

Thermodynamic and Transport Properties of Binary Liquid Mixtures of Methylaniline with Alkyl Acetates at 298 and 303K

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Abstract: Sound velocity, density and viscosity values have been measured at 298k & 303K in the four binary mixtures of methylaniline with alkyl acetates methylacetate, ethylacetate, propylacetate and butylacetate). From these data, acoustical parameters such as adiabatic compressibility (β), intermolecular free length (Lf), free volume (Vf), internal pressure (π) and their excess parameters have been calculated. These parameters are used to discuss the molecular interactions between the component molecules and the excess functions are found to be sensitive to the nature and extent of the interactions taking place in these binary mixtures.

Key words: Binary • Molecular interaction • Alkylacetates • Methylaniline

INTRODUCTION

Thermodynamic and transport properties of liquid mixtures have been extensively used [1, 2] to study the departure of a real liquid mixture from ideality. Further, these properties have been widely used to study the intermolecular interactions between the various species present in the mixture [3, 4]. In the chemical industry knowledge of the thermodynamic properties of non-electrolyte solutions is essential in the design involving chemical separation, heat transfer, mass transfer and fluid flow. Esters are one of the best candidates that exist as dipolar associates in their pure liquid state, available with not only aliphatic, aromatic and even acrylic nature. Methylaniline is an aniline derivative used in the production of dyes. Secondary amines like methylaniline are used as a latent and coupling solvent and is also used as an intermediate for dyes, agrochemicals and other organic products manufacturing. Alkyl acetates like methyl acetate, ethylacetate, butyl acetate and propyl acetate these are used as solvents which are having the acetic acid group. Methyl acetate also known as acetic acid methyl ester or methyl ethanoate, having a dipole moment of $\mu=1.72$ is a carboxylate ester. A major use of methyl acetate is as a volatile low toxicity solvent in glues, paints and nail polish removers. Acetic anhydride is produced by caronylation of methyl acetate. Ethyl acetate ($\mu=2.4$) is also known as ethyl ethanoate and it has plenty of

applications this colorless liquid has a characteristic sweet smell and is used in laboratory uses, Occurrence in wines, Entomological killing agent, glues, nail polish removers, decaffeinating, tea and coffee and cigarettes. Butyl acetate ($\mu=1.9$) is found in many types of fruit having a sweet smell. propyl acetate ($\mu=1.8$) is one of the best candidates that exist as dipolar associate in their pure state and find wide industrial applications. It is also called as propyl ethanoate. It is clear and colourless liquid is known by its characteristic odour of pears. Hence, the authors have performed a thorough study on the molecular interaction existing in the mixtures of alkyl acetates with methylaniline, using the sound velocity data. In order to study the thermodynamic and transport properties in the mixture of methylaniline with alkyl acetates, we report measurement of the ultrasonic velocity, density and viscosity at varying temperatures of 298 and 303 K. From the experimental properties, adiabatic compressibility (β), intermolecular free length (Lf), free volume (Vf), internal pressure (π), and their excess values have been evaluated. These parameters are used to discuss the intermolecular interaction of the mixtures.

Experimental Details: The mixtures of various concentrations in mole fraction were prepared by taking purified AR grade samples at 298k. The ultrasonic velocity (U) in liquid mixtures has been measured using an ultrasonic interferometer (Mittal type) working at 3 MHz

frequency with an accuracy of $\pm 0.1 \text{ ms}^{-1}$. The density, or the mass per unit volume (ρ) and viscosity (η) are measured using a pycnometer and an Ostwald's viscometer, respectively, with an accuracy of 3 parts in 10^5 for density and 0.001 Nsm^{-2} for viscosity.

Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (Lf), free volume (Vf) and internal pressure (π) and their excess parameters have been calculated using the following standard expressions:

$$\beta = (U^2 \rho)^{-1} \quad (1)$$

$$L_f = K T \beta^{1/2} \quad (2)$$

$$V_f = \left[\frac{M_{eff} U}{\eta k} \right] \quad (3)$$

$$\pi_i = b R T \left[\frac{k \eta}{U} \right]^{1/2} \left[\frac{\rho^{2/3}}{M_{eff}^{7/6}} \right] \quad (4)$$

where $M_{eff} = \sum x_i m_i$, where x_i is the mole fraction and m_i is the molecular weight of the i th component, R is the universal gas constant, b is a dimensionless constant having a value of 2 for all liquids.

The excess parameters are determined by $A^E = A_{exp} - A_{id}$ (5)

And $A_{id} = \sum x_i A_i$ (6)

where A^E stands for excess property of any given parameter, A_{exp} is the experimental value and A_{id} is the ideal value and x_i and A_i refers to the mole fraction and the relevant property of the i th component.

Sample Preparation: Liquid mixtures of different compositions were prepared by mixing measured amount of the pure liquids in cleaned and dried flasks. In this system, the first component and the second component (X1 and X2) were varied from 0.0 to 0.9, so as to have the mixtures of different compositions.

RESULTS

The experimental values of density (ρ), viscosity (η) and the ultrasonic velocity (U) for the binary system at 298, 303K are presented in Table 1 & 2. The values of adiabatic compressibility (β), intermolecular free length

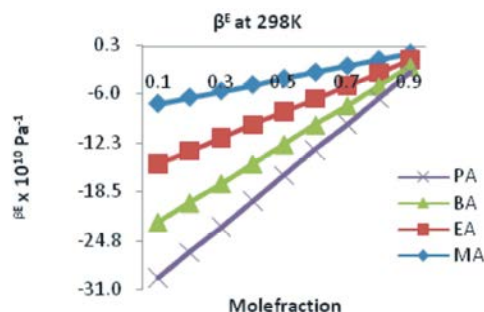


Fig. 1: Excess adiabatic compressibility at 298K

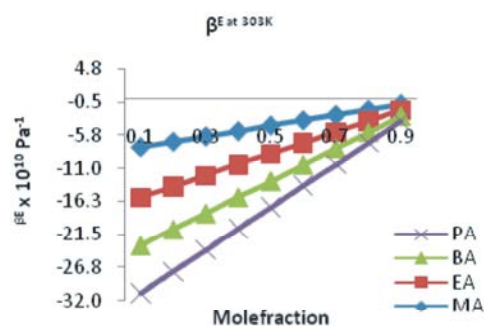


Fig 2: Excess adiabatic compressibility at 303K

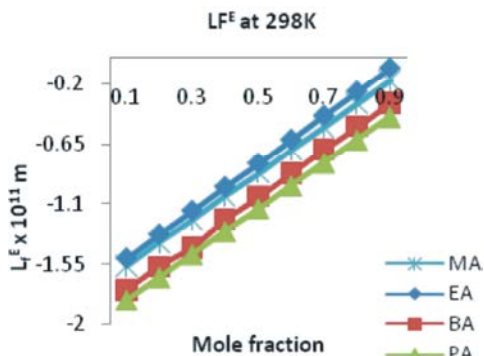


Fig 3: Excess free length at 298K

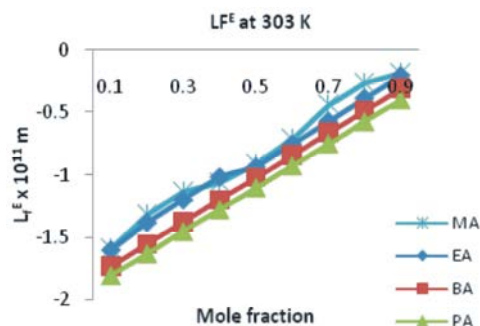


Fig 4: Excess free length at 303K

(L_f), free volume (V_f), internal pressure (π) at two different temperatures are given in table 2,3,4 & 5. The variation of β^E , L_f^E , V_f^E , π^E with molefraction of methylaniline are depicted in Fig 1-8.

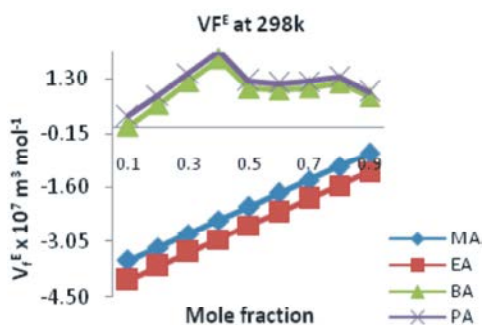


Fig 5: Excess free volume at 298K

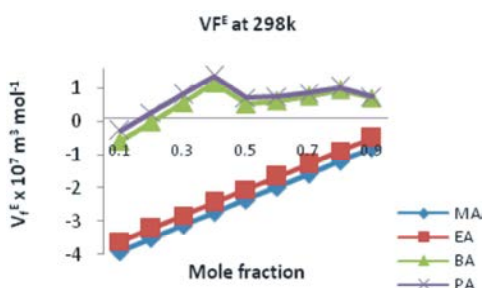


Fig 6: Excess free volume at 303k

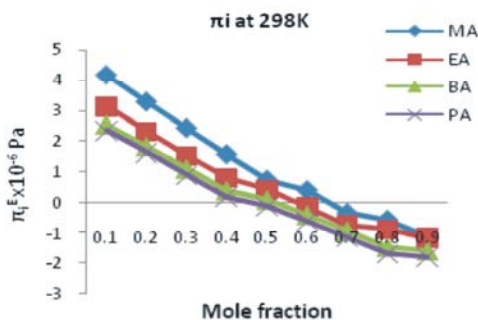


Fig 7: Excess internal pressure at 298K

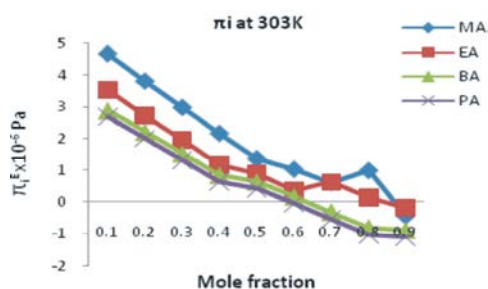


Fig 8: Excess internal pressure at 303K

DISCUSSION

The observed values for the system of methylaniline + methylacetate, ethylacetate, propylacetate, butylacetate are presented in Table 1& 2. The values of density (ρ), viscosity (η) and the ultrasonic velocity (U) show an increasing trend with increase in mole fraction of methylaniline in all the systems.

As ρ increases, the no of particles in a given region is increased and this leads to quick transfer of sound energy and thus velocity also increases [5-6]. As methylaniline is having a high boiling point, the energy between the molecules of methylaniline is so high that the molecular bonds of methylaniline cannot be ruptured, whereas for alkylacetates it is not so. The increasing molefraction of methylaniline supports non-rupturing of components and hence increase in viscosity [7] is expected. All the observed parameters vary non-linear and this indicates the existence of interactions in the medium. This is in line with the observations made by Jacek Glinski [8] in some binary systems.

Table 3&4 illustrates the variation of these parameters invariably show a decreasing trend in adiabatic compressibility (β) and Intermolecular free length (L_f), with increase in molefraction of methyl aniline with all the systems. Intermolecular free length is an important parameter that has association with adiabatic compressibility. The decreased compressibility brings the molecules to a closer packing resulting a decrease in intermolecular free length.

The compactness of the system with increase in mole fraction of methyl aniline is indicated by reduced β values and the same is favoured by the decreasing trend of L_f . Such trends were noticed in some similar liquid systems[9]. A Continuous decrease in β and L_f is a clear evidence for the existence of strong interactions. Such interactions may be due to charge transfer, dipole-dipole, dipole-induced dipole, etc [10]. L_f is a predominant factor in determining the variation of U in solutions. As L_f decreases U increases and vice versa, showing an inverse behaviour. The interdependence of L_f and U has been evolved from a model for sound propagation proposed by Eyring and Kincaid [11].

It is observed that V_f shows a monotonous increase, whereas a reverse trend is observed in internal pressure values with increase in mole fraction of methyl aniline. A continuous increase in V_f indicates that the components are packed in a cage-like structure; however, no complex formation is suspected. This compactness of the medium reduced the effective adhesive forces and thus π_i shows a decreasing trend[12-13]. In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters.

The excess values are shown in the Fig (1-4). The perusal of these figures indicates that β^E and L_f^E in the mixture are fully negative. It can be seen that excess adiabatic compressibility and excess free length in the mixture are fully negative which confirms the existence of strong interactions. From fig1 it is noticed that excess

Table 1: Values of density (ρ), viscosity (η) and velocity (U) of methylaniline (A) with methylacetate (MA), ethylacetate(EA), propylacetate(PA) and butylacetate(BA) at 298k

Mole fraction of A	$\rho \text{ kgm}^{-3}$				$\eta \times 10^3 \text{ Nsm}^{-2}$				U ms^{-1}			
	MA	EA	PA	BA	MA	EA	PA	BA	MA	EA	PA	BA
0.1007	827	899	974	1019	0.8634	0.8886	0.8988	0.9093	1201	1563	1813	1859
0.1995	832	912	987	1034	0.8738	0.8988	0.9094	0.9152	1219	1681	1915	1898
0.2996	838	926	1001	1050	0.8842	0.9202	0.9196	0.9258	1236	1799	2021	1937
0.4045	843	944	1019	1064	0.8947	0.9708	0.9298	0.9364	1254	1919	2127	1987
0.5000	849	962	1037	1078	0.9052	1.2456	1.2046	1.2112	1272	2040	2230	2047
0.6025	854	974	1049	1094	1.2139	1.4241	1.3831	1.3897	1356	2158	2338	2112
0.7046	860	986	1061	1107	1.5227	1.6026	1.5616	1.5682	1431	2277	2447	2168
0.8079	866	998	1073	1123	1.8315	2.2059	1.7399	1.7467	1511	2389	2556	2221
0.9003	872	1010	1085	1138	2.1403	2.8092	2.3432	2.3501	1585	2508	2658	2285

Table 2: Values of density (ρ), viscosity (η) and velocity (U) of methylaniline (A) with methylacetate (MA), ethylacetate (EA), propylacetate (PA) and butylacetate (BA) at 303k

Mole fraction of A	$\rho \text{ kgm}^{-3}$				$\eta \times 10^3 \text{ Nsm}^{-2}$				U ms^{-1}			
	MA	EA	PA	BA	MA	EA	PA	BA	MA	EA	PA	BA
0.1007	853	925	997	1038	0.9592	0.9844	0.9944	1.0049	1200	1559	1807	1867
0.1995	858	938	1010	1059	0.9699	0.9948	1.0050	1.0155	1216	1678	1909	1904
0.2996	864	951	1024	1075	0.9802	1.0054	1.0155	1.0257	1232	1791	2015	1945
0.4045	869	970	1042	1090	0.9907	1.0157	1.0259	1.0359	1248	1911	2121	1996
0.5000	875	986	1060	1105	1.0009	1.3266	1.3368	1.3468	1264	2035	2224	2053
0.6025	877	999	1072	1119	1.3097	1.5051	1.5153	1.5253	1347	2151	2332	2119
0.7046	881	1012	1084	1134	1.6185	1.7812	1.6938	1.7038	1423	2272	2441	2177
0.8079	883	1023	1096	1149	1.927	2.7092	1.8723	1.8823	1499	2379	2550	2232
0.9003	887	1034	1108	1164	2.2357	3.3125	2.4756	2.4857	1573	2501	2652	2294

Table 3: Values of adiabatic compressibility (β), free length (Lf) and free volume (Vf) of methylaniline (A) with methylacetate (MA), ethylacetate (EA), propylacetate (PA) and butylacetate (BA) at 298k

Mole fraction of A	$\beta \times 10^{10} \text{ Pa}^{-1}$				Lf $\times 10^{11} \text{ m}$				Vf $\times 10^7 \text{ m}^3 \text{ mol}^{-1}$			
	MA	EA	PA	BA	MA	EA	PA	BA	MA	EA	PA	BA
0.1007	8.3831	4.5533	3.1235	2.8397	5.7771	4.2576	3.5264	3.3623	0.7617	2.0023	1.5029	1.2163
0.1995	8.0885	3.8803	2.7628	2.6846	5.6746	3.9305	3.3165	3.2693	0.8532	3.6914	2.1993	1.8417
0.2996	7.8112	3.3368	2.4459	2.5383	5.5769	3.6448	3.1205	3.1790	0.9865	4.0662	2.4057	2.1139
0.4045	7.5435	2.8766	2.1692	2.3805	5.4802	3.3841	2.9387	3.0785	1.2138	4.5141	2.6762	2.4664
0.5000	7.2797	2.4978	1.9392	2.2138	5.3835	3.1535	2.7785	2.9688	1.2614	5.1168	3.0451	2.9277
0.6025	6.3682	2.2046	1.7440	2.0492	5.0352	2.9626	2.6350	2.8563	1.3491	5.9986	3.3641	4.0852
0.7046	5.6783	1.9561	1.5740	1.9219	4.7546	2.7907	2.5033	2.7661	1.4371	6.4762	3.6147	4.1249
0.8079	5.0577	1.7556	1.4265	1.8052	4.4872	2.6438	2.3831	2.6808	1.5289	6.8291	3.8821	4.1306
0.9003	4.5648	1.5741	1.3045	1.6830	4.263	2.5033	2.2790	2.5885	1.6229	6.8590	4.1528	4.1688

Table 4: Values of adiabatic compressibility (β), free length(Lf) and free volume(Vf) of methylaniline (A) with methylacetate (MA), ethylacetate(EA), propylacetate (PA) and butylacetate (BA) at 303k

Mole fraction of A	$\beta \times 10^{10} \text{ Pa}^{-1}$				Lf $\times 10^{11} \text{ m}$				Vf $\times 10^7 \text{ m}^3 \text{ mol}^{-1}$			
	MA	EA	PA	BA	MA	EA	PA	BA	MA	EA	PA	BA
0.1007	8.1412	4.3533	3.0235	2.7638	5.7077	4.0576	3.4264	3.3172	0.7054	1.5594	1.3793	1.1181
0.1995	7.8822	3.6803	2.6628	2.6048	5.6488	3.7305	3.2165	3.2203	0.7812	2.9691	1.9633	1.6464
0.2996	7.6254	3.1368	2.3459	2.4590	5.5486	3.4448	3.0205	3.1288	0.8927	3.4626	2.1218	1.8666
0.4045	7.3884	2.6766	2.0692	2.3028	5.4501	3.1841	2.8387	3.0279	1.0723	4.1412	2.3248	2.1449
0.5000	7.1532	2.2978	1.8392	2.1471	5.3513	2.9535	2.6785	2.9237	1.0759	4.6440	2.5943	2.4969
0.6025	6.2844	2.0046	1.6440	1.9903	4.995	2.7626	2.5350	2.8149	1.1493	5.1314	2.8765	3.5163
0.7046	5.6055	1.7561	1.4740	1.8607	4.7073	2.5907	2.4033	2.7217	1.2253	5.5518	3.0968	3.5291
0.8079	5.0401	1.5556	1.3265	1.7470	4.4327	2.4438	2.2831	2.6373	1.3027	5.9531	3.3305	3.5421
0.9003	4.5564	1.3741	1.2045	1.6325	4.2018	2.3033	2.1790	2.5494	1.3826	6.3826	3.5680	3.9582

Table 5: Value of internal pressure π_i at 298K and 303K

Mole fraction of A	$\pi_i \times 10^{-6}$ Pa 298K				303K			
	MA	EA	PA	BA	MA	EA	PA	BA
0.1007	4.9112	4.8568	4.4503	4.8871	5.3349	5.4532	4.7206	5.1765
0.1995	4.8756	4.4689	3.9032	4.1951	5.1803	5.1288	4.1793	4.4838
0.2996	4.8099	3.9552	3.7719	3.9469	5.1009	4.3176	4.0556	4.2408
0.4045	4.6644	3.8837	3.6242	3.6995	5.0950	4.1956	3.9173	3.9929
0.5000	4.6551	3.8427	3.4560	3.4412	4.9815	4.1344	3.7604	3.7444
0.6025	4.4587	3.7895	3.2481	3.016	4.8781	4.0461	3.5332	3.2695
0.7046	4.4339	3.6716	3.1890	2.9828	4.7812	4.0044	3.4659	3.2352
0.8079	4.2735	3.5421	3.1332	2.9382	4.6758	3.8395	3.4030	3.1916
0.9003	4.1061	3.4853	3.0902	2.9039	4.4923	3.6979	3.3538	3.1349

compressibility becomes decreasing negative and attains the minimum value at 0.9003, which again confirms the specific interaction between solute molecules for all the binary systems.

From Fig 2 it is observed that the negative excess free length in all four mixtures indicates that the sound waves needs to cover a larger distance [14] which may be attributed due to the dominant nature of interaction between the molecules. V_{fE} are negative for methyl acetate and ethyl acetate but for propyl acetate and butyl acetate show a decreasing trend with increase in mole fraction of methyl aniline. The negative deviation of excess free volume is an indication of the existence of strong interaction between the components [15]. But for propyl acetate and butyl acetate it shows positive values of excess properties correspond mainly to the existence of dispersive force which indicates structure breaking tendency while negative values is associated with structure forming tendency. In the present investigation, the deviation in V_{fE} shows that weak interaction between the molecules which is in agreement with shakila [16]. The positive but decreasing V_{fE} suggests that the dipole-dipole interactions need not to be of fully attractive type [17,18]. Excess internal pressure values are highly fluctuating at 298 & 303K it has the positive value and finally attain the negative value and at 308K it attains positive value. The negative excess internal pressure in all the mixtures indicates weak interaction between the component molecules [19,20].

All the four acetates are having acid group with increasing number of alkyl group. The acid group COOH in all the four acetates can interact with the methyl amino group of methyl aniline and thus dipole-dipole interactions are evident in all the four systems. In the case of propyl acetate and butyl acetate, the hydrocarbon chain acts as hydrophobic, whereas in other two acetates

such properties are not evident. Though the amino group is comparatively a strong electron donor, the H atoms in the methyl group can also play the role of electron acceptor centres [21] and hence the hydrophobic nature of propyl acetate and butyl acetate can create temporary dipoles in the methylamino group of methylaniline molecule thus dipole-induced dipole interactions are existing in the propyl acetate and butyl acetate system. The temporary dipoles are reflected in the fluctuations in the trend of excess free volume, internal pressure in the propylacetate and butylacetate systems.

In the propylacetate and butylacetate system, V_{fE} values are observed to be positive, whereas π_i values are negative and have haphazard variations. These fluctuations are reflect the possibility of new induced dipoles. Thus dipole-dipole and dipole-induced dipole types are confirmed in the system.

CONCLUSION

- Presence of Molecular interactions is confirmed in all the systems.
- These molecular interactions are strong in magnitude irrespective of the alkyl chain length.
- In addition to the existence of dipole-dipole interaction, dipole - induced dipole types are additionally present in the propylacetate and butylacetate system.

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