

On the Determination of Boron Mixed with Polyphenyls

Summary: The most suitable known organic compounds used in the organic cooled heavy water moderated nuclear reactors are polyphenyls. Therefore, many attempts have been and will be made by physicists to understand the dynamics of polyphenyl molecules, and also to measure the neutron parameters of these compounds. One technique for measuring the diffusion parameters of thermal neutrons is to add boron, at various concentrations, to the medium and to measure the relaxation length of the thermal neutrons. Thus, the accuracy of the extracted results is partly dependent upon the accuracy of the boron concentrations in the mixture.

Such a measurement was performed in Dowtherm-A (a eutectic mixture of 26.5% diphenyl and 73.5% diphenyl oxide by weight) at various temperatures (*t*) (Table I). Trihexyl-glycol bborate [tri-(2-methyl-2,4-pentanediol)borate], commercially known as Borester-7 was used to mix with Dowtherm-A at various concentrations. Unfortunately, the experimental arrangement did not allow the direct determination of boron concentrations by the addition of the known amount of Borester-7. The neutronic measurements were accurate to about one-half per cent, but some difficulties exist in determining the boron concentrations to a similar accuracy. This is an example of a common analytical problem that is difficult to solve. Chemical and physical methods of analysis have failed to give reliable results, but infrared spectra measurement method was found to be adequate.

The Borester-7 in the mixture was hydrolyzed with 5% sodium carbonate, the organic materials were removed by chloroform, and both the titration as the manitol complex and spectrophotometric estimation by carmine were performed.

The efficiency of the hydrolysis was demonstrated by finding the value of $5.66 \pm 0.01\%$ for boron in pure Borester-7, compared to 5.64% quoted by its supplier. But in mixtures with Dowtherm-A, low and random results were obtained. The error was found to increase with increasing quantities of Dowtherm-A, and extrapolation to zero weight of Dowtherm-A produced inconsistent results. Systematic variation of sample size, increase of hydrolysis time from 20 to 200 minutes, extraction by chloroform alone, chloroform after mechanical separation, and by other solvents failed to reveal the precise cause of error. No significant quantities of boron could be found in the separated organic material. The hydrolysates were noticed to develop a yellow hue after one or two days, indicating the incomplete removal of organic matter, but prolonged extraction and heating did not alleviate this situation. The hydrolysates were made strongly alkaline with sodium hydroxide, and were boiled under reflux up to three hours. This produced a significant improvement, in that recoveries rose to a level between 80 and 90%, but reproducibility was poor, extrapolation to zero Dowtherm-A weight became impossible, and the high salt concentrations gave rise to imprecise end points in titration.

The differences in the refractive indices of Dowtherm-A and Borester-7 suggested the refractometry method of analysis. The refractive indices were measured at 22 °C at the sodium wavelength. Samples of Dowtherm-A and Borester-7 showed no change in refractive index after heating either 24 or 148 hours at 180 °C. The results are the mean value of five refractive index measurements using the value of 5.66% by weight of boron in Borester-7. The variation between refractive index and per cent boron for synthetic samples was linear.

Infrared spectra measurement method is based upon the

(1) F. Sefidvash, Ph.D. Thesis, University of London, 1967.

Table I. Boron Content of Borester-7 Dowtherm-A Mixtures

Sample	Refractive index, % B by weight	Infrared spectra, % B by weight	Sample	Refractive index, % B by weight	Infrared spectra, % B by weight
A 80*	0.055	0.0081	E 20	0.156	0.0870
A 140	0.052	0.00815	E 80	0.166	0.0880
A 200	0.037	0.00782	E 200	0.147	0.0800
A 200	...	0.0085	F 20	0.232	0.155
B 20	0.030	0.0153	F 200	...	0.155
B 140	0.052	0.0155	G 20	0.276	0.226
B 200	0.063	0.0180	G 200	...	0.223
B 200	0.048	0.0162	H 20	0.369	0.292
C 20	0.063	0.0214	H 200	0.342	0.289
C 140	0.055	0.0209	I 20	0.652	0.524
C 200	0.063	0.0211	I 200	0.588	0.514
D 20	0.081	0.0295	J 20	1.03	1.00
D 200	0.085	0.0289			

* The letter indicates a particular mixture followed by a number giving the temperature (°C) of the medium at which the sample was taken.

measurement of absorption frequencies of the B-O-B bond which is present in the Boresters. Initial experiments, using the double beam technique, gave sharp absorptions at 1412 cm^{-1} and 1370 cm^{-1} , corresponding to the doublet associated with the B-O-B stretching frequency. For each sample a full spectrum was recorded, and then the portion of spectrum between 1600 cm^{-1} and 1200 cm^{-1} was repeated four times, each time with a different aliquot of sample in the sample cell. The mean of the four values for absorbance was used.

It seems unlikely that the chemical analysis of boron in these mixtures would be feasible without much further research. This view is supported by the notorious difficulty of precise boron determination in many materials. The results show the unreliability of the refractive index method. The infrared spectra measurement is the most suitable of all the presently tried methods.

There still remains the need for finding relatively cheap

boron compounds of high boron to hydrogen ratios, and stable with a high boiling point, to mix with various polyphenyls in large quantities, and to develop a simple and reliable method of determining their boron content to an accuracy of better than 1%. This then will provide physicists with a tool to make careful and detailed studies of the neutronic properties of polyphenyls.

FARHANG SEITDVASHI

Department of Technical Physics
Technical University of Helsinki
Otaniemi, Finland

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