Comments concerning the ‘solubility of buckminsterfullerene in tetrahydrofuran, thiophene, tetrahydrothiophene, 1,2,4-trichlorobenzene and n-butylyamine’

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In a recent article appearing in This Journal, Letcher et al. reported measuring the solubility of buckminsterfullerene, C_{60}, in tetrahydrofuran, thiophene, tetrahydrothiophene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene and n-butylyamine as a function of temperature from 298.1 K to 333.1 K. Results of the experimental measurements were used to calculate parameters of the Wilson and UNIQUAC equations.

The purpose of this communication is not unduly to criticize the authors’ work, but rather to point out two important errors/missstatements made in the paper in hopes that the authors would clarify these points. First, the authors state ‘it was assumed that ΔH_{m} = 748 kJ mol⁻¹ is temperature independent’ . Experimental values for the temperature T_m = 252 K and enthalpy ΔH_{m} = 8 kJ mol⁻¹ for the first order solid-solid phase transition were taken from reference 7. Using literature values for the standard gas phase enthalpy of formation of C_{60} at 298.15 K (ΔH_f^{B} = 2656 kJ mol⁻¹) and heat of sublimation of C_{60} powder (ΔH_s = 163 kJ mol⁻¹), the enthalpy of melting, ΔH_m, was found to be 2493 kJ mol⁻¹.

Readers will note the extremely large discrepancy between the two numerical values that presumably correspond to the enthalpy of melting. Unfortunately, the latter value is not the enthalpy of melting as the authors erroneously state. Using the cited values, and the corresponding reaction schemes to represent the processes to which the values refer,

\[60^\circ (\text{graphite, } 298.15 \text{ K}) \rightarrow C_{60}^\circ (\text{gas, } 298.15 \text{ K})\]
\[\Delta H_f^{B} = 2656 \text{ kJ mol}^{-1}\]
\[C_{60} (\text{powder, } T) \rightarrow C_{60}^\circ (\text{gas, } T)\]
\[\Delta H_s = 163 \text{ kJ mol}^{-1}\]

it is fairly easy to show using Hess’s law that the subtraction the authors used in obtaining the numerical value of 2493 kJ mol⁻¹ gives a value more in line with the enthalpy of formation of C_{60} powder. To derive the standard enthalpy of formation at 298.15 K correctly, one would have to use the value of the sublimation enthalpy extrapolated back to 298.15 K. The unspecified temperature in the second process would have to be T = 298.15 K. The matter of formation and sublimation processes is very clearly discussed in the paper by Steele and coworkers, from which the authors took the cited standard gas phase enthalpy of formation of C_{60} at 298.15 K. Curiously, Letcher and coworkers’ made exactly this same mistake in an earlier paper published in This Journal. In the earlier paper, only the single value of 2493 kJ mol⁻¹ for the enthalpy of melting is found.

A second problem with the manuscript concerns the calculation of the ideal mole fraction solubility of buckminsterfullerene. For informational purposes, the ideal mole fraction solubility was estimated as

\[-\ln X_1^{ideal} = (\Delta H_m^B R \left[ (1/T) - (1/T_m) \right])\]
\[\text{(1)}\]

This is equation 1 in the original manuscript with the activity coefficient set equal to unity. [Note The left-hand side of equations 1 and 2 in the original manuscript should read \(\ln X^{ideal} \).] The heat capacity term has been eliminated from the \(\ln X^{ideal} \) expression because the authors clearly state that the enthalpy of melting is assumed to be temperature independent. i.e. ΔC_p ≈ 0.

Substituting the actual numerical values that the authors give for the enthalpy of melting ΔH_m = 748 kJ mol⁻¹ and melting point temperature, T_m = 2023 K, into equation 1 above,

\[-\ln X_1^{ideal} = (74800/8.314) \left[ (1/298.15) - (1/2023) \right]\]
\[= 8496.87 \times 0.00353402 = 0.00049432\]
\[= 8996.87(0.0028597)\]
\[= 25.73\]

yielding an ideal mole fraction solubility of \(X_1^{ideal} \approx 6.7 \times 10^{-12}\). This value seems ridiculously small in light of published mole fraction solubility data for buckminsterfullerene in hexane (\(X_1^{hex} = 7.8 \times 10^{-5}\)), decane (\(X_1^{dec} = 1.92 \times 10^{-6}\)), cyclohexane (\(X_1^{cyc} = 5.4 \times 10^{-6}\)), methylcyclohexane (\(X_1^{methylcyc} = 3.1 \times 10^{-6}\)), ethylcyclohexane (\(X_1^{ethylcyc} = 4.9 \times 10^{-6}\)), and benzene (\(X_1^{benzene} = 2.11 \times 10^{-6}\)). There are over one hundred more examples of published solubility data that are considerably larger than the calculated ideal mole fraction solubility. The situation is even worse if the authors’ second value of the enthalpy of melting is used.

Now, there are a large number of examples in the published chemical literature of systems where the observed mole fraction solubility exceeds the ideal value. These systems give a calculated activity coefficient less than unity, and indicate negative deviations from Raoult’s law. Large negative deviations from Raoult’s law are often taken as indications that complex
formation occurs in solution. Given the rather inert nature of saturated hydrocarbons it is extremely hard to believe that complexation occurs in solutions of hexane, decane, cyclohexane and the other saturated hydrocarbons that are listed above. A more plausible explanation for why the published solubility exceeds \( X_i^{\text{ideal}} = 6.70 \times 10^{-4} \) is that something is wrong in the calculation of the ideal mole fraction solubility. Either the enthalpy of melting is not \( \Delta H_{\text{m,1}} = 74.8 \text{ kJ mol}^{-1} \), and/or the melting point temperature is not \( T_{\text{m,1}} = 298 \text{ K} \), and/or the assumption that the enthalpy of fusion is independent of temperature is invalid. There may be errors in the published values of \( \Delta H_{\text{m,1}} \) and \( T_{\text{m,1}} \) that the authors need to correct. It is not clear how the authors obtained their value of \( \Delta H_{\text{m,1}} = 74.8 \text{ kJ mol}^{-1} \). It is not clear if it is in their earlier cited paper.

Given the above observations, the ideal mole fraction solubility of buckminsterfullerene at 298.15 K is estimated as approximately equal to the measured mole fraction solubility in the solvent system that is expected to be the ‘most ideal, which is benzene’. A review article by Beck and Mandi\(^4\) tabulates published solubility values in 140 different organic and inorganic solvents. Admittedly, the choice of the ‘most’ ideal system would be subject to interpretation, but a value of \( X_i^{\text{ideal}} = 2.11 \times 10^{-4} \) is far more realistic than the value of \( X_i^{\text{ideal}} = 6.70 \times 10^{-12} \) calculated based upon the information contained in the Lether et al\(^1\) paper.

Finally, there is also a problem with the value of \( V_m = 600 \text{ cm}^3 \text{ mol}^{-1} \) that the authors used (without citation) for the molar volume of the hypothetical subcooled liquid solute. This particular numerical value is considerably larger than published partial molar volumes of \( C_{60} \) in several nonelectrolyte solvents. For example, Ruelle and coworkers\(^3\) calculated a value of \( V_m = 389 \text{ cm}^3 \text{ mol}^{-1} \) from high precision density measurements for buckminsterfullerene dissolved in 1,2-dichlorobenzene.

It should be noted that 1,2-dichlorobenzene was one of the six solvents studied by Lether et al\(^1\).

References