

Hydrogen-bonding. Part 22. Characterization of Soybean Oil and Prediction of Activity Coefficients in Soybean Oil from Inverse Gas Chromatographic Data

Michael H. Abraham* and Gary S. Whiting

Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom

Previously reported results on twenty-two gaseous compounds with soybean oil as the stationary gas chromatographic phase have been used to characterize soybean oil in terms of dipolarity/polarizability, hydrogen-bond basicity and lipophilicity. The solubility of these gases in soybean oil has been factored into components that show exactly the compound-soybean oil interactions that favor solubility. The same equation used to obtain this information also can be used to predict the gas chromatographic specific retention volume and then the weight-fraction activity coefficient for numerous other compounds on soybean oil, thus leading to predictions of the solubility behavior of these compounds as bulk liquids with soybean oil.

KEY WORDS: Hydrogen bonding, inverse gas chromatography, regression analysis, retention volume, solubility, solute descriptors, solute-solvent interactions, solvation, soybean oil, weight-fraction activity coefficient.

King and List (1) have recently used the technique of inverse gas chromatography (IGC) to obtain specific retention volumes of twenty-two compounds on soybean oil. In the IGC method, the soybean oil is used as a gas chromatographic stationary phase, and the various compounds studied are injected in such a small quantity that they are effectively at zero concentration in the stationary phase. From the specific retention volumes, either corrected to 0°C (V_G^0) or at the column temperature (V_G^T), it is possible to calculate quantities such as weight-fraction activity coefficients, mole-fraction activity coefficients, Henry's Law constants and, although not specified by King and List (1), the Flory-Huggins interaction coefficient by means of known equations (1,2).

In this study, we wish to show that the V_G values of King and List (1) can further be analyzed to obtain information on soybean oil in terms of fundamental chemical quantities. We shall also show that the interaction of the various chemicals with soybean oil can be dissected into specific compound-stationary phase components. Finally, we use the key equation in this analysis to predict further V_G values, and then further values of the weight-fraction activity coefficients that can be used to assess the solubilizing power of bulk liquids for soybean oil (1).

EXPERIMENTAL PROCEDURES

Abraham *et al.* (3-5) have used a model for the solvation of gaseous compounds, based on a cavity theory of solvation. In this model, solvation is broken down into two

steps: (i) a cavity of suitable size is created in the solvent; and (ii) the gaseous solute is inserted into the cavity. The first step involves the breaking of solvent-solvent bonds and is therefore energetically unfavorable, whereas in the second step various solvent-solute interactions are set up, all of which are energetically favorable. The extent of solvation, as measured by gaseous solubility, thus depends on the resultant energy from steps (i) and (ii). To use such a model for the quantitative analysis of solvation of a series of gaseous solutes in a given solvent, solute descriptors are needed for the various interaction terms in step (ii), and for the size or cavity effect in step (i). These descriptors have been assigned as follows: R_2 is an excess molar refraction (6) that corresponds to a solute-solvent polarizability interaction; π_2^H is the solute dipolarity/polarizability (3) that corresponds to solute-solvent interactions of the dipole/dipole or dipole/induced dipole type; α_2^H is the solute hydrogen-bond acidity that refers to an interaction between solute acid and solvent base (3-5); and β_2^H is the solute hydrogen-bond basicity that refers to an interaction of the type solute base/solvent acid (3-5). It has not been possible to devise a solute descriptor that refers only to the cavity effect in step (i), and Abraham *et al.* (3-5,7) suggest that gaseous solubility in hexadecane solvent at 25°C can be used as a combined measure of the energetically unfavorable cavity effect and an energetically favorable general van der Waals, or dispersion, solute-solvent interaction term.

As a measure of gaseous solubility, the Ostwald solubility coefficient, also referred to as the gas-liquid partition coefficient, is used and defined through Equation 1:

$$L = \frac{\text{concentration of solute in solution}}{\text{concentration of solute in the gas phase}} \quad [1]$$

The Ostwald solubility coefficient for solutes in hexadecane at 25°C is denoted as L^{16} , and the cavity effect plus dispersion interaction descriptor is then $\log L^{16}$ (7).

When all these various terms are linearly combined, the general solvation equation of Abraham *et al.* (3-5) results in:

$$\log SP = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad [2]$$

In Equation 2, SP is usually the Ostwald solubility coefficient, L, for a series of gaseous solutes on a given liquid phase. However, in gas chromatographic measurements it is usual to determine the specific retention volume for a series of gaseous solutes, rather than L. These two quantities are related through $L = V_G \cdot \rho_L$, where ρ_L is the density of the liquid phase, or solvent, at the experimental temperature. Thus $\log L = \log V_G + \log \rho_L$, where $\log \rho_L$ is a constant for series of measurements on a given liquid phase at a given temperature. Hence, use of V_G instead of L in Equation 2 will yield an identical equation, except that the c-constant will alter by $\log \rho_L$.

*To whom correspondence should be addressed at Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, U.K.

SHORT COMMUNICATION

TABLE 1

Descriptors of the Gaseous Compounds					
Compound	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
<i>n</i> -Hexane	0.000	0.000	0.000	0.000	2.668
<i>n</i> -Heptane	0.000	0.000	0.000	0.000	3.173
<i>n</i> -Octane	0.000	0.000	0.000	0.000	3.677
<i>n</i> -Decane	0.000	0.000	0.000	0.000	4.686
Cyclohexane	0.305	0.100	0.000	0.000	3.007
Benzene	0.610	0.520	0.000	0.140	2.786
Toluene	0.601	0.520	0.000	0.140	3.325
Ethylbenzene	0.613	0.510	0.000	0.150	3.778
Dichloromethane	0.387	0.570	0.100	0.050	2.019
Tetrachloromethane	0.458	0.380	0.000	0.000	2.823
Trichloroethene	0.524	0.400	0.080	0.030	2.997
Propanone	0.179	0.700	0.040	0.510	1.696
Butanone	0.166	0.700	0.000	0.510	2.287
4-Methylpentan-2-one	0.111	0.650	0.000	0.510	3.089
Furfural	0.690	1.130	0.000	0.430	3.262
Methanol	0.278	0.440	0.430	0.470	0.970
Ethanol	0.246	0.420	0.370	0.480	1.485
Propan-2-ol	0.212	0.360	0.330	0.560	1.764
Butan-1-ol	0.224	0.420	0.370	0.480	2.601
Acetic acid	0.265	0.650	0.610	0.410	1.750
Propanoic acid	0.233	0.650	0.600	0.430	2.290
Butanoic acid	0.210	0.620	0.600	0.430	2.830

Because each term in Equation 2 corresponds to a specific solute-solvent interaction (except for the combined $l \log L^{16}$ term), each term must contain both a solute descriptor and a parameter that is related to the corresponding solvent property. These solvent parameters are the constants c , r , s , a , b and l in Equation 2 and are found by the method of multiple linear regression analysis. Their relationship to the chemical properties of the solvent or liquid phase follows automatically from the definition of the solute descriptors. Thus the r -constant corresponds to the tendency of the liquid phase to interact with polarizable solutes, the s -constant is a measure of the liquid phase dipolarity/polarizability, the a -constant is a measure of the liquid-phase hydrogen-bond basicity (because this is the complementary property to solute hydrogen-bond acidity), and the b -constant measures the liquid-phase acidity. The l -constant will include both the solvent-solvent unfavorable bond-breaking cavity process and the favorable solvent dispersion property. Interestingly, it turns out that the l -constant is a good measure of the lipophilicity of the solvent phase, relative to hexadecane at 25°C for which, by definition $l = 1$.

Hence, not only can Equation 2 be used to estimate further values of SP, either L or V_G , but the constants in Equation 2 provide definite chemical information on the properties of the given liquid phase. The descriptors required for Equation 2 are available (3-7) for all 22 compounds studied by King and List (1) and are given in Table 1.

RESULTS AND DISCUSSION

When Equation 2 was correlated to the $\log V_G$ values of King and List (1), we found that decane was an outlier by several standard deviations at all four temperatures. Therefore, we omitted this compound and give (in Table 2) the results of correlating Equation 2 to the twenty-one remaining compounds. At all four temperatures, the terms in rR_2 and $b\beta_2^H$ were statistically not significant, as judged by Student's t -test.

TABLE 2

Application of Equation 1 to $\log V_G$ Values for 21 Gaseous Solutes in Soybean Oil

Temperature (°C)	c	s	a	l	n^a	g^b	SD ^c
58.7	-0.415	0.815	1.602	0.820	21	0.988	0.09
79.0	-0.421	0.735	1.322	0.744	21	0.990	0.08
100.9	-0.414	0.649	1.089	0.671	21	0.990	0.07
123.4	-0.427	0.584	0.901	0.611	21	0.991	0.06

^aNumber of data points (decane omitted).

^bOverall correlation coefficient.

^cStandard deviation in $\log V_G$.

Inspection of Table 2 shows that soybean oil is moderately dipolar/polarizable, a hydrogen-bond base and lipophilic but has no hydrogen-bond acidic properties ($b = 0$). This is as expected on general chemical grounds, but more meaning to the constants in Table 2 can be obtained by comparison with other liquids at a common temperature of 120°C. (Note that the constants in Equation 2 [s , a and l] decrease regularly with temperature, so that comparisons must be made at a common temperature.) We have interpolated constants in Equation 2 for soybean oil to 120°C, and in Table 3 give a number of liquid phases for comparison (4,8). The constants for soybean oil are quite close to those for a number of long-chain esters, for example, di-2-ethylhexyladipate, although soybean oil seems slightly more lipophilic. Thus, soybean oil has the same dipolarity/polarizability and the same hydrogen-bond basicity as long-chain esters of aliphatic dicarboxylic acids.

Equation 2 can be used not only to characterize soybean oil, but to quantitatively detail the factors that influence the solubility of gaseous compounds. Some examples are given in Table 4 for the experimental temperature of 100.9°C. The main term is always the $l \log L^{16}$ term, composed of a cavity term that opposes solution and a general dispersion or van der Waals interaction term that favors solution; the latter dominates and is the largest gas-oil interaction in all cases. In general, the larger the gaseous solute, the larger the van der Waals interaction, and the larger is $\log V_G$ (i.e., the gas is more soluble). Ethanol is rather small, and although the dipolarity/polarizability and the hydrogen-bond acidity both contribute to the overall solubility, ethanol is still one of the least soluble gaseous compounds in soybean oil.

TABLE 3

Comparison of Solvation Properties of Soybean Oil with Other Liquids at 120°C

Liquid ^a	c	r	s	a	l
Apiezon J	-0.48	0.24	0.15	0.13	0.596
Polyphenyl ether	-0.69	0.14	0.92	0.61	0.560
Diethylphthalate	-0.52	0.14	0.67	0.77	0.587
Diethylsebacate	-0.35	0.12	0.49	0.79	0.594
Di-2-ethylhexyladipate	-0.36	0.13	0.55	0.87	0.590
Diethyleneglycol succinate	-0.97	0.26	1.76	1.80	0.375
Carbowax 1540	-0.75	0.22	1.37	1.92	0.456
Carbowax 300	-0.79	0.33	1.50	2.28	0.434
Soybean oil	-0.42	—	0.59	0.92	0.618

^aFrom refs. 4 and 8.

TABLE 4

The Factors That Influence the Solubility of Gaseous Compounds in Soybean Oil at 100.9°C, as Log V_G

Compound	c	$s\pi_2^H^a$	$a\alpha_2^H^b$	$l \log L^{16^c}$	Log V_G	
					Calculated	Observed
Octane	-0.414	0	0	2.467	2.05	1.92
Toluene	-0.414	0.337	0	2.231	2.15	2.18
Propanone	-0.414	0.454	0.044	1.138	1.22	1.23
Ethanol	-0.414	0.273	0.403	0.996	1.26	1.18
Propionic acid	-0.414	0.422	0.653	1.537	2.20	2.26

^a Gas-oil dipole/dipole or induced dipole/dipole interaction.

^b Gas-oil acid/base interaction.

^c Gas-oil general dispersion interactions plus cavity effect.

Now that the constants in Equation 2, where $SP = V_G$, are known, values of $\log V_G$, and thence V_G , may be predicted for any compound for which the descriptors π_2^H , α_2^H and $\log L^{16}$ are available. Since these are known for several hundred compounds (3,4,9), a large number of V_G values can be estimated. Knowing V_G , the corresponding weight-fraction activity coefficient, Ω^∞ , of the compound can then be calculated (1,2) *via* Equation 3, so that predictions of V_G are, in effect, also predictions of Ω^∞ :

$$\Omega^\infty = \frac{RT}{V_G P_1 M_1} \exp \left[\frac{P_1 (B_{11} - V_1)}{RT} \right] \quad [3]$$

In Equation 3, P_1 , M_1 , B_{11} and V_1 are the compound saturated vapor pressure, molecular weight, second virial coefficient and molar volume, respectively.

Now Ω^∞ corresponds to the reciprocal of the weight-fraction solubility of the bulk liquid compound in soybean oil at the given temperature. Unless one of the components is associated, as is the case for alcohols, activity coefficients in two-component systems tend to be rather symmetrical. Thus, a low value for Ω^∞ , which corresponds to a high solubility of the bulk liquid in soybean oil, will indicate a high solubility of soybean oil in the bulk liquid compound. King and List (1) have shown through direct determinations of V_G and Ω^∞ that chlorinated solvents tend to be compatible with soybean oil, with values of Ω^∞ around 2.0 at 79°C (Table 5). We have predicted V_G values at 79°C from Equation 2 for a number of compounds as an example of our method. These are in Table 6, together with the corresponding Ω^∞ values. As found by King and List (1), other chlorinated solvents, such as

TABLE 5

Some Values of Log V_G and of Ω^∞ Determined by King and List (ref. 1) for Compounds on Soybean Oil at 79°C

Compound	Log V_G	Ω^∞
Butan-1-ol	2.17	12.9
Propanone	1.42	9.7
<i>n</i> -Hexane	1.65	5.8
Benzene	2.08	3.3
Ethyl benzene	2.76	3.0
Dichloromethane	1.65	2.4
Trichloroethene	2.22	1.8
Tetrachloromethane	2.02	1.7

TABLE 6

Some Predicted Values of Log V_G and of Ω^∞ for Compounds on Soybean Oil at 79°C, from Equation 2 and 3

Compound	Log V_G	Ω^∞
Acetonitrile	1.65	17.9
Ethyl acetate	1.76	5.5
Benzyl alcohol	3.92	5.4
Dimethylformamide	2.92	5.1
Cyclohexanone	3.03	3.2
Tetrahydrofuran	1.94	3.2
1,2-Dichloroethane	2.10	2.7
Trichloromethane	1.98	1.5

1,2-dichloroethane and trichloromethane, are predicted to have rather low Ω^∞ values, although the predicted Ω^∞ values of cyclohexanone and tetrahydrofuran are only a little higher.

Our method of analysis of V_G values *via* Equation 2 thus not only provides an explanation of solvation in soybean oil, but also leads to the prediction of V_G and the practically important weight-fraction activity coefficient, Ω^∞ . Thus, if V_G values can be determined by IGC for about 20–30 well-selected compounds on a particular liquid phase, it is now possible to predict further V_G values, and Ω^∞ values as well, for a huge number of other compounds for which descriptors are available. Thus, with a comparatively small amount of calculation, it is possible to select a number of compounds with good solubility properties toward the given liquid phase without any further testing at all.

REFERENCES

- King, J.W., and G. List, *J. Am. Oil Chem. Soc.* 67:424 (1990).
- Romdhane, I.H., and R.P. Danner, *J. Chem. Eng. Data* 36:15 (1991).
- Abraham, M.H., G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.* 587:213 (1991).
- Abraham, M.H., G.S. Whiting, R.M. Doherty and W.J. Shuely, *Ibid.* 587:229 (1991).
- Abraham, M.H., I. Hamerton, J.B. Rose and J.W. Grate, *J. Chem. Soc. Perkin Trans.* 2:1417 (1991).
- Abraham, M.H., G.S. Whiting, R.M. Doherty and W.J. Shuely, *Ibid.* 2:1451 (1990).
- Abraham, M.H., P.L. Grellier and R.A. McGill, *Ibid.* 2:523 (1988).
- Abraham, M.H., G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.* 518:329 (1990).
- Abraham, M.H., and G.S. Whiting, *Ibid.* 594:229 (1992).

[Received June 16, 1992; accepted September 20, 1992]