J. Chim. Phys. (1999) **96**, 923-933

Influence of some physico-chemical characteristics of non-associated liquids on sound velocity therein

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(Received 27 August 1998; accepted 21 January 1999)

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RÉSUMÉ

L'équation, qui a été proposée pour les liquides non-associés, décrit une nouvelle relation fonctionnelle entre la vitesse du son dans ces liquides et les caractéristiques physico-chimiques de ces derniers (volume critique, tension superficielle, densité et masse moléculaire). Il a été démontré que cette équation peut être utilisée pour les calculs de la vitesse du son à différentes températures.
Mots-clés : Vitesse du son, liquids non-associés, caractéristiques physico-chimiques.

ABSTRACT

The equation proposed for non-associated liquids describes a new functional dependence of the sound velocity in these liquids on their physico-chemical characteristics (critical volume, surface tension, density and molecular mass). It is shown that this equation can be used for the adequate calculation of the sound velocity at different temperature.
Key words: Sound velocity, non-associated liquids, physico-chemical characteristics.

INTRODUCTION

Many correlations were proposed in order to describe the relationship between physico-chemical characteristics of non-associated liquids and sound velocity in them [1-6]. These correlations were designed mainly on the basis of various thermodynamical relations, which exist between sound velocity and different physico-chemical characteristics of these liquids. However, possible dynamical aspects, which define sound velocity and are connected with vibrational motion of molecules involved.

into a spreading sound wave, weren't taken into account properly. As a consequence of this fact the use of these correlations is most successfully within the framework of one separate homologous series of investigated compounds. Transitions to new homologous series, possessing new types of chemical structure, require additional changes (or modification) of their semi-empirical constants [7, 8].

At the same time there are some correlations, describing (as it will be seen below) sound velocity on the basis of physico-chemical parameters, which are connected with the above mentioned dynamical aspects. One of them is the correlation, which was given in the work [9]:

$$c = 5.663\sigma^{1/2} (N/d^2M)^{1/6}. \quad (1)$$

Here σ, d, and M are respectively surface tension, density, and molecular mass of the liquid under investigation. N is Avogadro's number. Equation (2) received in the work [10] connects c at absolute temperature T with critical molar volume V:

$$c = 0.1049\ V^4d^4(RT/M^4)^{4/3}. \quad (2)$$

In Eqn. (2) R is universal gas constant. Eqns. (1) and (2) hold for non-associated liquids; and their calculation errors are equal to ±2.5% [11].

The existence of Eqns. (1) and (2) shows that both these quantities (σ and V) are important for the adequate quantitative description of sound velocity in the liquid phase. The aim of the present work consists in the attempt to find the equation, which connects sound velocity with these physico-chemical quantities.

THEORY

We shall consider all the molecules of the non-associated liquid under investigation as the spherical particles, which have the molecular mass M and may vibrate around their equilibrium centres. Further, we shall discuss the frontier surface of spreading sound wave, which is situated between the following regions: one of them is the

region compressed by this wave, the second one is the normal liquid phase in the direction of its spreading. Let the highest possible values of molecular frequency and amplitude of the molecules situated on this surface be equal to ν and A respectively. The average velocity-u of these frontier molecules at the segment, which is normal to the plane of the above mentioned frontier surface and has the value of its lenght - 2A, will be equal to:

$$u = 4A\nu. \tag{3}$$

Let the process of spreading of sound wave consist of two processes. Let, further, the first slowest process, which takes place due to the compression in the first region and defines mainly the value of c, be the displacement of the frontier molecule under consideration from its equilibrium point at some distance - D, which is less than A and is supposed to be proportional to A for different liquids. When this distance (at the frequency ν) is reached, the second faster process of passing of sound wave impulse will take place. This process is caused by the intermolecular repulsion between this frontier molecule and one of the molecules of the second region. The first process requires the following time: D/u and isn't accompanied by any significant interatomic interaction in the direction of sound wave spreading. It takes place in the free volume, which is accessible to this molecule. In other words, for any non-associated liquid D is the upper limit of the approximate description of its bimolecular potential by means of the corresponding one-dimensional potential well. Then the value of c will be defined by the first equality of (4). Thus, bearing in mind all the above mentioned reasons, we may consider that c is propotional to u:

$$c = Au/D = su = 4sA\nu, \tag{4}$$

where s is coefficient of proportionality, which equals to A/D and is constant for various non-associated liquids.

In order to appreciate ν we shall consider the vibrations of the frontier molecules