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Specific Heat of Biphenyl and Other Polyphenyls. Correlation of Specific Heat Data for Phenyl Type Compounds

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The increasing applications for heat transfer media at high temperatures have created a greater demand for high temperature physical property studies of various materials. In recent years, several groups of investigators at this laboratory have been involved with precise measurements of various physical properties, such as viscosity, surface tension, thermal electromotive force, thermal conductivity, heat transfer coefficients, and specific heat on substances of interest as heat transfer media.

The specific heat of biphenyl, metaterphenyl, metaquaterphenyl, and the polymer-biphenyl mixture was measured as part of a program concerned with organic coolants. The program involved heat transfer studies (measurement of heat transfer coefficients, fouling, and polymerization effects on heat transfer) in a pumped loop, and investigation of the physical properties of these coolants.

EXPERIMENTAL

The apparatus has been described (*6*) in some detail. Briefly, the calorimeter is a modified version of Southard's apparatus (*5*), in which the drop method is utilized. The sample is dropped at a known temperature into the calorimeter which measures the heat evolved from the furnace temperature to the operating temperature of the calorimeter (86°F.). The heat capacity is then derived from the enthalpy measurements by the usual methods.

The samples were vacuum sealed in Type 304 stainless steel buckets, which were calibrated in the calorimeter system over the desired temperature range (200° to 600°F.). The weights, in vacuo, of the samples and the containers are as follows:

Biphenyl 8.2130 grams
Type 304 S.S. container 22.9605 grams
Metaterphenyl 8.7157 grams
Type 304 S.S. container 23.8820 grams
Biphenyl polymer 7.9917 grams
Type 304 S.S. container 23.0524 grams
Metaquaterphenyl 7.7731 grams
Type 304 S.S. container 23.0059 grams

The heat content results for biphenyl and metaterphenyl are listed in Table I. The heat content results for the loop polymer and the metaquaterphenyl are not included, because a supercooling effect was evident in each. Therefore, the values determined do not represent the true heat contents of the materials, as the heats of fusion, ΔH_f, were not recorded. To obtain these heat values, runs would have had to be extended over a considerable period of time (several hours), and possibly this would introduce additional error and actually add very little data. The enthalpy equations for biphenyl and metaterphenyl in engineering units are as follows:

Table I. Heat Content of Biphenyl and Metaterphenyl

Temp., °F.	$H_t - H_{86}$, B.t.u./Lb. Obsd.	Calcd.	% Deviation Calcd.-Obsd.
	Biphenyl		
204.89	97.39	97.58	+0.19
205.92	98.22	98.03	−0.19
421.56	200.02	201.24	+0.61
423.16	202.08	202.07	0.00
423.64	203.51	202.32	−0.59
577.90	285.73	285.89	+0.06
578.14	286.20	286.02	−0.06
			Mean ±0.24
	Metaterphenyl		
215.89	87.62	88.04	+0.48
216.75	88.97	88.42	−0.62
421.93	184.71	184.97	+0.14
422.29	185.42	185.15	−0.15
581.92	269.62	270.00	+0.14
581.92	270.40	270.00	−0.15
			Mean ±0.28

Table II. Heat Capacity of Biphenyl, Biphenyl-Tar, Metaterphenyl, and Metaquaterphenyl

Temp., °F.	Cp B.t.u./Lb. °F. Obsd.	Calcd.	% Deviation Calcd.-Obsd.	Cp Monsanto (*3*)	% Deviation Monsanto-Obsd.
		Biphenyl			
314.1	0.479	0.479	0.0	0.473	−1.3
391.7	0.505	0.505	0.0	0.508	+0.7
500.4	0.542	0.542	0.0	0.558	+2.9
		Biphenyl-Tar (60% Biphenyl, 15% Terphenyls, 25% Higher Polymers)			
312.2	0.470	0.468	−0.5	0.464	−1.3
393.2	0.496	0.495	−0.3	0.501	+0.9
501.3	0.531	0.531	+0.1	0.550	+3.5
		Metaterphenyl			
318.4	0.470	0.470	0.0		
399.1	0.497	0.497	0.0		
502.0	0.531	0.531	+0.1		
		Metaquaterphenyl			
316.9	0.466	0.466	0.0		
395.0	0.490	0.490	0.0		
501.6	0.523	0.523	0.0		

Table III. Heat Content of Biphenyl Compared to Heat Content of Other Investigators

Temp., °F.	$H_t - H_{250}$			
	NRL equation	(4)	(2)	(3)
340	42.5	42.3	42.2	40.5
430	87.7	87.0	90.2	84.6
520	135.7	134.0	144.4	132.5
610	186.4	183.5	202.3	183.9

$$(H_t - H_{86}) = 0.3725\,t + (1.691 \times 10^{-4})\,t^2 + 14.17 \text{ (biphenyl 200°–600°F.)}$$

$$(H_t - H_{86}) = 0.3638\,t + (1.671 \times 10^{-4})\,t^2 + 1.71 \text{ (metaterphenyl 200°–600°F.)}$$

The heat capacities of the four sample materials are indicated in Table II. The equations for the heat capacities in engineering units (B.t.u. per pound and degrees F.) are as follows:

Table IV. Specific Heat Correlation of Phenyl Compounds

Material	Ref.	Av. Atomic Weight	Temp., °F.	C_p B.t.u./Lb. °F. Calcd.	C_p B.t.u./Lb. °F. Obsd.	% Deviation (Calcd.-Obsd.)
Biphenyl	NRL	7.009	300	0.474	0.474	0.0
			400	0.508	0.508	0.0
			500	0.542	0.542	0.0
Biphenyl	(3)	7.012	300	0.474	0.467	+1.5
			400	0.508	0.512	−0.8
			500	0.542	0.557	−2.9
			600	0.575	0.603	−4.6
Biphenyl-tar[a] 60% biphenyl 15% terphenyls 25% high polymers	NRL	7.076	300	0.469	0.464	+1.1
			400	0.503	0.498	+1.0
			500	0.536	0.531	+0.9
Biphenyl-tar[a] 75% biphenyl 25% tar[a]	(3)	7.071	300	0.470	0.463	+1.5
			400	0.503	0.508	−1.0
			500	0.537	0.553	−2.9
			600	0.570	0.597	−4.5
Biphenyl-tar[a] 50% biphenyl 50% tar[a]	(3)	7.097	300	0.468	0.458	+2.2
			400	0.501	0.503	−0.4
			500	0.535	0.547	−2.2
			600	0.568	0.592	−4.1
Biphenyl-tar[a] 25% biphenyl 75% tar[a]	(3)	7.135	300	0.466	0.453	+2.9
			400	0.499	0.498	+0.2
			500	0.532	0.543	−2.0
			600	0.565	0.587	−3.7
100% tar[a]	(3)	7.186	300	0.462	0.448	+3.1
			400	0.495	0.493	+0.4
			500	0.528	0.537	−1.7
			600	0.561	0.582	−3.6
Metaterphenyl	NRL	7.197	300	0.462	0.464	−0.4
			400	0.495	0.498	−0.6
			500	0.527	0.531	−0.8
Metaquaterphenyl	NRL	7.295	300	0.455	0.461	−1.3
			400	0.488	0.492	−0.8
			500	0.520	0.523	−0.6
Monoisopropyl biphenyl (MIPB)	(3)	6.290	300	0.528	0.513	+2.9
			400	0.566	0.562	+0.4
			500	0.603	0.610	−1.2
			600	0.641	0.659	−2.7
Diisopropyl biphenyl (DIPB)	(3)	5.954	300	0.558	0.522	+6.9
			400	0.598	0.568	+5.3
			500	0.638	0.613	+4.1
			600	0.677	0.658	+2.9
MIPB-tar[b] 50% MIPB 50% tar[b]	(3)	6.382	300	0.521	0.495	+5.3
			400	0.558	0.539	+3.5
			500	0.595	0.583	+2.0
			600	0.632	0.627	+0.8
MIPB-tar[b] 75% MIPB 25% tar[b]	(3)	6.382	300	0.521	0.495	+5.3
			400	0.558	0.539	+3.5
			500	0.595	0.583	+2.0
			600	0.632	0.627	+0.8
Tertiary eutectic Biphenyl *o*-Terphenyl *m*-Terphenyl	(3)	7.113	300	0.467	0.453	+3.1
			400	0.500	0.489	+2.3
			500	0.534	0.544	−1.8
			600	0.567	0.589	−3.7

[a] Radiolytic tar made by irradiating biphenyl.
[b] Tar made by irradiating MIPB.

$$c_p = 0.3725 + (3.382 \times 10^{-4})t$$
(biphenyl, 200°-600°F.)

$$c_p = 0.3638 + (3.343 \times 10^{-4})t$$
(metaterphenyl, 200°-600°F.)

$$c_p = 0.3638 + (3.343 \times 10^{-4})t$$
(biphenyl polymer, 200°-600°F.)

$$c_p = 0.3672 + (3.119 \times 10^{-4})t$$
(metaquaterphenyl, 200°-600°F.)

The heat capacities of biphenyl and the polymer-biphenyl mixture are compared to those obtained at Monsanto (*3*) in Table II. The NRL polymer-biphenyl mixture was a mixture of biphenyl and pyrolytic tars consisting roughly of 60% biphenyl, 15% mixed terphenyls, and 25% mixed higher polyphenyls. The heat content for biphenyl ($H_t - H_{250}$) is compared to that obtained by other investigators in Table III. The probable error in this calorimetric system has been estimated to be ±0.3% in heat content and ±2% in heat capacity. This estimate is apparently somewhat high, as evidenced by results attained with a calorimetric standard material, aluminum oxide. The aluminum oxide results agreed with those attained at the National Bureau of Standards to less than ±0.2% in heat content and ±0.5% in heat capacity (*6*). The present results should certainly be within the estimated limits, despite possible uncertainties in the purity of the materials.

CORRELATION OF SPECIFIC HEAT DATA

Specific heat results for phenyl type compounds can be correlated by the use of average weight per atom. If the NRL specific heat-temperature equation for biphenyl (Equation 1) is adjusted for the change in average weight per atom as shown in Equation 2, the same equation is very effective in predicting specific heat values for all the phenyl type compounds tested. Taking the theoretical average weight per atom for biphenyl as 7.009, the general equation reduces to the form of Equation 3 in engineering units.

$$c_p = 0.3725 + (3.382 \times 10^{-4})t \quad (1)$$

$$c_p = 0.3725 + (3.382 \times 10^{-4})t\,\frac{A\phi_2}{A_x} \quad (2)$$

$$c_p = \frac{2.611 + (23.704 \times 10^{-4})t}{A_x} \quad (3)$$

This general equation was used to calculate specific heat values at various temperatures for a number of phenyl compounds for which measured results were available from the NRL and Monsanto studies. The results of these calculations are shown in Table IV. Where carbon-hydrogen analyses were given in the Monsanto report (*3*), the average weights per atom for the Monsanto materials are based on these analyses. All other average atom weights are based on the theoretical carbon-hydrogen contents. For the four compounds or mixtures measured at NRL, the mean deviation of the calculated values from those observed is ±0.6%. The mean deviation for all the results in Table IV is ±2.3%. The above equation was obtained empirically, but correlations, based on the additivity and constancy of atomic specific heats, have been established for certain groups of substances, such as solid elements and inorganic compounds, liquid metals, and inorganic liquid salts (*1*). This particular correlation is unique in the fact that it is applicable over a considerable temperature range and, furthermore, may be applied to phenyl compounds containing a carbon-hydrogen ratio different from the theoretical ratio. In heat transfer calculations, specific heat values are often required for complex decomposition products resulting from thermal or radiolytic decomposition of phenyl compounds or mixtures. This equation permits the estimation of specific heat values for such complex mixtures of higher polyphenyls from the measured carbon-hydrogen ratios, without regard to the exact composition of the mixtures. It is felt, therefore, that this general equation can be useful in predicting specific heat values for other phenyl type compounds of interest to the organic coolant program.

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