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Relationships of Some Useful Thermodynamic Properties of Liquid with Sound Velocity and Density Data

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Abstract: In order to compute various useful and importance thermodynamic properties of liquids from sound velocity and density data, a number of correlations have been presented. Sound velocity and density data for numerous liquids are available in literature and the experimental measurements of these properties are very simple and convenient, also very economical. Such data provides very simple methods of determining the thermodynamic properties. Expressions of heat capacity at constant pressure C_p, heat capacity at constant volume C_v, heat capacities ratio (γ), internal pressure (P_{int}), energy of vaporisation (ΔE_v), cohesive energy density (c) and solubility parameter (δ) are obtained in terms of density (ρ) and sound velocity (u) on the basis of empirical relations for thermal expansivity (α) and isothermal compressibility (β_T) proposed earlier from this lab.

Keywords: Thermodynamics, Sound velocity, Density, Heat capacity.

1. Introduction

Correlations between various thermodynamic and transport properties of a liquid have been found to be very useful in the study of physicochemical and structural behaviour. Some of the properties of liquid which are very difficult to determine experimentally even not possible. In such case the correlation with other known property is carried out. Sound velocity is one of the very important thermodynamic property of liquid which can be determined very easily using low cost technique. Sound velocity and density data in conjunction with the equation of state provides a lot of information about the interactions occurring in liquid system. Correlation between sound velocity and surface tension has been made by earlier worker[1-3]. These interrelationships have been employed by many researchers[4-9]. In the year 1999, Markus[10] presented a critical review on the relationship between transport and thermodynamic properties of pure organic liquids at ambient conditions. Interrelationships between other properties are also available in literature[11,12].

Considering sound velocity and density as tools (since their experimental measurements are simple and economical), expressions[13-16] for thermal expansivity (α) and isothermal compressibility (β_T) were deduced in terms of these properties. These relations are tested and applied for pure liquids, binary and multicomponent liquid system.

(1) $$\alpha = (0.0191 \times \beta_T)^{1/4} = \frac{75.6 \times 10^{-3}}{T^{1/9} U^{1/2} \rho^{1/3}}$$

(2) $$\beta_T = \frac{1.71 \times 10^{-3}}{T^{4/9} U^2 \rho^{4/3}}$$

In the present work, expressions for estimating the heat capacities (at constant volume and at constant pressure) are deduced in terms of ρ and U, so that C_v and C_P of liquid can be obtained directly from the experimental values of density and sound velocity.
Starting with the thermodynamic relation

(3) $$\beta_S = (U^2 \rho)^{-1}$$

and remembering that

(4) $$V = \frac{M}{\rho}$$

(5) $$\beta_S - (U^2\rho)^{-1} = \frac{\alpha^2 TM}{\rho C_P}\quad .$$

We obtain

(6) $$\frac{1.71\times10^{-3}}{T^{4/9}u^2\rho^{4/3}} - (U^2\rho)^{-1} = \frac{\alpha^2 TM}{\rho C_P}$$

Using eqs (1) and (2) for α and β_T, above equation reduces to

$$C_P = \frac{5715.36\times10^{-4}MU}{\rho^{1/3}(1.71 - T^{4/9}\rho^{1/3}}$$

which on simplification gives

(7) $$\gamma = \frac{C_p}{C_v} = \frac{\beta_T}{\beta_S}\,.$$

There are two routes of arriving the interrelation for C_v, one is to start with the thermodynamic relation

(8) $$C_p - C_v = \frac{\alpha^2 TV}{C_P}$$

and using the value of C_p and α in terms of u and ρ. This is a lengthy procedure. Another way is to use equation for γ i.e.

(9) $$\gamma = \frac{C_p}{C_v} = \frac{\beta_T}{\beta_S}\quad .$$

By substituting the values of β_T and β_s in terms of u and ρ. γ is obtained as

(10) $$\gamma = \frac{1.71\times10^{-3}}{T^{4/9}\rho^{1/3}}$$

here, C_V is given by

(11) $$C_V = \frac{C_p}{\gamma} = \frac{5715.36.M.u.T^{5/3}}{17.1(17.1 - \rho^{1/3}T^{1/9})} .$$

In the year 1997[13], the interrelationship between internal pressure (P_{int}) and sound velocity was obtained as

(12) $$P_{\text{int}} = 44.2 \times T^{4/3} u^{3/2} \rho .$$

Now we shall obtained the relationship for cohesive energy, density, c, and solubility parameter, (δ) , introduced by Hildebr and co-workers[12] in their regular solution theory. They discussed the significance of these thermodynamic properties. The internal pressure is related to the energy of vaporization, U_{vap}, by the equation

(13) $$P_{\text{int}} = \frac{U_{vap}}{V}$$

where V is the molar volume.

U_{vap} is obtained by the relation

(14) $$U_{vap} = H_{vap} - RT .$$

Using the value of heat of vaporisation H_{vap}. The cohesive energy density, c, and the solubility parameter, δ, are obtained as

(15) $$c = n\frac{U_{vap}}{V} \approx \frac{U_{vap}}{V}$$

(16) $$\delta = \sqrt{C}$$

n is taken as unity of non-polar liquids.

Using equations (12), (15) and (16)

(17) $$C = 44.2.T^{4/3}.\rho.U^{3/2}$$

and $$\delta = (44.2.T^{4/3}.\rho.U^{3/2})^{1/2}$$

(18) $$\delta = T^{2/3}.\rho.U^{3/4}.$$

Hence

(19) $$\delta = T^{2/3}\rho^{1/3}U^{3/4}.$$

Thus we have succeeded in relating sound velocity and density with a number of useful and important thermodynamic properties viz C_P, C_v, γ, P_{int}, U_{vap}, c_{ed} and δ of liquids. This will enable to obtain these thermodynamic properties with help of only sound velocity and density data. In the subsequent paper we shall describe the experimental verification of these equations.

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References

1. N. Auerbach, Oberfl,ӓchens panning and Schallgaschwindigheit, *Experimentia*, **4** (1978) 473-475.
2. J. D. Pandey, N. Pant, N. Agrawal and Shikha, Ultrasonic velocity in quaternary liquid mixtures, *Acoustica*, **68** (1989) 225-227.
3. J. D. Pandey, V. Sanguri, A. K. Singh, and G. P. Dubey, Interrelationship between surface tension and ultrasonic velocity of liquid & liquid mixtures, *J.Pure & Appl.Ultrasonics,* **19** (1997) 47-49.
4. R. L. Mishra, Extension of Flory's statistical theory of elevated pressures, *J. Chem.Phys*., **73** (1980) 5301-5304.
5. J. D. Pandey, Sound velocity and surface tension from flory's statistical theory, J. Chem.Soc., *Faraday Transactions-I*, **75** (1973) 2160-2164.
6. J. D. Pandey and R. P. Pandey, Surface tension and sound velocity of Pb-Sn alloys in the liquid state, *Phys.Chem Liq*., 1984.
7. Shipra Baluja, Prediction of surface tension in ternary systems, *J.Pure.Appl.Ultrasonic*, **21**(1999)119-121.

8. S. L. Oswal, P. Oswal, P. S. Modi, J. P. Dave and R. L. Gardas, Acoustic, volumetric, compressibility and refractive properties of alkyl alkanaotes from $298.15-333.15.$ *K, Thermochimica Acta*, **410**(2004) 1-14.

9. J. D. Pandey, P. Jain and V. Vyas, Isothermal compressibility and sound velocity of binary liquis systems, *Pramana*, **43**(1994) 361-372.

10. Y. Marcus, On the relationships between transport and thermodynamic properties of organic liquids at ambient conditions, *Fluid phase equilibria*, **154**(1999) 311-321.

11. H. Schonhorn, Surface tension-viscosity relationship for liquids, *J.Chem.& Eng.Data*, **12**(1967) 524-525.

12. R. C.Reid, J. M. Prausnitz and B. E. Rolling, *The properties of gases and liquids*, McGraw-Hill, Inc, New York, Chapter-12, 1987, $632-656.$

13. J. D. Pandey, G. P. Dubey, Neelima Tripathi, and A. K. Singh, Evaluation of internal pressure of multicomponent liquid mixtures using velocity and density data, *J. International Acad.Phys.Sciences,* **1**(1997) 117-124.

14. J. D.Pandey, R. Dey, V. Sanguri, N. K.Soni, M. K. Yadav and Niti Pandey, Non-linearity Parameter (B/A) of cycloalkanes at varying temperatures and pressures, *J. Ind.Chem.Soc.,* **83**(2006) 649-651.

15. J. D. Pandey and R. Verma, Inversion of the Kirkwood-buff theory of solutions: application to binary systems, *Chemical physics*, **270**(2001) 429.

16. J. D. Pandey, V. Sanguri, , M. K. Yadav and Aruna Singh, Intermolecular free length and free volume of pure liquids at varying temperatures and pressures, *Ind.J.Chem.*, **47**A(2008) 1020-1025.

17. J. D. Pandey, J. Chhabra, R. Day, and R. Verma, Non-linearity parameter(B/A) of binary liquid mixtures at elevated pressures, *Pramana*, **55**(2000) 433-439.