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Computational Study of Debye Temperature for Liquid Mixtures-Thermal Energy Variations

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In an analytical way, effective Debye temperature computations of functional materials are extended to organic liquid mixtures using ultrasonic velocity and density measurements. Thermal properties of an organic liquid mixture containing Aniline + Toluene, Aniline + o-Xylene and Aniline + Mesitylene with different mole fractions have been explained using Debye temperature variations and they are scrutinized to bring out the molecular association due to thermal energy changes of binary liquid mixtures. The results including computation of Debye temperatures using standard formula, ideal mixture relation and modified Lorentz-Bertholet combination mixing rule and their deviations are used to explain thermal energy changes of component molecules in liquid mixtures and their association.

Keywords: Debye temperature, Thermal behavior, Ideal mixture relation, Deviation, Mesitylene

INTRODUCTION

Physical, chemical and thermal properties of polar and non polar solutions of binary liquid mixtures are very much essential for chemical industries in design processing involving chemical separation, heat transfer, mass transfer and fluid flow. In engineering applications, liquid mixture rather than single component liquid system is used in processing and product formulations [1-6]. Ultrasonic velocity measurements have been carried out to bring out physical, chemical and thermal properties of liquids, liquid mixtures, polar and non polar solutions [7,8]. Recently the method of computation of Debye Temperature for solids having several approximations has been modified and applied to binary liquid mixtures. However, the study of atomic motions in liquids plays a very significant role in understanding the solid-like behavior of liquids. The dynamical behavior of liquids can be studied by the accurate measurements of the thermal energy changes due to the scattering. This technique was implemented by Hughee *et al*. [9] and Frenkel10. Such types of calculations have recently been extended to other liquids by assuming that the atomic motions in these liquids are similar to those of solids. Thermodynamics and related properties of liquids and liquid mixtures are useful in studying the internal structures, clustering phenomenon and other quasi-crystalline properties [11,12]. The estimated Debye temperature of liquids and liquid mixtures from the data of ultrasonic velocity and density found to be useful in explaining the molecular interactions in the mixtures for thermal energy changes and consequently the specific heat contribution of respective liquid mixtures. Here, we report the results of Debye temperatures for the binary liquid mixtures of Aniline + Toluene, Aniline + o-Xylene and Aniline + Mesitylene, and compare the thermal energy changes using ideal mixture relation as well as modified Lorentz-Bertholet combination mixing rule with deviations from experimental values [13-16].

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MATERIALS AND METHODS

The chemicals used are of AR grade (analytical reagents) and are obtained from SDFCL chemicals. Aniline and MERCK chemicals (Mesitylene) are purified by standard procedure. Ultrasonic pulse echo interferometer (3 MHz Mittal Enterprises India) is used for ultrasonic velocity measurements. The temperature of the pure liquids or liquid mixtures is adjusted by using temperature controlled water bath. Specific gravity bottle is used for the measurement of densities of pure liquids and liquid mixtures. An electronic weighing balance (Shimadzu AUY220, Japan-precision + or - 0.1 mg) is used for the measurements of mass of pure liquids or liquid mixtures. The temperature of the solution under study is maintained constant using the electronic thermostat. This thermostat is equipped with a heater, stirrer, and a highly accurate platinum thermo meter; a regulator and automatic viscosity correction (range 0-70 ºC, ±0.01 ºC).

THEORY

The basic equation employed for the calculation of the effective Debye temperature is written as [17],

$$\theta_D = \frac{h}{k_B}\left[\frac{9N/4\pi V}{\left(\frac{1}{U_l^3}\right)+\left(\frac{2}{U_t^3}\right)}\right]^{1/3} \tag{1}$$

where U_l and Ut are the propagation velocities for longitudinal and transverse modes respectively. V is the molar volume, h is Planck's constant, k_B is Boltzmann's constant and N is Avogadro's number.

The two wave velocities expressed in terms of density (ρ), the adiabatic compressibility (β_a) and Poisson's ratio (σ) for liquids are as follows:

$$\left(\frac{1}{U_l^3}\right)+\left(\frac{2}{U_t^3}\right) = (\rho\beta_a)^{3/2}\left[\left\{\frac{1+\sigma}{3(1-\sigma)}\right\}^{3/2} + 2\left\{\frac{1+\sigma}{3(1-2\sigma)}\right\}^{3/2}\right] \tag{2}$$

The Poisson's ratio (σ) is given by

$$\sigma = \frac{3A-2}{6A+2} \tag{3}$$

and

$$A = \left(\frac{4}{3}\right)\left(\frac{1}{\gamma}\right) \tag{4}$$

where, γ is the ratio of specific heats.

From the ideal mixture relation

$$\theta_D = \Sigma\, X_i\, \theta_{Di} \tag{5}$$

where X_i is the mole fraction of i^{th} component and θ_{Di} is the Debye temperature of i^{th} component.

According to Lorentz-Bertholet combination rule:

$$m_1 s_1 (t_1 - t) = m_2 s_2 (t - t_2) \tag{6}$$

By changing mass 'm' into molecular weight, specific heat 's' into molar heat capacity and temperature 't' into Debye temperature then modified mixing relation for computation of Debye temperature becomes [18],

$$\theta_D = \frac{\sum X_i C_{pi} \theta_{Di}}{\sum X_i C_{pi}} \tag{7}$$

where C_{pi} is the molar specific heat capacity of i^{th} component, X_i is the mole fraction of i^{th} component and θ_{Di} is the Debye temperature of i^{th} component.

Using these methods, the Debye temperature of mixtures have been computed and compared with the experimental values obtained with the help of Eq. (2).

RESULTS AND DISCUSSION

Using experimental values of ultrasonic velocity and density, Debye temperatures for respective liquid mixtures are calculated. The obtained values of Debye temperature (θ_D) of pure samples are given in Table 1. The standard values of Debye temperature (θ_D) along with their theoretical estimations using Eqs. (5), (7) and their deviations over the mole fraction range of aniline at T = 303.15 K are given in Table 2. The corresponding variations of theoretical values from the experimental

Table 1. Standard Values of Debye Temperature of Pure Liquids with their Experimental Values of Ultrasonic Velocity and Density at T = 303.15 K

Liquid sample (Pure)	U ($m\ s^{-1}$)	ρ ($Kg\ m^{-3}$)	θ_D (K)
Aniline	1614.15	1020.14	87.99
Toluene	1273.52	867.11	66.31
O-xylene	1339.93	870.72	66.39
Mesitylene	1314.15	856.30	62.00

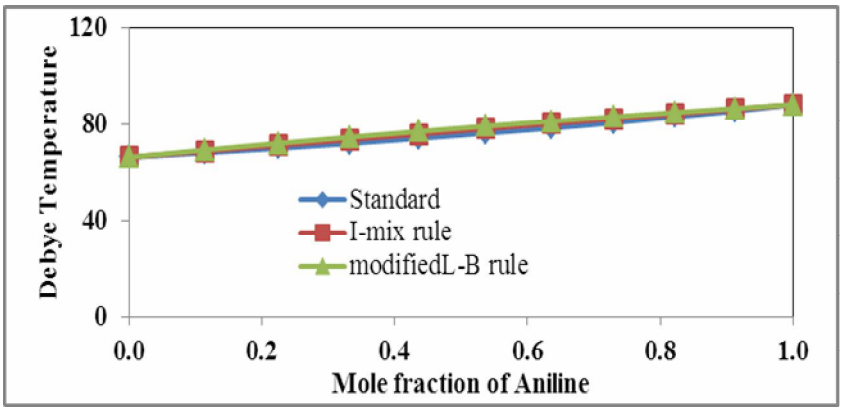

Fig. 1. Variations of Debye temperature with mole fraction of Aniline for Aniline + Toluene liquid mixture at T = 303.15 K.

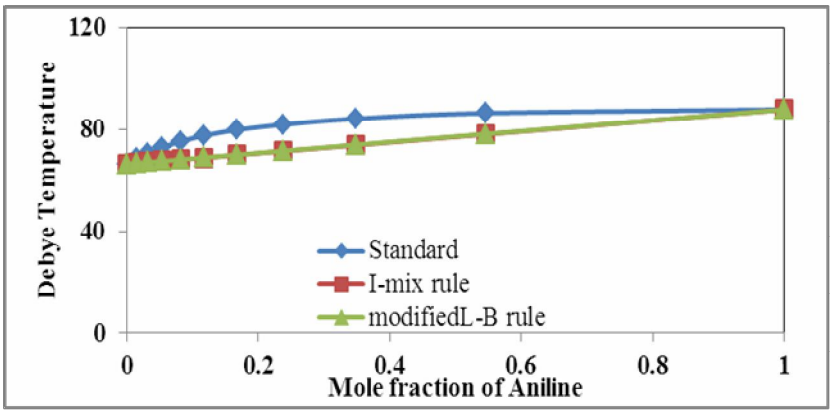

Fig. 2. Variations of Debye temperature with mole fraction of Aniline for Aniline + o-Xylene liquid mixture at T = 303.15 K.

Table 2. Standard Values of Debye Temperature (θ_D), Theoretical Estimations and Deviations for the Liquid Mixtures of Aniline + Toluene, Aniline + o-Xylene and Aniline + Mesitylene with the Mole Fraction of Aniline at T = 303.15 K

Mole fraction of Aniline (X)	Ultrasonic velocity (U) (m s^{-1})	Density (ρ) (kg m^{-3})	Experimental debye temperature (θ_D) (K)	Ideal mixture relation (θ_D) (K)	LB Combination mixing rule (θ_D) (K)	Average deviation (%)
Aniline + Toluene at T = 303.15 K						
0.0000	1273.52	867.11	66.31	66.30	66.30	0.02
0.1145	1303.82	880.49	68.16	68.78	69.27	-1.27
0.2254	1332.45	895.72	69.99	71.19	72.01	-2.30
0.3328	1361.76	915.69	71.99	73.52	74.54	-2.84
0.4369	1392.23	935.69	74.06	75.78	76.88	-3.06
0.5379	1423.36	954.89	76.17	77.97	79.06	-3.08
0.6358	1453.47	974.89	78.26	80.10	81.09	-2.99
0.7309	1488.10	991.69	80.52	82.16	82.99	-2.55
0.8232	1527.73	1005.16	82.98	84.16	84.77	-1.79
0.9129	1567.36	1014.39	85.33	86.11	86.43	-1.10
1.0000	1614.15	1020.14	87.99	88.00	88.00	-0.02
Aniline + o-Xylene at T = 303.15 K						
0.0000	1339.93	870.72	66.39	66.40	66.40	-0.01
0.0146	1370.23	882.49	68.56	66.72	66.72	2.68
0.0323	1398.86	897.72	70.74	67.10	67.12	5.14
0.0541	1428.17	913.69	73.00	67.57	67.60	7.42
0.0816	1458.64	930.69	75.36	68.16	68.20	9.52
0.1176	1489.77	944.89	77.69	68.94	69.00	11.23
0.1667	1519.88	957.89	79.95	70.00	70.08	12.40
0.2373	1544.51	974.69	82.05	71.53	71.63	12.76
0.3478	1574.14	989.40	84.36	73.91	74.04	12.30
0.5455	1600.77	1005.39	86.55	78.18	78.32	9.59
1.0000	1614.15	1020.14	87.99	88.00	88.00	-0.02

Table 2. Continued

Aniline + Mesitylene at T = 303.15 K						
0.0000	1314.15	856.30	62.00	62.00	62.00	0.00
0.0166	1338.51	881.30	64.47	62.43	62.40	3.18
0.0367	1368.14	892.53	66.86	62.95	62.89	5.89
0.0613	1397.77	915.50	69.55	63.59	63.48	8.65
0.0922	1427.40	936.50	72.22	64.40	64.24	10.94
0.1322	1457.03	957.70	74.91	65.44	65.22	12.79
0.1860	1486.66	970.70	77.40	66.84	66.55	13.84
0.2622	1516.29	988.50	80.04	68.82	68.44	14.25
0.3786	1545.92	1003.97	82.63	71.84	71.39	13.33
0.5782	1575.55	1017.20	85.19	77.03	76.55	9.85
1.0000	1614.15	1020.14	87.99	88.00	88.00	-0.02

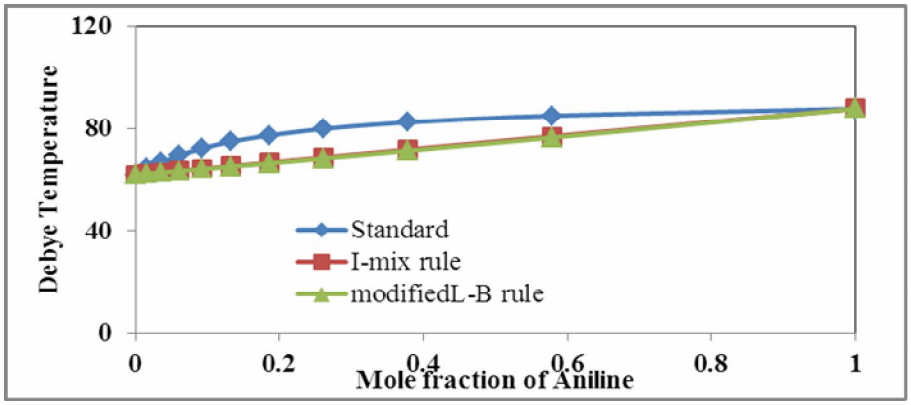

Fig. 3. Variations of Debye temperature with mole fraction of Aniline for Aniline + Mesitylene liquid mixture at T = 303.15K.

findings are represented in Figs. 1, 2 and 3.

According to Debye theory, if the bonds among the atoms are stronger, it will require more energy to heat up the substance hence Debye temperature is also more. The results in Table 2 and the deviations of Debye temperature in Figs. 1, 2 and 3 more clearly reveal as mole fraction of Aniline increases, the estimated Debye temperatures increase for the binary liquid mixtures. In Aniline + Toluene liquid mixture, negative deviations of experimental results from theoretical estimations are observed, but in other two remaining mixtures, the deviations are positive. Pandey *et al.* [19] discussed that as Debye temperature increases, the mole fraction of solvent having higher molecular weight decreases in a liquid mixture. Here, the molecular weight

and specific heat values of Toluene are less when compared with Aniline and are more for o-Xylene and Mesitylene. Thus the deviations are less and negative in the case of Aniline + Toluene liquid mixture and the deviations are more and positive in the case of Aniline + o-Xylene and Aniline + Mesitylene liquid mixtures.

Lorentz-Bertholet combination rule and ideal mixing relation give same trend in all the binary liquid mixtures, whereas deviations are observed in the experimental results. Lesser specific heat contribution and molecular weight of Toluene than those of Aniline cause negative deviations, and higher specific heat and molecular weight of o-Xylene and Mesitylene than those of Aniline give positive deviation as discussed by Pandey *et al.* [20] Therefore, the experimental results show both positive and negative deviations, indicating the non-ideal behavior of the liquid mixtures studied.

CONCLUSIONS

In the present paper, Debye temperatures are calculated from the experimental values of ultrasonic velocity, density for the binary liquid mixtures of Aniline + Toluene, Aniline + o-Xylene and Aniline + Mesitylene with respect to change in mole fraction of Aniline at T = 303.15 K. The results obtained for the mixtures show an increasing trend in Debye temperature while decreasing the mole concentration of the component having higher molecular weight. The Debye temperatures were estimated at various other temperatures and found that their values decrease with an increase in temperature. Under observation, the data stress at a point that the positive deviations for Aniline + o-Xylene and Aniline + Mesitylene are due to polar and non-polar associations and negative deviation in the case of Aniline + Toluene liquid mixture is due to polar-polar dispersion. Hence, both the positive and negative deviations indicate that there exist larger molecular associations in A + X, A + M and lesser associations in A + T among the molecules of the binary liquid mixtures studied.

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