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Ultrasonic Velocity- Viscosity Correlation for Quaternary Liquid Systems

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Abstract: On the basis of dimensional analysis and free volume concept of liquid a relationship between ultrasonic velocity and viscosity has been derived. This equation has been applied to two binary and (Diglyme+Octane+2,2,4,Trimethyl pentane) and two quaternary (n-Pentane+Toluene+Cyclohexane and n-Decane+n-Hexane+Cyclohexane+Benzene) liquid mixtures. The agreement is found to be quite satisfactory.

Keywords: ultrasonic velocity, Diglyme+Octane+2,2,4,Trimethyl pentane, n-Pentane+Toluene+Cyclohexane and n-Decane+n-Hexane+Cyclohexane+Benzene.

1. Introduction

Viscosity of a liquid provides useful basis for understanding the nature of liquid state and has been widely used to study the physiochemical behaviour and molecular interactions in varieties of liquids and liquid mixtures. It has been customary in the past to correlate transport properties a liquid with thermodynamic properties. A critical review of such correlation has been presented by Marcus[1]. Since sound velocity in conjunction with density provides a lot of information about the thermodynamic behaviour of liquids and liquid mixtures. Experimental techniques involved in the determination of density and sound velocity are very simple and economical. It is worthwhile to correlate this property with the transport property of liquid. Viscosity is the most important transport property among the other transport properties viz. diffusion coefficient and conductivity. Bosworth[2] deduced a relationship between viscosity and sound velocity on the basis of kinetic theory of gases. But this relation does not give satisfactory results for most liquids and their mixtures. A correlation between surface tension and sound velocity has been proposed recently[3], and successfully applied to pure liquid and liquid mixtures including binary ternary and quaternary ones. Although statistical mechanical theories[4-8] have been employed for the viscosity of liquids, but such simple correlation between sound velocity and viscosity has so far not available. Here we have obtained correlation equation on the basis of dimensionless analysis and applied to three quaternary liquid mixtures.

2. Theoretical

It is well known that viscosity of a liquid is related to the free volume. The idea of free volume is that each molecule is enclosed by its neighbours in a cell and is defined as the average volume in which the centre of the molecule can be ade in the hypothetical cell due to the repulsion of the surrounding molecules. Experimentally it is found that as the temperature increases the viscosity of liquid decreases while isentropic compressibility increases. Hence it can be assumed that for liquids viscosity (η) depends upon free volume(V_f), isentropic compressibility (β_S), and molar mass (M).

Let us suppose that

(1) $$\eta \propto (V_f)^x (\beta_s)^y (M)^z .$$

Hence

(2) $$\eta = constant \times (V_f)^x (\beta_s)^y (M)^z .$$

Since proportionality constant has no dimension

(3) $$[\eta] = (V_f)^x (\beta_s)^y (M)^z$$

$$[\mathrm{M L^{-1} T^{-1}}] = [\mathrm{L^3}]^{\mathrm{x}} [\mathrm{M^{-1} L T^2}]^{\mathrm{y}} [\mathrm{M}]^{\mathrm{z}}$$

(4) $$[\mathrm{M L^{-1} T^{-1}}] = [\mathrm{M^{z-y} L^{3x+y} T^{2y}}].$$

From the principle of homogeneity of dimensions, equating the powers of mass (M), length(L), and time(T) on both the sides, we get

(5) $$2\mathrm{y} = -1, \qquad \mathrm{y} = 1/2$$

(6) $$z - y = 1, \quad z = 1/2$$

(7) $$3x + y = -1, \quad x = -1/6$$

So that

(8) $$\eta \propto (V_f)^{-1/6}.(\beta_s)^{-1/2}(M)^{1/2} \; .$$

The free volume of a liquid is related to the ultrasonic velocity by the well known equation

(9) $$\left(\frac{V}{V_f}\right)^{1/3} = \frac{1}{u}\left(\frac{\gamma RT}{M}\right)^{1/2} ,$$

where V is the molar volume, u the ultrasonic velocity, γ the heat capacities ratio, R gas constant, M the molar mass and T is the absolute temperature. From (9), we have

(10) $$\begin{aligned}(V_f)^{1/6} &= (u^{1/2}M^{1/4})/(\gamma^{1/4}T^{1/4}V^{1/6}R^{1/4}) \\ &= (u^{1/2}M^{1/4}\ell^{1/6})/(\gamma^{1/4}T^{1/4}M^{1/6}) \\ &= (u^{1/2}M^{1/12}\ell^{1/6})/(\gamma^{1/4}T^{1/4}) .\end{aligned}$$

The isentropic compressibility β_S, is given by

(11) $$\beta_S = (u^2\ell)^{-1} \; .$$

From equations (8), (10) and (11), we get

$$\eta = \left[(u^{1/2}M^{1/12}\ell^{1/6})/\gamma^{1/4}T^{1/4}\right]\left[u^{1/2}M^{1/2}\right] ,$$

(12) $$\eta = const \times (u^{3/2}.M^{7/12}.\ell^{2/3})/(\gamma^{1/4}.T^{1/4}) .$$

The specific heat ratio γ is related to the density ℓ and temperature T as

(13) $$\gamma = 17.1/(T^{4/9}.\ell^{1/3}) .$$

From equations (12) and (13)

$$\eta = const \times (u^{3/2}\ell^{2/3}M^{7/12}T^{1/9}\ell^{1/12}/T^{1/14}) ,$$

(14) $$\eta = const \times (u^{3/2}M^{7/12}\ell^{3/4}/T^{5/36}) \; .$$

Table 1: Calculated and experimental values of viscosity (cP) of binary liquid mixture Diglyme (x1) +Octane (x2).

T=308.15 K

x1	η(exp)	η(cal)	Percentage Deviation
0.0946	0.458	0.470	-2.64
0.2030	0.475	0.486	-2.31
0.2985	0.501	0.503	-0.32
0.3956	0.523	0.525	-0.39
0.4955	0.556	0.545	2.06
0.5945	0.596	0.571	4.19

T=313.15 K

x1	η(exp)	η(cal)	Percentage Deviation
0.0946	0.432	0.455	-5.21
0.2030	0.448	0.470	-5.0
0.2985	0.473	0.484	-2.32
0.3956	0.493	0.502	-1.9
0.4955	0.524	0.530	-1.2
0.5945	0.559	0.555	0.75
0.6970	0.604	0.575	4.85
0.7972	0.650	0.604	7.02
0.8977	0.712	0.656	7.93

T=318.15K

x1	η(exp)	η(cal)	Percentage Deviation
0.0946	0.410	0.437	-6.64
0.2030	0.425	0.442	-3.98
0.2985	0.446	0.466	-4.53
0.3956	0.466	0.485	-4.16
0.4955	0.493	0.505	-2.44
0.5945	0.523	0.536	-2.57
0.6970	0.575	0.569	0.99
0.7972	0.610	0.589	3.49
0.8977	0.667	0.633	5.17

Table 2: Diglyme (x1) + 2,2,4, Trimethyl Pentane(x2)

T=308.15K

x1	η(exp)	η(cal)	Percentage Deviation
0.0931	0.435	0.416	4.47
0.1978	0.455	0.435	4.29
0.2916	0.478	0.459	4.03
0.4016	0.512	0.486	5.02
0.4538	0.529	0.502	5.19
0.5881	0.584	0.547	6.40
0.6870	0.632	0.585	7.51
0.7926	0.690	0.625	9.44

T=313.15K

x1	η(exp)	η(cal)	Percentage Deviation
0.0931	0.413	0.407	1.41
0.1978	0.430	0.424	1.44
0.2916	0.451	0.445	1.42
0.4016	0.482	0.475	1.48
0.4538	0.500	0.487	2.56
0.5881	0.548	0.531	3.16
0.6870	0.592	0.566	4.46

T=318.15K

x1	η(exp)	η(cal)	Percentage Deviation
0.0931	0.389	0.390	-0.16
0.1978	0.405	0.409	-0.88
0.2916	0.425	0.431	-1.48
0.4016	0.453	0.460	-1.61
0.4538	0.468	0.471	-0.64
0.5881	0.512	0.519	-1.27
0.6870	0.553	0.548	0.85
0.7926	0.601	0.592	1.57
0.8997	0.602	0.632	-4.93

Table 3: Calculated and experimental values of viscosity (cP) of quaternary liquid mixture n-Pentane(x1)+Toluene(x2)+n-Heptane(x3)+Cyclohexane(x4) at 298.15K

x1	x2	x3	η(exp)	η(cal)	Percentage Deviation
0.056	0.5737	0.1284	0.5145	0.5215	-1.36
0.0735	0.5474	0.1120	0.5101	0.5097	0.07
0.0935	0.5282	0.0959	0.5090	0.4980	2.16
0.1141	0.5054	0.0793	0.5013	0.4900	2.26
0.1134	0.4948	0.0660	0.5198	0.4933	5.09
0.1511	0.4602	0.0487	0.5153	0.4795	6.95
0.1709	0.4395	0.0338	0.5048	0.4734	6.22

Table 4: Calculated and experimental values of viscosity (cP) of quaternary liquid mixture n-Decane(x1)+n-Hexane (x2)+Cyclohexane(x3)+Benzene(x4) at 298.15K

x1	x2	x3	η(exp)	η(cal)	Percentage Deviation
0.1171	0.1748	0.1883	0.4903	0.4981	-1.59
0.1169	0.1772	0.2769	0.5042	0.4961	1.61
0.1275	0.3826	0.2080	0.4364	0.4835	-10.79
0.1195	0.2478	0.1951	0.4677	0.4925	-5.3
0.1158	0.1758	0.1911	0.4914	0.4980	-1.34
0.1243	0.1898	0.4047	0.5363	0.4932	8.03
0.1241	0.2570	0.3445	0.5072	0.4895	3.48
0.1253	0.3435	0.2560	0.4590	0.4854	-5.75
0.1749	0.1908	0.2045	0.5066	0.5040	0.51
0.1170	0.1766	0.1894	0.5004	0.4996	0.16
0.0897	0.1721	0.1863	0.4989	0.4967	0.44

Using the above experimental data for viscosity of liquid, the constant in the equation (14) was found to vary from $1.2x10^{-6}$ to 4.0×10^{-6}
Here we consider

(15) $$\eta = 2.2\times10^{-6}(u^{3/2}M^{7/12}\ell^{3/4})/T^{5/36}$$

where the units η, u, ℓ, M and T are in centipoises (cP), ms^{-1}, gcm^{-3}, g and °K respectively. The importance of above equation is that to compute the viscosity of liquid system directly, we need only to measure ultrasonic velocity, density and temperature.

3. Results and discussion

From the present study three quaternary liquid mixtures namely,

I - n-pentane(x_1)+toluene(x_2)+n-heptane(x_3)+ cyclohexane(x_4)

II - n-decane(x_1)+n-hexane(x_2)+ cyclohexane(x_3)+benzene(x_4)

III- n-pentane(x_1)+n-hexane(x_2)+benzene(x_3)+toluene(x_4)

have been considered. The experimental data of density(ℓ), ultrasonic velocity(u), and viscosity(η) for the aforesaid systems were taken from literature (12). In using eq. (15) for the computation of η of quaternary liquid systems, the value of M will be obtained from mole fraction additivity i.e.

(16) $$M_{1234}=x_1M_1+x_2M_2+x_3M_3+x_4M_4$$

The theoretical values of η for all the systems calculated from eqs. (15) and (16) using density and sound velocity data reported in table1,2 and 3. For the comparison experimental values of η are also given. All the reported vales are at temperature of 298.15 K. In the last column of each table, the percentage deviations are reported.

A perusal of table 1,2 and 3 shows that the average percentage deviations in the calculated viscosity values are 2.90, 0.73 and 12.70 for the systems 1,2 and 3 respectively. Considering the approximations made in the derivation of eqn.(15), excellent agreement is achieved. The little deviations are due to the experimental uncertainties in the viscosity values.

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