Ultrasonic investigation of effective Debye temperature in multi-component liquid systems at 298.15 K

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ULTRASONIC INVESTIGATION OF EFFECTIVE DEBYE TEMPERATURE IN MULTI-COMPONENT LIQUID SYSTEMS AT 298.15 K

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Assuming the quasi-crystalline model for the multi-component liquid systems, the effective Debye temperature has been investigated from the density and sound velocity measurements of three ternary and three quaternary liquid systems containing *n*-alkanes over the entire range of mole fractions at 298.15 K. The results obtained have been interpreted in terms of intermolecular interactions and modifications of the internal structure of the mixtures.

1. INTRODUCTION

By assuming the quasi-crystalline model for the liquids which has been justified by cold neutron scattering and other experimental techniques, the concept of effective Debye temperature has been given earlier [1,2]. Ultrasonic propagation parameters along with density and other related properties have been used by a number of workers [3,4] to estimate this temperature in many pure liquids and liquid metals. In the year 1975 the original approach for evaluating the effective Debye temperature has been modified to yield a simpler method which many workers [5,6] have later used. The concept of Debye temperature has been successfully applied, for the first time, to homogenous liquid mixture. Recently the study of effective Debye temperature has been extended to a few other ordinary binary liquid mixtures [7,8].

During recent years [9–13] the theoretical and experimental studies of equilibrium and transport properties of multi-component liquid systems have gained much

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importance due to their relevance in industries where multi-phase equilibria are involved. It appears from the literature that nobody has, so far, investigated the concept of effective Debye temperature in multi-component homogenous liquid mixtures due to lack of desired experimental data. In the present work the theoretical formalism of the effective Debye temperature (θ_D) has been made for multi-component homogenous liquid mixtures assuming the quasi-crystalline model for such systems. The resulting expressions are used to estimate the effective θ_D in different ternary and quaternary liquid systems.

2. EXPERIMENTAL

All the organic liquids used were of analytical reagent grade and were obtained from BDH Chemicals Ltd., England. These chemicals were further purified by double distillation. Densities and speeds of sound were measured at 298.15 K. Densities were determined with a precalibrated bicapillary pyknometer with an accuracy of ± 0.3 kg/m^3 (approx. 0.05%). Speeds of sound measurements were made with a single crystal variable path ultrasonic interferometer at 2 MHz frequency and the data were accurate to $\pm 0.01\%$. The purity of the samples was checked by comparing the measured density of the compounds with those reported in literature [14].

3. THEORETICAL

The effective Debye temperature, 'θ_D' of multi-component systems can be evaluated by using the following expression

$$\theta_D = \frac{h}{k}\left\{\left[\frac{9N}{4\pi V}\right]\middle/\left[\frac{1}{\mu_1^3} + \frac{2}{\mu_t^3}\right]\right\}^{1/3}.$$ (1)

In the above formula h, k, N, V, μ_1 and μ_t represent Planck's constant, Boltzmann's constant, Avagadro number, molar volume, longitudinal wave velocity and transverse wave velocity respectively. For liquids exhibiting the quasi-crystalline properties, two wave velocities may be expressed in terms of density, ρ, the instantaneous adiabatic compressibility, $\beta_{a,\infty}$ and the Poisson's ratio, σ, as follows:

$$\frac{2}{\mu_t^3} + \frac{1}{\mu_1^3} = (\rho, \beta_{a,\infty})^{3/2} 2\left[\left\{\frac{2(1+\sigma)}{3(1-2\sigma)}\right\} + \left\{\frac{(1+\sigma)}{3(1-\sigma)}\right\}\right]^{3/2}$$ (2)

where Poisson's ratio, σ, is given by

$$\sigma = (3A - 2)/(6A + 2).$$ (3)

A is related to the ratio of two principal heat capacities, accordingly:

$$A = (4/3) \cdot (1/\gamma)$$ (4)

Using the relation $\gamma = \beta_T/\beta_S$, Eq. (3) can be transformed into Eq. (5) with the help of Eq. (4) as

$$\sigma = (2\beta_T - \beta_S)/(4\beta_T + \beta_S) \tag{5}$$

The value of θ_D thus can be obtained with the help of Eqs. (1), (2) and (5). For this we need the experimental values of adiabatic compressibility (β_S), isothermal compressibility (β_T) and the molar volume (V) of the systems under consideration, β_S can be obtained directly from the experimental values of density (ρ) and ultrasonic velocity (u) in the multi-component liquid systems through the relation, $\beta_S = (u^2\rho)^{-1}$. For an n-component system, the isentropic compressibility, $\beta_{S,n\text{-mix}}$ is given by

$$\beta_{S,n\text{-mix}} = (u^2_{n\text{-mix}}\rho_{n\text{-mix}})^{-1} \tag{6}$$

For estimating the value of the isothermal compressibility of n-component liquid systems, we have used the well-tested empirical equation [15]

$$\beta_{T,n\text{-mix}} = \frac{17.1 \times 10^{-4}}{u^2_{n\text{-mix}} T^{4/9} \rho^{4/3}_{n\text{-mix}}} \tag{7}$$

where $u_{n\text{-mix}}$ and $\rho_{n\text{-mix}}$ represent the experimental values of ultrasonic velocity and density of the mixtures. Thus, θ_D can be obtained with the help of Eqs. (1) to (7).

4. RESULTS AND DISCUSSION

For demonstrating the existence of Debye temperature in multi-component liquid systems and its physical significance, three ternary [n-pentane + n-hexane + benzene (1), n-hexane + cyclohexane + benzene (2), cyclohexane + n-heptane + toluene (3)] and three quaternary [n-pentane + n-hexane + cyclohexane + benzene (1), n-pentane + n-hexane + benzene + toluence (2), n-pentane + toluene + n-heptane + cyclohexane (3)] liquid systems were considered in the present investigation.

The experimental values of speed of sound (u) and density (ρ) of all pure component liquids of various ternaries and quaternaries have been determined at 298.15 K and recorded in Table I along with other thermodynamic parameters. Density and speed of sound of all the ternary and quaternary liquid systems have been measured

TABLE I Effective Debye temperature, θ_D, densities ρ and ultrasonic speeds u of pure component liquids at 298.15 K

Pure components	ρ (kg m^{-3})	u (ms^{-1})	β_T (T Pa^{-1})	θ_D (K)
n-Pentane	621.6	991.2	2123.3	53.15
n-Hexane	655.2	1078.2	1709.0	55.46
Cyclohexane	773.6	1253.0	1140.0	69.18
Benzene	873.3	1295.6	967.0	76.66
n-Heptane	679.3	1130.6	1424.0	55.94
Toluene	862.6	1304.6	921.5	71.99

as a function of composition at 298.15 K and the values are recorded in columns three and four of Tables II–IV and columns four and five of Tables V–VII respectively.

Theoretically evaluated values of effective Debye temperature (θ_D) of all the pure components along with isothermal compressibility values have also been recorded in Table I. Effective θ_D values have been computed with the help of Eqs. (1)–(7), using experimental values of ultrasonic velocity and density.

TABLE II Effective Debye temperature, θ_D, Poisson's ratio, σ, specific heat ratio, γ, density, ρ, and ultrasonic speed, u, of ternary system; n-pentane (x_1) + n-hexane (x_2) + benzene (x_3) at 298.15 K. $x_3 = 1 - (x_1 + x_2)$

x_1	x_2	$\rho \times 10^{-3}$ (kg m^{-3})	u (m/s)	γ	Poisson's ratio, σ	θ_D (K)
0.0966	0.4171	0.7432	1201.1	1.500	0.0908	66.95
0.1428	0.3739	0.7416	1197.5	1.502	0.0906	66.88
0.2017	0.3388	0.7361	1193.2	1.505	0.0898	66.67
0.2590	0.3038	0.7286	1187.7	1.510	0.0889	66.33
0.2984	0.2877	0.7218	1177.2	1.515	0.0879	65.66
0.3075	0.2945	0.7195	1175.2	1.512	0.0884	65.31
0.3420	0.3143	0.7073	1173.4	1.525	0.0859	65.07
0.3685	0.3523	0.6953	1170.2	1.534	0.0842	64.52
0.4099	0.3888	0.6838	1178.4	1.543	0.0825	64.63
0.4082	0.4665	0.6688	1163.2	1.554	0.0802	63.21

TABLE III Effective Debye temperature, θ_D, Poisson's ratio, σ, specific heat ratio, γ, density, ρ, and ultrasonic speed, u, of ternary system; hexane (x_1) + cyclohexane (x_2) + benzene (x_3) at 298.15 K. $x_3 = 1 - (x_1 + x_2)$

x_1	x_2	$\rho \times 10^{-3}$ (kg m^{-3})	u (m/s)	γ	Poisson's ratio, σ	θ_D (K)
0.0771	0.4315	0.8062	1278.1	1.460	0.0988	72.86
0.1269	0.4149	0.7935	1267.5	1.468	0.0973	71.83
0.1795	0.3854	0.7852	1261.2	1.473	0.0962	71.18
0.2279	0.3501	0.777	1251.2	1.478	0.0952	70.34
0.2616	0.3342	0.7734	1263.5	1.481	0.0948	70.87
0.2812	0.3348	0.7672	1256.3	1.485	0.0940	70.26
0.3021	0.3643	0.7618	1260.2	1.488	0.0933	70.23
0.3062	0.3823	0.7584	1248.4	1.491	0.0928	69.45
0.3448	0.4566	0.748	1259.1	1.497	0.0915	69.54
0.3231	0.4851	0.7484	1244.2	1.496	0.0916	68.71

TABLE IV Effective Debye temperature, θ_D, Poisson's ratio, σ, specific heat ratio, γ, density, ρ, and ultrasonic speed, u, of ternary system; cyclohexane (x_1) + n-heptane (x_2) + toluene (x_3) at 298.15 K. $x_3 = 1 - (x_1 + x_2)$

x_1	x_2	$\rho \times 10^{-3}$ (kg m^{-3})	u (m/s)	γ	Poisson's ratio, σ	θ_D (K)
0.1124	0.3962	0.7861	1328.8	1.473	0.096	71.55
0.1761	0.3766	0.7801	1319.2	1.476	0.096	71.04
0.2452	0.3379	0.7807	1317.4	1.461	0.093	71.46
0.3027	0.3032	0.7812	1307.3	1.476	0.096	70.83
0.3479	0.2837	0.7825	1321.5	1.475	0.096	71.77
0.3766	0.2895	0.7792	1318.5	1.477	0.095	71.56
0.3907	0.305	0.7773	1323.2	1.478	0.095	71.76
0.4198	0.3416	0.7669	1308.2	1.485	0.094	70.65
0.4468	0.3796	0.7607	1321.4	1.489	0.093	71.17
0.4525	0.4393	0.7495	1303.2	1.496	0.092	69.77

TABLE V Effective Debye temperature, θ_D, Poisson's ratio, σ, specific heat ratio, γ, density, ρ, and ultrasonic speed, u, of quaternary system; n-pentane $(x_1)+n$-hexane $(x_2)+$cyclohexane $(x_3)+$benzene (x_4) at 298.15 K. $x_4 = 1 - (x_1 + x_2 + x_3)$

x_1	x_2	x_3	$\rho \times 10^{-3}$ (kg m^{-3})	u (m/s)	γ	Poisson's ratio, σ	θ_D (K)
0.0488	0.1238	0.1831	0.8051	1240.1	1.4609	0.0987	71.02
0.0658	0.1078	0.2036	0.8004	1239.9	1.4638	0.0981	70.98
0.0813	0.0934	0.2238	0.7988	1237.2	1.4648	0.0979	70.79
0.1006	0.0778	0.243	0.7995	1236.6	1.4643	0.0980	70.70
0.118	0.0629	0.2615	0.7941	1230.2	1.4676	0.0974	70.30
0.1243	0.0466	0.2842	0.7908	1240.1	1.4697	0.0969	70.90
0.141	0.1304	0.3129	0.7709	1205.4	1.4822	0.0944	67.97
0.156	0.1262	0.1513	0.7828	1213.5	1.4747	0.0959	69.03
0.1285	0.1192	0.5888	0.7549	1206.2	1.4926	0.0924	67.11
0.1537	0.0925	0.1685	0.7906	1226.4	1.4698	0.0969	70.00
0.1649	0.1013	0.5177	0.7547	1194.3	1.4928	0.0923	66.68
0.1368	0.1258	0.1507	0.7851	1210.5	1.4732	0.0962	68.98
0.091	0.1721	0.6137	0.7509	1201.6	1.4953	0.0918	66.52
0.0649	0.1378	0.1103	0.8048	1263.7	1.4611	0.0987	72.47
0.181	0.1656	0.2971	0.7542	1197.4	1.4931	0.0923	67.09

TABLE VI Effective Debye temperature, θ_D, Poisson's ratio, σ, specific heat ratio, γ, density, ρ, and ultrasonic speed, u, of quaternary system; n-pentane $(x_1)+n$-hexane $(x_2)+$benzene $(x_3)+$toluene (x_4) at 298.15 K. $x_4 = 1 - (x_1 + x_2 + x_3)$

x_1	x_2	x_3	$\rho \times 10^{-3}$ (kg m^{-3})	u (m/s)	γ	Poisson's ratio, σ	θ_D (K)
0.0943	0.0918	0.4587	0.8216	1260.1	1.4511	0.1007	71.53
0.13	0.1373	0.2974	0.8011	1233.2	1.4634	0.0982	69.11
0.1278	0.1288	0.3589	0.8054	1237.3	1.4608	0.0987	69.62
0.145	0.1291	0.3376	0.7991	1225.7	1.4646	0.0980	68.87
0.1492	0.1384	0.3421	0.7974	1217.9	1.4656	0.0978	68.39
0.1843	0.1484	0.2711	0.7855	1200.1	1.4730	0.0963	67.05
0.1823	0.164	0.3613	0.7838	1197.9	1.4741	0.0961	67.18
0.1819	0.1606	0.3842	0.7824	1200.1	1.4749	0.0959	67.41
0.125	0.1665	0.2455	0.7975	1223.1	1.4655	0.0978	68.22
0.1691	0.2041	0.2218	0.7769	1201.3	1.4784	0.0952	66.71
0.1866	0.0826	0.125	0.7995	1229.3	1.4643	0.0980	68.44
0.1372	0.158	0.5548	0.7926	1211.4	1.4686	0.0972	68.77
0.066	0.1053	0.7033	0.8273	1268.1	1.4478	0.1014	72.97
0.0524	0.1434	0.4201	0.8176	1260.5	1.4534	0.1002	71.20
0.1586	0.0468	0.4582	0.8184	1256.3	1.4530	0.1003	71.44

The sum of mole fractions of all the components is taken as equal to one. In a ternary mixture x_1, x_2 and x_3 are the mole fractions of components 1, 2 and 3 respectively. Similarly in a quaternary mixture x_1, x_2, x_3 and x_4 are the mole fractions of components 1, 2, 3 and 4 respectively. Computed values of θ_D for the above mentioned ternary and quaternary liquid systems as a function of composition have been listed in columns 7 and 8 of Tables II–IV and V–VII respectively. Experimental values of density and ultrasonic velocity of all the ternary and quaternary systems have also been presented in columns three and four of Tables II–IV and four and five of Tables V–VII respectively.

The values of specific heat ration (γ) and Poisson's ratio (σ) have been recorded in columns five and six of Tables II–IV for all the ternary liquid systems. The computed values of specific heat ratio and the Poisson's ratio for all the quaternary liquid

TABLE VII Effective Debye temperature, θ_D, Poisson's ratio, σ, specific heat ratio, γ, density, ρ, and ultrasonic speed, u, of quaternary system; n-pentane (x_1) + toluene (x_2) + n-heptane (x_3) + cyclohexane (x_4) at 298.15 K. $x_4 = 1 - (x_1 + x_2 + x_3)$

| x_1	x_2	x_3	$\rho \times 10^{-3}$ (kg m^{-3})	u (m/s)	γ	Poisson's ratio, σ	θ_D (K)
0.0404	0.6358	0.1544	0.8073	1270.1	1.4595	0.0990	69.55
0.056	0.5737	0.1284	0.8026	1256.3	1.4625	0.0984	68.97
0.0735	0.5474	0.112	0.7995	1243.5	1.4643	0.0980	68.36
0.0935	0.5282	0.0959	0.7965	1230.2	1.4661	0.0977	67.73
0.1145	0.5054	0.0793	0.7927	1223.7	1.4685	0.0972	67.47
0.1134	0.4948	0.066	0.7909	1232.3	1.4696	0.0970	68.05
0.1511	0.4602	0.0487	0.7857	1218.7	1.4729	0.0963	67.39
0.1709	0.4395	0.0338	0.784	1213.2	1.4739	0.0961	67.16
0.1071	0.4099	0.0783	0.7855	1234.5	1.4731	0.0963	68.07
0.1126	0.4267	0.1137	0.7837	1218.1	1.4741	0.0961	66.89
0.1783	0.2174	0.1637	0.7498	1201.5	1.4959	0.0917	65.54
0.1991	0.22	0.1674	0.7465	1199.2	1.4982	0.9126	65.37
0.1794	0.602	0.1551	0.7842	1233.2	1.4738	0.0961	67.46
0.1351	0.11	0.1484	0.7492	1217.2	1.4964	0.0916	66.53
0.0948	0.3338	0.2524	0.7615	1227.5	1.4884	0.0932	66.44
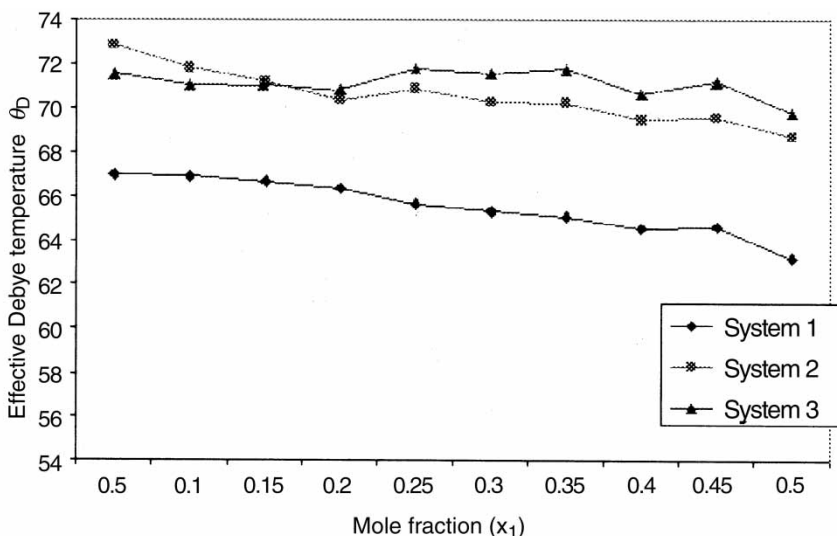
FIGURE 1 Variation of effective Debye temperature with mole fraction of component 1 for the ternary systems 1–3.

systems have also been presented in columns six and seven of Tables V–VII. The variation of effective Debye temperature with composition for all the ternaries and quaternaries has also been graphically represented in Figs. 1 and 2 respectively.

Examination of the data presented in Tables II–IV for the ternary liquid systems (1–3) shows that the values of θ_D decrease with increasing mole fraction of component one for all the three mixtures. Similar trends have also been observed in the experimental values of ultrasonic velocity and density. But the specific heat ratio values show regular increase with increasing concentration of component one for all three systems.
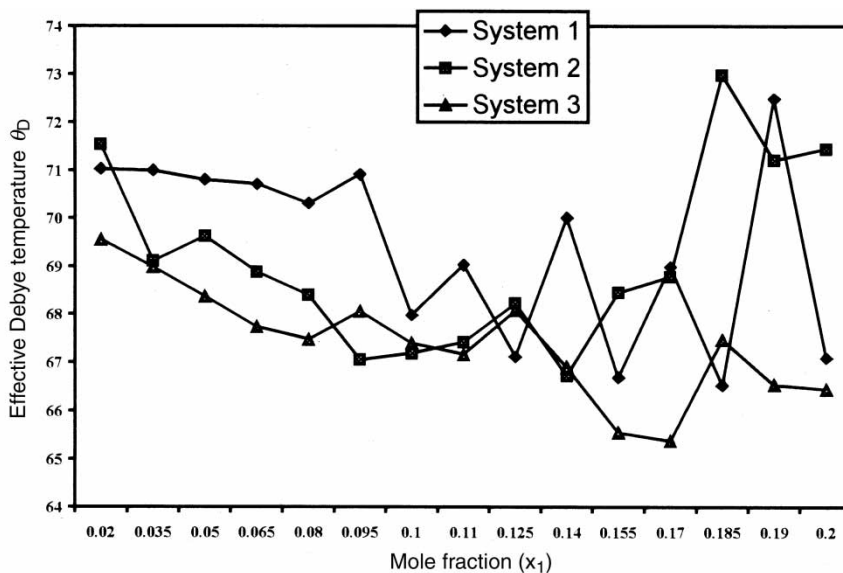
FIGURE 2 Variation of effective Debye temperature with mole fraction of component 1 for the quaternary systems 1–3.

The data presented in Tables V–VII shows that the values of effective Debye temperature (θ_D) for all the three quaternary liquid systems are lowered as the mole fraction of component one increases. Similar trends have been also observed in the ultrasonic velocity but the isentropic compressibility increases with increasing mole fraction of component one.

The results of the calculations presented here clearly indicate the utility of an effective Debye temperature in all the multi-component liquid systems under investigation. It is interesting to note that the magnitude of θ_D obtained for all the liquid systems at all the compositions lie between the values of pure components. Inconsistent values of θ_D in quaternary liquid systems are the resultant of the collapse of order in the mixture. This trend must reflect the superposition of size effects on one-another, which causes contraction. The contraction may arise from the disruption by the mixing process of a somewhat expanded-dipole structure due to the addition of third and fourth components. Additional contributions can be envisaged as coming from the restrictions in rotational motion, which arises when the chain component liquids are accommodated interstitially within the substituted or ring structured liquids. It appears that the difference in molecular size, the nature of intermolecular interactions and r-meric relationships play a significant role in determining the effective Debye temperature and other thermodynamic properties.

It is primarily the compressibility that changes with structure. This leads to a change in ultrasonic velocity. The greater the attractive forces among the molecules of the liquid, the smaller will be the distance between the single molecules, and the smaller will be the compressibility. The main effect of addition of n-alkanes is the disruption of the structure of the pure components and restriction of their rotational motion. Interstitial accommodation and orientational order led to a more compact structure and to an observed decrease in the effective Debye temperature and ultrasonic velocity. In n-alkanes, the dipole is shielded more, and this leads to a lowering of cohesive forces

between molecules and a consequent increase in compressibility. Since most of the component liquids are nearly similar in nature i.e. they are inert solvents having least polarity in the configuration, so interactions in these systems will not be appreciable. Size of the ring, molecular configuration, orientations and concept of charge transfer provides better information for molecular interaction studies. It appears that the strength of interaction between two components in weakened by addition of third and fourth components as evident in ternary and quaternary liquid systems.

4. CONCLUSION

Since intermolecular interactions are sensitive to thermal fluctuations, which in turn are dependent on the quasi-crystalline structure existing in the liquid state similar to those of solids, and on the basis of above discussion, it appears that the multi-component liquid systems can be treated successfully on the basis of a quasi-crystalline model. The present study explores the utility of effective Debye temperature data in under-standing the molecular interactions and structural changes in multi-component liquid systems.

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