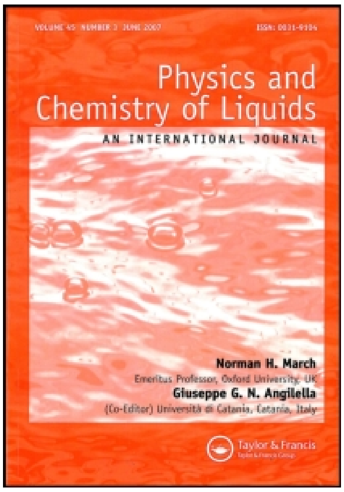

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J. Amorós[a]; S. Ravi[b]; M. Kalidoss[c]
[a] Departamento de Física Aplicada, Universidad de Cantabria, Santander, Spain [b] Department of Physics, National College, Tiruchirappalli - 620 001, India [c] Department of Physics, St. Joseph's College, Tiruchirappalli - 620 002, India

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A NOVEL METHOD OF DETERMINING HARD-CORE RADIUS AND ROUGHNESS FACTOR FOR ORGANIC MIXTURES

J. AMORÓS[a,*], S. RAVI[b] and M. KALIDOSS[c]

[a]*Departamento de Física Aplicada, Universidad de Cantabria, 39005, Santander, Spain;*
[b]*Department of Physics, National College, Tiruchirappalli – 620 001, India;*
[c]*Department of Physics, St. Joseph's College, Tiruchirappalli – 620 002, India*

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The translational–rotational coupling factor or the roughness factor coefficient introduced by Chandler has been evaluated for a number of organic mixtures containing hydrocarbons from their shear viscosity. The hard-core radius and hence the radial distribution function at contact, required in such an evaluation is obtained through a novel method. Its variation with temperature and concentration is discussed. With the available shear viscosity measurements, the roughness factor is also calculated and analyzed.

Keywords: Hard-core radius; Hydrocarbon; Roughness factor; Shear viscosity

1. INTRODUCTION

The transport coefficients for real fluids and hard-sphere fluids can be related by means of two characteristic parameters of the fluid viz.: (i) the translational–rotational coupling factor A_X, where X is the corresponding transport property and (ii) the hard-sphere core σ.

It is conventional that the hard-sphere model forms the basis of the zero-order perturbation for extending the description to real fluids. Chandler [1] assumed that X coincides with its corresponding experimental value for the rough hard-sphere model i.e. X_{RHS}, and gave the relation as

$$X = X_{\mathrm{RHS}} = A_X X_{\mathrm{SHS}}(\sigma) \tag{1}$$

where X_{SHS} is the value for smooth hard-sphere and σ, the hard-core diameter.

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*Corresponding author. E-mail: amorosj@unican.es

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Though the experimental values for the assumed transport property (shear viscosity, A_η, in our case) and the simulation data for $\eta_{\mathrm{SHS}}/\eta_E$, where η_E is the Enskog value, are available, the choice of σ is of much importance. So far with the available data the roughness factor has been calculated for a number of different pure (nonpolar) liquids by Amorós [2–5]. The highlight of this article is that, probably for the first time, the roughness factor A_η is determined for a number of different mixtures (at different mole fractions) containing hydrocarbons. The repulsive part of the interaction which is the essential feature of the fluids at high densities can only be described with a knowledge of the roughness factor and the hard-core diameter.

The knowledge of both parameters (A_η and σ) and their variation with the basic quantities are fundamental for the clarification of the problem. The advantages of this method is that instead of considering individual isotherms, one can consider all the transport coefficient data for a given fluid together. Also, the acoustic determination of σ and $g(\sigma)$ have greater degree of accuracy than the calorimetric measurements. The procedure adopted is as follows.

2. PROCEDURE

Equation (1) can be rewritten as

$$\eta = \eta_{\mathrm{RHS}} = A_\eta \eta_E \frac{\eta_{\mathrm{SHS}}}{\eta_E} \tag{2}$$

where η_E is the Enskog value [6] given by

$$\eta_E = \eta_0 \left[\frac{1}{g(\sigma)} + 0.8\frac{b}{V} + 0.761 g(\sigma)\left(\frac{b}{V}\right)^2 \right] \tag{3}$$

where the covolume is given by $b = (2\pi/3)\rho\sigma^3$ and the number density is $\rho = N/V$. η_0 is the viscosity coefficient of dilute gas composed of hard spheres given by [6]

$$\eta_0 = \frac{5}{16\sigma^2}\left(\frac{mk_BT}{\pi}\right)^{1/2} \tag{4}$$

where m is the mass of one molecule and k_B the Boltzmann's constant. Again in Eq. (3), $g(\sigma)$ is the radial distribution function at contact.

In earlier works, the compressibility factor Z of hard spheres was obtained from a good empirical equation such as the Carnahan–Starling equation [7] or preferably from a simulation method such as the Erpenbeck and Wood [8,9] procedure in the stable range and the Woodcock [10] procedure in the metastable range.

Previous workers obtained $g(\sigma)$ using virial theorem of Clausius [11]. But in the present work, a new relation obtained by Ravi *et al.* [12] that takes up a very elementary form

$$g(\sigma) = \frac{\alpha + \beta + \delta}{(1-y)^4} \tag{5}$$

where

$$\alpha = (1+2y)^2; \quad \beta = -6y(1+y/2)^2; \quad \delta = \frac{y}{2}(1+2y)^3 \quad \text{and} \quad y = \pi\rho\sigma^3/6 \tag{6}$$

has been employed. Even though Eq. (5) was originally derived for atomic liquids, the same relation has been successfully extended to liquid mixtures [13].

Also, the packing factor y is obtained through a very simple relation given by Kalidoss *et al.* [13,14] as

$$U = \frac{1+2y}{(1-y)^2}\left(\frac{\gamma RT}{M}\right)^{1/2} \tag{7}$$

where R is the gas constant, γ is the ratio of specific heat and M is the molecular weight. With the experimental ultrasonic velocity as input in the above equation, y is varied for the best fit. σ follows from y.

It is not the general practice to approximate the molecular systems to a system of rough hard spheres. The work of Kalidoss *et al.* [14] compares the calculated hard-core radii of pure liquids with that obtained from viscosity and surface tension data and the same methodology has been extended to liquid mixtures. For the case of a hard-sphere fluid, the dependence of hard-sphere diameter on temperature and density relates this model to a real fluid, although the molecules of the latter are obviously nonspherical. For mixtures, besides temperature and density, this quantity would depend on composition. But the concept remains.

While previous researchers have studied the variation of σ with temperature and pressure (an extensive recopilation of the main contributions in this field has been done by Silva *et al.* [15]), the present work focuses on the composition dependence.

The advantage of this method is that, if we employ the usual mixing rule, $B = \sum_i x_i B_i$ (with x_i being the mole fraction of the ith component liquid and B_i any of its experimentally observable parameters such as compressibility), large deviation or so called "excess value" of the parameter from the experimental value will be observed. No such discrepancy arises while using the above procedure, since y for pure liquids and their mixtures (at various concentrations) at different temperature are determined directly using ultrasonic velocity. Once y is thus estimated, $g(\sigma)$ and σ follows from Eqs. (5) and (6).

With $(\eta_{\text{SHS}}/\eta_E)$ taken from the simulation data [16–19], η_E from Eq. (3) and the experimental values of η, A_η is readily computed using Eq. (1).

3. RESULTS AND DISCUSSION

The experimental velocity data at 1 MHz for bromoform with hydrocarbons [20], styrene (ethenylbenzene) with alkanes at 1 kHz [21], cyclohexanone with alkanes at 1 kHz [22] and hexane and octane with 1-butanol, 1-hexanol and 1-octanol [23] are taken from literature. Most of our calculations were done with the experimental data at 298.15 K, while hexane and octane with 1-butanol, 1-hexanol and 1-octanol [23] were studied at 288.15, 293.15, 298.15, 303.15 and 308.15 K.

The hard-sphere diameters were evaluated in all these cases. When the shear viscosity data were available, the roughness factor was also evaluated if the density does not exceed the limit of the transition of solid–fluid for hard spheres.

For the hard-sphere diameter, the ultrasonic velocity is the relevant quantity. Besides, shear viscosity coefficient is needed for the calculation of roughness factor. The involved error is about 5%. Adding the remaining uncertainties, A_η is valid within 10%.

Figure 1 shows the results obtained in mixtures of bromoform with alkanes. Starting with pure bromoform ($x = 0$), the hard-sphere diameter increases with the concentration of alkane with a slope increasing as the chain length increases.

Figure 2 shows the results obtained in mixtures of bromoform with other hydrocarbons such as 2,2,4-trimethylpentane (TMP) and tetralin together with the alkanes with the same number of carbon atoms. The variation with the mass and the chain length is clearly appreciable. In fact, the smaller values correspond to tetralin, those corresponding to octane and TMP are almost coincident, and larger values correspond to decane.

The variation of hard-sphere diameter for the mixtures of styrene (ethenylbenzene) with alkanes is shown in Fig. 3, the general features of which are the same as the previous two cases (for alkanes and hydrocarbons). However there is a decrease for the hexane, whose molar mass is appreciably lower than styrene.

The results of the same study for the binary mixtures of cyclohexanone with alkanes and TMP are presented in Fig. 4. The tendency is similar. The values for octane and TMP are again practically coincident, suggesting independence of the other component in their mixtures.

Figure 5 shows the results in the mixtures of hexane with the three alcohols (1-butanol, 1-hexanol and 1-octanol) at 288.15 K. The hard-sphere diameter increases for the case of 1-butanol (the results are similar for the rest of the available temperatures) and decreases in the other two in the order of their molar masses.

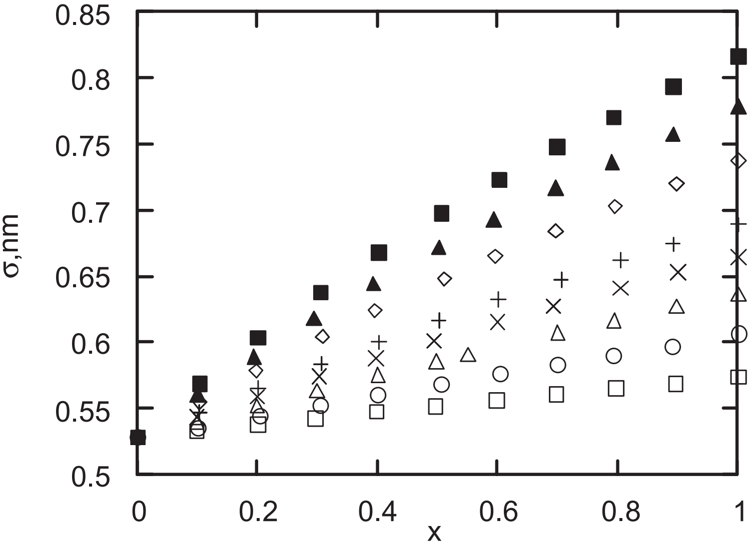

FIGURE 1 Hard-sphere diameter as a function of mole fraction of alkane in binary mixtures of bromoform with alkanes: □ hexane; ○ heptane; △ octane; × nonane; + decane; ◇ dodecane; ▲ tetradecane; ■ hexadecane.

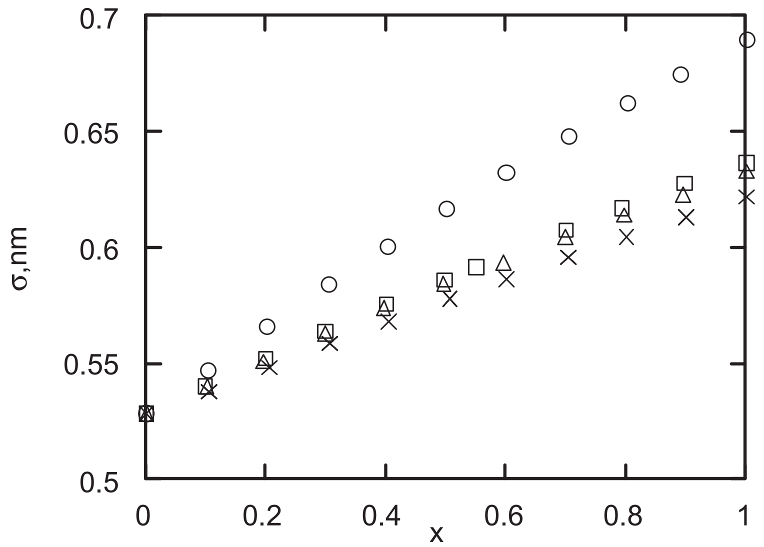

FIGURE 2 As in Fig. 1 for hydrocarbons: □ octane; ○ decane; △ 2,2,4-trimethylpentane (TMP); × tetralin.

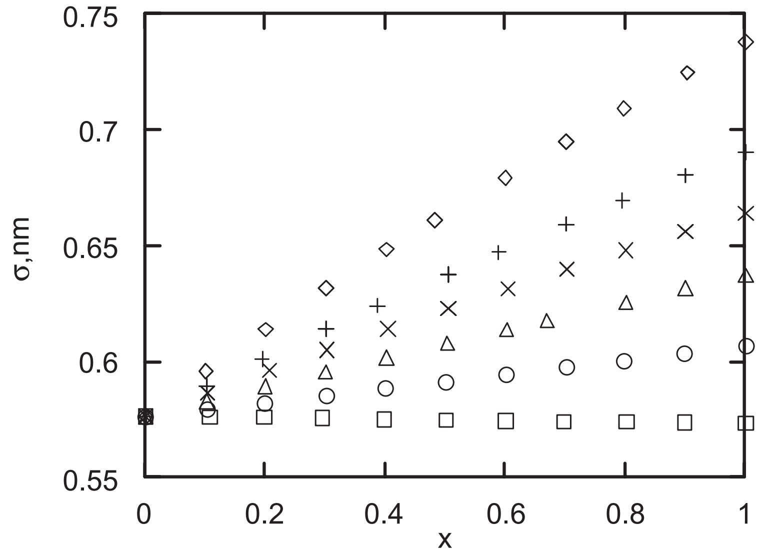

FIGURE 3 As in Fig. 1 in binary mixtures of ethenylbenzene with alkanes.

Figure 6 shows the results for the mixtures of hexane + 1-butanol and Fig. 7 that of hexane + 1-hexanol at five available temperatures. The temperature effect is negligible if the carbon atoms number of both the components is different (Fig. 6). However, there is an appreciable separation in Fig. 7 for the case of 1-hexanol. The same behavior is observed for the mixture of octane with 1-octanol. This can be interpreted by assuming that the variations with respect to concentration assumes importance when the two component liquid molecules have the different number of carbon atoms.

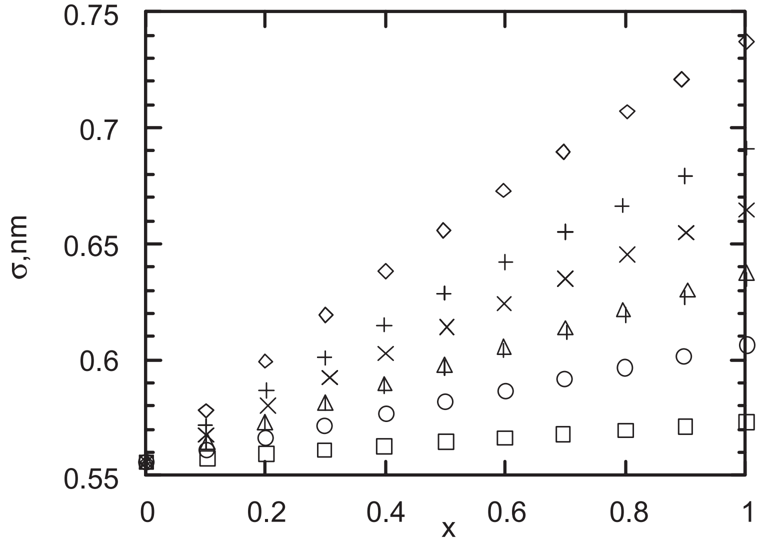

FIGURE 4 As in Fig. 1 in binary mixtures of cyclohexanone with alkanes and | trimethylpentane (TMP).

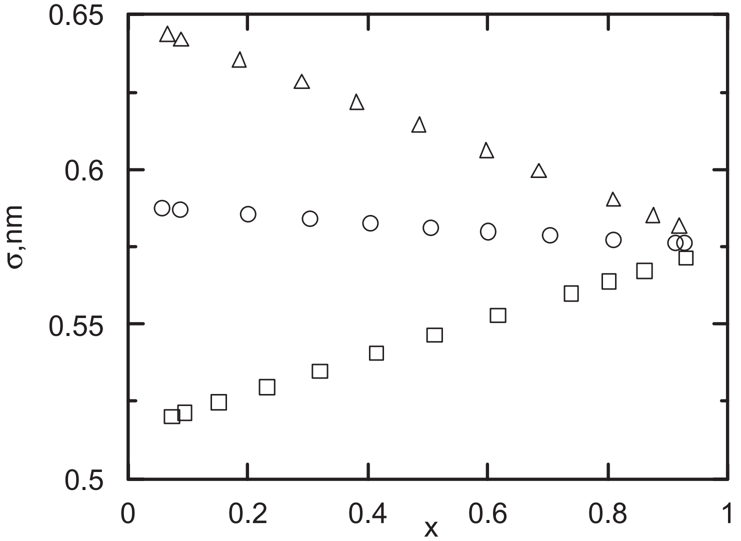

FIGURE 5 As in Fig. 1 in binary mixtures of hexane with alcohols: □ 1-butanol; ○ 1-hexanol; △ 1-octanol at 288.15 K.

The determination of the roughness factor A_η is limited owing to two requirements:

(1) the simultaneous existence of data for ultrasonic velocity and shear viscosity
(2) the peculiar limitations of Chandler's method.

Therefore, only generic conclusions can be inferred.

The roughness factor A_η results are given in Fig. 8. A_η varies strongly for hydrogen bonded liquids. This feature was already established for the variation with temperature

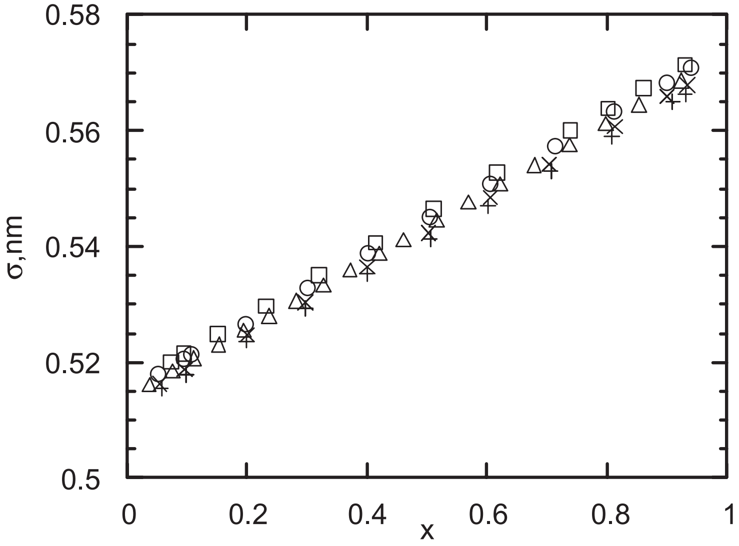

FIGURE 6 As in Fig. 1 in binary mixtures at 288.15 K (□), 293.15.K (○), 298.15 K (△), 303.15 K (×) and 308.15 K (+) of hexane with 1-butanol.

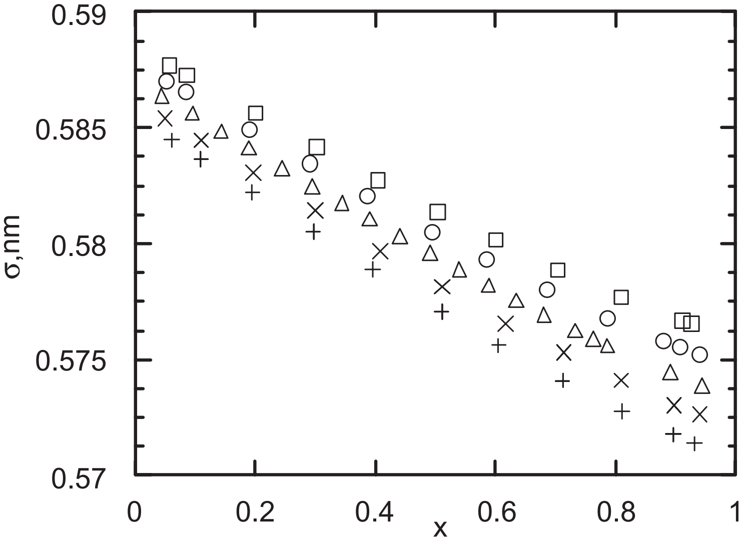

FIGURE 7 As in Fig. 6 with 1-hexanol.

for pure substances [24] and can be attributed to strongly anisotropic interactions resulting from hydrogen bonding. The remaining substances present a very smooth variation in hexane mixtures. In the case of bromoform, A_η is practically uniform.

A_η is calculated from the experimental viscosity data. Its difference with respect to unity reveals the deviation from the hard-sphere system. If an alkane is present in the mixture, this deviation is greater when its concentration diminishes probably due to the increase of the effects of electrical polarity.

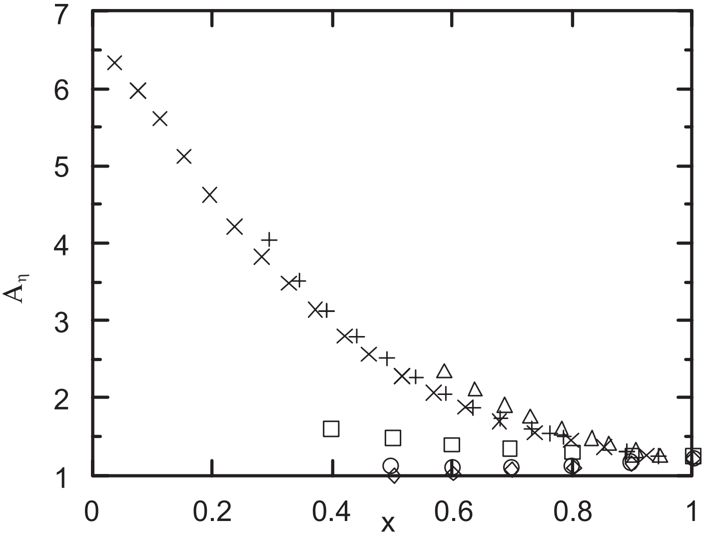

FIGURE 8 Roughness factor A_η as a function of mole fraction of hexane in binary mixtures with several organic compounds: ○ bromoform; ◇ ethenylbenzene; □ cyclohexanone; × 1-butanol; + 1-hexanol; △ 1-octanol.

As A_η were calculated fitting the available values along an isotherm, the comparison of $\eta_{\mathrm{RHS}} = A_\eta \eta_{\mathrm{SHS}}$ with each individual experimental value of η would be useful. However, we obtain each value of A_η from the experimental viscosity coefficient and therefore the comparison is not possible.

Thus the method proposed by Kalidoss and Ravi [13,14] for calculating hard-core diameters and hence $g(\sigma)$ makes it possible to determine the roughness factor for any pure liquid or liquid mixture subject to the availability of experimental data of ultrasonic velocity and shear viscosity.

Work is in progress for other liquid mixtures.

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