium has been developed. The values of 13 contributions for individual membrane relative expansions were determined on the basis of experimental data on relative expansion of Nafion membrane in 26 organic liquids (evaluational set). The predictive ability of the proposed contribution method was tested by comparing the calculated values of relative expansion for 12 independent compounds (testing set) with the experimental ones. Obtained results are in good agreement with experimental data. Maximum differences between experimental and calculated values are nearly the same, only twice greater than the experimental error.

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