Density And Viscosity Studies Of Methyl Acrylate And Aromatic Hydrocarbons At 313.15k

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ABSTRACT

The experimental results of densities (ρ), viscosities (η), and the excess properties such as excess viscosity (η^E), excess Volumes (v^E), excess Gibbs free energy (ΔG^{*E}) were calculated for the binary mixtures of Methyl Acrylate (MA) with Aromatic Hydrocarbon molecules like Benzene (B), Methyl Benzene (MB) and Ethyl Benzene (EB) at 313.15K.The comparative study of theoretical mixing rule relations for the viscosities of liquids has been carried out. The data obtained from the binary mixture were calculated and the interaction parameters were fitted with the Redlich – Kister Polynomial equation. The computed parameters were discussed based on the nature of molecular interactions.

Keywords: Methyl Acrylate, Benzene, Methyl Benzene, Ethyl Benzene, density, viscosity, Thermochemical, and excess properties, Redlich–Kister Polynomial equation, Molecular interaction.

INTRODUCTION

The Information on the volumetric properties of non–electrolyte solutions are necessary for the study of heat transfer, mass transfer, chemical separation, and fluid flow. Thermophysical properties are vital tools as knowing the liquid state and also the bond between the liquid structures [1-6]. Aromatic hydrocarbon molecules play major parts in the modernization of our science society. This research is focused on MAwithAromatic Hydrocarbon molecules like Benzene, Methyl Benzene, and Ethyl Benzene at 313.15K.

Methyl Acrylate is a very important industrial solvent that is used commercially in the production of technically important high polymeric and latex compounds. It is relatively polar (dipole moment, l = 1.77 D at 298.15 K, 1 D=3.334 x 10^{-3} Cm) [7], aprotic and associated liquid. The aromatic hydrocarbons have large quadrupole moments [8], instigating an orientational order among molecules due to the partial alignment of neighboring segments or whole molecules [8]. Acrylates are frequently used in industries like, leather, textiles, adhesives, paints, antioxidant agents, inks, amphoteric surfactants, paper, detergents, surface coatings, etc. [9]. Also, the liquid mixtures containing aromatic hydrocarbons find applications in the studies of polymer phase diagrams and preferential interaction in mixed media [10]. Therefore, the mixtures of Methyl Acrylate with Aromatic Hydrocarbon molecules will be highly useful in many chemical and industrial applications. Methyl Acrylate due to lone electron pairs possesses electron-donor ability [11] towards the aromatic rings which act like electron-acceptors [12] and may be involved in charge-transfer interactions which may be influenced by the presence of alkyl groups on the ring. A survey of the literature shows that exist some studies [3–6, 13, 14 & 15].

Aromatic Hydrocarbon molecules [Benzene, Methyl Benzene, and Ethyl Benzene] are quite important organic solvents due to their favorable physicochemical properties such as the blood temperature range corresponding to their liquid state and good donor and acceptor properties and possess large quadrupole moments[16] causing an orientational order in these liquids.

Modern scientific research generates great curiosity in hypothetical and trial investigations of the thermo physical properties of solutions [17-19]. The Redlich–Kister polynomial equation is applied to recognize the standard deviation in hypothetical and untried values of the liquid solutions. The different theoretical mixing rules are applied in these readings,in this investigation, the interaction behavior of Aromatic Hydrocarbon molecules like Benzene, Methyl Benzene, and Ethyl Benzene at 313.15K were studied.

EXPERIMENTAL MATERIALS AND METHODS

Methyl acrylate (MA), Benzene (B), Methyl Benzene (MB), and Ethyl Benzene (EB) were purchased from Merck and were used as purchased.

Mixtures [MA + B, MA + MB, and MA + EB] were prepared by mixing weighed amounts of the pure liquids adopting the method of a closed system.The weighings were done by using a Mettler balance with a precision of $\pm$ 0.1 mg. The precision in the mole function was estimated to be less than $\pm 1\times10^{-4}$. Mixtures were allowed to stand for some time before every measurement to avoid air bubbles.

The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer having a bulb capacity of $\approx$ 10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The uncertainty in density measurements was within $\pm 2\times10^{-5}$ g cm^{-3}.

Viscosity measurements were carried out with a precision of $\pm$ 0.2% using a calibrated Schott-Gerate AVS 400 viscometer, whose flow time for doubly distilled water was found to be 375 seconds at 25^{0}C. The temperature of the test liquids during the measurements was maintained within the precision of $\pm$ 0.01 K in an electronically controlled thermostatic water bath. The measurements were made with proper care in an AC room to avoid evaporation loss. The purities of the liquids were checked by comparing the values of densities and viscosities with literature data (Table 1) and formed well in general [5, 20-21].

Table 1: Comparison of experimental density and viscosity of pure liquids with literature values at 313.15 K

Liquid	Density (ρ) x 10^{-3} Kg m^{-3}		Viscosity (η) x 10^{-3} Kg m^{-1} s^{-1}	
	Exptl.	Lit.	Exptl.	Lit.
Benzene	0.8574	0. 8576 [15]	0.4981	0.4980 [24]
Methyl Benzene	0.8488	0.8587 [22]	0.4662	0.4662 [22]
Ethyl Benzene	0.8484	0.8486 [23]	0.5378	0.5378 [25]
Methyl Acrylate	0.9292	0.9292 [24]	0.3551	0.3550 [24]

RESULTS AND DISCUSSIONS

The experimental results of measurements of densities and viscosities of binary mixtures are presented in Table 2. The excess volume V^E, excess viscosity η^E the excess Gibbs free energy of activation of flow G^{*E} were calculated from the measured data using the following equations:-

$$V = (X_1M_1 + X_2M_2) / \rho \qquad \dots \qquad (1)$$
$$V^E = V - (X_1 V_1 + X_2 V_2) \qquad \dots \qquad (2)$$
$$\eta^E = \eta - (X_1 \eta_1 + X_2 \eta_2) \qquad ... \qquad (3)$$
$$G^{*E} = RT [ln \, \eta \, V - (X_1 ln \, \eta_1 \, V_1 + X_2 ln \, \eta_2 \, V_2)] \qquad \dots \qquad (4)$$

Where ρ, η, and V are the density, viscosity, and molar volume of the mixture, M_1 and M_2 are the molar masses, η_1 and η_2 are the viscosities V_1 and V_2 are the molar volumes of the benzenes and methyl acrylate respectively and x is the mole fraction of MA.

The dependence of η^E, V^E, and G^{*E} on the mole fraction of methyl acrylate (X_{MA}) for all three systems were fitted to the following Redlich-Kister equation by the least-squares method.

$$Y^E = x(1-X)\sum_{i} A_i (2x-1)^{i} \dots(6)$$

Where Y^E is η^E, V^E, and G^{*E} parameters.

The parameters A_i, obtained by a linear least squares polynomial fitting procedure, are also given in Table 3 together with the standard deviations (σ) values.

The measured density [ρ] and a viscosity [η] at 313.15 K for the mixtures of Methyl Acrylate, withAromatic Hydrocarbon molecules like Benzene, Methyl Benzene, and Ethyl Benzeneare used to calculate V^E, η^E, and G^{*E} and the results are presented in Tables 2.

The variation of the parameters V^E, η^E, and G^{*E} with mole fraction of Methyl Acrylate (X_{MA}) for the systems under study are shown graphically in Fig. 1 to 3 respectively.

FromFig. 1 It is clear thatthe negative excess Volume values (V^E) for all three systems, indicate the presence of strong molecular interactions between the unlike components of mixtures. The negative V^Evalues fall in the sequence.

$$(MA + EB) > (MA + MB) > (MA + B)$$

According to,Subha et al.[2] several effects may contribute to the sign and values of V^E and the following three effects may be considered as being important.

I. Break up of hydrogen bonds and dipolar interactions in MA and intermolecular Hydrogen bonded interactions in Benzenes.
II. Interstitial accommodation of one component molecule into the other unlike Component molecules due to their differences in Sizes and
III. The possible intermolecular interactions like hydrogen bonding between unlike molecules.

The actual volume change would, therefore, depend on the relative strength of these three opposing effects.

S. Parthasarathi and workers [26]have reported negative excess volumes for the mixtures of Methyl Acrylate with polar components; this observation is supported by the present work where V^E values are negative for all the MAwithAromatic Hydrocarbon molecules. The negative excess volumes reported by Vijaya Lakshmi et al. [27]for Methyl Acrylate withBenzene and substituted benzenes at 308.15K concluded that this is due to the interaction between the oxygen atom of Methyl Acrylate and hydrogen atom of Benzene and substituted benzenes. Anothersimilar study supported by Anil Kumar Nain [15], a study of intermolecular interactions in binary mixtures of methyl acrylate with benzene and methyl-substituted benzenes at different temperatureslike 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15K.

The interactions between Methyl Acrylate and Aromatic hydrocarbon molecules may be due to the formation of strong intermolecular hydrogen-bonded complexes which are responsible for the negative excess volume. The negative excess volumes of Methyl Acrylate+ Aromatic Hydrocarbon molecules over the whole range of composition suggest that the IInd and IIIrdeffects are responsible for this situation i.e. formation of hydrogen bond interaction between >C=O group of MA and H-C- groups of Aromatic Hydrocarbon molecules [>C=O--------H-C-] and the accommodation of smaller size Methyl Acrylate molecules in the bigger size Aromatic Hydrocarbon molecules i.e. interstitial accommodation. These two effects lead to the negative V^E values, also these two effects outweigh the 1st effect. The formation of strong hydrogen-bonded complexes is sufficient to compensate for the physical effect caused during mixing.

Another effect of interaction between the two components becomes more and more predominant as the increased chain of AromaticHydrocarbon molecules becomes more due to their electron-donating ability to Methyl Acrylate. Also, the size of Aromatic Hydrocarbon molecules increases from Benzene to Ethyl Benzene, which in turn makes a larger difference in the size of Methyl Acrylate and Aromatic Hydrocarbon molecules. This gives more possibilities for, more interstitial accommodation resulting in negativeV^E to confirm the negative excess volumes the following explanation can also be considered as a reasonable one.

Fig. 2 shows it is observed that η^Evalues are positive for the whole composition range for all three systems. A correlation between signs of η^E and V^Ehas been observed for several binary solvent systems [28, 29], η^Ebeing positive where V^E is negative or vice-versa. In general for systems, where dispersion and dipolar interactions are operating η^E values are found to be negative, whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules thereby resulting in positive η^E values.The algebraic values of $\eta^E$for all the three mixtures of MA + Aromatic Hydrocarbon molecules like Benzene, Methyl Benzene, and Ethyl Benzene fall in the order.

$$(MA + EB) > (MA + MB) > (MA + B)$$

This order suggests that the presence of charge transfer and hydrogen bonding between unlike molecules increases with the increase in chain length in Aromatic Hydrocarbon molecules. A similar observation was reported by Vijaya Lakshmiet al. [30] and Manapragada et al. [31] in their viscosity study of binary liquid mixtures.

Fig. 2 shows it is observed that, The variation of excess Gibbs free energy of activation of viscous flow (G^{*E}) with X_{MA} for all the three systems.the magnitude of the positive values is an excellent indicator of the strength of specific interactions. G^{*E} values for the systems under study suggest the following order.

$$(MA + EB) > (MA + MB) > (MA + B)$$

Reed and Taylor[32]and Meyer *et al.*, [33] reported that,G^{*E} parameter can as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. Similar behavior was reported by Manapragada *et al.*,[31] in the case of G^{*E} values for mixtures of methyl formate, ethyl formate, propyl formate, and benzyl acetate with bromo-, chloro-, nitro benzenes at 303.15,308.15 and 313.15 K.

CONCLUSION

The present study concluded that the densities and viscosities of the binary mixtures of Methyl Acrylate with Aromatic Hydrocarbon molecules like Benzene, Methyl Benzene and Ethyl benzene over the whole composition range at 313.15K have been measured and the values of V^E, η^E, and G^{*E} were calculated.

The V^E values were found negative for all three mixtures whereas η^E and G^{*E} values were found positive for the presence of specific interactions between methyl acrylate with Aromatic Hydrocarbon molecules. The magnitude of the interactions were shown in the following order

$$(MA + EB) > (MA + MB) > (MA + B)$$

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Table 1: Values of density (ρ), viscosity (η), excess viscosity (η^E), molar volume (V), excess volume (V^E) and excess Gibbs free energy of activation of viscous flow (G^{*E}) for the binary liquid mixtures of Methyl Acrylate (MA) + Aromatic Hydrocarbon molecules like Benzene, Methyl Benzene, Ethyl Benzene at 313.15 K.

Mole fraction of MA (X_{MA})	$\rho \times 10^{-3}$ Kg m^{-3}	$\eta \times 10^3$ Kg m^{-1} s^{-1}	$\eta^E \times 10^3$ Kg m-1 s^{-1}	V$\times 10^6$ m^3 mol^{-1}	$V^E \times 10^6$ m^3 mol^{-1}	$G^{*E} \times 10^3$ N mol^{-1}
			Methyl Acrylate (MA) + Benzene (B)			
0.0000	0.8574	0.4981	0.0000	91.1010	0.0000	0.0000
0.0916	0.8646	0.4838	-0.0012	91.1897	-0.0531	0.7907
0.1849	0.8718	0.4695	-0.0022	91.2928	-0.0945	1.4827
0.2800	0.8789	0.4552	-0.0029	91.4104	-0.1242	2.0527
0.3769	0.8861	0.4409	-0.0033	91.5425	-0.1422	2.4752
0.4757	0.8933	0.4266	-0.0035	91.6893	-0.1483	2.7210

|						
0.5764	0.9005	0.4123	-0.0034	91.8510	-0.1426	2.7576
0.6792	0.9077	0.3980	-0.0030	92.0277	-0.1251	2.5484
0.7840	0.9148	0.3837	-0.0023	92.2196	-0.0955	2.0516
0.8909	0.9220	0.3694	-0.0013	92.4268	-0.0538	1.2200
1.0000	0.9292	0.3551	0.0000	92.6496	0.0000	0.0000
Methyl Acrylate (MA) + Methyl Benzene (MB)						
0.0000	0.8488	0.4662	0.0000	108.5533	0.0000	0.0000
0.1063	0.8568	0.4551	0.0007	106.7842	-0.0788	3.1957
0.2111	0.8649	0.4440	0.0012	105.0584	-0.1378	5.7214
0.3145	0.8729	0.4329	0.0016	103.3744	-0.1779	7.5654
0.4164	0.8810	0.4218	0.0018	101.7308	-0.2001	8.7141
0.5170	0.8890	0.4107	0.0019	100.1263	-0.2052	9.1522
0.6162	0.8970	0.3995	0.0018	98.5598	-0.1939	8.8624
0.7141	0.9051	0.3884	0.0016	97.0300	-0.1670	7.8254
0.8106	0.9131	0.3773	0.0012	95.5357	-0.1253	6.0194
0.9059	0.9212	0.3662	0.0007	94.0760	-0.0694	3.4200
1.0000	0.9292	0.3551	0.0000	92.6496	0.0000	0.0000
Methyl Acrylate (MA) + Ethyl Benzene (EB)						
0.0000	0.8484	0.5378	0.0000	125.1379	0.0000	0.0000
0.1205	0.8565	0.5195	0.0037	121.1324	-0.0903	11.7304
0.2357	0.8646	0.5013	0.0065	117.3265	-0.1555	20.7217
0.3458	0.8726	0.4830	0.0084	113.7066	-0.1978	27.0563
0.4512	0.8807	0.4647	0.0094	110.2602	-0.2192	30.7982
0.5522	0.8888	0.4465	0.0095	106.9759	-0.2215	31.9928
0.6491	0.8969	0.4282	0.0090	103.8433	-0.2064	30.6670
0.7421	0.9050	0.4099	0.0077	100.8529	-0.1754	26.8283
0.8314	0.9130	0.3916	0.0057	97.9958	-0.1298	20.4644
0.9173	0.9211	0.3734	0.0032	95.2638	-0.0710	11.5410
1.0000	0.9292	0.3551	0.0000	92.6496	0.0000	0.0000
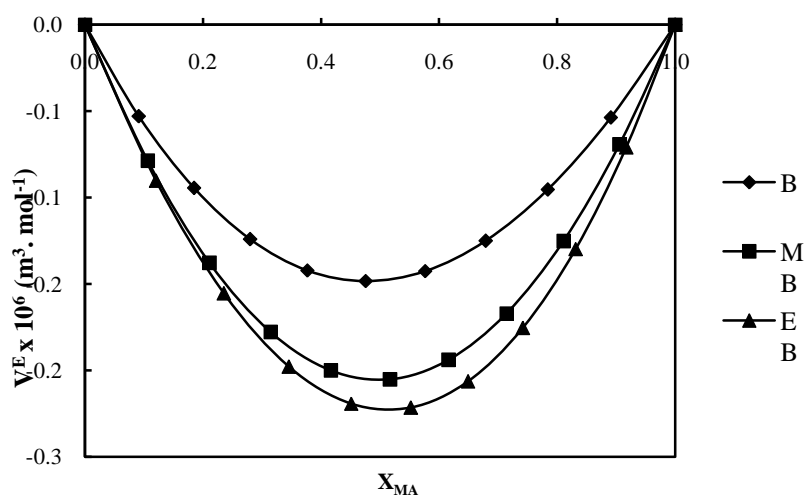
Fig: 1: Plots of excess volumes (V^E) for various Aromatic Hydrocarbon molecules like Benzene (-♦-), Methyl Benzene (-■-), and Ethyl Benzene (-▲-) vs mole fraction ofMethyl acrylate (X_{MA}) at 313.15 K
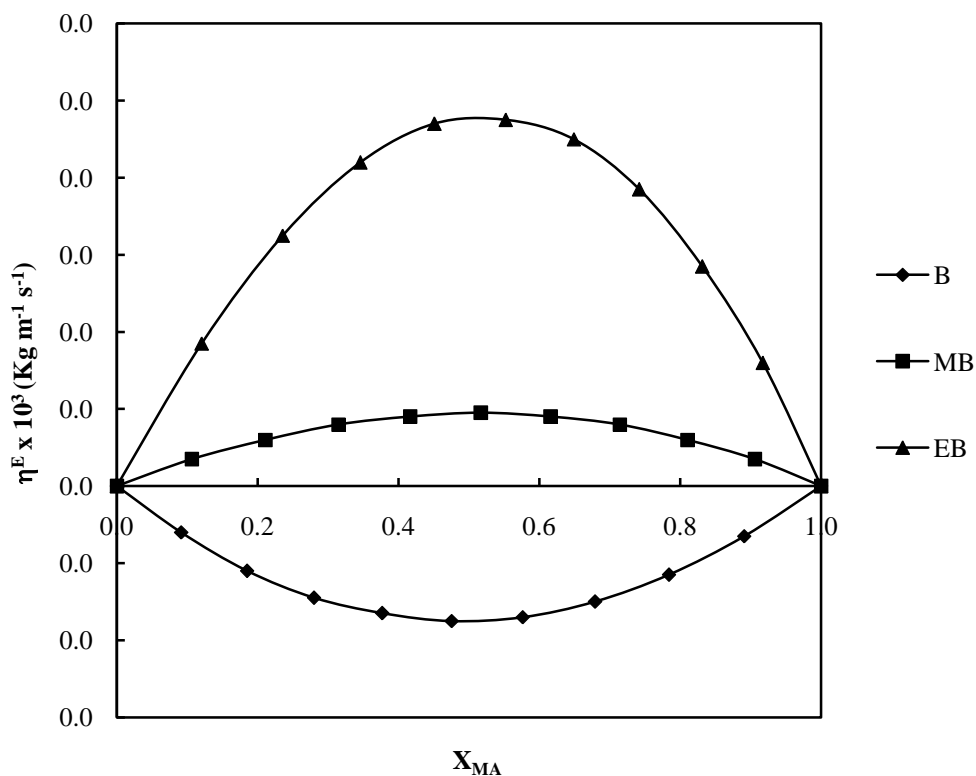
Excess Viscosities

Fig: 2: Plots of excess viscosities (η^E) for various Aromatic Hydrocarbon molecules like Benzene (-♦-), Methyl Benzene (-■-), and Ethyl Benzene (-▲-) vs mole fraction ofMethyl acrylate (X_{MA}) at 313.15 K

Fig:3: Plots of Excess Gibbs free energy of activation of viscous flow (G^{*E}) for various Aromatic Hydrocarbon molecules like Benzene (-♦-), Methyl Benzene (-■-), and Ethyl Benzene (-▲-) vs mole fraction ofMethyl acrylate (X_{MA}) at 313.15 K
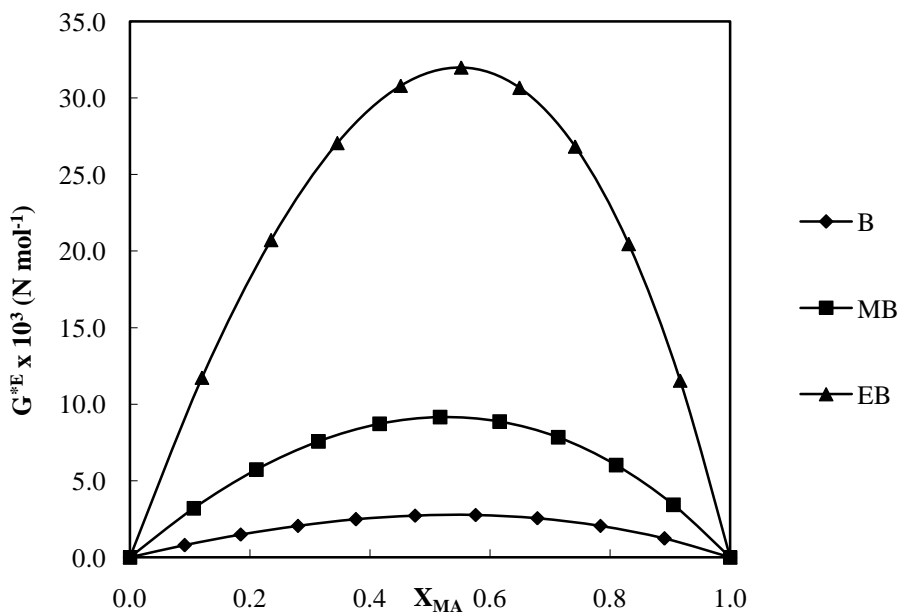
Table 2: Parameters of Eq. (6) and Standard deviations						
Excess Property	**A_0**	**A_1**	**A_2**	**A_3**	**A_4**	**σ**
Methyl Acrylate (MA) + Benzene (B)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.000003	-0.0148	0.01653	-0.0020	0.0002	0.00001
V^E x 10^6 m^3 mol^{-1}	-0.000003	-0.6492	0.77283	-0.1422	0.01869	0.00003
G^{*E} x 10^3N mol^{-1}	-0.00001	9.19117	-5.75584	-3.0605	-0.37453	0.00027
Methyl Acrylate (MA) + Methyl Benzene (MB)						
η^E x 10^3 Kg m^{-1} s^{-1}	0.000002	0.00718	-0.00685	0.0003	-0.0006	0.000015
V^E x 10^6 m^3 mol^{-1}	-0.00001	-0.83107	0.84925	-0.01789	-0.0002	0.000029
G^{*E} x 10^3N mol^{-1}	-0.00274	122.89509	-117.5114	3.79963	-9.17769	0.00482
Methyl Acrylate (MA) + Ethyl Benzene (EB)						
η^E x 10^3 Kg m^{-1} s^{-1}	-0.000009	0.03423	-0.02596	-0.0086	0.0003	0.00003
V^E x 10^6 m^3 mol^{-1}	-0.000003	-0.8403	0.74534	0.08492	0.01004	0.00001
G^{*E} x 10^3N mol^{-1}	-0.00959	107.36603	-80.02792	-4.46084	-22.85224	0.02134
Methyl Acrylate (MA) + Butyl Benzene (BB)						
η^E x 10^3 Kg m^{-1} s^{-1}	-0.00001	0.15666	-0.11186	-0.00597	-0.03879	0.00004
V^E x 10^6 m^3 mol^{-1}	0.00003	-0.93327	0.68582	0.1153	0.13204	0.00009
G^{*E} x 10^3N mol^{-1}	-0.21729	366.71629	-335.5674	303.90889	-334.2562	0.66089