Study of Acceptor–Donor Interactions at the Polymer Interface by Inverse Gas Chromatography Data Analysis

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ABSTRACT: Analysis of inverse gas chromatography (IGC) data supports Fowkes's theory of acceptor–donor (acid–base) interactions at the polymer interface. Moreover, this analysis allows one to estimate Drago parameters of some polymers and IGC probes.

Introduction

In fields of polymer science such as composites, blends, and adhesion, interfacial interactions may play a critical role in determining material properties. The magnitude of these interfacial forces ranges from the strong covalent or ionic chemical bonds to the comparatively weak van der Waals interaction. In many systems of interest, however, chemical bonds are essentially absent and hence do not contribute significantly to the interfacial strength. Thus, interfacial properties are often determined by the strength of nonbonded interactions. In contrast to the degree of understanding that we currently have of the chemical bond, knowledge of nonbonded interactions is essentially limited to a qualitative level. The focus of the present work is on nonbonded interfacial forces at the polymer interface.

Fowkes[1] has proposed a quantitative description of polymer interfaces based on acceptor–donor interactions. This theory involves the acid–base interaction heat at the polymer interface, ΔH^{ab}, a parameter that is difficult to obtain by normal calorimetry. The method of IGC, however, can provide a related parameter, namely, the adsorption heat in the "infinite" dilution region ΔH. This parameter can be precisely calculated from the slope of the plot of ln V_g versus $1/T$, where V_g is the specific retention volume and T is the absolute temperature. It is suggested here that ΔH^{ab} can be calculated from ΔH, and thus IGC data can be used to verify the theory of Fowkes.

It is known that ΔH values computed from IGC data acquired above the glass transition temperature, T_g, are the sum of surface and bulk (solution) contributions. To eliminate these complications, one could use IGC data taken below the polymer T_g. As will be described, however, the calculation of ΔH^{ab} can only be performed from IGC data that meet specific requirements. Unfortunately, there are almost no IGC data available that were acquired below T_g and meet these special requirements. An important point to be noted here, however, is that since ΔH values obtained from IGC data are calculated under the condition of infinite dilution of probe molecules, it is reasonable to expect that they represent predominately a surface contribution. Yang[2] has recently carried out an IGC study of several polymer–probe pairs, taking data below the polymer T_g. These data were then compared to ΔH values obtained from IGC data acquired above T_g. Interestingly, no significant difference was found. In fact, the results of the IGC data plotted as a ln V_g versus $1/T$ curve reveal that the linear segment above T_g is always approximately parallel to that below T_g. Therefore, it is reasonable to assume that ΔH values calculated from IGC data acquired above T_g are approximately equivalent to the adsorption heat of probe molecules on the polymer surface.

In this article several sets of published IGC data have been analyzed. The results of this study support Fowkes' theory quite well and also provide several sets of Drago parameters of polymers and probes.

Theory

The thermodynamic work of adhesion can be defined as

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1}$$

where γ_1 and γ_2 are the surface free energy of phase 1 and phase 2, respectively. γ_{12} is the interface free energy between phase 1 and phase 2. According to the geometric mean assumption

$$\gamma_{12} = \gamma_1 + \gamma_2 + 2\psi(\gamma_1\gamma_2)^{1/2} \tag{2}$$

where ψ is a parameter close to unity. The surface free energy of a substance is assumed to be the sum of several types of intermolecular interactions:

$$\gamma = \sum_i \gamma^i \tag{3}$$

where γ^i represents various contributions to γ such as dispersion (i = d), dipole (i = p), and hydrogen bond (i = h) interactions.

An expression for the thermodynamic work of adhesion can be obtained[3] by combining eq 1–3:

$$W_q = 2\psi(\gamma_1\gamma_2)^{1/2} = \sum_i W_a^i \tag{4}$$

If $\psi = 1$, it can be assumed that $W_a^d = 2(\gamma_1^d\gamma_2^d)^{1/2}$ and $W_a^p = 2(\gamma_1^p\gamma_2^p)^{1/2}$. It is important to note that, in general, $W_a^h \neq 2(\gamma_1^h\gamma_2^h)^{1/2}$, since hydrogen bonding acceptors such as ethers or esters cannot themselves form hydrogen bonds. Therefore, γ^h is 0 for such materials, even though they have large W_a^h values with hydrogen donors.

From polymer solution theory, the heat of mixing ΔH_m and the solubility parameter δ are divided into several independent components:[4]

$$\Delta H_m = \sum_i \Delta H_m^i \tag{5}$$

$$\delta^2 = \sum_i (\delta^i)^2 \tag{6}$$

According to the geometric mean assumption, ΔH_m^d can be given by the Hildbrand relationship $\Delta H_m^d = V_m\varphi_1\varphi_2(\delta_1^d - \delta_2^d)^2$, and similarly ΔH_m^p can be given as $\Delta H_m^p = V_m\varphi_1\varphi_2(\delta_1^p - \delta_2^p)$. In these equations, V_m represents the total volume of solution and φ_1 and φ_2 are the volume fractions of component 1 and component 2, respectively. ΔH_m^h cannot however be expressed as $V_m\varphi_1\varphi_2(\delta_1^h - \delta_2^h)^2$.

A useful approach for describing hydrogen bonding as well as dipole–dipole interactions at an interface has been proposed by Fowkes[1] based on acid–base type interactions. According to Drago,[5] an empirical correlation exists for the

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enthalpy of mixing an acid (i.e., electron acceptor) and a base (i.e., electron donor):

$$-\Delta H^{ab} = C_a C_b + E_a E_b \quad (7)$$

Two empirical parameters are assigned to each acid (C_a and E_a) and each base (C_b and E_b), so that when substituted into eq 7, they give the correct ΔH^{ab} for the acid–base pair. The values of C and E are then used to predict ΔH^{ab} for other acid–base pairs. Values of ΔH^{ab} calculated in this way for a great variety of materials agree very well with those experimentally determined, usually within 5% or less.

Applying these concepts to interactions at polymer interfaces, Fowkes proposed two basic assumptions. First, the interaction at the polymer interface can be divided into dispersion and acid–base components. The hydrogen bonding interactions have been included in the acid–base term, and the dipole–dipole interactions are often negligibly small. These assumptions yield

$$W_a = W_a^d + W_a^{ab} \quad (8)$$

$$\Delta H_m = \Delta H_m^d + \Delta H_m^{ab} \quad (9)$$

Second, Fowkes assumed that Drago's four-parameter equation (eq 7) can be applied to polymer systems.

To verify Fowkes's assumptions mentioned, one must obtain the dispersion component ΔH^d and the acid–base component ΔH^{ab} of polymer interfacial interaction. It is, however, very difficult to obtain these parameters by normal calorimetry. Therefore, it is suggested here that IGC data may be useful in addressing this problem. According to chromatography theory, the adsorption heat ΔH between the probe molecule and the polymer of stationary phase can be expressed as follows:

$$-\Delta H = R\,\partial \ln V_g/\partial(1/T) = \Delta H_1 + \Delta H_2 - \Delta H_{12} \quad (10)$$

where R is the gas constant, ΔH_1 is the latent heat of evaporation of the probe molecule, and ΔH_2 is the heat of "hole formation", determined by the heat expended on formation of a vacancy in a stationary-phase environment when a probe molecule takes its place. ΔH_{12} is the probe–stationary phase interaction heat. According to the Fowkes' assumption

$$\Delta H_{12} = \Delta H^d + \Delta H^{ab} \quad (11)$$

Substitution in eq 10 gives

$$-\Delta H = \Delta H_1 + \Delta H_2 - \Delta H^d - \Delta H^{ab} \quad (12)$$

With a series of normal alkanes as probes and a given polymer as the stationary phase, it is possible to determine the corresponding ΔH over a given temperature range. In this case ΔH^{ab} is 0 because the normal alkanes are neutral. At the same time, it is reasonable to assume that $(\Delta H^d)_{M\to 0} = 0$, where M is the molecular weight of the probe. Therefore, we can obtain the ΔH_2 for a given column from the following expression:

$$\Delta H_2 = (-\Delta H)_{M\to 0} - (\Delta H_1)_{M\to 0} \quad (13)$$

In eq 13 $(-\Delta H)_{M\to 0}$ is the extrapolated value of $-\Delta H$, and $(\Delta H_1)_{M\to 0}$ is the extrapolated value of ΔH_1, which can be obtained from literature data. Furthermore, we can obtain ΔH^d for a series of normal alkanes for a given column using

$$-\Delta H^d = -\Delta H - \Delta H_1 - \Delta H_2 \quad (14)$$

The relationship between $-\Delta H^d$ and M of a series of normal alkanes is given by

$$-\Delta H^d = KM \quad (15)$$

At this point, an additional assumption is introduced. Specifically, it is assumed that ΔH^d values of the all other probes (besides normal alkanes) used in the same column obey eq 15. This allows ΔH^{ab} to be determined for any probe molecule–polymer pair in a given column from the expressions

$$-\Delta H^{ab} = -\Delta H - \Delta H_1 - \Delta H_2 + \Delta H^d = -\Delta H - \Delta H_1 - \Delta H_2 - KM \quad (16)$$

The next step is to verify eq 7. Unfortunately, few polymer Drago parameters are reported, and only a few of materials listed by Drago[6] are suitable as probes for IGC. So that this problem can be circumvented, it is suggested to collect a group of IGC data for l normal alkanes and m acid and/or base probes in n different columns. All ΔH values obtained by the IGC method are to be measured under identical conditions. From the ΔH values of normal alkanes we can get ΔH_2 and the relationships between ΔH^d and M (molecular weight of the probe) for each column. From ΔH of acid and base probes we can obtain the corresponding ΔH^{ab} and then establish the following $m \times n$ equations:

$$-\Delta H^{ab}{}_k = (C_a)_i(C_b)_j + (E_a)_i(E_b)_j \quad (17)$$

where $i = 1, 2, 3, \ldots, m$, $j = 1, 2, 3, \ldots, n$, and $k = 1, 2, 3, \ldots, (m \times n)$. It is to be noted that there are $(2m + 2n)$ unknown Drago parameters and mn equations. When $mn > 2m + 2n$, we can obtain $(mn)!/(2m + 2n)!(mn - 2m - 2n)!$ solutions. If the previously mentioned assumptions are correct, then all solutions should be similar. By averaging, we can obtain a set of best Drago parameters for each of the m probes and n polymers. Substitution of these values into eq 7 provides a calculated value for ΔH. Comparing these values with the corresponding values obtained from IGC data, we can verify all of the previously mentioned assumptions.

Results and Discussion

As a simple example, the IGC data of low-density polyethylene (LDPE) reported by Tseng et al.[7] are analyzed first. The specific retention volumes of 13 probes at 6 temperatures within the range 50–175 °C have been collected in Table I. It can be seen that there is a linear relationship between ln V_g and $1/T$. Thus ΔH can be calculated from the slopes of the plot ln V_g versus $1/T$ by eq 10. On the other hand, it is difficult to obtain ΔH_1 values of probes at a given temperature (in this example, 120 °C has been chosen) since ΔH_1 has notable temperature dependence. From the literature,[8] the only available data of ΔH_1 of probe molecules are values at 25 °C and at the probe boiling point. As an approximate calculation, it was thus assumed that the relationship between ΔH_1 and T is linear within the region between 25 °C and the boiling point of the probe. With this assumption, the probe's ΔH values at 120 °C can be calculated from their known values at 25 °C and the boiling point. All of the ΔH and ΔH_1 values are listed in Table II.

From the data of the four normal alkanes, it was found that there is a very good linear relationship between ΔH and the probe molecular weight M as well as between ΔH_1 and M. These relationships and their coefficient of correlation, r, were found to be

$$-\Delta H = -17.5 + 0.372M \qquad r = 0.998$$

$$\Delta H_1 = -1.26 + 0.316M \qquad r = 1.000$$

Thus we can obtain

$$\Delta H_2 = (-\Delta H)_{M\to 0} - (\Delta H_1)_{M\to 0} = -17.5 + 1.26 = -16.2 \text{ kJ/mol}$$

Table I
Specific Retention Volume Data of LDPE Column[a]

probe	V_g, cm³/g					
	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C
tetrahydrofuran	33.86	19.24	14.40	11.92		
1-octene	175.38	76.57	49.08	35.70	19.24	10.24
1-nonene	446.30	174.77	99.40	67.45	33.47	17.81
heptane	79.08	37.77	36.73	21.69	12.27	
octane	207.47	87.73	54.91	39.45	21.96	12.55
nonane	542.19	198.00	112.21	74.04	36.73	19.17
decane	1434.85	452.90	233.71	139.22	63.97	31.26
benzene	58.01	32.52	22.59	18.96	11.79	
toluene	169.74	81.46	50.90	40.17	22.18	12.94
chlorobenzene	347.65	150.76	93.35	64.65	34.71	19.43
p-xylene	481.42	188.26	112.99	74.37	38.56	21.50
cumene	626.61	246.15	142.37	94.99	49.38	25.11
n-butylbenzene	2172.69	729.39	380.05	221.75	100.61	49.15

[a] Taken from Table 1 of ref 7.

Table II
$-\Delta H$, ΔH_1, and $-\Delta H^{ab}$ Data of LDPE Column

probe	M	$-\Delta H$, kJ/mol	ΔH_1, kJ/mol	$-\Delta H^{ab}$, kJ/mol
tetrahydrofuran	72	14.7	26.4	0.5
heptane	100	19.3	30.3	0
octane	114	25.4	34.90	0
nonane	128	30.4	39.3	0
decane	142	35.0	43.6	0
1-octene	112	25.4	33.8	1.5
1-nonene	126	29.3	38.3	0.1
benzene	78	16.9	28.4	0.3
toluene	92	23.2	32.6	1.6
chlorobenzene	113	26.2	37.2	−1.1
p-xylene	106	28.7	36.9	2.1
cumene	120	29.2	39.4	−0.7
n-butylbenzene	134	34.8	43.9	−0.4

Using these values of ΔH, ΔH_1, and ΔH_2, the $-\Delta H^d$ values of heptane, octane, nonane, and decane are found to be 5.2, 6.7, 7.4, and 7.6 kJ/mol, respectively. Thus, we can establish the following linear equation:

$$-\Delta H^d = 0.056M \qquad r = 0.996$$

From eq 16, $-\Delta H^{ab}$ values of the other nine probes can be calculated. These have also been summarized in Table II.

As seen in Table II, all values of ΔH^{ab} are close to 0. This result is not surprising in light of the neutral character of LDPE. In fact, using the Drago parameters of benzene [C_b = 1.44 (kJ/mol)$^{1/2}$, E_b = 0.991 (kJ/mol)$^{1/2}$], *p*-xylene [C_b = 3.63 (kJ/mol)$^{1/2}$, E_b = 0.849 (kJ/mol)$^{1/2}$], and tetrahydrofuran [C_b = 8.71 (kJ/mol)$^{1/2}$, E_b = 2.00 (kJ/mol)$^{1/2}$], as can obtain the corresponding Drago parameters of LDPE: C_a = 0.4 (kJ/mol)$^{1/2}$ and E_a = −0.2 (kJ/mol)$^{1/2}$. They are very close to 0. The maximum deviation of ΔH^{ab} from 0 (about 2 kJ/mol) can be considered as an estimate of error in the ΔH^{ab} values determined by our method. From the example of LDPE it can be concluded that the previously mentioned method works well for determining the ΔH^{ab}. This example, however, cannot be used to verify Fowkes' theory as a consequence of the neutrality of LDPE. For this purpose some more complicated examples must be analyzed.

The specific retention volumes of six normal alkanes and several alcohols as well as benzene, toluene, and ethylbenzene were reported by Castells and Mazza[9] at several temperatures between 120 and 150 °C. The stationary phase consisted of four different copolymers of vinyl acetate and vinyl alcohol with 94.8, 74.4, 60.9, and 43.4 mol % of the vinyl acetate unit (mol % VAC). With the method described previously, a group of corresponding $-\Delta H^{ab}$ data can be obtained, as listed in Table III. According to eq 17, there are 32 unknown parameters and 48 equations in this example. It is clear that the volume of such a calculation is too large to solve this problem exactly. For this reason, a simplified calculation has been suggested as will be described.

Table III
$-\Delta H^{ab}$ and $-\Delta H^{ab}$(calcd) of Probe–Copolymer Pairs

probe	$-\Delta H^{ab}$ ($-\Delta H^{ab}$(calcd)), kJ/mol			
	43.4 mol % VAC	60.9 mol % VAC	74.4 mol % VAC	94.8 mol % VAC
benzene	10.3 (11.6)	8.1 (8.7)	8.5 (6.5)	−0.9 (3.4)
toluene	9.6 (12.7)	8.5 (8.9)	7.6 (6.0)	−3.5 (1.8)
ethylbenzene	8.6 (12.5)	7.8 (9.2)	6.5 (6.6)	−1.6 (2.9)
n-propyl alcohol	10.9 (14.3)	7.6 (7.0)	1.7 (1.2)	−12.7 (−8.7)
n-butyl alcohol	5.1 (9.9)	6.2 (4.8)	2.4 (0.8)	−13.3 (5.9)
n-pentyl alcohol	10.3 (13.0)	5.7 (6.5)	2.8 (1.4)	−11.2 (−6.8)
n-hexyl alcohol	8.3 (10.5)	3.4 (4.4)	0.6 (−0.5)	−11.5 (−8.3)
isopropyl alcohol	12.4 (15.3)	6.4 (6.8)	0.3 (0.0)	−13.5 (−10.8)
sec-butyl alcohol	12.6 (14.9)	8.3 (7.9)	4.0 (2.3)	−11.9 (−6.4)
tert-butyl alcohol	17.2 (21.5)	14.4 (14.4)	9.7 (8.8)	−5.5 (0.5)
sec-pentyl alcohol	10.0 (12.2)	5.7 (4.2)	−3.3 (−2.1)	−14.7 (−12.4)
cyclohexanol	9.4 (11.6)	5.7 (5.1)	−0.3 (−0.1)	−11.7 (−8.4)

It is interesting to note that there is a linear relationship between the $-\Delta H^{ab}$ of benzene–copolymers and the mole percent VAC:

$$-\Delta H^{ab} = 20.5 - 0.21 \text{ mol \% VAC}$$

This implies that the acid (or base) strength of the four copolymers varies linearly with mole percent VAC. There are similar relationships for toluene and for ethylbenzene:

$$-\Delta H^{ab} = 22.5 - 0.25 \text{ mol \% VAC} \qquad \text{toluene}$$

$$-\Delta H^{ab} = 18.7 - 0.20 \text{ mol \% VAC} \qquad \text{ethylbenzene}$$

These equations indicate that all three materials have almost identical acid (or base) strength. By averaging, we can obtain the following relationship:

$$-\Delta H^{ab} = 20.6 - 0.22 \text{ mol \% VAC} \qquad (18)$$

At the same time, there are similar linear relationships for all of the alcohols listed in Table III. Thus, averaging as before gives

$$-\Delta H^{ab} = 31.9 - 0.44 \text{ mol \% VAC} \qquad (19)$$

With these relationships in hand, we can recalculate the values of $-\Delta H^{ab}$(av) between benzene and the four copolymers by eq 18. Similarly, the values of $-\Delta H^{ab}$(av) between *tert*-butyl alcohol and the four copolymers can be recalculated by eq 19. Fortunately, the Drago parameters of benzene [C_b = 1.44 (kJ/mol)$^{1/2}$, E_b = 0.991 (kJ/mol)$^{1/2}$] and *tert*-butyl alcohol [C_a = 0.612 (kJ/mol)$^{1/2}$, E_a = 4.14 (kJ/mol)$^{1/2}$] are available from ref 6. These cal-

Table IV
Drago Parameters of Vinyl Acetate/Vinyl Alcohol Copolymers

Drago parameter	43.4 mol % VAC	60.9 mol % VAC	74.4 mol % VAC	94.8 mol % VAC
C_b, $(kJ/mol)^{1/2}$	−11.3	−7.1	−3.8	1.2
E_b, $(kJ/mol)^{1/2}$	4.8	2.4	0.5	−2.5

Table V
Drago Parameters [$(kJ/mol)^{1/2}$] of Several Probes

probe	C_a	E_a
benzene	−2.0	−2.3
toluene	−1.8	−1.6
ethylbenzene	−2.0	−2.1
n-propyl alcohol	0.1	3.2
n-butyl alcohol	−0.1	2.3
n-pentyl alcohol	0.0	2.7
n-hexyl alcohol	0.6	3.6
isopropyl alcohol	0.6	4.6
sec-butyl alcohol	−0.3	2.4
tert-butyl alcohol	−2.5	−1.4
sec-pentyl alcohol	1.3	5.6
cyclohexanol	0.5	3.6

culations, however, yield negative $-\Delta H^{ab}$ in some cases. According to ref 6, benzene has only base parameters, and *tert*-butyl alcohol has only acid parameters. To use the two sets of Drago parameters, we must introduce a further assumption; namely, for all materials $C_b = -C_a$ and $E_b = -E_a$. By this assumption we can calculate the Drago parameters of the four copolymers from the corresponding $-\Delta H^{ab}$(av) and the Drago parameters of benzene and *tert*-butyl alcohol. The results of these calculations are listed in Table IV. It is interesting to note that the Drago parameters of these copolymers vary linearly with mole percent VAC:

$$C_b = -22 + 0.24 \text{ mol \% VAC} \qquad r = 1.000$$

$$E_b = 11 - 0.14 \text{ mol \% VAC} \qquad r = 1.000$$

With the data of Table IV and the corresponding $-\Delta H^{ab}$, six sets of Drago parameters can be obtained for each probe. The optimum values can be found by averaging, and they are collected in Table V.

Finally, $-\Delta H^{ab}$(calcd) of each probe combined with each copolymer can be calculated from data of Tables IV and V. The results are listed in Table III in parentheses. With consideration of the inherent error of the method, the agreement between $-\Delta H^{ab}$ and $-\Delta H^{ab}$(calcd) is good. Therefore, it can be concluded that Fowkes' theory and all the previously mentioned assumptions are reasonable.

The Drago parameters of probes listed in Table V are useful for further study. For example, the IGC data of poly(vinyl isobutyl ethers) (PVIBE) reported by Deshpanda and Tyagi[10] have included the ΔH of benzene and toluene. With the Drago parameters listed in Table V, the Drago parameters of isotactic PVIBE are calculated to be $C_a = 2.0$ $(kJ/mol)^{1/2}$ and $E_a = -0.3$ $(kJ/mol)^{1/2}$. With the Drago parameters of chloroform,[6] $-\Delta H^{ab}$ between chloroform and PVIBE can be calculated. By this method of analysis, the value is found to be 1.4 kJ/mol and agrees with the value obtained from IGC data (1.9 kJ/mol).

As a final note, we mention here that the IGC analysis described above could be useful in studying a wide range of material problems that are dependent on interfacial interactions. For example, one could obtain Drago parameters of several polymers and a series of fillers that have undergone various surface treatments. By tests of the physical properties of composites that are made from these materials, it would be possible to establish quantitative relationships between interfacial interactions and the properties of the composites.

Conclusions

This work has shown that IGC can be used as a method for studying polymer interfacial interactions. The necessary procedures for data analysis have been outlined. This method of IGC data analysis has reinforced the validity of Fowkes's theory. Thus, it is reasonable to assume that polymer interfacial interaction need be divided into only two terms, i.e., dispersion and acid–base. The acid–base interaction heat can be described by Drago's four-parameter equation. Moreover, this method allows Drago parameters of polymers and probes to be calculated from IGC data. Interestingly, the Drago parameters of copolymers of vinyl acetate and vinyl alcohol were found to vary linearly with copolymer composition.

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Registry No. LDPE, 9002-88-4; (vinyl acetate)(vinyl alcohol) (copolymer), 25213-24-5; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; propyl alcohol, 71-23-8; butyl alcohol, 71-36-3; pentyl alcohol, 71-41-0; hexyl alcohol, 111-27-3; isopropyl alcohol, 67-63-0; *sec*-butyl alcohol, 78-92-2; *tert*-butyl alcohol, 75-65-0; *sec*-pentyl alcohol, 26635-63-2; cyclohexanol, 108-93-0; tetrahdyrofuran, 109-99-9; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5; 1-octene, 111-66-0; 1-nonene, 124-11-8; chlorobenzene, 108-90-7; *p*-xylene, 106-42-3; cumene, 98-82-8; butylbenzene, 104-51-8.

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