

The soft-solid model for liquids. Application to biodiesel and other materials of technological interest[†]

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ABSTRACT: The coefficient of cubic expansion of liquids (α) correlates inversely with the corresponding value of enthalpy of vaporisation. The theoretical interpretation is based on the molecular view of liquids as modified solids made of molecules packed in a way that a few neighbouring molecules have been removed. The general equation for the coefficient of cubic expansion of solids was modified to describe the case of liquids regarded as *soft solids*. The empirical equation $\alpha = 0.087/\Delta H_{\text{vap}}$ was obtained for long-chain liquids of low polarity such as *biodiesel* materials, when the enthalpy value is given in kJ/mol. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: biodiesel; coefficient of cubic expansion; enthalpy of vaporisation; Hildebrand solubility parameter; isothermal compressibility

INTRODUCTION

Sustainable industrial practices promote economic and social development, because environmental equilibrium has become the key issue for global survival.

The replacement of petroleum derivatives for hydrocarbon-like materials from renewable sources constitutes a *cleaner-production* approach to the problem of petroleum availability, due to decreasing oil reserves, increasing fuel cost and air, water and soil pollution, amongst other reasons.

Most researchers and their organisations have mainly devoted their efforts to find a replacement for diesel fuel. A lesser degree of interest is found on the evaluation and production of petroleum substitutes suitable for use as industrial solvents, lubricants or fluids for transmission of mechanical energy. The assessment of the potential applications of these materials requires the knowledge of their chemical, thermodynamic and rheologic properties.

Therefore, we should like to discuss a molecular model that allows the estimation of thermodynamic properties for molecular liquids, from the experimental determination of the coefficient of cubic expansion. This work focuses on the fatty-acid ethyl and methyl esters (*biodiesel*) from soybean (*Glycine max*) and palm

(*Elaeis guineensis*). The thermodynamic parameters sought are: the molar enthalpy of vaporisation (ΔH_{vap}), the Hildebrand solubility parameter (δ_{H}), the isothermal compressibility (κ_{T}) and the so-called thermal pressure coefficient $(\partial p/\partial T)_{\text{V}}$.

Qualitative statement of the molecular model

Liquids can be regarded as modified solids made of molecules packed in a way that a few neighbouring molecules have been removed.^{1–3} The van der Waals scheme for the liquid state⁴ depicts a collection of interacting hard spheres. This model points predominantly to the dominant role of the short-ranged repulsive intermolecular forces in determining the microscopic features of liquids. Thus, weak attractive interactions help fix the volume of the liquid system, but the relative particle positions and their motions within that volume are determined primarily by the local packing and steric exclusion resulting from the strong repulsive forces. Indeed, it has been observed that the basic features of the supramolecular solid-state configuration of covalent tetrachlorides,^{5,6} benzene^{5,7} or carbon disulphide⁵ remain in the liquid state. These observations suggest the possibility of treating liquids as *soft solids*.

In the soft-solid model for the liquid state, liquids can be regarded as modified solids made of particles packed in such a way that a few neighbours have been removed.

Most materials expand upon heating. The magnitude of the effect is given by the isobaric coefficient of cubic

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expansion $\alpha = 1/V(\partial V/\partial T)_T$. Macroscopic expansion is the result of the increase in particle kinetic energy, as temperature rises. This leads to wider amplitudes of molecular oscillations about their equilibrium positions in the lattice, and larger inter-particle distances. The macroscopic result is the increase of the system volume as a whole. Cubic expansion can be expected to vary inversely proportional to the degree of cohesion of systems. This proposal finds agreement with the finding that $\alpha = 1.27 \times 10^{-3} \text{ K}^{-1}$ for CCl_4 , whilst only $2.57 \times 10^{-4} \text{ K}^{-1}$ for water. Thus, if one considers that the enthalpy of vaporisation is a suitable measure of the intermolecular forces of liquids, intuitiveness leads to expect a general mathematical relationship of the type $\alpha = \text{constant}/\Delta H_{\text{vap}}$. The empirical correlation of α and ΔH_{vap} for 311 liquids produces the relation

$$\alpha = \frac{(4.30 \pm 0.05) \times 10^{-2}}{\Delta H_{\text{vap}}} \quad (1)$$

when the enthalpy of vaporisation is given in kJ/mol. Figure 1 shows the correlation in the linear form α versus $1/\Delta H_{\text{vap}}$ (Student $t = 15.8$, $p < 0.005$). The test liquids subjected to the fit were small non-polar, polar as well as hydrogen-bonding molecules, with molecular weights less than about 150.⁸ The group of compounds included: 26 alkanes, 10 olefins, 13 aromatics, 4 fluorohydrocarbons, 139 polar non-hydrogen-bonding molecules, 40 alcohols, 63 carboxylic acids and 16 amines. The empirical fit was done to each group of compounds separately. The proportionality parameters resulted: 0.0428 ± 0.0006 , 0.043 ± 0.001 , 0.043 ± 0.001 , 0.043 ± 0.007 , 0.0427 ± 0.0006 , 0.043 ± 0.001 , 0.043 ± 0.002 and 0.044 ± 0.001 . It is an important fact that the same result is observed for all the compounds, included the associated liquids.

This qualitative result indicates the model is realistic, even taking into account that the data were obtained from four different databases,⁸ which undoubtedly contain data of different degrees of accuracy.

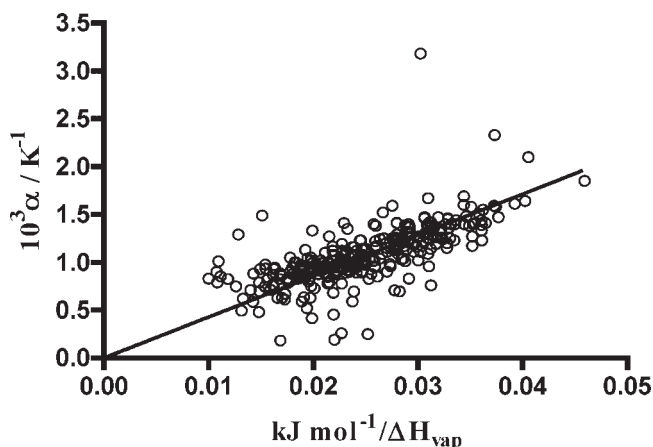


Figure 1. Correlation of the coefficient of cubic expansion of 311 liquids with the enthalpy of vaporisation

Quantitative statement of the molecular model

The thermal coefficient of linear expansion, $\alpha_1 = 1/l(\partial l/\partial T)_p$ can be obtained from fundamental considerations for materials made of nearly spherical particles as:⁹

$$\alpha_1 = \frac{7}{216\varepsilon N_A} C_p \quad (2)$$

where ε is the energy of interaction between a central particle and its neighbours, N_A is Avogadro's number and C_p is the heat capacity of the material.

Since the cubic expansion coefficient is given by $\alpha = 3\alpha_1$, one obtains the relation:

$$\alpha = \frac{7}{72\varepsilon N_A} C_p \quad (3)$$

From the qualitative molecular considerations discussed in the previous section, one can deduce that a relationship $\varepsilon N_A = \lambda \Delta H_{\text{vap}}$ must exist, and

$$\alpha = \frac{7C_p}{72\lambda\Delta H_{\text{vap}}} \quad (4)$$

The use of heats of vaporisation as assessment of intermolecular forces in liquids is a common approach. Two examples are the formal treatment of surface tension¹ and the estimation of the energy of activation for viscous flow of liquids.²

The proportionality constant λ can be obtained by the following rationale. The coordination numbers in non-polar liquids vary from 8 to 12.¹ The molar enthalpy of vaporisation is the measure of the cost for separation of the constituting particles from their configuration in the liquid state to the degree of molecular freedom of the gaseous state. For a small $(\partial V/\partial T)_p$ it suffices to move apart 3 of the average 10 isotropically distributed neighbours (one along each Cartesian coordinate). This gives a basis to propose that $\varepsilon N_A \approx (3/10)\Delta H_{\text{vap}}$. An average C_p value for common liquids is $0.15 \text{ kJ K}^{-1} \text{ mol}^{-1}$. Insertion of these figures in Eqn (3) yields $\alpha = 4.8 \times 10^{-2}/\Delta H_{\text{vap}}$. This predicted equation is in good agreement with the observed empirical result [Eqn (1)].

EXPERIMENTAL

For many of the test liquids, the cubic expansion coefficients were calculated from reported densities (ρ) at different temperatures as $\alpha = -(\partial \ln \rho / \partial T)_p$.

The determination of α for the different *biodiesel* materials was done by measuring their densities at different temperatures, by means of a pycnometer provided with thermometer. The procedure is the usual described in standard textbooks of experimental physical

chemistry. Plots of $\ln \rho$ versus T gave good straight lines ($r^2 = 0.99$) whose slopes are equal to the negative of α .

RESULTS AND DISCUSSION

Enthalpies of vaporisation and solubility parameters

Biodiesel materials are mixtures of fatty-acid methyl or ethyl esters. These non-hydrogen bonding materials are not expected to obey Eqn (1), because the packing density is different from that of simple spheres and the average C_p values are now about fourfold greater ($C_p \sim 0.6 \text{ kJ K}^{-1} \text{ mol}^{-1}$).

A simple rationale is expected to yield an acceptable result for λ , based on the idea that these long-chain esters should be regarded as rods (either straight or bent), rather than spheres. 'Liquid structure', that is, the intermolecular configuration and correlations are determined primarily by the local packing and steric effects produced by the resulting action of short-ranged repulsive and attractive intermolecular forces. Since Eqn (1) conforms to nearly spherical small-size molecules, it is logical that the proportionality parameter ($7C_p/72\lambda$) for longer-chain molecules must have a different value, based on molecular shape features that define local molecular packing.

For example, one can take one yellow pencil tightly surrounded by six radially distributed blue pencils, plus two more flanking at head and tail. In order to allow the yellow pencil have a wider degree of movement along the three Cartesian coordinates, it is necessary to *push apart* the two flanking objects plus three more around its length. This geometrical model gives $\lambda = 5/8 = 0.6$. Equation (4) is now $\alpha = 0.09/\Delta H_{\text{vap}}$.

The correlation of the α - ΔH_{vap} data of triethyleneglycol acetate, dibutyl sebacate, butyl stearate and methyl oleate yield the empirical relation:

$$\alpha = \frac{(0.087 \pm 0.005)}{\Delta H_{\text{vap}}} \quad (5)$$

a result in good agreement with the expected relationship.

The thermodynamic parameters

The cohesion energy density¹⁰ of liquids is given by $\Delta U_{\text{vap}}/V_m = (\Delta H_{\text{vap}} - RT)/V_m$, where V_m is the molar

Table 1. Cohesion energy density and internal pressure for non-polar liquids at 25 °C

Compound	$\Delta U_{\text{vap}}/V_m$ (J/cm ³)	$(\partial U/\partial V)_T$ (J/cm ³)
CCl ₄	308	337
CS ₂	420	362
C ₆ H ₆	351	372
<i>n</i> -C ₆ H ₁₄	219	239
<i>c</i> -C ₆ H ₁₂	280	326

volume of the liquid ($V_m = \text{molecular mass/density}$). For the case of liquids of low polarity and within 10% precision, this quantity is known to be equal to the thermodynamic *internal pressure* of the system, $(\partial U/\partial V)_T$. Table 1 gives some examples from the literature.¹⁰

$(\partial U/\partial V)_T$ can be physically interpreted as the energy needed for a unitary isothermal expansion, and thus is a measure of the degree of cohesion of the system. The so-called thermodynamic equation of state¹¹ allows the calculation of the internal pressure of a system from the isobaric coefficient of cubic expansion and the isothermal compressibility (κ_T):

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (6a)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T}{\kappa_T} - p \quad (6b)$$

When $(\partial U/\partial V)_T$ is substituted in Eqn (6b) for $\Delta U_{\text{vap}}/V_m$, one can readily show that for moderate values of pressure:

$$\kappa_T \approx \frac{\alpha T}{\Delta U_{\text{vap}}/V_m} \quad (7)$$

Table 2 gives thermodynamic properties of the four types of *biodiesel* materials studied. The mean value of ΔH_{vap} of the four *biodiesel* materials is $106 \pm 2 \text{ kJ/mol}$. This value is in agreement with those of pure analogous substances such as methyl palmitate (94 kJ/mol), ethyl palmitate (101 kJ/mol), methyl stearate (98 kJ/mol), ethyl stearate (109 kJ/mol), ethyl oleate (92 kJ/mol), methyl linoleate (102 kJ/mol) and methyl linolenate (102 kJ/mol).

Biodiesels from different sources are potentially useful substitutes of industrial solvents derived from petroleum.

Table 2. Thermodynamic properties of the four types of *biodiesel*

Material	$10^4 \alpha$ (K ⁻¹)	ΔH_{vap} (kJ mol ⁻¹)	δ_H (J cm ⁻³) ^{1/2}	$10^{10} \kappa_T$ (Pa ⁻¹)	$10^{-6} (\partial p/\partial T)_V$ (Pa K ⁻¹)
Soybean methyl <i>biodiesel</i>	8.3 ± 0.2	105 ± 6	17.5 ± 0.3	7.7 ± 0.2	1.08 ± 0.04
Soybean ethyl <i>biodiesel</i>	8.0 ± 0.6	109 ± 9	17.4 ± 0.8	7.6 ± 0.6	1.1 ± 0.1
Palm methyl <i>biodiesel</i>	8.2 ± 0.1	106 ± 6	18.0 ± 0.5	7.2 ± 0.2	1.14 ± 0.03
Palm ethyl <i>biodiesel</i>	8.2 ± 0.4	106 ± 8	17.3 ± 0.6	8.0 ± 0.4	1.02 ± 0.07

This is especially true for the case of agrochemical formulations, due to the low toxicity of these fatty esters and readily biodegradation.¹² The utility of the different biodiesels as solvents depends on their capacities of dissolving the particular solutes of interest.

Hildebrand's solubility parameter, $\delta_H = \sqrt{\Delta U_{\text{vap}}/V_m}$ for particular liquids, can be calculated from their ΔH_{vap} and apparent molar volumes V_m . For biodiesels, this last quantity is the weighted average of the molar volumes of the constituting fatty esters. The solubility parameter gives a numerical value indicating the solvency behaviour of a specific solvent. Since the solubility of two materials is only possible when their intermolecular forces are similar, one expects that materials with similar δ_H values would be miscible.

Table 2 includes the δ_H data. The biodiesels of this work can be considered potential substitutes in industry, for health risky solvents such as toluene ($\delta_H = 18.2$) and *m*-xylene ($\delta_H = 18.0$).

Lubricity is another potential application for biodiesels. A good lubricant must have high viscosity and low compressibility. Under stress, the molecular layers of this type of long-chain molecules between sliding surfaces must not get *squeezed out*. Therefore, an easier way to obtain κ_T is certainly useful.

All the biodiesel materials show a mean $\kappa_T = (7.6 \pm 0.3) \times 10^{-10} \text{ Pa}^{-1}$. This figure is concordant with the corresponding values observed at 20 °C for *n*-C₁₂H₂₆ (9.87×10^{-10}), *n*-C₁₅H₃₂ (9.1×10^{-10}), *n*-C₁₆H₃₄ (8.67×10^{-10}) and machine oils (6×10^{-10} – 8×10^{-10}). It seems that polarity (esters *vs.* hydrocarbons) increases the degree of molecular packing in liquids of similar molecular dimensions.

The thermal pressure coefficient $(\partial p/\partial T)_V$, measures the resistance of the system to stress. Since $(\partial p/\partial T)_V = \alpha/\kappa_T$, this third thermodynamic coefficient

can be obtained from the other two. The values are listed in Table 2.

CONCLUSION

Useful thermodynamic characterisation of liquids of low polarity can be achieved by measuring their coefficient of cubic expansion. This parameter is easily obtained from density measurements at different temperatures, even when using a simple pycnometer and analytical balance. The enthalpy of vaporisation and the basic thermodynamic coefficients obtained for liquid materials of low polarity such as *biodiesel* resulted in numerical data that agreed with expectation.

REFERENCES

1. Tabor D. *Gases, Liquids and Solids*. Penguin Books: Baltimore, 1969; 199–204.
2. Glasstone S, Laidler KJ, Eyring H. *The Theory of Rate Processes*. McGraw-Hill: New York, 1941, 477–480.
3. Frenkel J. *Kinetic Theory of Liquids*. Clarendon: Oxford, 1946, chapter 3, section 1.
4. Chandler D, Weeks JD, Andersen HC. *Science* 1983; **220**: 787–794.
5. Lowden LJ, Chandler D. *J. Chem. Phys.* 1974; **61**: 5228–5241.
6. Jóvári P, Mészáros G, Pusztai L, Sváb E. *J. Chem. Phys.* 2001; **114**: 8082–8090.
7. Schoer JW, Monson PA. *J. Chem. Phys.* 2000; **112**: 8950–8957.
8. The α and ΔH_{vap} data were obtained from different sources such as: (a) *CRC Handbook of Chemistry and Physics*, (b) *The Merck Index*, (c) Riddick JA, Bunger WB. *Techniques of Organic Chemistry. Organic Solvents*, vol. 2, (d) Chickos JS, Acree WE Jr, *J. Phys. Chem. Ref. Data* 2003; **32**: 519–878.
9. Flowers BH, Mendoza E. *Propiedades de la Materia*, Spanish ed. Limusa: Mexico, 1979, 273–278.
10. Barton AFM. *Chem. Rev.* 1975; **75**: 731–753.
11. Berry RS, Rice SA, Ross J. *Physical Chemistry*, 2nd ed. Oxford University Press: New York, 2000, 620.
12. Lutz G, Chavarría M, Arias ML, Mata-Segreda JF. *Rev. Biol. Trop.* 2006; **54**: 59–63.