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VELOCITY OF ULTRASOUND PROPAGATION IN SOLUTIONS

OF HELIUM IN CRYOGENIC LIQUIDS

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The speed of ultrasound propagation is measured in neon—helium solutions. The effect of a helium impurity on ultrasound propagation speed in cryogenic liquids is analyzed.

The propagation speed of ultrasound in the low-frequency region where dispersion is absent is a purely thermodynamic quantity which relates compressibility and specific heat. Since, as a rule, the caloric properties of low-temperature liquids can be measured only with insignificant uncertainties, one can obtain the most complete information on equilibrium volume properties of such systems by using results of ultrasound velocity measurements together with the equation of state. It is also possible to use such data to verify theoretical models at a level significantly higher than is possible with the equation of state.

The solubility of helium in argon, and at sufficiently low temperature and pressure, in neon and hydrogen as well, is relatively low. This fact allows treating the general problem of describing the change in speed of ultrasound in solutions of He in Ar, Ne, and H_2 (for definiteness, pH_2) as one in which the He concentration is a small parameter. This problem has been solved within the framework of a model based on the method of distribution functions in the statistical physics of mixtures of simple liquids.

Experimental Results. Studies of ultrasound speed in Ne—He solutions were performed by the impulsive method at a frequency of 5 MHz along five isotherms at T = 26.95, 29.91, 32.89, 35.9, and 38.88°K at pressures up to 150 atm. The range of He concentration in the liquid Ne then comprised x_2 = 0-27 mol.%. The measurement technique and experimental equipment were described by the present authors in [1, 2]. The uncertainty in the ultrasound speed measurements was no greater than 0.1%. The experimental results are presented in Table 1. The He concentration in the solutions was determined from equilibrium phase diagrams [3]. The gaseous impurity (He) reduces the speed of ultrasound in Ne—He solutions as compared to the pure solvent (Ne), as in Ar—He [4] and pH_2—He [2], studied previously by the present authors. The higher the temperature, the higher the solubility of He in liquid Ne [3] and the more intense the reduction in ultrasound speed in the solution. Thus, at T = 26.95°K and p = 60 atm $|\Delta(p)| = u - u_{11}$ (where u_{11} is the speed of ultrasound in pure Ne, u, the speed in the Ne—He solution) comprises ∿10 m/sec, while at T = 38.88°K and the same pressure $|\Delta u| \simeq 46$ m/sec.

Using density values for the Ne—He solutions calculated from data on dielectric permittivity [5] the adiabatic compressibility $\beta_S = 1/\rho u^2$ was determined. As is evident from Fig. 1, the He impurity increases β_S of liquid Ne.

TABLE 1. Ultrasound Propagation Speed in Neon—Helium Solutions

p, atm	x_2, mol.%	u, m/sec	p, atm	x_2 mol.%	u, m/sec
$T = 26{,}95$ K			38,0	5,35	511,3
0,96*	0	597,2	47,2	7,9	518,5
11,1	0,7	602,6	77,2	12,1	526,4
29,0	1,93	612,6	93,15	15,15	533,1
50,8	3,6	625,9	112,7	19,83	542,4
81,0	5,3	639,0	125,8	23,45	546,1
106,0	6,57	646,4	134,0	25,8	545,6
131,6	7,85	658,4	144,0	28,6	552,1
147,3	8,52	657,0	$T = 35{,}9$ K		
			7,52*	0	427,5
$T = 29{,}91$ K			16,5	1,62	436,0
			30,3	4,67	449,3
2,15*	0	547,5	43,1	7,7	459,5
13,5	1,16	557,0	53,7	10,45	464,5
33,6	3,15	563,2	65,0	14,05	470,0
46,1	4,57	571,0	82,5	21,6	476,1
70,0	7,1	583,1	90,0	25,5	479,0
89,7	8,97	587,2			
105,1	10,35	594,3	$T = 38{,}88$ K		
127,6	12,45	603,5	13,41*	0	355,3
145,1	14,1	606,3	24,0	2,95	373,0
			35,8	6,65	385,5
$T = 32{,}89$ K			46,7	10,55	402,2
4,24*	0	491,2	63,6	23,6	412,2
13,4	1,4	492,6			
22,2	2,81	501,3			

*Saturated vapor pressure of pore Ne.

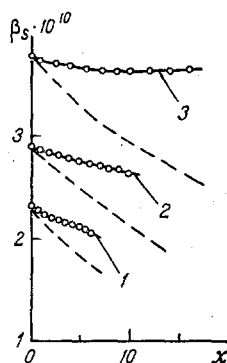

Fig. 1. Adiabatic compressibility β (cm²/dyn) vs He concentration (mol.%) in Ne—He solutions along isotherms at T = 26.95°K (1), 29.91 (2), 32.89 (3); dashed curves, pure Ne at corresponding pressures.

Evaluation of Results. We will consider the following model of the solution, a generalization of that proposed in [6]. For the pressure p and internal energy e per single particle we have

$$p = \rho kT - \frac{2}{3}\pi\rho^2 \sum_{i,j} x_i x_j \int_0^\infty (d\varphi_{ij}(r)/dr)\, g_{ij}(r)\, r^3 dr, \tag{1}$$

$$e = \frac{3}{2} kT + 2\pi\rho \sum_{i,j} x_i x_j \int_0^\infty \varphi_{ij}(r)\, g_{ij}(r)\, r^2 dr, \tag{2}$$

where $x_1 = N_i/N$ is the concentration of the i-th component of the mixture. We choose the interaction potentials in Lennard-Jones form

$$\varphi_{ij}(r) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6], \tag{3}$$

where we define ε_{12} and σ_{12} with refined Lorentz—Bertello rules $\varepsilon_{ij} = \zeta_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{1/2}$; $\sigma_{ij} = 0.5(\sigma_{ii}+\sigma_{jj})$, and we take the potential parameters for the pure components of the mixture the same as in [7]. We define the value of the parameter ζ_{12} according to [8] (in [6] the case $\zeta = 1$ was considered, i.e., the traditional rule). The subscripts i and j in the present case take on the values of 1 for the solvent and 2 for the He.

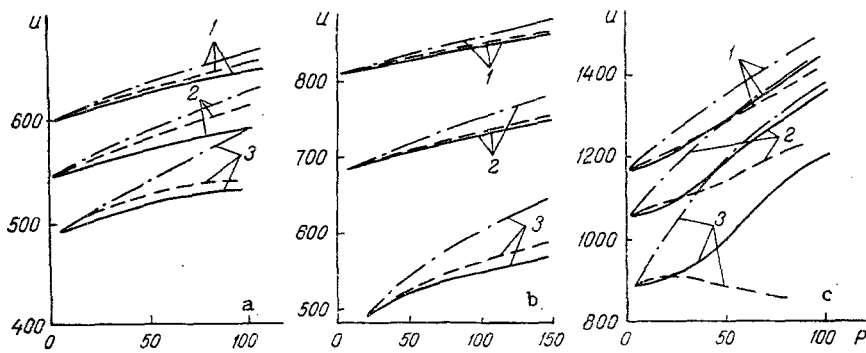Since x_2 is considered as a small parameter, from Eqs. (1) and (2), neglecting terms quadratic in x_2 we obtain

Fig. 2. Comparison of experimental speed of ultrasound u(p) (solid curves) vs theoretical calculations (dashed lines): a) for Ne—He solutions at T = 26.95°K (1), 29.91 (2), 32.89 (3); b) Ar—He solutions at T = 91.34°K (1), 108.03 (2), 130.08 (3); c) pH$_2$—He at T = 18.0°K (1), 22.03 (2), 26.6 (3); dash—dot curves, u(p) for pure solvents (Ne [1], Ar [12], pH$_2$ [13]). u, m/sec, p, atm.

$$p = p_{11} + \frac{4\pi}{3}\, \rho^2 x_2 \int_0^\infty [(d\varphi_{11}(r)/dr)\, g_{11}(r) - (d\varphi_{12}(r)/dr)\, g_{12}(r)]\, r^3 dr, \tag{4}$$

$$e = e_{11} - 4\pi\rho x_2 \int_0^\infty [\varphi_{11}(r)\, g_{11}(r) - \varphi_{12}(r)\, g_{12}(r)]\, r^2 dr. \tag{5}$$

Here we distinguish the quantities p_{11} and e_{11}, the pressure and energy of the pure solvent in the thermodynamic state (T, ρ) of the solution. Commencing from expressions presented in [7], for the speed of ultrasound in the solution we obtain

$$u^2 = (x_1 m_1 + x_2 m_2)^{-1} \left[(\partial p/\partial\rho)_T + T\left(\frac{\partial p}{\partial T}\right)^2_\rho \Big/ \rho^2 \left(\frac{\partial e}{\partial T}\right)_\rho \right], \tag{6}$$

where m_1, m_2 are the molecular masses of the solution components. Upon substitution of Eqs. (4), (5) in Eq. (6), considering only terms produced by interaction, we have

$$u^2 = m_1 (x_1 m_1 + x_2 m_2)^{-1} u_{11}^2 + \left(\frac{\partial}{\partial\rho}\right)_T \frac{4\pi\rho^2 x_2}{3(x_1 m_1 + x_2 m_2)} \int_0^\infty [(d\varphi_{11}(r)/dr)\, g_{11}(r) - (d\varphi_{12}(r)/dr)\, g_{12}(r)]\, r^3 dr \tag{7}$$

(the essence of this approximation will be clarified below). Here u_{11} is the speed of ultrasound in the pure solvent:

$$u_{11}^2 = \frac{1}{m_1} \left[(\partial p_{11}/\partial\rho)_T + T\left(\frac{\partial p_{11}}{\partial T}\right)^2_\rho \Big/ \rho^2 \left(\frac{\partial e_{11}}{\partial T}\right)_\rho \right]. \tag{8}$$

In this case to calculate the small additions to u_{11} we may approximate the radial distribution function by steps of unit height and length r^0_{ij}, since calculations of the speed of sound itself in such an approximation produce usable results for a number of liquids [9]. The effects of particle correlation are considered by suitable definition of r^0_{ij} (ρ, T). According to [10]:

$$2z_{ij}^5 - z_{ij}^3 + \frac{T^*_{ij}}{12}\, z_{ij} = \frac{\pi\sigma_{ij}^3 \rho T^*_{ij}}{6} \exp[4/T^*_{ij}(z_{ij}^2 - z_{ij}^4)], \tag{9}$$

where $T^*_{ij} = kT/\varepsilon_{ij}$; $z_{ij} = (\sigma_{ij}/r^0_{ij})^3$. Since it follows from this that the derivative $(\partial r^0_{ij}/\partial T)_p \simeq \varphi_{ij}(r^0_{ij})/T(\partial\varphi_{ij}/\partial r)|_{r=r^0_{ij}}$ is small, the meaning of the approximation used in transforming from Eq. (6) to Eq. (7) becomes clear: additions due to derivatives with respect to ρ (while terms linear in x_2 depend on T only in terms of g(r; ρ, T)). The desirability of the approximations used for the radial distribution function in calculating small changes in the ultrasound velocity $\Delta u = u - u_{11}$ are confirmed by a comparison of the derivatives $(\partial p/\partial\rho)_T$ in the present approximation and a more precise one, for example, the so-called mean spherical approximation model of [11]. Calculations are presented in the appendix.

Equation (9) was solved numerically on an ES-1033 computer for the required temperatures

and pressures (densities). The Mueller method (parabola) based on quadratic interpolation was used to find the roots.

For the difference between the squares of the ultrasound speeds in the solution and the pure solvent $\Delta(u^2) = u^2 - u_{11}^2$ in similar states (T, ρ) we obtain from Eq. (7)

$$\Delta(u^2) = u_{11}^2 \frac{\gamma_m - 1}{1 + \gamma_x \gamma_m} - \frac{128 \pi \rho}{\gamma_x m_1 + m_2} [\sigma_{11}^3 \varepsilon_{11}(4z_{11}^3 - 3z_{11}) - \sigma_{12}^3 \varepsilon_{12}(4z_{12}^3 - 3z_{12})], \quad (10)$$

where $\gamma_x(p) = x_1/x_2$; $\gamma_m = m_1/m_2$. From this we determine the value of $\Delta u = -u_{11}[-(1 + \Delta(u^2)/u_{11}^2)^{1/2}]$ the change in ultrasound velocity upon solution of He in the liquid. These data were used to construct graphs of ultrasound speed vs pressure in Ne−He, Ar−He, and pH$_2$− He solutions shown in Fig. 2. For comparison experimental results on ultrasound speed from the present study (Ne−He solutions), [4] (Ar−He), and [2] (pH$_2$−He) are shown. The agreement between calculated and experimental results is satisfactory within the framework of the approximations used. It is evident that the best description is achieved at lower temperatures, apparently because the transition from Eq. (6) to Eq. (7) is then more correct, and x_2 decreases for equal pressures. This appears especially markedly in the case of the system pH$_2$−He (Fig. 2c); thus the behavior of the calculated dependence $u(p)$ at $T = 26.6°K$ is explained by the good solubility of He in hydrogen at such a temperature [14], so that the quantity x_2 cannot be considered a small parameter. With decrease in temperature the solubility of He in pH$_2$ decreases markedly, and Eq. (10) produces satisfactory results if the pressure is not too high.

Appendix. We will express the derivative $(\partial p/\partial \rho)_T$ in terms of the direct correlation function $c(r)$ [15]:

$$(\partial p/\partial \rho)_T = kT - 4\pi \rho kT \int_0^\infty c(r) r^2 dr. \quad (11)$$

This means that

$$\left(\frac{\partial}{\partial \rho}\right)_T \frac{2}{3} \pi \rho^2 \int_0^\infty (d\varphi(r)/dr) g(r) r^3 dr = 4\pi \rho kT \int_0^\infty c(r) r^2 dr. \quad (12)$$

If the pressure is written in the form of Eq. (3), then by using Eq. (12), as in the derivation of Eq. (7), we have

$$(x_1 m_1 + x_2 m_2)^{-1} (\partial p/\partial \rho)_T = \frac{m_1}{x_1 m_1 + x_2 m_2} u_{11}^2 + \frac{8\pi \rho kT x^2}{x_1 m_1 + x_2 m_2} \int_0^\infty [c_{11}(r) - c_{12}(r)] r^2 dr. \quad (13)$$

We will compare the expressions

$$\left(\frac{\partial}{\partial \rho}\right) \frac{4\pi \rho^2 x^2}{3(x_1 m_1 + x_2 m_2)} \int_0^\infty (d\varphi_{ij}(r)/dr) g_{ij}(r) r^3 dr \quad (14)$$

and

$$\frac{8\pi \rho x_2 kT}{x_1 m_1 + x_2 m_2} \int_0^\infty c_{ij}(r) r^2 dr. \quad (15)$$

Since the structure of these expressions, and consequently, their relative difference for $ij = 11$ and 12, are identical, we will perform the evaluation for the first case, omitting the indices ij.

The mean spherical model of [11] proposes the following form for $c(r)$:

$$c(r) = \begin{cases} g(r)[1 - \exp(-\varphi(r)/kT)], & 0 < r < \sigma, \\ -\varphi(r)/kT, & r > \sigma. \end{cases} \quad (16)$$

Calculations of thermodynamic characteristics in the mean spherical model give satisfactory results for a number of properties and a wide class of systems. Using the approximation of Eq. (16) to calculate the integral in Eq. (15), integrating by parts we have

$$\int_0^\infty c(r) r^2 dr \simeq \int_0^\sigma [1 - \exp(-\varphi(r)/kT)] g(r) r^2 dr + \frac{1}{3kT} \int_\sigma^\infty (d\varphi(r)/dr) r^3 dr. \quad (17)$$

Evaluating the integral of Eq. (14) in our approximation and using the condition $g(r) \simeq g(\sigma)\exp[-\varphi(r)/kT]$ at $r < \sigma$ (see [16]) and the closeness of r^0 to σ to evaluate Eq. (17), we find for the temperature $T = \varepsilon/k$ that the relative difference between Eqs. (14) and (15) does not exceed 12% and decreases with decrease in temperature. This justifies the approximation used.

NOTATION

p, pressure; V, molar volume; T, temperature; x, concentration; u, speed of ultrasound; ρ, density; β_S, adiabatic compressibility; e, internal energy; k, Boltzmann's constant; $g_{ij}(r)$, radial distribution function for mixture of particles with effective interaction pair potential $\varphi_{ij}(r)$; ε and σ, parameters of Lennard-Jones potential; m, molecular mass; c(r), direct correlation function.

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DEPENDENCE OF THE VISCOSITY OF PLASTISOLS
ON TEMPERATURE AND TIME

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The method of rapid heating of the medium was used for investigating the dependence of the viscosity of polyvinyl chloride plastisols on the temperature and time in connection with isothermal molding in casting practice.

For injection molding in long molds with small clearances, plastisols are often used; these are materials consisting basically of a mixture of a polymer and a plasticizer. Fixation of the mold is attained by gelling the polymer material at elevated temperatures where the viscosity of the system rapidly increases up to curing. To optimize casting and choose correctly its parameters, it is important to know the rheological properties of the processed plastisols.

It was found that the temperature has a considerable effect on the gelling process of industrial plastisols above 40-60°C. At low temperatures, where the viscosity does not change with time, the rheological properties of plastisols in steady shear have been accurately determined (viz., e.g., [1]). It is interesting to investigate the behavior of these