Relative Gas Solubilities Correlate Linearly to the Refractive Indices of Aprotic Solvents

Toshimasa Katagiri* and Kenji Uneyama

Department of Applied Chemistry,
Faculty of Engineering, Okayama University,
3-1-1 Tsushimanaka, Okayama 700-8530

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E-mail: tkata@cc.okayama-u.ac.jp

A linear correlation between the relative gas solubilities (O_2/CO_2) and refractive indices of aprotic solvents is shown. This empirical linear correlation would be useful to estimate relative gas solubilities of aprotic solvents.

Estimation of gas solubility has been an important issue, especially in development of artificial bloods.[1,2] The temperature and pressure effects on gas solubility have been understood as Henry's law.[3,4] Meanwhile, the correlation of solvent species and solubility has not been well understood.

Refractive index is an intrinsic property of organic liquid.[5] Though the refractive indices of organic compounds are included in some reagent catalogs,[6] they are hardly used in modern organic chemistry. Because, the indices are affected by the temperature (due to change of densities of the liquid) and the wavelength of the light source.

On the other hand, the indices represent electronic polarizabilities of the liquids.[5,7] That is, the refractive indices of the liquids well correlate with intrinsic energies of the aprotic liquids. Thus, the indices can be a tool for evaluation of liquid properties, such as boiling points.[8] The refractive indices should be appreciated more highly in the field of organic chemistry.

Correlation between gas solubilities and refractive indices has been repeatedly considered. Multivariate analysis has suggested that the refractive indices, as well as dielectric constants, cohesive energies, basicities, and electrophilicities of solvents have some correlation to the solubilities.[9] Although a method could be applicable to a wide range of solvents including protic solvents, it would be tough to use by organic chemists.

Table 1 summarizes gas (non-polar) solubilities of some aprotic solvents.[1,10–12] Table 1 shows that the higher the boiling points of the gases, the higher their solubilities are; and the lower the refractive indices of the solvents, the higher the solubilities of gases are. These results are consistent with the extremely useful rule of thumb "Like dissolves like."[13] Their low boiling points suggest gaseous species have small intrinsic energy caused by small electronic polarizability. Thus, gas would well dissolve in a solvent with a smaller refractive index and a smaller intrinsic energy.

Figure 1 summarizes a linear correlation between relative gas solubilities ($[O_2]/[CO_2]$) and refractive index of the solvent. The figure shows a linear correlation within the range of usual aprotic organic solvents, except for acetone and DMSO. Here, the higher the refractive indices are, the higher the selectivities are. Worthy of note, these two factors, refractive index and relative gas solubility, are non-dimensional values.

Acetone and DMSO are such polar solvents that they show polar interactions. Moreover, they can show hydrogen-bonding interaction via their enol forms.[14,15] Thus, we may exclude these polar solvents, acetone and DMSO, as well as protic solvents, alcohols from the linear correlation, because they may have additional interactions.

In conclusion we showed the relative amounts of gas solvations linearly correlate to the refractive indices of aprotic liquids. This correlation would be easy-to-use for design of artificial blood, as well as intuitive understanding of gas solubilities, although it needs some justification by theory. Anyway, we should respect the refractive index as a tool for understanding properties of the liquid.

Table 1. Gas Solubilities into Some Solvents [$\times 10^4$, at 298.15 K and 1 atm Partial Gas Pressure][1,10–12]

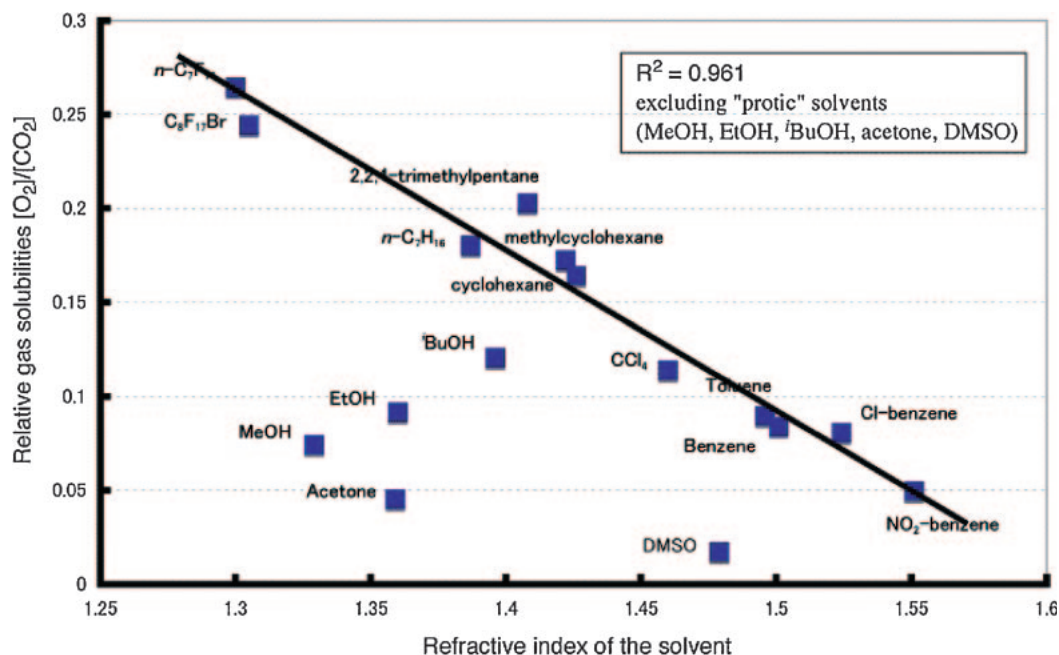| Solvent	n_D^{20}	He bp: 4 K	H$_2$ bp: 20 K	N$_2$ bp: 77 K	O$_2$ bp: 90 K	CO$_2$ bp: 195 K
n-C$_7$F$_{16}$	1.300	8.862	14.03	38.80	55.08	208.2
Hexane	1.379	2.604	6.315	14.02	19.30	—
Octane	1.398	2.397	6.845	13.04	20.83	—
Cyclohexane	1.426	1.217	4.142	7.610	12.48	76.00
Toluene	1.496	0.974	3.171	5.740	9.090	101.3
m-Xylene	1.497	1.121	4.153	—	—	—
Benzene	1.501	0.771	2.580	4.461	8.165	97.30
C$_6$H$_5$Cl	1.524	0.691	2.609	4.377	7.910	98.06

Figure 1. A linear correlation between relative gas solubilities ($[O_2]/[CO_2]$) and refractive indeces of the solvents.

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