

# Generalization of Polymer/Organic Solvent Interaction Processes by Means of Linear Polyparameter Equations. I. Swelling of Polyethylene

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**ABSTRACT:** A solvent's molar volume is the factor that determines its ability to penetrate into a polymer structure. However, the available data for polyethylene swelling in organic solvents may be quantitatively linked with their physicochemical properties only by use of polyparameter equations, which take into account not only the molar volume of solvents but also their ability for specific and nonspecific solvation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3133–3140, 2001

**Key words:** swelling; organic solvents; polyethylene; molar volume; solvation

## INTRODUCTION

Polymer/organic solvent interaction processes, particularly the ability of solvents to penetrate into polymer structures (i.e., their swelling behavior), are at present usually considered from the standpoint of both Hildebrand's regular solutions theory<sup>1</sup> and the Flory–Huggins model.<sup>2</sup> These are based on the assumption that the degree of solvent adsorption is determined by a solvent's cohesion energy density  $\delta$  or, even better, by the difference of solvent and polymer solubility parameters  $\delta_1 - \delta_2$ . However, in reality these dependencies give only a semiquantitative bell-like picture, with a maximum for solvents characterized by  $\delta$  values that are the same as or nearly the same as the  $\delta$  values of polymers. At

the same time, one frequently observes numerous deviations from these dependencies, even when examining solvents divided into separate groups (e.g., Richards<sup>3</sup>); thus, to obtain acceptable outcomes it is often necessary to introduce empirical corrective coefficients.<sup>4</sup>

Recent reviews have been published concerning the work of Aminabhavi and coworkers, who investigated solvent penetration into the structure of diverse polymer membranes.<sup>5</sup> These authors proposed the solvent molar volume  $V_m$  as the parameter that determines the degree of polymer swelling. Such a supposition should be considered as logical because, undoubtedly, the larger the molecular dimensions of a solvent, the more difficult it will be for the solvent to penetrate into the polymer structure. In reality, however, one observes a linear dependence between the logarithm of the degree of polymer swelling ( $\log S$ ) in various solvents and their  $V_m$  (even conceding that there are a number of exceptions)

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when considering three distinct solvent groups: the aliphatic hydrocarbons, monocyclic aromatics, and esters.

Obviously such discrepancies in the proposed models (particularly in Aminabhavi et al.<sup>5</sup>) are caused by the use of physical factors only, setting aside consideration of possible chemical solvation processes.<sup>6</sup> At the same time, however, one should realize that attempts to describe the swelling process by chemical characteristics alone (e.g., Reichard's electrophilicity parameter  $E_T$ ) are successful only for distinct groups of solvents.<sup>7</sup> Thus it seems presumptuous to maintain that the processes of polymer/organic solvent interaction are significantly more complicated and, further, that their generalization by means of a single parameter is impossible.

Therefore we suggest that the swelling process be considered as an equilibrant intersolution of components and that the obtained experimental results be generalized on the basis of the principle of free energy linearity, which takes into account various possible aspects of interactions. Such an approach was developed in the area of chemical kinetics by Koppel and Palm<sup>8</sup> and by Kamlet et al.<sup>9</sup> We set forth this proposition in the following equation:

$$\log S = a_0 + a_1 \left( \frac{n^2 - 1}{n^2 + 2} \right) + a_2 \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) + a_3 B + a_4 E_T + a_5 \delta^2 \quad (1)$$

in which  $S$  is the degree of swelling in mol %, which allows us to generalize with adequate accuracy the results of swelling for both synthetic butadiene-styrene rubber<sup>10,11</sup> and polyethylene<sup>12</sup>;  $n$  is the solvent's refraction index;  $\epsilon$  is the solvent's dielectric permeability;  $B$  is basicity (according to Koppel and Palm<sup>8</sup>), which is the change of -OH frequency in the PhOH IR spectrum in the presence of the corresponding solvent in  $\text{cm}^{-1}$ ;  $E_T$  is Reichard's electrophilicity (according to Jonquieres et al.<sup>7</sup>); and  $\delta^2$  is the solvent's cohesion energy density in kJ/mol. The first two terms characterize nonspecific polymer solvation processes generated by solvent polarizability and polarity; the two next terms delineate the specific solvation caused by possible acid-base interactions; and the last term defines the expenditure of energy needed to isolate absorbed solvent molecules from the liquid structure. However, despite adequate results obtained from these calculations, eq. (1) does not take into account the influence of molec-

ular dimensions, characterized by their molar volume  $V_m$ , which as stated earlier are of a great importance. In addition, the initial data used in Pyrih et al.<sup>10,11</sup> are given in vol %, although when considering equilibrant processes one should use mol %; however, because of the comparatively large molecular masses of polymers in the cases examined here, this distinction may be of no vital significance.

Thus it may be expedient to generalize the data from Aminabhavi et al.<sup>5</sup> on polymer/organic solvent interactions by means of eq. (1) but supplemented with a term that takes into account the influence of molar volume  $V_M$ , expressed in mol/mL:

$$\log S = a_0 + a_1 \left( \frac{n^2 - 1}{n^2 + 2} \right) + a_2 \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M \quad (2)$$

In the present study we consider the swelling data of the membrane samples from ethylene-propylene copolymer, structured by the addition of 3-8% divinyl followed by vulcanization in the presence of sulfur. Table I presents data, from Aminabhavi et al.,<sup>5</sup> on the degree of swelling  $S_M$  of these samples in organic solvents at 25, 44, and 60°C in mol %, as well as the swelling enthalpies  $\Delta H_s$  in kJ/mol. The necessary solvent characteristics are given in a previous study<sup>13</sup> and the calculations were made according to the recommendations of the Group of Correlation Analysis in Chemistry (CAC) at IUPAC.<sup>14</sup>

Here we note that, by means of eq. (2), all  $\log S$  values at 25°C yield an unsatisfactory generalization because the value of the multiple correlation coefficient  $R$  is only 0.915. However, after excluding from consideration (as recommended by the CAC<sup>14</sup>) data for the poorest solvent (i.e., nitrobenzene), we may satisfactorily correlate the remaining 26 solvents by the following equation, which characterizes the distinct influence of the solvation effect on  $\log S$ :

$$\begin{aligned} \log S = & 2.82 + (6.91 \pm 1.63)f(n^2) \\ & + (4.20 \pm 1.05)f(\epsilon) - (1.91 \pm 0.66)10^{-3}B \\ & - (0.14 \pm 0.03)E_T - (2.11 \pm 1.30)10^{-3}\delta^2 \\ & - (3.18 \pm 0.61)10^{-3}V_M \end{aligned} \quad (3)$$

The value of  $R$  for eq. (3) is 0.955; the pair-correlation coefficients  $r_i$  for the separate terms are

**Table I Degree of Swelling ( $S_M$ ) and Adsorption Enthalpies of Swelling ( $\Delta H_s$ ) of Ethylene-Propylene-Butadiene Copolymer Membrane Samples at 25, 44, and 60°C**

Sample	Solvent	$S_M$ (mol %)			$\Delta H_s$ (kJ/mol)
		25°C	44°C	60°C	
1	Hexane	0.79	0.76	0.74	-1.70
2	Heptane	0.71	0.68	0.66	-1.95
3	Octane	0.65	0.63	0.61	-1.44
4	Nonane	0.60	0.59	0.58	-0.92
5	Decane	0.54	0.53	0.52	-0.84
6	Dodecane	0.46	0.45	0.44	-1.10
7	Tetradecane	0.39	0.38	0.38	-0.48
8	Hexadecane	0.34	0.33	0.23	-1.10
9	Isooctane	0.57	0.55	0.54	-1.18
10	Cyclohexane	1.28	1.27	1.23	-0.87
11	Tetraline	0.88	0.89	0.89	0.30
12	Benzene	1.05	1.11	1.16	2.34
13	Toluene	1.09	1.09	1.09	0.18
14	<i>m</i> -Xylene	1.05	1.04	1.04	-0.18
15	1,3,5-Trimethylbenzene	0.91	0.89	0.88	-0.78
16	Fluorobenzene	0.88	0.94	0.96	2.17
17	Chlorobenzene	1.15	1.17	1.18	0.68
18	Bromobenzene	1.03	1.07	1.11	1.82
19	Nitrobenzene	0.09	0.12	0.14	11.83
20	Aniline	0.03	0.06	0.07	20.90
21	Cyclohexanone	0.25	0.32	0.39	10.66
22	Anisole	0.36	0.45	0.52	8.66
23	Methylacetate	0.087	0.11	0.12	50.72
24	Ethylacetate	0.13	0.17	0.20	34.90
25	<i>n</i> -Propylacetate	0.18	0.23	0.27	37.04
26	Butylacetate	0.22	0.27	0.30	34.19
27	Isoamylacetate	0.23	0.26	0.30	35.29

Values derived according to Aminabhavi et al.<sup>5</sup>

0.176, 0.549, 0.804, 0.664, 0.302, and 0.08, respectively; and the average square error  $s$  is  $\pm 0.118$ .

Analysis of the signs of the separate equation terms leads to the following conclusions: increases of the solvent's molecular dimensions and energy expenditure for its extraction from the liquid structure both cause a decrease in the solvent's ability to be assimilated into the polymer structure (the minus signs at the corresponding equation terms). Moreover, the increased propensity for acid-base interactions, characterized by the terms  $B$  and  $E_T$ , depresses the absorption process that conforms to the neutral hydrophilic character of the polyethylene polymer. However, some nonspecific interaction between polymer and solvent is evidently possible because the terms that denote the polarizability and polarity of solvent have a plus sign.

The adequacy of eq. (3) and appropriate  $R$  values is confirmed, as in all subsequent cases as

well, by comparing the calculated values of Fisher's criterion  $F_{\text{calc}}$ , which are greater than the tabulated values  $F_{\text{tab}}$  for the corresponding number of degrees of freedom at a degree of reliability  $\alpha = 0.95$ .

Nevertheless, both the absolute values of regression coefficients and those of pair-correlation coefficients do not reliably characterize their influence on  $\log S$ . It may be determined only by excluding, in turn, each separate equation term and recalculating  $R$  values each time for the obtained equations with the identified number of terms.<sup>14</sup> This procedure confirms the predominant influence of the molar volume factor  $V_M$ ; in that its exclusion lowers the  $R$  value of the obtained five-parameter equation to an intolerably low value of 0.880. Similarly, the exclusion of  $f(n^2)$ ,  $f(\epsilon)$ , or  $E_T$  terms lowers  $R$  to 0.918–0.924; the  $\delta^2$  and  $B$  terms are shown to be of only slight significance because their exclusion lowers  $R$  to

**Table II** Experimental and Calculated Values of  $\log S_M$  at 25°C for Ethylene-Propylene-Butadiene Copolymer Swelling

Sample	Solvent	$\log S_{\text{exp}}$	$\log S_{\text{calc}}$	$\Delta \log S$
1	Hexane	-0.0993	-0.1287	0.0294
2	Heptane	-0.1478	-1.5218	0.0044
3	Octane	-0.1851	-1.7423	0.0109
4	Nonane	-0.2167	-1.8339	0.0334
5	Decane	-0.2682	-2.1962	0.0485
6	Dodecane	-0.3332	-3.1261	0.0206
7	Tetradecane	-0.4093	-4.1532	0.0061
8	Hexadecane	-0.4707	-4.5359	0.0169
9	Isooctane	-0.2443	-8.6462	0.1578
10	Cyclohexane	0.1076	15.095	0.0434
11	Tetraline	-0.0555	1.6820	0.2237
12	Benzene	0.0212	-1.0186	-0.1231
13	Toluene	0.0374	-0.9526	-0.1327
14	<i>m</i> -Xylene	0.2119	-0.9631	-0.1175
15	1,3,5-Trimethylbenzene	-0.4096	-1.2767	-0.0867
16	Fluorobenzene	-0.0555	-0.9159	-0.0361
17	Chlorobenzene	0.0607	-0.3818	-0.0988
18	Bromobenzene	0.0128	0.0555	-0.0073
19	Nitrobenzene	-1.0458	0.2346	0.8111
20	Aniline	-1.5229	-13.563	0.1665
21	Cyclohexanone	-0.6056	-6.6015	-0.0546
22	Anisole	-0.4437	-3.4182	0.1019
23	Methylacetate	-1.0605	-9.0451	0.1560
24	Ethylacetate	-0.8861	-6.9082	0.1952
25	<i>n</i> -Propylacetate	-0.7376	-6.9910	0.0385
26	Butylacetate	-0.6498	-8.7462	-0.2249
27	Isoamylacetate	-0.6383	-9.3019	0.2919

Calculated values are derived from eq. (4).

0.950 or 0.939. Thus, the link between  $\log S$  values and physicochemical solvent properties may be adequately described by means of the following five-parameter equation:

$$\begin{aligned} \log S = & 3.15 + (4.64 \pm 0.90)f(n^2) \\ & + (3.31 \pm 0.94)f(\epsilon) - (1.85 \pm 0.70)10^{-3}B \\ & - (0.15 \pm 0.03)E_T - (3.52 \pm 0.62)10^{-3}V_M \\ R = & 0.950; \quad s = \pm 0.125 \end{aligned} \quad (4)$$

Comparisons of experimental  $\log S$  values and those calculated by means of eq. (4) as well as divergences of these values ( $\Delta \log S$ ) are given in Table II.

It is obvious that the  $\Delta \log S$  values (excluding that for nitrobenzene, which was rejected) approach limits of  $s$  of  $\pm 0.125$  or only negligibly exceed these limits (esters, tetraline, and aniline). In addition the following four-parameter equation

is adequate according to Fisher's criterion, even though the  $R$  value here is somewhat lower:

$$\begin{aligned} \log S = & 4.94 + (5.60 \pm 0.93)f(n^2) \\ & + (4.30 \pm 0.16)f(\epsilon) - (0.22 \pm 0.02)E_T \\ & - (3.86 \pm 0.68)10^{-3}V_M \\ R = & 0.934; \quad s = \pm 0.141 \end{aligned} \quad (5)$$

However, the subsequent exclusion of any term would destroy the correlation because the value of  $R$  falls below 0.9.

In this way we see that eq. (2), as proposed, is essentially more adequate to describe the influence of solvent properties on swelling than that used by Aminabhavi et al.,<sup>5</sup> which depends solely on the molar volume. For the function  $\log S = f(V_M)$  for 26 solvents (after excluding  $\text{PhNO}_2$ ), the value of  $R$  is only 0.879; corresponding  $R$  values for divided solvent groups are still lower:

for low-polarity solvents (Table I, samples 1–18)  $R$  is 0.726; for more polar solvents (Table I, samples 19–27)  $R$  is 0.590.

Similar results, in terms of the signs and significance of separate terms on  $\log S$  values, were obtained by generalizing  $\log S$  data at 44 and 60°C (Table I). Here we give only the six-parameter equations [eq. (2) type] for 26 solvents (data for nitrobenzene are excluded):

For 44°C:

$$\begin{aligned} \log S = & 2.38 + (6.82 \pm 1.40)f(n^2) \\ & + (3.76 \pm 0.90)f(\epsilon) - (1.44 \pm 0.57)10^{-3}B \\ & - (0.12 \pm 0.03)E_T - (1.99 \pm 1.11)10^{-3}\delta^2 \\ & - (3.70 \pm 0.53)10^{-3}V_M \\ R = & 0.954; \quad s = \pm 0.102 \end{aligned} \quad (6)$$

For 60°C:

$$\begin{aligned} \log S = & 2.57 + (6.86 \pm 1.43)f(n^2) \\ & + (4.02 \pm 0.91)f(\epsilon) - (1.15 \pm 0.58)10^{-3}B \\ & - (0.13 \pm 0.03)E_T - (2.21 \pm 1.13)10^{-3}\delta^2 \\ & - (4.10 \pm 0.54)10^{-3}V_M \\ R = & 0.947; \quad s = \pm 0.105 \end{aligned} \quad (7)$$

Nonetheless, we must indicate that the separate treatment of the two solvent groups [i.e., hydrophobic solvents of only low polarity and practically incapable of specific interaction (Table I, samples 1–18) and the more polar heteroatomic solvents (Table I, samples 19–27)] allows us to obtain equations with even greater degrees of correlation and distinct validity of separate factors. Thus, the molar volume factor is decisive for the first group of solvents as the pair-correlation coefficient of  $\log S$  at 25°C with  $V_M$  is 0.953, and inserting the other terms in the calculation increases the correlation only negligibly. For the six-parameter equation,  $R = 0.976$ , although the following three-parameter equation is also adequate:

$$\begin{aligned} \log S = & 0.42 + (1.96 \pm 0.55)f(n^2) \\ & + (0.020 \pm 0.007)E_T \\ & - (2.81 \pm 0.21)10^{-3}V_M \\ R = & 0.973; \quad s = \pm 0.04 \end{aligned} \quad (8)$$

Here the influence of individual factors is the same as that in the summary eqs. (3)–(5).

For polar solvents 19–27, correlation with  $V_M$  is considerably poorer ( $R = 0.884$ ). The influence of other solvation factors is more important, although their validity and signs are often opposite as in eq. (3) or for low-polarity solvents as in eq. (8):

$$\begin{aligned} \log S = & 4.40 + (3.47 \pm 2.76)f(n^2) \\ & + (1.48 \pm 2.16)f(\epsilon) - (0.90 \pm 0.53)10^{-3}B \\ & - (0.19 \pm 0.02)E_T - (6.29 \pm 3.05)10^{-3}\delta^2 \\ & - (7.53 \pm 2.26)10^{-3}V_M \\ R = & 0.968; \quad s = \pm 0.082 \end{aligned} \quad (9)$$

and

$$\begin{aligned} \log S = & 4.51 + (0.90 \pm 0.55)10^{-3}B \\ & - (0.19 \pm 0.03)E_T - (3.09 \pm 0.89)10^{-3}\delta^2 \\ & - (5.76 \pm 1.96)10^{-3}V_M \\ R = & 0.966; \quad s = \pm 0.096 \end{aligned} \quad (10)$$

The subsequent exclusion of the  $B$  term leads to the decrease of  $R$  to 0.948, of the  $\delta^2$  term to 0.900, and of the  $E_T$  term to 0.706.

Thus we may presume that there are two essentially different mechanisms of ethylene-propylene copolymer interaction with solvents, depending on their characteristics. The swelling in low-polarity solvents depends only on their molar volume, although for higher-polarity solvents the solvents' ability for electrophilic solvation, which diminishes the value of  $\log S$ , remains important. We note that because Aminabhavi et al.<sup>5</sup> did not correctly divide the solvents into distinct groups, they did not arrive at a satisfactory interpretation. Thus, in the aliphatic hydrocarbons group they placed the polar cyclohexanone, and in the group of monocyclic aromatics they included both low-polarity solvents, such as hydrocarbons and halogenohydrocarbons, and high-polarity solvents, such as nitrobenzene and aniline.

Additionally, the adsorption enthalpy values  $\Delta H_s$  from Table I may be generalized by means of a common multiparameter equation, although in this case it is necessary to exclude the data for cyclohexanone and to consider other factors as valid, as is the case of  $\log S$ . It is obvious that, in most instances, the signs on separate terms are opposite to those in eqs. (3)–(6).



$$\begin{aligned}\Delta H_s &= 87.04 - (417.1 \pm 54.4)f(n^2) \\ &+ (42.3 \pm 38.7)f(\epsilon) - (0.11 \pm 0.02)B \\ &- (0.10 \pm 1.37)E_T - (0.16 \pm 0.05)\delta^2 \\ &- (0.02 \pm 0.02)V_M \\ R &= 0.960; \quad s = \pm 3.87\end{aligned}\quad (11)$$

and

$$\begin{aligned}\Delta H_s &= 68.64 - (43,431 \pm 39.6)f(n^2) \\ &+ (0.09 \pm 0.01)B + (0.10 \pm 1.37)E_T \\ &+ (0.16 \pm 0.02)\delta^2 \\ R &= 0.966; \quad s = \pm 4.07\end{aligned}\quad (12)$$

Moreover, Aminabhavi et al.<sup>5</sup> do not state any simple dependencies between adsorption enthalpy  $\Delta H_s$  and  $V_M$ . It is clear that  $\Delta H_s$  values acquire not only various magnitudes but even various signs, depending on the peculiarities of the solvent structures.

By analogy with the  $\log S$  case here it is also possible to separate calculations for polar and nonpolar solvents, although such an operation yields only slightly satisfactory results. For nonpolar solvents the results are appreciably poorer ( $R = 0.884$ ) and to achieve a satisfactory correlation ( $R = 0.964$ ) it is necessary to exclude the data for two solvents, isooctane and cyclohexane, from the calculations. The determinative factor here is the cohesion energy density ( $R = 0.863$ ), although for satisfactory generalization of available data it is necessary to use a five-parameter equation without the basicity term. For nine polar solvents an equation with  $R = 0.979$  is obtained, although the following four-parameter equation yields sufficiently accurate results:

$$\begin{aligned}\Delta H_s &= -350.10 - (384.0 \pm 34.0)f(n^2) \\ &+ (181.6 \pm 35.1)f(\epsilon) - (0.07 \pm 0.02)B \\ &- (6.31 \pm 0.93)E_T - (0.16 \pm 0.05)\delta^2 \\ &- (0.02 \pm 0.02)V_M \\ R &= 0.976; \quad s = \pm 3.20\end{aligned}\quad (13)$$

The slipshod results obtained by attempts to construct some dependencies between  $\Delta H_s$  values and solvent characteristics are possibly caused by the not fully reliable results given in Aminabhavi et al.<sup>5</sup> The corresponding magnitudes of  $\Delta H_s$  are

derived from the  $\log S$  values for only three temperatures (i.e., on three points) and by construction of any linearity in  $\log S - 1/T$  coordinates one often observes significant deviations.

One may ascertain some one-sidedness in solvent selection in Aminabhavi et al.,<sup>5</sup> particularly the absence of aliphatic halogenohydrocarbons and hydrophylic alcohols. Therefore, we examined by analogous mathematical treatment the swelling data from Richards<sup>3</sup> on polyethylene samples (MW = 9400) in 30 solvents of varying characteristics. We previously showed<sup>12</sup> that these data may be generalized with satisfactory accuracy by means of the five-parameter equation [eq. (1) type], although we did not take into account the important factor  $V_M$ . Moreover, the data in Richards<sup>3</sup> are given in volume percentages (vol %) of solvent adsorbed by 1 vol of polymer, whereas in this case it is more accurate to use mol % in the calculations. Table III shows both the volumes of adsorbed solvents  $S_V$  (according to Richards<sup>3</sup>) and the mol % of solvent  $S_M$  adsorbed by the sample. The generalization of these data by means of eq. (2) results in an equation with  $R = 0.937$ , and the exclusion of the poorest data for acetone (sample 30) leads to the following equation, with a satisfactory degree of correlation:

$$\begin{aligned}\log S_M &= 2.36 + (0.85 \pm 1.57)f(n^2) \\ &+ (0.24 \pm 1.01)f(\epsilon) - (0.36 \pm 0.48)10^{-3}B \\ &- (0.14 \pm 0.02)E_T - (1.02 \pm 1.03)10^{-3}\delta^2 \\ &- (8.20 \pm 1.30)10^{-3}V_M \\ R &= 0.956; \quad s = \pm 0.245\end{aligned}\quad (14)$$

and the pair-correlation coefficients with individual factors  $r_I$  are 0.186, 0.771, 0.531, 0.862, 0.639, and 0.05, respectively. Here, we may presume that the noncoordinate  $S_v$  value 0.02 for acetone is, in all likelihood, understated in Richards<sup>3</sup> by 10-fold compared to that in structure esters or benzaldehyde, in which the value of solvent adsorbed by the polymer sample is 0.02.

After excluding insignificant terms, we arrive at an adequate three-parameter equation:

$$\begin{aligned}\log S_M &= 2.71 - (0.15 \pm 0.01)E_T \\ &+ (1.48 \pm 0.85)10^{-3}\delta^2 \\ &- (7.95 \pm 1.27)10^{-3}V_M \\ R &= 0.955; \quad s = \pm 0.248\end{aligned}\quad (15)$$

**Table III** Volume Percentage ( $S_v$ ), Weight Percentage ( $S_g$ ), and Mole Percentage ( $S_M$ ) Values for Polyethylene (MW = 9400) Swelling

Sample	Solvent	$S_v$ (vol %)	$S_g$ (wt %)	$S_M$ ( $\times 10^3$ ) (mol %)
1	Pentane	0.21	0.13	1.8
2	Hexane	0.28	0.19	2.1
3	Heptane	0.31	0.21	2.1
4	Benzene	0.22	0.19	2.5
5	Toluene	0.25	0.22	2.4
6	<i>m</i> -Xylene	0.29	0.25	2.4
7	Cyclohexane	0.40	0.31	3.7
8	Tetraline	0.29	0.28	2.1
9	Decaline	0.39	0.34	2.5
10	CHCl <sub>3</sub>	0.28	0.42	3.5
11	CCl <sub>4</sub>	0.40	0.64	4.1
12	Trichloroethylene	0.43	0.62	4.7
13	Dibromoethane	0.08	0.17	0.9
14	Chlorobenzene	0.25	0.28	2.5
15	Ethanol	0.002	0.0016	0.034
16	<i>n</i> -Propanol	0.004	0.0032	0.054
17	<i>n</i> -Pentanol	0.005	0.0041	0.046
18	<i>n</i> -Octanol	0.0009	0.00074	0.0057
19	Diethylether	0.14	0.10	1.4
20	Acetic acid	0.001	0.0010	0.017
21	Benzaldehyde	0.024	0.025	0.23
22	Ethylacetate	0.025	0.023	0.26
23	Butylacetate	0.070	0.062	0.53
24	Amylacetate	0.070	0.061	0.47
25	Dibutylphthalate	0.006	0.0063	0.023
26	Aniline	0.008	0.0082	0.088
27	Methylaniline	0.025	0.025	0.23
28	Dimethylaniline	0.110	0.105	0.87
29	Nitrobenzene	0.019	0.023	0.19
30	Acetone	0.002	0.0016	0.027

Data are from Richards.<sup>3</sup>

After excluding the  $\delta^2$  term,  $R$  decreases to 0.950. Both the signs and magnitudes of regression coefficients are similar to those in eqs. (4) and (5), which generalize the results from Aminabhavi et al.<sup>5</sup> We should note that eq. (14), the  $R$  value of which is 0.956, is of the same degree of trustworthiness as the equation given in Makitra et al.<sup>12</sup> At the same time an attempt to generalize the swelling data  $S_g$  given in wt % (Table III) gives unsatisfactory results: to obtain a value of  $R > 0.950$ , it is necessary to exclude from consideration the data for six solvents.

We may note that here, as in the previous case, it is possible to discretely examine the data for both polar and nonpolar solvents, including in the latter halogenohydrocarbons. But unlike eq. (8) for the case of a low-polarity solvent with the structural factors  $\delta^2$  and  $V_M$ , which here are in-

significant, the determinative role belongs to non-specific solvation factors that favor adsorption and the ability for electrophilic solvation, which diminishes it. The unimportant role of structural factors is possibly the result of the nearly identical dimensions of the solvents under investigation, excluding the higher  $n$ -alkanes. The following three-parameter equation, thus obtained for 12 of the solvents [Table III, solvents 1–14, after excluding data for tetraline (solvent 8) and chlorobenzene (solvent 14)], is characterized by  $R = 0.980$ ; moreover, this equation, which corresponds to eq. (8), yields adequate results:

$$\begin{aligned} \log S_g = & 3.00 + (2.30 \pm 0.86)f(n^2) \\ & - (10.90 \pm 1.51)f(\epsilon) - (0.21 \pm 0.03)E_T \\ R = & 0.951; \quad s = \pm 0.07 \end{aligned} \quad (16)$$

For the 15 polar solvents, which include the alcohols [Table III, samples 15–29 but without acetone (sample 30)], we obtain a six-parameter equation with  $R = 0.958$  and the simplified four-parameter equation with the same significant terms, analogous to eq. (9), which describes the polar solvent influence on the swelling of ethylene–propylene copolymer:

$$\begin{aligned} \log S_g &= 3.89 + (0.63 \pm 0.51)10^{-3}B \\ &\quad - (0.14 \pm 0.02)E_T - (1.05 \pm 0.92)10^{-3}\delta^2 \\ &\quad - (3.49 \pm 1.29)10^{-3}V_M \\ R &= 0.957; \quad s = \pm 0.207 \end{aligned} \quad (17)$$

This investigation thus confirms the above-mentioned opinion that the degree of polymer swelling is determined not only by solvent molar volume (i.e., solvent molecule dimensions) but also by the influence of other characteristics. To obtain a quantitative relation between these diverse magnitudes, one must consider the basis of the principle of free-energy linearity by means of linear polyparameter equations. In the case of polyethylene polymers, their degree of swelling decreases with the increase of solvent molar volume  $V_M$  and their ability for electrophilic solvation, which is really linked with their hydrophilicity, increases with an increase of solvent polarizability.

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