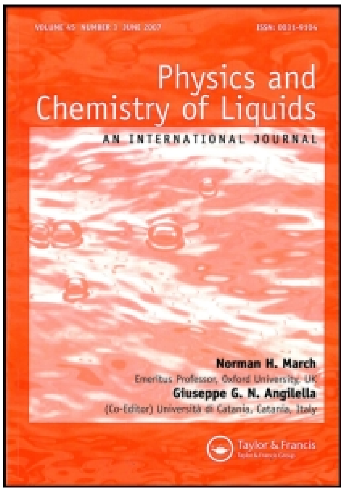

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Relation of surface tension to compressibility at room temperature and wetting index also involving viscosity for 22 organic liquids

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Recent work on surface tension σ of liquid organic solvents by Egemen *et al.* (Environ. Sci. Technol. **34**, 2596–2600 (2000)) prompts us first to draw attention to a simple correlation at 298 K between σ and bulk isothermal compressibility. While a little less accurate (~12%) than some available predictions, these later generally involve at least three chemical or physical descriptors to obtain σ. For some 20 organic liquid solvents, the spread of wetting index (again with restriction to 298 K) involving viscosity η and density ρ is also reported, using the fact that σ/η has units of speed. The search for 'greener' organic solvents may be aided by considerations such as those reported here. The most favourable cleaning agents for the electronic industry require solvents with high density ρ, high compressibility κ_T, and high velocity v_{char} (assumed to be equivalent to the sound velocity).

Keywords: liquid organic solvents; surface tension; bulk isothermal compressibility; wetting index; sound velocity

1. Introduction

The motivation for the present study comes from the appearance of a paper by Egemen *et al.* with predictions of surface tension for organic liquid solvents [1]. Following Reid and Sherwood [2], the authors of ref. [1] first draw attention to a few of the more common empirical models available in the literature. Two of these involve the parachor P, and one of these requires refractive index n and molar refraction R as additional input. While group contribution methods exist to estimate both P and R, n often is taken from experiment.

Egemen *et al.* [1] emphasise that the important role of surface tension σ of cleaning agents in the mass production of truly 'clean' surfaces, or of components of computational and medical applications, is by now widely recognised. Another factor to be taken into account is the persistence of volatile organic compounds in the atmosphere, as they may contribute to global warming (or to the depletion of the ozone layer if the solvent contains halogen atoms such as fluorine, chlorine or bromine). Because of substantial regulatory control of several traditional cleaning agents (or 'solvents') as well as because of toxicity

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and other hazards, industries continue to seek 'greener' solvents as substitutes. While the surface tension σ has been selected as one of the key quantities in the assessment of such alternative solvents, a further quantity, involving not only σ but also viscosity η and density ρ, has also been singled out [1], namely the so-called wetting index (WI), for characterising cleaning agents.

It seems important here, to avoid possible confusion in the future, to point out that there is a misprint in the definition of the WI in the article by Egemen *et al.* [1]. The corrected formula reads

$$\mathrm{WI} = 1000\rho/\sigma\eta \tag{1}$$

This clearly shows that a 'heavy' solvent with high density (ρ), low surface tension (σ) and low viscosity (η) should have a high WI, and be a better cleaning agent. Equation (1) is one of the focal points of the present article.

2. Surface tension

Beginning with surface tension, we stress that early work by Cahn and Hilliard, which is summarised in the book by March and Tosi [3], anticipated the study by Egelstaff and Widom [4] who showed using experimental data that, for a variety of liquids near the triple point, the multiplication of surface tension σ and isothermal compressibility κ_T (to give a quantity ℓ having the dimensions of length)

$$\sigma\kappa_T = \ell \tag{2}$$

was relatively constant. This study motivated Bhatia and March [5] to give a first-principles statistical mechanical derivation of such a relation between σ and κ_T for monatomic liquids by utilising gradient expressions in the density $\rho(x)$ through the liquid–vapour interface. Subsequently, Freeman and March [6] have shown for some 20 organic liquids near 298 K that Equation (2) is well obeyed. There they demonstrated that the (microscopic) length ℓ in Equation (2) is given by (see also Table 1 and Figure 1):

$$\ell = (27 \pm 3) \times 10^{-12}\,\mathrm{m} \tag{3}$$

Though the error shown in Equation (3) is somewhat larger than that quoted in ref. [1] for the two predictions mentioned above involving the parachor P, namely 3–4%, these latter predictions each involve three descriptors for σ, rather than just one, κ_T, in Equation (2) above.

3. Wetting index

Let us turn next to consider a little further the WI defined in Equation (1). Using admittedly cruder statistical mechanical approximations than involved in the theory of Equation (2) given by Bhatia and March [5] as already mentioned above, Alonso and March [7] have written for monatomic liquids, that the ratio σ/η, which has units of speed, can be considered therefore in relation to two characteristic velocities: (i) the thermal velocity v_T defined by $(k_BT/M)^{1/2}$, where k_BT is the thermal energy associated with temperature T, and M is the molecular mass, or alternatively (ii) the sound velocity v_s, which in turn is related to the (now adiabatic) compressibility.

Table 1. Data for 22 organic liquids at 298 K (from ref. [6]).

Organic liquid	Surface tension (σ) (10^{-3} kg s^{-2})	Isothermal compressibility (κ) (10^{-10} m $\times$ s^{-2} kg^{-1})	$\sigma\kappa/270$ (10^{-13} m)	$1/\kappa$ (10^{-10} kg m^{-1} $\times$ s^{-2})
Aniline	42	4.7	0.73	0.213
Bromobenzene	36	6.7	0.89	0.149
Carbon disulfide	32	9.5	1.13	0.105
Iodoethane	29	9	0.97	0.111
Benzene	28	9.7	1.01	0.103
Toluene	28	9.3	0.96	0.108
Dichloromethane	27.2	10.3	1.04	0.097
Acetic acid	27	9.4	0.94	0.106
n-Dodecane	25	9.9	0.92	0.101
Cyclohexane	25	11.3	1.05	0.088
Bromoethane	24	13.6	1.21	0.074
n-Decane	23	11	0.94	0.091
Acetone	23	13	1.11	0.077
n-Propanol	23	10	0.85	0.100
trans-1,2-Dichloroethylene	23	11.2	0.95	0.089
Methanol	22	12.6	1.03	0.079
Ethanol	22	11.4	0.93	0.088
n-Octane	21.2	12.8	1.01	0.078
n-Heptane	19.6	14.4	1.05	0.069
n-Hexane	18.4	16.7	1.14	0.060
Diethyl ether	17	19.7	1.24	0.051
n-Pentane	15.6	18	1.04	0.056

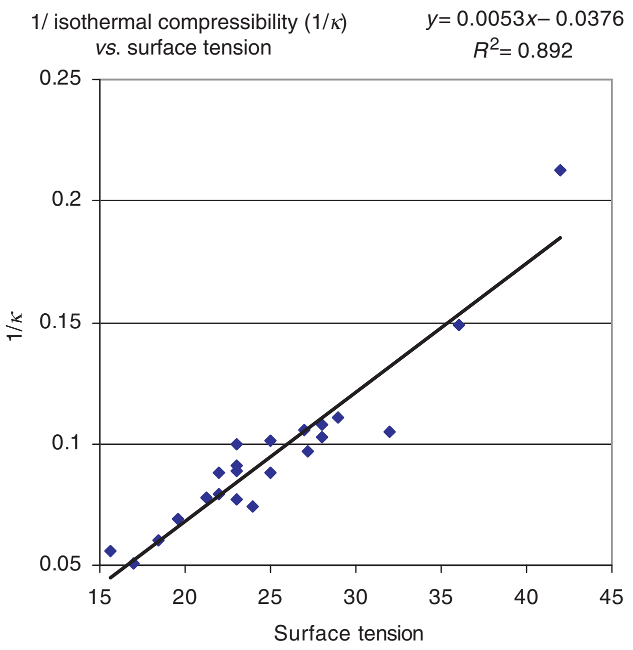

Figure 1. Plot of the reciprocal isothermal compressibility (10^{-10} kg m^{-1} $\times$ s^{-2}) *vs.* the surface tension (10^{-3} kg s^{-2}) for 22 organic liquids at 298 K.

Unfortunately, as also stressed by Freeman and March [6], when one goes from monatomic liquids to organics, or a selection of the latter liquids given in Table 1 of ref. [6], the values of $(\sigma/\eta)\ v_T^{-1}$ now range over a factor of ≈ 9, so that the application of the monatomic liquid result to organics does not provide a very useful correlation. We suggest therefore that, when experimental values of sound velocity become more readily available, the possible correlation of the ratio σ/η for organics at 298 K with the above velocity should be reopened.

To press this point, let us write, by invoking merely dimensional analysis, the ratio σ/η in terms of a characteristic velocity v_{char} as

$$\sigma/\eta = v_{\text{char}} \tag{4}$$

Let us now use Equation (4) in Equation (1), plus Equation (2), to rewrite the WI in terms of the bulk isothermal compressibility κ_{T}, the microscopic length ℓ (compare Equation (3)) and the characteristic velocity defined by Equation (4). We then readily obtain the result

$$\text{WI} = 1000\rho v_{\text{char}}/\sigma^2 = 1000\rho\, v_{\text{char}}\kappa_{\text{T}}^2/\ell^2 \tag{5}$$

Thus, since the length ℓ is rather constant through a wide range of organic liquids (compare Equation (3)), we can say that favourable cleaning agents require solvents with a high density ρ, high compressibility κ_{T} and a high velocity v_{char}. As discussed above, the most likely candidate for v_{char} in the organic solvents under discussion is the velocity of sound v_{s} and it would be interesting in the future in this general area to have experimental measurements of v_{s} for many environment-friendly solvent candidates.

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