Solubilities of BHT in Various Solvents

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BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) is a widely used antioxidant in polymers as well as in many other applications. The solubilities of BHT in various solvents, such as *n*-heptane, ethanol, water, ethanol/water mixtures, 1-octanol, and corn oil, have been determined. The solubility of BHT in *n*-heptane is found to be slightly less than the ideal solubility predictable from calorimetric constants of BHT. Equilibrium absorption of BHT by several polyolefins have also been determined. Partition coefficients of BHT between solvents and polymers as derived from the solubility and absorption data are compared and discussed with partition coefficients observed from extraction and migration experiments.

Introduction

BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) is one of the most widely used antioxidants for polyethylene and other polymers. It is also used in a variety of products including foods. The study of the solubilities of BHT in a variety of solvents (including food-oil simulating solvents) and in polymers will allow an estimation of the partition coefficients of BHT between the solvent and the polymer. This will yield the equilibrium concentration of BHT in a foodstuff when the polymer is used as food packaging material.

Experimental Section

***Techniques*.** Solubilities of BHT were determined either by a radiotracer technique for low concentrations or by visually observing the dissolution process as the temperature of a mixture is changed. Both of these methods were described in detail in a previous publication (*1*) for the solubilities of *n*-alkanes. Corrections to the solution concentration of highly concentrated solutions, due to the evaporation of the solvent in a closed vial, have been applied as described previously (*1*).

Calorimetric measurements were performed with a commercial differential scanning calorimeter to determine the temperature and the enthalpy of fusion of BHT. Calorimetric procedures were also described previously (*1*).

***Materials*.** Commercially available samples of BHT were used directly without further purification. Some degradation or the presence of an impurity is evident as a slightly yellowish tint in a BHT, sample 1, Eastman Kodak Tenox BHT, that has been stored in the laboratory for more than a decade. (Note: Certain commercial materials are identified in this paper to adequately specify the experimental procedure. This identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.) Another sample of food-grade BHT, sample 2, was obtained through F. Wehar, Jr. of Koppers Chemicals and Coatings. The purity of this sample was quoted as at least 99% pure. All percentage figures related to the composition in this paper are expressed in terms of weight percent, unless stated otherwise. Only slight systematic differences in solubility characteristics were detected between these two samples.

Radioactive ^{14}C-labeled BHT, 3,5-di-*tert*-butyl-4-hydroxytoluene-7-^{14}C, with an original specific activity of 12.8 Ci/mol or 58 mCi/g, was diluted with unlabeled BHT to yield a specific activity of about 50 μCi/g or about 110 dpm/μg for observations of the solubility in water. To test the absorption of BHT by polyolefins through ethanol, a large amount of low activity BHT at about 0.25 μCi/g or about 550 dpm/mg was used.

Table I. Solubility of BHT in *n*-Heptane

sample 1, 96.5% *n*-heptane		sample 2			
		96.5% *n*-heptane		99.99% *n*-heptane	
t, °C	wt %	*t*, °C	wt %	*t*, °C	wt %
29.5	55.9	29.2	55.1	31.1	57.3
30.8	57.4	33.5	60.1	39.9	67.6
32.9	60.1	37.8	65.2	52.4	82.1
37.3	65.8	41.9	70.1	61.2	91.2
41.2	70.1	46.3	75.2	67.0	97.4
45.1	74.8	50.5	80.0		
49.9	80.4	55.2	85.2		
55.5	87.4	59.8	90.1		
60.0	91.2	62.7	93.1		
		64.7	95.1		
		65.7	96.1		
		66.6	97.0		
		67.8	98.2		
		68.7	99.1		

Table II. Solubility of BHT in Ethanol

sample 1		sample 2	
t, °C	wt %	*t*, °C	wt %
28.7	34.0	56.4	84.4
30.4	35.9	57.4	87.2
32.2	37.9	59.2	90.3
34.2	40.1	60.3	92.3
34.5	40.5	61.6	94.0
41.6	50.1	62.9	95.0
46.0	60.0	63.7	96.1
46.4	60.1	65.0	97.2
50.1	69.8	66.6	98.1
54.2	80.0	67.7	99.0
54.3	80.0		
59.6	90.2		

Commercially available solvents were used directly without further purification. Their characteristics are described in the previous paper (*1*). In addition to the more readily available "distilled-in-glass" heptane used in the previous paper, a sample of high purity *n*-heptane, 99.988%, from ELF Aquitane of France was also used for comparison. The latter sample is being certified as the National Bureau of Standards—Standard Reference Material 1815A as a reference fuel standard for the octane scale. The "distilled-in-glass" heptane contained approximately 96.5% of *n*-heptane. Analysis performed on a typical lot by the manufacturer, Burdick and Jackson Laboratories, Inc., indicated that the impurities are predominately aliphatic isomers of heptanes, with the presence of small amounts of methyl cyclohexane and ethyl cyclopentane. As shown later in this paper, the results of solubilities in these two samples of heptane are indistinguishable within the precision of the measurement.

Results

Solubilities of BHT in *n*-heptane, ethanol, and 1-octanol are listed in Tables I, II, and III, respectively. The measured dissolution temperature and the precipitation temperature agree

Table III. Solubility of BHT in 1-Octanol

sample 1		sample 2	
t, °C	wt %	t, °C	wt %
29.5	31.1	29.7	31.4
37.3	39.8	33.4	35.1
44.3	50.2	40.9	44.8
48.4	57.5	49.6	60.1
		54.3	70.2
		58.4	80.3
		63.1	90.1
		66.0	95.0
		66.8	96.2
		67.6	97.3
		68.2	98.2
		68.9	99.1

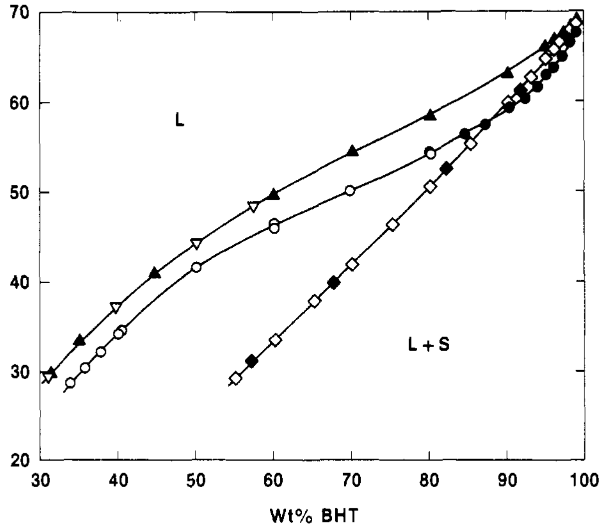

Figure 1. Phase diagram of BHT in various solvents. Sample 1: O, ethanol, ∇, 1-octanol; sample 2: ●, ethanol, ▲, 1-octanol, ◇, 96.5% *n*-heptane, ◆, 99.99% *n*-heptane.

in most cases to within 0.1 K. These results are shown in Figure 1 as phase diagrams for the weight percent of BHT as a function of temperature and in Figure 2 for the mole fraction of BHT as a function of inverse temperature (K^{-1}). The results of the less pure sample 1 in *n*-heptane are about 1% higher than that for the purer sample 2, and are therefore omitted in the figures for clarity. For solubilities of sample 2 in *n*-heptane, the filled symbols indicate the results obtained with the high purity *n*-heptane. For solubilities in ethanol and 1-octanol, the data for sample 1 are represented by unfilled symbols in the figures, while filled symbols are used for sample 2.

Above 58 °C, the solubility expressed in weight percent is higher in ethanol than that in *n*-heptane, as shown in Figure 1. However, when the solubility is expressed in mole fraction, the solubility of BHT in ethanol is always less than that in 1-octanol, which is in turn less than that in *n*-heptane, as shown in Figure 2. The mole fraction, N_2, and the weight fraction, X_2, of the solute may be converted from one to the other as follows

$$N_2 = 1/[1 + (1/X_2 - 1)M_2/M_1] \quad (1)$$

$$X_2 = 1/[1 + (1/N_2 - 1)M_1/M_2] \quad (2)$$

where M_1 and M_2 are the molecular weights of the solvent and the solute, respectively.

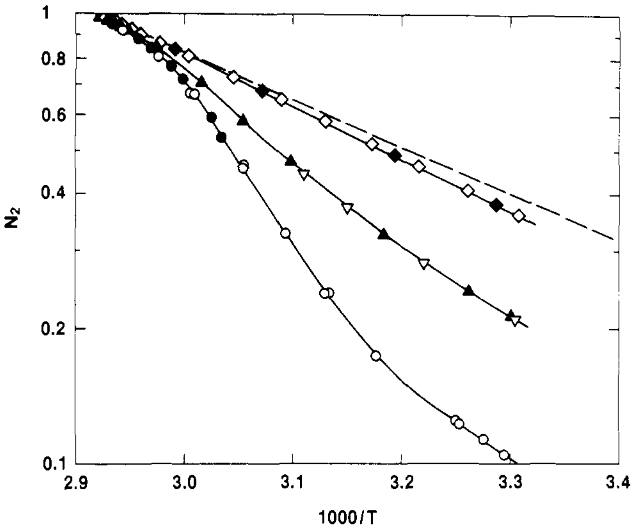

Figure 2. Solubilities of BHT as functions of inversed temperature (K^{-1}). Same legends as in Figure 1.

Solubilities of BHT in corn oil are only observed to an imprecision of approximately ±1%. The high viscosity of the oil tends to slow down both dissolution and crystallization processes, thus making precise observation of the temperatures of dissolution and crystallization difficult. Furthermore, the composition of triglycerides in corn oil may vary from batch to batch. The solubility of BHT in corn oil is about 58% at 60 °C and 28% at 30 °C. The solubility of BHT in corn oil is near those in ethanol or 1-octanol at 30 °C but much less than those in ethanol or 1-octanol at 60 °C.

The low solubility of BHT in distilled water is determined with radioactive ^{14}C-labeled BHT and by liquid scintillation counting measurements. The determination of the solubility of BHT in water and aqueous media by this technique is complicated by the steady degradation of BHT in contact with water. The reaction of BHT with water and oxygen leads to a large variety of products. A main yellow fraction was identified as a stilbenequinone and its precursor, a dimer of BHT (*2*). More than 20 transformation products from BHT were found in polyethylene (*3*). As the time of observation is prolonged, these degradation fragments remaining in the solution will lead to an increasingly higher value of accumulated radioactivity in the solution and hence an increasingly higher value of apparent concentration of BHT (including both unreacted BHT and all degradation products still remaining in the solution) with time.

When BHT is mixed with distilled water, the specific radioactivity of the aqueous solution rises quickly for about 4 h and then slowly increases. The initial rise is believed to be caused predominately by the kinetics of dissolution and the later slower rise is due predominately to the degradation reaction. The specific radioactivity observed after 4 days of contact is equivalent to 6 ppm of BHT by weight at 30 °C and 45 ppm at 60 °C. The specific radioactivity is expected to rise continuously, indicating that the degradation products may be more soluble in water than unreacted BHT. Extrapolation to time zero from the observations longer than 4 hours yields an estimate of the solubility of BHT to be of the order of 1.5 ppm at 30 °C and 6 ppm at 60 °C. A more precise estimation of the solubility would require the modeling of the complicated degradation reaction and its kinetics, and the analyzing of the composition of the solution by techniques such as HPLC to identify the presence of various species of reactants and products in the solution. The solution of a sparingly soluble substance may be obtained by the use of a generator column method (*4*).

Inui et al. (*5*) gave a value of solubility of BHT in water as 0.6 ppm at 25 °C, without giving any details about how this value is derived. Guziak and Gaydoz (*6*) of Koppers determined the solubility of BHT in water to be 1.7 ppm at ambient temperature. They added 1 g of BHT to 1 L of distilled water and heated the mixture at 40 °C for 36 h before allowing the mixture to cool to ambient temperature and to stand there for 24 h. The mixture was filtered and the filtrate was extracted with methyl ether. The extract was analyzed for BHT by gas chromatography.

The solubility of BHT in a 50/50 water/ethanol mixture by weight is also determined by the radio-tracer technique and estimated by extrapolating the long-time observations. At 30 °C, the short-time solubility is estimated as 0.025%. After 2 days the total radioactivity in the solution is equivalent to 0.07% at 30 °C. At 60 °C, the solubility is about 1% after 2 h and does not seem to increase rapidly afterward.

Similarly, the extrapolated short-time solubility of BHT in 40% ethanol is estimated to be 0.01% at 30 °C. The specific radioactivity seems largely stabilized at 0.06% after 200 h.

Above its melting point of 69.8 °C, BHT is miscible with any one of the solvents: *n*-heptane, ethanol, 1-octanol, or corn oil.

Solubilities of BHT are listed in manufacturers' literature by Koppers at 20 °C and by Kodak at 25 °C. The solubility of BHT in ethanol, 26% at 20 °C, is perhaps only 1-2% lower than that which may be extrapolated from this work. The value of 25% at 25 °C is about 5% too low. The water content in an alcohol solvent may have rather pronounced effects on the solubility of BHT. The solubility in methyl or isopropyl alcohol was given as 20% at 20 °C. The solubility in petroleum ether, 50% at 20 °C, is about 5% higher than that which may be estimated from the solubility in *n*-heptane. The solubility in mineral oil was listed as 30% at 20 °C and only 5% at 25 °C. The solubility in soya oil, peanut oil, corn oil, cottonseed oil, and coconut oil at 25 °C are all listed as 30%. Other solubility values for oils are 25% at 25 °C for olive oil, and 28% at 20 °C for linseed oil. The solubilities of BHT in lard are given as 40 and 48% at 50 °C by the two manufacturers. All of these values seem to be within 2-3% of those which may be estimated from the solubility of BHT in corn oil from this work.

The melting point of BHT is determined as 342.9 ± 0.2 K or 69.8 °C by differential scanning calorimetry. The enthalpy of fusion is determined as 90.0 ± 2.6 J/g. Therefore, the entropy of fusion can be calculated as 58 J/K/mol.

Discussion

The ideal solubility as a function of temperature, shown as the dashed line in Figure 2, can be calculated from the melting point, T_m, and the enthalpy of fusion, ΔH_m, by the relation

$$\ln N_2 = (\Delta H_m/R)(1/T_m - 1/T) \qquad (3)$$

where R is the gas constant. The experimentally measured solubility of BHT in *n*-heptane is only slightly lower than the ideal solubility, calculated by assuming that the enthalpy of fusion is independent of temperature. The nonideality is the result of the activity coefficient being less than unity. This slight difference may be accounted for by applying the Flory-Huggins theory of solutions (*7*) or by allowing for the additional temperature dependency of the solubility parameter (*8*). The applicability of the temperature-independent solubility parameter theory for describing the behavior of antioxidants in hydrocarbon solvents has been recognized previously (*9*). However, neither of these two methods would provide a precise description of the more complicated solubility behavior of the hindered phenol in alcohols. The solubility parameter theory is considered to be very poor when applied to antioxidant solubility in polymers (*10*).

In order to establish the upper and the lower bounds of equilibrium absorption of BHT by polyolefins, the following experiments were performed. The lower bound was established simply by immersing the untreated polyolefin plaques of less than 0.3-mm thickness in a bed of BHT crystals for about 1 yr at 30 or 60 °C. The upper bound of absorption was established by first saturating the polyolefin plaques in molten BHT for 1 week at 70 °C, and then holding the mixture for about 1 yr at either 30 or 60 °C. In the molten state of BHT at 70 °C, the lower bound of absorption was observed by immersing the plaques in liquid BHT for 10 days. The upper bound at 70 °C was established by leaving the plaques in liquid BHT at 76 °C for 5 days, followed by holding at 70 °C for 5 days.

Table IV. Absorption of BHT by Polyolefins[a]

	linear poly-ethylene		branched poly-ethylene		isotactic poly-propy-lene	
	L[b]	U[b]	L	U	L	U
	30 °C					
direct contact (G)[b]	2.3	2.4	2.3	4.1	3.4	4.5
ethanol (R)[b]	1.9	1.9	2.1	2.4	2.9	3.8
ethanol (G)	1.8	2.1	2.2	2.5	3.3	4.1
	60 °C					
direct contact (G)	5.7	5.5	9.0	10.4	7.5	7.9
ethanol (R)	5.3	5.6	9.2	10.4	7.8	8.7
ethanol (G)	5.2	5.4	8.7	9.5	7.0	7.5
	70 °C					
direct contact (G)	6.4	6.3	14.7	16.0	9.7	8.4

[a] Weight percent of BHT in final sample. [b] L = lower bound, U = upper bound, G = gravimetric, and R = radiotracer.

With saturated ethanol solution of BHT and with excess solid BHT present, BHT may also be absorbed by polyolefin plaques in similar quantities as the absorption experiments mentioned above. The amounts of BHT absorbed with ethanol as the transportation medium were monitored gravimetrically as well as by means of ^{14}C-labeled BHT and liquid scintillation techniques. The total weight gained is a less precise way of indicating the amount of BHT absorbed, as a small amount of ethanol may be absorbed by the polyolefins and as some oligomer fraction of the polymer may be removed by ethanol, especially at high temperatures. The results for these BHT absorption experiments are all listed in Table IV. The closeness of the bounds permits the estimation of the equilibrium absorption of BHT by polyolefins to within 0.5 wt %.

Moisan (*11*) estimated the solubility of BHT in branched polyethylene from diffusion studies. Their estimated values of solubilities are about 1.2% at 30 °C and 12% at 60 °C. The curve in Figure 5 of ref 11 seems to suggest a complete miscibility (100%) at the temperature of fusion of BHT. The solubility of BHT in isotactic polypropylene at 120 °C was determined as 9-18% by vapor absorption (*10*).

By assuming that the equilibrium absorption of BHT in polyolefin is the solubility of BHT in polyolefins, the partition coefficient, defined as $C_{\mathrm{solv}}/C_{\mathrm{poly}}$, would be on the order of 10-20 for BHT distributed between ethanol and polyolefins. With the weight ratio of ethanol and the polymer plaque on the order of 50 for typical extraction experiments, more than 99.8% of BHT is expected to be in the solvent phase. In our studies on the migration of BHT from polymers into various contacting solvents (*12*), equilibrium partitioning was observed only in aqueous extractions. In other solvents (such as *n*-heptane, ethanol, 95% ethanol, 1-octanol, a synthetic triglyceride mixture [HB-307], and corn oil), the solubilities of BHT are rather high. Therefore, almost all of the available BHT may be extracted by these solvents from the polymers studied: polyolefins, ethylene-vinyl acetate copolymers, and impact modified polystyrene.

From the extraction experiments (*12*), the partition coefficient BHT between water and polyethylene is estimated on the order of 0.05, and about 0.01 between water and polypropylene at 60 °C. If the solubility of BHT in water at 60 °C is assumed to be around 10 ppm, then the solubility of BHT in these polyolefins would be on the order of 0.02-0.1%, or at about 2 orders of magnitude less than that observed for equilibrium absorption. Experiments were performed to observe the absorption by polyethylene of BHT from ethanol and from 50/50 water/ethanol solutions. In contrast to the case of immersing the polymer in saturated ethanol solution of BHT with the presence of excess BHT crystals, practically no BHT was absorbed from the unsaturated ethanol solution of BHT. Only a small amount of BHT was absorbed by polyethylene from the 50/50 ethanol/water mixture, yielding a partition coefficient of about 0.4. By applying the measured solubility of BHT in 50/50 ethanol/water mixture, the solubility of BHT in polyethylene should be on the order of 0.1% or less at 30 °C.

There are also other indications that the true solubility of BHT in either linear or branched polyethylene may be very low. In polyethylenes loaded with about 100 ppm of ^{14}C-labeled BHT and remolded several times by compression, we still find evidence, by means of autoradiography, that the distribution of the radioactivity is highly nonuniform and that the radioactivity seems to aggregate into small concentrated particulate forms in the molded polymer plaques. It is possible that even the distribution of BHT in the amorphous regions of the plaque is not necessarily uniform. In separate experiments (*12*), BHT was noticed to escape from thin sheets of polyolefins and ethylene–vinyl acetate copolymers at room temperature into air at a rate more rapid than by solvent extraction. It appears that the rapid rate of loss may be associated with the sublimation from a large surface area of finely divided BHT particles mixed in the loose polymer matrix.

Thus, the solubility of BHT in polyethylene from equilibrium partitioning studies is much less than that estimated from the upper and lower bounds of absorption as mentioned above, from vapor uptake studies (*10*), and from diffusion studies (*11*). These discrepancies between the observations of solubilities of BHT in polymers from equilibrium partition and those from diffusion or vapor absorption require further investigation.

Registry No. BHT, 128-37-0; heptane, 142-82-5; ethanol, 64-17-5; 1-octanol, 111-87-5; polyethylene, 9002-88-4; polypropylene, 9003-07-0.

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Bond–Bond Interactions in Alkanes and Their Heteroanalogues. Allen-Type Group Increments for Estimating Enthalpies of Formation of Alkanes and Their Oxygen, Sulfur, and Nitrogen Analogues and Aliphatic Ketones

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Experimental values for the enthalpies of formation of 21 alcohols, 17 ethers, 7 acetals, and 71 alkanes were used to derive the values of the different group increments for alkanes and their oxygen analogues. The average difference between the calculated and estimated values for these 116 compounds is ±1.1 kJ/mol. The bond–bond interaction scheme so obtained was extended to saturated sulfur and nitrogen containing compounds and to aliphatic ketones by using enthalpies of formation of 45 sulfur and 21 nitrogen compounds and 18 ketones. The average differences between the calculated and the experimental values are ±0.8 kJ mol^{-1} for the sulfur and nitrogen compounds and ±1.0 kJ mol^{-1} for the aliphatic ketones. The values of the necessary bond energies have been corrected in accordance with the latest recommended values for the enthalpies of formation of gaseous atoms and selected model compounds.

Table I. Bond Energies in the Gaseous State

bond	E_b(g)/(kJ/mol)	compd	$-\Delta H_f°$(g)/(kJ/mol)	ref
C–C	330.1	CH_3CH_3	83.8	*16*
C–H	415.85	CH_4	74.7	*16, 17*
C–O	327.95	CH_3OH	201.1	*2b*
O–H	463.5	H_2O	241.8	*9*
C–S	274.15	CH_3SH	22.8	*2a, 9*
S–H	366.8	H_2S	20.6	8
S–S	246.2	H_2S_2	−10.2	*2b*
C–N	273.05	CH_3NH_2	23.0	*9*
N–H	390.9	NH_3	45.9	*9*
N–N	158.6	H_2NNH_2	−95.2	*17*
C=O	678.8	CH_2O	108.6	*2b*

Introduction

An Allen-type (*1*) bond–bond interaction scheme can be used for many purposes like evaluation of enthalpies of formation, nonbonded interactions, and conformational energies (*2a*). Kalb

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