ANL/RA/CP-96998

*Summary to be presented at the American Nuclear Society winter meeting, November 15-19, 1998, Washington, DC

Solubility Investigations in Support of Ultrasensitive Noble Gas Detector Development

by

Kenny C. Gross and Amity Andersen

Reactor Analysis Division
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

and

William R. Russ, David Stuenkel and John D. Valentine
Dept. of Mechanical, Industrial and Nuclear Engineering
University of Cincinnati
P. O. Box 210072
Cincinnati, OH 45221

*Work supported by the U. S. Department of Energy, Nuclear Energy Programs under Contract W-31-109-Eng-38

DISCLAIMER

Solubility Investigations in Support of Ultrasensitive Noble Gas Detector Development

Kenny C. Gross and Amity Andersen
Argonne National Laboratory
and
William R. Russ, David Stuenkel and John D. Valentine
University of Cincinnati

Introduction

Argonne National Laboratory (ANL) and the University of Cincinnati (UC) have been developing a new class of ultrasensitive noble gas detectors that are based upon the ANL discovery[1] that corn oil has a high affinity for heavy noble gas absorption at room temperature, but releases the noble gases with warming or by other low-energy-input means[2]. Environmental applications for this new class of fluid-based detectors include: ultrahigh sensitivity radioxenon detectors for Comprehensive Test Ban Treaty Surveillance[2,3], improved fission gas detectors for enhanced environmental surveillance in the vicinity of DOE, DOD, and NRC-licensed facilities, and improved integrating Rn detectors for earthquake prediction. The purpose of the present paper is to present the results of theoretical and experimental investigations into the solubility phenomena of heavy noble gases (Rn, Xe, and Kr) in triglyceride oils. It is the authors' intention that the findings presented herein may be used to guide future selection, development, and refinement of vegetable and other hydrocarbon oils to bring further enhancements to noble gas detection efficiencies.

Solubility Theory

Screening of potential working fluids for the ultrasensitive noble gas detector can be accomplished on the basis of gas-liquid solubility theory. Hildebrand et al.[4] proposed a solubility

parameter, δ, which is the square root of the cohesive energy density of a substance:

$$\delta = \sqrt{-\frac{E}{V}}$$

where δ is the solubility parameter, E is the molar internal energy of a substance (with a numerically negative value for a condensed material), and V is the molar volume. If the temperature of a liquid is well below its boiling point, the parameter can be estimated by using the molar vaporization energy (see Ref. 5, p. 23), ΔE^v, in place of $-E$. The internal energy of vaporization can in turn be replaced by the thermodynamic expression, $\Delta E^v = \Delta H^v - RT$, and, therefore, the final expression is:

$$\delta = \sqrt{\frac{\Delta H^v - RT}{V}}$$

where ΔH^v is the enthalpy of vaporization, R is the ideal gas constant, and T is the temperature.

The most promising technique identified for calculating the solubility parameter for various organic oils is the group molar cohesive energy contribution method (see Ref. 5, Sec. 6.2) in which the Hildebrand solubility parameter for an organic molecule is calculated as the sum of its constituent functional groups' cohesive energy densities. Vegetable oils comprise a mixture of triglycerides along with trace amounts of sterols, carotenoids, phospholipids, and waxes. Triglycerides are esters of fatty acids (carboxylic acids) with a glycerol backbone and three fatty acid chains. The fatty acids consist of a carboxyl group with a chain of carbons and hydrogens

of various lengths. A fatty acid is said to be "saturated" when no double-bonding occurs within the chain. Out of all the electrostatic force parameters considered, the most widely used partial solubility parameters for our purposes are the Hansen parameters[5,6] which divide the cohesive energy density among three electromagnetic forces: London dispersion, polar, and hydrogen bonding forces, with the dispersion force being the dominating force. Thermodynamic data were extracted from Barton[5] for the relevant triglyceride organic groups on the London dispersion, polar, and hydrogen bonding factors for these groups.

Results and Conclusions

Hildebrand solubility parameters were calculated for a number of pure saturated and unsaturated triglyceride molecules that make up vegetable oils. Results are summarized in Table 1.

From the calculated results for the saturated triglycerides, the solubility parameter decreases slightly with increasing fatty acid chain length. The solubility parameter for unsaturated triglycerides increases with increasing number of double bonds, but only by very small increments.

As part of this investigation, a variety of vegetable oils were tested in ANL experiments for absorptive capacity. Radon gas was used for these radiochemistry experiments, but absorption trends among the tested oils are expected to be similar--albeit at smaller magnitudes--for Xe and Kr. Concentration factors, defined as the radon concentration attained in oil divided by the radon concentration of the input air stream, were measured for peanut, corn, soybean, olive, walnut, and safflower oils. The highest mean concentration factor among the vegetable oils tested is for corn at 8.85; the lowest is safflower, 4.45. On the basis of solubility theory considerations it is not expected that any vegetable oils will be identified that can concentrate

heavy noble gases significantly better than corn oil. For this reason, and because of easy availability and modest cost, corn oil has been selected for all prototype designs of the ultrasensitive noble gas detection system built by the ANL/UC team to date.

In summary, noble gas solubility decreases slightly as the fatty acid chain length increases in saturated fatty acids and triglycerides, but levels off. The effect of unsaturation is found to be a very slight increase with a increasing number of double bonds according to the group contribution calculations. Implications are that increasing the length of the fatty acid chains in a long-chain triglyceride will not significantly increase the solubility of the noble gas. Corn oil favorably absorbs heavy noble gases and is nonvolatile, nontoxic, and inexpensive. Corn oil also has the added advantage that it absorbs noble gas radionuclides at temperatures just under room temperature and releases the gases when heated above this temperature range. The other chemistry aspects cannot be ignored, however. Corn oil is known to undergo oxidation and polymerization, which will necessitate the addition of antioxidants for long-term field deployment of environmental radionuclide detectors. For future research, it is recommended that the molar group contribution method presented here be extended to other fluids with similar properties to those of the triglyceride oils.

References

1. "Fluid-Based Radon Mitigation Technology Development for Decontamination and Decommissioning," K. V. Liu, J. D. Gabor, K. C. Gross and R. E. Holtz, ***Proc. 4th Intnl.***

Conf. on Nuclear Engineering, New Orleans, La. (Mar 10-14, 1996).

2. "Low-Energy Degassing Mechanisms for a Fluid-Based Radioxenon Detection System," D. Stuenkel, W. R. Russ, J. D. Valentine, and K. C. Gross, *Proc 20th Annual Research Symposium on Monitoring a Comprehensive Test Ban Treaty*, Santa Fe, NM (Sept 21-23, 1998).
3. "A Fluid-based Measurement System for Airborne Radioxenon Surveillance," B. Rooney, K. C. Gross, R. Nietert, J. Valentine and W. Russ, *Proc. 19th Research Symposium on Monitoring a Comprehensive Test Ban Treaty*, Orlando, Fla (Sept 23-25, 1997).
4. *Regular and Related Solutions*, Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L., Van Nostrand Reinhold Co., New York, 1970.
5. *Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed., A. F. M. Barton, CRC Press, Inc., Boca Raton, FL, 1991.
6. "On the Use of Cohesion Parameters to Characterize Surfaces," C. M. Hansen and E. Wallstrom, Journal of Adhesion, Vol. 15 (1983).

Table 1

Molar Group Cohesive Energy Contribution Calculations

Triglyceride	Group Contribution Solubility Parameter ($MPa^{½}$)	Molar Volume (cm^3/mol)
C12:0 *	19.8	282
C18:0	19.3	379
C24:0	18.9	476
C30:0	18.7	572
C36:0	18.5	669
C42:0	18.4	765
C48:0	18.3	862
C54:0	18.2	959
C60:0	18.2	1055
C48:3	18.3	895
C54:3	18.3	943
C54:6	18.3	927
C54:9	18.4	912

* The first number is the number of carbon atoms in the triglyceride, and the second number is the number of double bonds in the triglyceride.