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Theoretical derivation of Wada's and Rao's relations

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Abstract. Starting from the appropriate equation of state for the liquid medium and taking a suitable form of the interaction potential, general expressions have been derived relating the velocity of sound to density, compressibility, and molecular weight of the liquid. The general relations reduce to the empirical relations of Wada and Rao as a special case.

1. Introduction

A number of empirical relations relating physico–chemical parameters of liquids and liquid mixtures have been given from time to time. The two prominent amongst these are (i) Wada's (1949) relation ($M\chi_s^{-1/7}/\rho$ = constant) and (ii) Rao's (1940, 1941) relation ($MC^{1/3}/\rho$ = constant) where M denotes molecular weight, ρ the density, χ_s the adiabatic compressibility and C the velocity of sound. The constants in the two cases, called the molecular sound velocity and the molecular compressibility, are found to be independent of temperature and pressure in most of the cases. While considerable work has been done to show the experimental validity of these expressions (Beyer and Letcher 1969), very little progress has been made to give theoretical foundations to these relations.

Starting from the appropriate equation of state for the liquid medium and taking a suitable form of the interaction potential, we have derived expressions connecting liquid density, compressibility, sound velocity and molecular weight. The special case in which these relations reduce to Wada's and Rao's relations has been brought out.

2. Theory

Lependin (1953) obtained, on the basis of molecular kinetic theory, an equation of state for condensed systems in which the pressure p is given by the relation

$$p = \frac{kT}{v} - \frac{\partial \varphi}{\partial v} \tag{1}$$

where k is the Boltzmann constant, T the absolute temperature and v denotes the volume per molecule. The interaction potential φ is defined by

$$\varphi = -\alpha v^{-\mu} + \beta v^{-\nu} \tag{2}$$

where the first term gives the contribution due to Coulombic interaction and the second term represents the short-range repulsive interaction; the value of μ is always equal to 2 but the value of ν is not well defined and different authors have used values ranging from 4 to 6. The equation relating adiabatic sound velocity C, γ the specific heat ratio and the molecular volume v is given by

$$C^2 = -\frac{v^2\gamma}{m}\left(\frac{\Delta p}{\Delta v}\right)_T. \tag{3}$$

From (1) and (3) we get

$$\frac{mc^2}{\gamma} = kT + v^2 \frac{\partial^2 \varphi}{\partial v^2} \tag{4}$$

where γ is the ratio of specific heats C_p and C_v, and m is the mass of each liquid molecule. Equations (2) and (3) lead to the relation

$$\frac{v}{\gamma \chi_s} - kT = \beta\nu(\nu+1)v^{-\nu} - \alpha\mu(\mu+1)v^{-\mu} \tag{5}$$

where C^2 has been replaced by $1/\chi_s\rho$. For the particular case of toluene at 273 K

$$\chi_s = 78 \times 10^{-11}\, m^2/N$$

$$\rho = 8{\cdot}80 \times 10^2\, \mathrm{kg\,m^{-3}}$$

and

$$v = 1{\cdot}8 \times 10^{-30}\, \mathrm{m^3}$$

which gives

$$\frac{v}{\gamma \chi_s} = 2{\cdot}3 \times 10^{-17}\, \mathrm{joules}$$

and

$$kT = 4{\cdot}2 \times 10^{-21}\, \mathrm{joules}.$$

Thus kT is very small in comparison with $v/\gamma\chi_s$ and can be neglected. Differentiating (5) with temperature and putting

$$\alpha_v = \frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}T}$$

and

$$\alpha_{\chi_s} = \frac{1}{\chi_s}\frac{\mathrm{d}\chi_s}{\mathrm{d}T}$$

we get

$$\frac{\alpha_v - \alpha_{\chi_s}}{\alpha_v} = 2 - K(\nu+2) \tag{7}$$

where

$$K = \left(1 - \frac{\alpha\mu(\mu+1)(\mu+2)v^{\nu-\mu}}{\beta\nu(\nu+1)(\nu+2)}\right)\left(1 - \frac{\alpha\mu(\mu+1)v^{\nu-\mu}}{\beta\nu(\nu+1)}\right)^{-1}$$

where the variation of γ with temperature is neglected. This gives the relation

$$\alpha_{\chi_s} = \{K(\nu+2) - 1\}\alpha_v \tag{8}$$

on integrating we get

$$\frac{M}{\rho}\chi_s^{-1/\{K(\nu+2)-1\}} = \text{constant}. \tag{9}$$

Since

$$\alpha_v = \frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}T} = -\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}T} = -\alpha_\rho$$

we have from (8)

$$\alpha_{\chi_s} = -\{K(\nu+2) - 1\}\alpha_\rho \tag{10}$$

and differentiating the expression $C^2 = 1/\rho\chi_s$ with respect to temperature and combining this with (10) gives

$$2\alpha_c = -\{K(\nu+2) - 2\}\alpha_v. \tag{11}$$

Integrating this expression we get

$$\frac{MC^{2/\{K(\nu+2)-2\}}}{\rho} = \text{constant} \tag{12}$$

The relations (9) and (12) resemble the empirical relations of Wada and Rao respectively. It is seen that if

$$K(\nu+2)-2 = 6 \tag{13}$$

these relations reduce to

$$\frac{M\chi_s^{-1/7}}{\rho} = \text{constant} \tag{14}$$

and

$$\frac{MC^{1/3}}{\rho} = \text{constant} \tag{15}$$

which are the well known Wada and Rao relations. The only thing necessary therefore is to justify (13).

Looking at the expression for K, it is apparent that its value is very nearly equal to unity because of the smallness of terms both in the numerator and denominator compared with unity. This must be so for $\nu > \mu$ which is always the case. A reinforcement of this approximation can also be provided by comparing the potential with the Lennard–Jones potential in which $\nu = 4$.

$$\varphi(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

for which the parameters σ and ϵ are known in many cases (Bird *et al.* 1967). For carbon tetrachloride, for example,

$$\frac{\epsilon}{k} = 327\ \text{K}$$

and

$$\sigma = 5881\ \text{Å}$$

and it is a simple calculation to verify that K is almost equal to unity. For greater values of ν this approximation will be even better.

Thus, putting $K = 1$, we find that the relations (9) and (12) reduce to Wada's and Rao's relations respectively provided we assume $\nu = 6$. As pointed out earlier the values of ν reported in the literature range from 4 to 6 and therefore we conclude that Wada and Rao's relations are a special case of the general relations (9) and (12) when $\nu = 6$.

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