Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **3(5),** 43-46, May **(2013)** *Res. J. Chem. Sci.*

Investigations on the Binary Mixtures of Organic Additives in Lubricating Oil - SAE15W40 through Ultrasound Velocity Measurements

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Available online at: www.isca.in
Received 21st March 2013, revised 3rd April 2013, accepted 15th April 2013

Abstract

Thermo, Acoustical and Dielectric (TAD) parameters such as adiabatic compressibility (β), intermolecular free length (L_f), acoustical impendence (Z), dielectric constant (ε), surface tension (S), relaxation time (τ), Gibb's free energy (ΔG) and its excess functions (A^E) have been calculatedfor the binary mixtures of lubricating oil-SAE15w40 with toluene and benzene from ultrasound velocity (u),density (ρ) and viscosity (η)measurements. These measurementswere carried out at various concentration of oil from 0% to 100% in steps of 20% at 308.15K.From the data's of TAD parameters and their excess values, it is very obvious that there exist a hetero interaction existing between the unlike molecules.

Keywords: Lubricating oil, additives, non-polar, dipolar forces, excess parameters.

Introduction

Lubricating oil used in various production machineries, power plants, automobiles etc. for reducing friction, carrying away heat, protecting against rust and wear and sealing out contaminant[1] and pure organic fluids also called as additives such as toluene, acetone, methanol and n-pentane[2], are advantageous when the plant runs at low temperature or low power in comparison to water. For engineering applications, liquid mixtures rather than single component liquid system are used in processing and product formulations. Most of the physical properties of liquid mixtures such as melting point, boiling point, dielectric constant, density, viscosity, surface tension and solubility are actually controlled by strength of intermolecular attractive forces[3] It defines the shape, size, structure and the properties of the compounds formed[4]. To discuss the properties of mixtures, we must understand the intermolecular forces. TAD parameters obtained in ultrasonic study yield valuable information regarding intermolecular association and behavior of liquid systems. Therefore, it is of interest to examine TAD parameters of mixtures. Owing to these considerations, the authors have carried out the ultrasonic studies on the following systems i. lubricating oil-SAE15w40 in toluene and ii. lubricating oil-SAE15w40 in benzene.

Material and Methods

Castrol GTD - SAE15w40 (API CF4) (Lubricating oil) is supplied by Castrol India Ltd. The pure chemicals toluene and benzene are supplied by E-Merck. They were used as such without further purification. The density (ρ) were measured by relative density method using 20ml specific gravity bottle was employed. An electronic digital balance (Model: SHIMADZU ELB300) was used for weighing and the losses due to evaporation of the sample were minimized. The ultrasonic velocity (u) have been measured using an Ultrasonic interferometer (Model: F81) supplied by Mittal Enterprises, New Delhi working at 2MHz and viscosity (η) were measured by using Ostwald's viscometer. All the measurements at various concentrations of pure liquids and liquid mixtures of each sample were made at 308.15K. The constant temperature was maintained by water circulating thermostat supplied by Raaga industries, Chennai, India. The fluctuation in temperature was ±0.1K.

Calculation of TAD parameters: TAD parameters of liquid mixtures have been calculated from the experimental values of density ρ, viscosity η and ultrasonic velocity u, using the following standard relations[5-8].

$$\beta = 1/u^2 \rho \quad (1)$$

$$L_f = K/u\rho^{1/2} \quad (2)$$

$$Z = u\rho \quad (3)$$

$$\varepsilon = 0.001667\rho + 0.785 \quad (4)$$

$$u = (S/6.3X10^{-4}\rho)^{2/3} \quad (5)$$

$$\tau = (4/3)\eta\beta \quad (6)$$

$$\Delta G = K_B T \ln(K_B T\tau/h) \quad (7)$$

$$A^E = A_{\exp} - A_{id}$$
$$A_{id} = \sum A_i X_i \quad (8)$$

where , K is a temperature – dependent constant, [= $636x10^{-6}$ at 308.15K], K_B is the Boltzmann's constant [=$1.23x10^{-23}$J/K], h is the Planck's constant [=$6.626x10^{-34}$Js], T is the absolute temperature, A_i is any acoustical parameters and X_i is the mole fraction of the liquid component

Results and Discussion

The experimentally measured values ρ,η,u and observed values TAD parameters such as β, L_f, Z, ε, S, τ, ΔG and their excess functions A^E for the systems I and II at 308.15Kare given in table 1-3. It is seen from table 1 that the ρ, η and u values of the system I and system II is found to be increases with increasing concentration of oil. This suggests that as ρ increases, the number of particles in a given region is increased and it makes the systems more compact. As the medium becomes more and more compact, velocity also increases as is observed in both the system. This leads to quick transfer of sound energy in the compact region[9]. So thatfrom the values of ultrasonic velocity, it is apparent that a definite structural re-adjustment of molecular packing is taking place in solution. Further, an examination of table 1 shows that the increasing value of η indicates an increase of frictional resistance force that may be due to change in effective molecular area or the cohesive/adhesive forces or relative random velocity between the compounds of mixtures or combination of these[10]. Table 2 gives the values of β for both the system, shows an exactly reverse trend that of velocity variation, as expected. The decrease in compressibility brings the molecules to a closer packing resulting into a decrease of intermolecular free length. As L_f decreases, u increases and vice versa, showing an inverse behavior. Similar results are reported by Palaniappan[11] for Benzene - alcohol mixtures. Further, the values of Z for the studied systems are found to be increased. This factor is governed by the inertial and elastic properties of the medium[12], which can be attributed to the effective molecular interaction between oil and non - polar aromatic compounds.A dielectric constant (ε) measures the forces between molecules of a substance. This is relevant to oils where the interaction between molecules is weak (which gives it lubricating properties) and the dielectric constant of oils is relatively small (because the interaction between molecules is small). Hydrocarbon lubrication oils have a dielectric constant from 2.1 to 2.8, which depends on the viscosity of the oil, the paraffinic/naphthenic content, and additive package. Perusal of the table 3 shows that the ε value of the mixtures, such as lubricating oil SAE15w40 + Toluene and lubricating oil SAE15w40 + Benzene increases with the increasing concentration of the lubricating oil. This is the effect of structural changes. The hetero interaction between lubricating oil SAE15w40 and non-polar aromatic compounds (Toluene, Benzene) is responsible for this kind of behavior. Similar conclusions have been reported by Parthipan et al[13], in his dielectric studies on liquid mixtures. Table 3 shows that the surface tension of both the mixtures increases with the concentration of oil. This means that interactions in the mixture are not strong and hence rise in the S value was observed when concentration increases[14]. From table 3, it can be seen that, the relaxation time(τ) increases with increase in concentration which is in the order of 10^{-12} s, is due to relaxation process and in such situation it is suggested that the molecules gets rearranged due to co-operative process[15]. The increase of τ may also be due to the enhancement of the cluster size. Mixing of two liquids results in the formation of bigger molecular size which enhances the relaxation time (τ) and the hetero interaction exists in between oil and non-polar aromatic compounds is such as to form linear multimer. The term ΔG is defined as the change in "free energy". This is the energy that can be used for a specific purpose and is available from a process. Values of ΔG at 308.15K, for the different concentrations of lubricating oil are reported in table 3. Positive value of ΔG[16], implies that the process is endergonic (non-spontaneous) which means that hetero interaction may be such that more ordered configuration exists. Excess parameters are regarded as more suitable for evaluating the degree of interaction[17]. The non-zero excess values of η^E indicates the presence of molecular interaction and also the difference size and shape of the component molecules and large difference in the viscosities of pure components may contribute negative deviations of η^E. Similar conclusions have been reported by Dalai et al[18]. The excess adiabatic compressibility (β^E) are mostly negative and indicate the presence of hetero interaction in liquid mixtures through charge transfer, dipole-dipole interactions and dipole-induced dipole interaction interstitial accommodation and orientational ordering, leading to more compact structure making which leads to negative L_f^E values[19]. According to Rajagopal and Chenthilnath[20], the positive trends in ΔG^E indicate the presence of specific interactions between unlike molecules. From table 3, it is interesting to observe that negative ε^E indicates that molecules of the mixtures may form multimer structures. This means that there is an association of oil and non-polar aromatic compounds[21].

Conclusion

The TAD parameters such as ρ, η, u, β, L_f, Z, α/f^2, ε, S, τ and ΔG for the mixtures lubricating oil SAE15w40 + toluene and lubricating oil SAE15w40 + benzene at 308.15K of various concentrations have been reported. The increase in velocity, impedance and decrease in compressibility and free length with the addition of toluene and benzene indicates that, intermolecular forces increase with the addition of solvents. The results are further confirmed by its respective excess parameters. A comparative study of these tables of the systems I and II gives some idea about the strength of the interaction in the mixtures is in the order of toluene > benzene.

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Table-1

Values of density (ρ), viscosity (η), ultrasonic velocity (u) and its excess parameters for the systems I&II at 308.15 K

X_2 (oil)	ρ Kg/m^3	η x 10^{-3} Nsm^{-2}	u x10^3 m/s	ρ^E Kg/m^3	η^E Nsm^{-2}	u^E m/s
System I Lubricating oil SAE15w40+Toluene						
0%	830.2823	0.5172	1.2500	0.0000E+00	0.0000E+00	0.0000E+00
20%	841.8946	0.8206	1.3200	-8.1290E-01	-1.7655E-02	-4.8000E+00
40%	847.7008	1.5891	1.3840	-7.4319E+00	-3.4845E-02	-1.5600E+01
60%	864.5387	3.9387	1.4640	-3.0192E+00	-5.0454E-02	-1.0400E+01
80%	873.8286	14.181	1.5200	-6.1545E+00	-5.8170E-02	-2.9200E+01
100%	892.4083	90.309	1.6240	0.0000E+00	0.0000E+00	0.0000E+00
System II Lubricating oil SAE15w40+Benzene						
0%	818.0893	0.5062	1.2000	0.0000E+00	0.0000E+00	0.0000E+00
20%	834.9272	0.8112	1.3040	1.9741E+00	-1.7656E-02	1.9200E+01
40%	846.5396	1.5533	1.3600	-1.2773E+00	-3.4874E-02	-9.6000E+00
60%	850.0233	3.7928	1.4000	-1.2657E+01	-5.0595E-02	-5.4400E+01
80%	861.0550	13.430	1.4400	-1.6490E+01	-5.8918E-02	-9.9200E+01
100%	892.4083	90.309	1.6240	0.0000E+00	0.0000E+00	0.0000E+00

Table -2

Values of adiabatic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z), and its excess parameters for the systems I&II at 308.15 K

X_2 Oil	ε	S N/m	τ s	ΔGx10^{-20} KJ/mol	ε^E	S^E N/m	τ^E s	ΔG^E KJ/mol
System I Lubricating oil SAE15w40+Toluene								
0%	2.1691	23116	0.5316	0.5214	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
20%	2.1884	25436	0.7459	0.6653	-1.4000E-03	-4.1590E+02	-9.9114E-12	-2.4426E-21
40%	2.1981	27497	1.3049	0.9030	-1.2400E-02	-1.0909E+03	-1.9478E-11	-3.9476E-21
60%	2.2262	30509	2.8342	1.2328	-5.0000E-03	-8.1391E+02	-2.8074E-11	-4.5327E-21
80%	2.2417	32623	9.3655	1.7408	-1.0900E-02	-1.4354E+03	-3.1669E-11	-3.3348E-21
100%	2.2726	36794	51.160	2.4625	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
System II Lubricating oil SAE15w40+Benzene								
0%	2.1488	21424	0.5729	0.5532	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
20%	2.1768	24768	0.7618	0.6743	3.2400E-03	2.7023E+02	-9.9285E-12	-2.6072E-21
40%	2.1962	26748	1.3227	0.9088	-2.1200E-03	-8.2428E+02	-1.9485E-11	-4.0808E-21
60%	2.2020	28051	3.0354	1.2619	-2.6880E-02	-2.5946E+03	-2.7890E-11	-4.3689E-21
80%	2.2204	29642	10.029	1.7699	-2.7440E-02	-4.0780E+03	-3.1014E-11	-3.1075E-21
100%	2.2726	36794	51.160	2.4625	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00

Table-3
Values of dielectric constant (ε), surface tension (S), relaxation time (τ), Gibb's free energy (ΔG), and its excess parameters for the systems I&II at 308.15 K

X_2 Oil	$\beta x10^{-10}$ m^2/N	L_f x 10^{-9} m	Zx 10^6 $Kg/m^2/s$	β^E m^2/N	L_f^E m	Z^E $Kg/m^2/s$	$(\alpha/f^2)^E$ s^2/m
System I Lubricating oil SAE15w40+Toluene							
0%	7.7082	17.658	1.0379	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
20%	6.8170	16.606	1.1113	-1.9932E-11	-1.4126E+00	-8.8800E+03	-1.9544E-10
40%	6.1586	15.783	1.1732	-1.6584E-11	-1.0595E+00	-2.9260E+04	-3.8408E-10
60%	5.3968	14.775	1.2657	-2.3576E-11	-7.0632E-01	-1.9040E+04	-5.5359E-10
80%	4.9532	14.155	1.3282	1.2520E-12	-3.5316E-01	-3.8820E+04	-6.2446E-10
100%	4.2488	13.110	1.4493	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
System II Lubricating oil SAE15w40+Benzene							
0%	8.4886	18.530	0.9817	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
20%	7.0436	16.879	1.0887	-5.9720E-11	-5.6700E-10	1.3472E+04	-1.9578E-10
40%	6.3867	16.073	1.1513	-4.0610E-11	-2.8900E-10	-1.7446E+04	-3.8422E-10
60%	6.0022	15.582	1.1900	5.7400E-12	3.0400E-10	-7.2264E+04	-5.4994E-10
80%	5.6007	15.051	1.2399	5.0390E-11	8.5700E-10	-1.1588E+05	-6.1154E-10
100%	4.2488	13.110	1.4493	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00

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