NOTE

Appropriate Use of Fick's Equation To Compute Diffusion Coefficients in Pervaporation Experiments

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The permeation of solvents through nonporous polymeric membranes is usually described in terms of the sorption and molecular diffusion of liquid molecules. The sorption of liquid molecules occurs at the liquid–membrane interface, and it is assumed that there exists thermodynamic equilibrium at this surface. The chemical nature of the polymer and solvents can determine the extent of sorption as well as sorption selectivity. In pervaporation (PV) experiments, the driving force for diffusion is the existence of a concentration gradient maintained at a steady state by solvent evaporation from the membrane surface. The consideration of the diffusion of solvent molecules through membranes is important in PV experiments, and so diffusion coefficients are calculated. When the diffusion coefficients of water molecules in water–organic mixtures are calculated, Fick's first law of diffusion is used:[1]

$$[J_i = (D_i / h)[C_{i(\text{feed})} - C_{i(\text{permeate})}] \quad (1)$$

where D_i is assumed to be constant across the effective membrane thickness (h); $C_{i(\text{feed})}$ and $C_{i(\text{permeate})}$ are the compositions of the liquids present in the feed and permeate, respectively; and subscript i represents water or an organic component for which the diffusion coefficients are to be calculated.

In a series of articles from our laboratory,[2–9] we have computed values of D_i, using eq. (1), from the flux data and thickness of the membranes. Previous calculations have been performed done with the mass percentage of the liquid in the feed and permeate. These data have been published in our earlier articles;[2–9] we refer to this as method I. We have performed specimen calculations by taking one set of data from Kurkuri et al.[6] for water/tetrahydrofuran (THF) mixtures for three membranes: (1) pure sodium alginate (NaAlg), 10 mass % poly(ethylene glycol) 200 (PEG 200), and 5 mass % poly(vinyl alcohol) (PVA; designated membrane M1); (2) 46% polyacrylamide (pAAM)-*g*-NaAlg, 10 mass % PEG 200, and 5 mass % PVA (designated membrane M2), and (3) 93% pAAM-*g*-NaAlg, 10 mass % PEG 200, and 5 mass % PVA (designated membrane M3). These are presented in Table I by method I. This way of calculating the diffusion coefficients is erroneous because the volumes are not taken into consideration in all calculations. Therefore, we propose the following procedure, called method II, which may be recommended in the future for computing D_i. The program, written in the programming language C, is given in the appendix.

In the proposed procedure, the values of D_i have been calculated with eq. (1); we have considered the correct use of the concentration of the liquid in the feed and in the permeate, instead of the mass percentage. Therefore, we are providing the program, written in the programming language C (see the appendix), to calculate D_i with the concentration of water (or even an organic component) from its mixture with THF as an example.[6] This program computes the concentration by taking the volume of the feed and permeate into consideration for calculating the D_i values for the binary system used. The values of D_i calculated for water from water/THF mixtures with M1, M2, and M3 are compared in Table I.

In conclusion, we made an inadvertent mistake, as suggested in method I, but method II is correct.

APPENDIX

Variables used in the program

betao	enrichment factor of the organic solvent
betaw	enrichment factor of water
cof	concentration of the organic solvent in the feed (mol/m^3)
cop	concentration of the organic solvent in the permeate (mol/m^3)
cwf	concentration of the water in the feed (mol/m^3)
cwp	concentration of the water in the feed (mol/m^3)
deno	density of the organic solvent (kg/m^3)
dso	diffusion coefficient of the organic solvent (m^2/s)
dw	diffusion coefficient of water (m^2/s)
h	thickness of the membrane (m)
jo	organic solvent flux (g/m^2 h)
jw	water flux (g/m^2 h)
mwo	molecular weight of the organic solvent

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TABLE I
Diffusion Coefficients of Water (D_w) in Water/+THF Mixtures Calculated by methods I and II

	$D_w \times 10^9$ (m^2/s), method I			$D_w \times 10^{14}$ (m^2/s), method II		
Water (mass %)	M1	M2	M3	M1	M2	M3
10	3.94	4.06	5.67	0.84	0.87	1.22
20	5.19	5.56	6.67	1.11	1.19	1.43
30	7.72	8.14	9.78	1.65	1.74	2.093
40	19.3	20.6	29.2	2.06	2.19	3.123
50	22.2	43.3	81.4	2.36	4.63	8.693
60	32.8	74.2	281.0	3.49	7.90	29.99
70	75.6	322	47.5	8.04	34.23	8.94
80	486	111	2.59	51.61	11.76	12.96

vf volume of the feed (m^3)
vp volume of the permeate (m^3)
wof weight of the organic solvent in the feed (g)
wop weight of the organic solvent in the permeate (g)
wwf weight of water in the feed (g)
wwp weight of water in the permeate (g)

Program

```
/* A 'C' program to find the diffusion coefficients and
   stripping coefficient. */
#include<stdio.h>
#include<conio.h>
#include<math.h>
void main()
{
double wwp,wop,wwf,wof,deno,mwo,jw,jo,h-
   ,vf,vp,vfw,vfo,vpo,vpw;
double cwf,cwp,cof,cop,dw,dso,betaw,betao;
clrscr();
printf("Enter the wt. of the water & organic solvent in
   feed in gms:
\n");
scanf("%lf %lf",&wwf,&wof);
printf("Enter the wt. of the water & organic solvent in
   feed in gms:
\n");
scanf("%lf %lf",&wwp,&wop);
printf("Enter the mol.weight organic solvent:\n");
scanf("%lf",&mwo);
printf("Enter the Density of Organic solvent:\n");
scanf("%lf",&deno);
printf("Enter the water flux & Organic solvent in g/sq.m
   - hr:\n");
scanf("%lf %lf",&jw,&jo);
printf("Enter the thickness of the membrane in mts:\n");
scanf("%lf",&h);
/* calculating the total volume of feed */
vfw = wwf*0.001 / 1000.0;
vfo = wof*0.001 / deno;
vf = vfw + vfo;
/* calculating the total volume of the permeate. */
vpw = wwp * 0.001 / 1000.0;
vpo = wop * 0.001 / deno;
vp = vpw + vpo;
/* calculation of concentration of water in feed and per-
   meate */
cwf = wwf/(18.0 * vf);
cwp = wwp/(18.0 * vp);
/* Calculation of concentration of organic compound in
   Feed & permeate */
cof = wof/(mwo * vf);
cop = wop/(mwo * vp);
/* calculation of diffusion coefficients */
dw = (jw * h) / (18.0 * 3600.0 * (cwp - cwf) ) * 1e13;
dso = (jo * h) / (mwo * 3600.0 * (cof - cop) ) * 1e14;
/* calculation of enrichment factor */
betaw = cwp / cwf;
betao = cop / cof;
/* printing the results */
printf("*************************************************\n");
printf("Diffusion coefficient of water X 1e13 = %lf sq. mts
   / sec.\n",dw);
printf("Diffusion coefficient of organic solv.X 1e14 = %lf
   sq.mts/sec.\n",dso);
printf("Enrichment factor of water = %lf\n",betaw);
printf("Enrichment factor of organic solvent
   = %lf\n",betao);
printf("*************************************************\n");
getch();
}
```

References

1. Crank, J. The Mathematics of Diffusion, 2nd ed.; Clarendon: Oxford, 1975.
2. Aminabhavi, T. M.; Naik, H. G. J Appl Polym Sci 2002, 83, 244.
3. Toti, U. S.; Kariduraganavar, M. Y.; Soppimath, K. S.; Aminabhavi, T. M. J Appl Polym Sci 2002, 83, 259.
4. Aminabhavi, T. M.; Naik, H. G. J Appl Polym Sci 2002, 83, 273.
5. Toti, U. S.; Aminabhavi, T. M. J Appl Polym Sci 2002, 85, 2014.
6. Kurkuri, M. D.; Kumbar, S. G.; Aminabhavi, T. M. J Appl Polym Sci 2002, 86, 272.
7. Kurkuri, M. D.; Toti, U. S.; Aminabhavi, T. M. J Appl Polym Sci 2002, 86, 3642.
8. Kurkuri, M. D.; Aminabhavi, T. M. J Appl Polym Sci 2003, 89, 300.
9. Kurkuri, M. D.; Naik, H. G.; Aminabhavi, T. M. J Appl Polym Sci, to appear.