

# ‘Measurements of temperature of maximum density (TMD) of aliphatic amines in water at low concentration and calculation of limiting excess volumes at different temperatures.’

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## **Abstract:**

*The alcohols produce a rise in the temperature of maximum density at least at low concentration, while amines lower it at all concentrations similar to the normal electrolytes. Shifts in the TMD of water solutions ( $\Delta\theta$ ) are an effective way to probe the nature of the hydrogen-bonded structure of those solutions; solutes that promote a more stable hydrogen bonded network should yield solutions with higher TMDs, whereas those that break the HB network should decrease the TMD value. In the present study a systematic measurement of densities of aliphatic amine in water at low concentration is carried out and calculate the limiting excess volumes at different temperatures. At low concentrations amines (methylamine, n-propylamine, t-butylamine, Dimethylamine and Tri-methylamine) are known to undergo considerable hydrolysis, it was also necessary to examine the applicability of method of hydrolysis correction suggested by Cabani*

Key words: TMD, HB, aliphatic amines

## **I. INTORUCTION:**

In the studies of temperature of maximum density (TMD) indicates that, some alcohols produce a rise in the temperature of maximum density at least at low concentration, while amines lower it at all concentrations similar to the normal electrolytes. Shifts in the TMD of water solutions ( $\Delta\theta$ ) are an effective way to probe the nature of the hydrogen-bonded (HB) structure of those solutions; solutes that promote a more stable HB network should yield solutions with higher TMDs, whereas those that break the HB network should decrease the TMD value. In most cases, the  $D_y$  values are proportional to the amount of added solute, as stated by the Despretz rule.[1-2] It must be stressed that such a rule does not entail a colligative property such as the freezing point depression of aqueous solutions; whereas the latter property does not depend on the nature of the solute (just on its added amount), the shifts in the TMD of the aqueous solutions will depend on the ability of different solutes to interfere with the HB network of liquid water. Moreover, the Despretz rule should be understood as a limiting law; in the absence of solute–solute interactions (low solute concentrations) the amount of interference with the HB network of water should be proportional to the amount and nature of the solute present; that is not necessarily the case for more concentrated solutions or for solutes that tend to self-aggregate even at fairly low concentrations (e.g. surfactant molecules with long alkyl chains). Finally, most authors<sup>4–10</sup> have dissected the observed TMD shifts into two contributions:  $\Delta\theta = \Delta\theta_{id} + \Delta\theta_{str}$ . Careful observation of the values of structural contribution in the TMD ( $\Delta\theta_{str}$ ) corresponding parameter ‘a’ ( $a = [d(\Delta\theta_{str})/dx]_{x \rightarrow 0}$ ) values according to the above equation though positive for both alcohols and amines are greater in magnitude for alcohols than corresponding amines. However, the careful observation of the curves ( $(\Delta\theta_{str}/x) \text{ Vs } x$ ) obtained for amines indicates that at low concentration the points for the amines distinctly shows a nonlinearity and tendency to

curve down, this rather more marked for methyl amine and less for n-butylamine. This nonlinearity nature of the curve at low concentrations cannot be said to be in errors as  $\Delta\theta$  for lowest concentration are quit large ( - 0.14 0C for methyl amine and – 0.25 0C for n-butyl amine) as compared to the reported uncertainty of TMD ( i.e.  $\pm 0.02^{\circ}\text{C}$ ) . Hence in our view, the intercept determined under this situation will not give true values for parameter ‘a’ and this nonlinearity may be due to the presence of ionic species formed as a result of hydrolysis which is not accounted by the researchers. The true value for parameter ‘a’ for amines must have be much different than alcohols. TMD for binary aqueous solutions of amino acids and were also studied [3]. The temperature of maximum density and excess thermodynamics of aqueous mixtures of methnols were studied by some researchers. [4-7]

Moreover, as it is clear from the survey of the work that there is a close relationship between TMD and excess volume and its temperature derivative. Systematic work on the density of amines at different temperatures and at low concentration is lacking. In the present paper a systematic measurement of densities of aliphatic amine in water at low concentration is carried out and calculate the limiting excess volumes at 5,15, and 25<sup>0</sup>C. Since at such low concentrations amines are known to undergo considerable hydrolysis, it was also necessary to examine the applicability of method of hydrolysis correction suggested by Cabani [8]. For this study ammonia, methylamine, n-propylamine, t-butylamine, Di-methylamine and Tri-methylamine are chosen.

## II. EXPERIMENTAL:

### 2.1 Material used and their purification:

n- Propylamine (Reidle de Haen A. G.), n- butylamine (Merck) and t- butylamine (Fluka) were dried over fresh potassium hydroxide for 48 hours and distilled twice. The purity of liquid before used was established by density measurements. Table –I shows the comparison of the observed densities with those from literature [9].

In case of volatile amines, methylamine ( BDH) 40% and ethylamine (Reidle de Haen A. G.) 50% were used. In order to prepare dilute stock solutions the following procedure is adopted; about 100 ml of concentrated solution mentioned above was taken in a round bottom flask and warm carefully on a heating mantle. The vapours of the amines evolved there off were led by means of corning glass bent tube fitted with slandered joints in to degassed conductivity water in another similar flask kept in ice cold water in which the vapours distilled. In this process only the middle fraction of amine was allowed to dissolve. The solutions so obtained were quit concentrated was used to prepare stock solution. The solution of trimethyl amine (BDH) and dimethylamine (BDH) have also been prepared by similar procedure.

Table –I : Densities of liquid Amines at 25<sup>0</sup>C

Amines	Experimental	Literature
n- PrNH <sub>2</sub>	0.7126	0.7122
n- BuNH <sub>2</sub>	0.7348	0.7346
t- BuNH <sub>2</sub>	0.6905	0.6908

### 2.2 Preparation of Amine Hydrochloride solution:

For the preparation of hydrochlorides a concentrated solution (1M) of purified amines was prepared in a double distilled water. About 200 ml of this solution was taken in a beaker and cooled in a ice bath. To the cold solution a calculated quantity of concentrated cold solution of HCl (AR) was added slowly with stirring till the solution was just acidic and turned methyl red solution pink when tested separately on a porcelain tile. To this solution cold dilute solution of amine was added with constant stirring though separating funnel till the solution gives the test for basic nature. The excess amine was boiled off till the out coming vapours when tested for amine by holding a piece of filter paper soaked in methyl red did not produce any colour change. The water was boiled off on a water bath under reduced pressure till solid amine hydrochloride separated out. The amine hydrochloride was recrystallized for conductivity water at least three times. It was finally dried under reduced pressure at 100 0C and placed first over KOH and then over CaCl<sub>2</sub> in vacuum desicator for several days. The purity of salt was established by estimation of chloride by conductometric titration against standard AgNO<sub>3</sub>

solution. The table –II shows the comparison of the estimated chloride with theoretical ones calculated from the molecular weight of all hydrochlorides used in this work.

The solutions of amine hydrochlorides required for measurement was prepared as follows; about 500 ml of double distilled water is accurately weighed by using 100 ml of Stoppard conical flask and placed in dry Stoppard flat bottom flask. After accurately determining its weight a calculated quantity of purified amine hydrochloride was added to the weighed quantity of double distilled water. This give solution of amine hydrochloride of known molality which is then filled in dilatometer.

Table- II : Estimated percentage of chlorides in the amine hydrochloride salts

Salt	Molecular weight	% of Chloride ( Theoretical)	% of Chloride (Estimated)	% Purity
MeNH <sub>3</sub> Cl	67.519	52.508	52.63	99.9
EtNH <sub>3</sub> Cl	81.546	43.476	43.43	99.9
n-PrNH <sub>3</sub> Cl	95.573	37.095	37.06	99.9
n-BuNH <sub>3</sub> Cl	109.599	32.348	32.31	99.9
t-BuNH <sub>3</sub> Cl	109.599	32.348	32.37	99.9
Me <sub>2</sub> NH <sub>3</sub> Cl	81.546	43.476	43.41	99.9
Me <sub>3</sub> NH <sub>2</sub> Cl	95.573	37.095	37.13	99.9

### 2.3 Measurement of TMD for solutions of amines:

About 500 ml dilute solution is prepared by diluting the stock solution. The concentration of dilute amine solution which is prepared for measurements is further determine by titrating against standard 0.02 M HCl solution using Bromocresol purple as indicator. This solution is filled in dilatometer taking the precaution to prevent carbonization from atmospheric CO<sub>2</sub> and measurement for TMD were made. Taking into consideration the possibility of diffusion of some dissolved amine during the process of filling of dilatometer the concentration of amine solution was determined again after the measurements. This will account for the loss of amine if any takes place by diffusion. The TMD of amine and amine hydrochloride solutions are then determined. The plot of meniscuss height ( $h_1 + h_2$ ) Vs temperature are shown in figure (1- 4) for methyl amine ( $m = 0.171$ ), n- Butylamine ( $m = 0.0465$ ), Ethylamine hydrochloride ( $m = 0.0826$ ) and t- Butyl amine hydrochloride ( $m = 0.0385$ ) respectively. The corresponding plots of  $dh/dT$  Vs mean temperature from which TMD for given solution is determined are shown in figure (4-7). Table (III – VI) show the values of ( $\Delta\theta_{obs}$ ) determine for all amines concentrations handled in this work. Figure 4 and 5 represent the plots of ( $\Delta\theta_{obs}$ ) Vs. x for amine and corresponding hydrochlorides respectively.

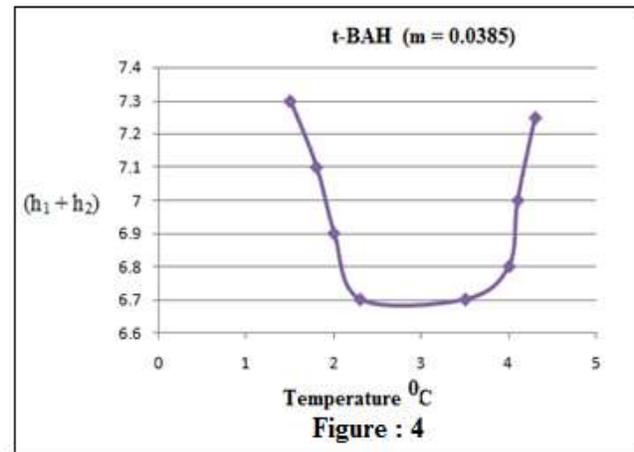
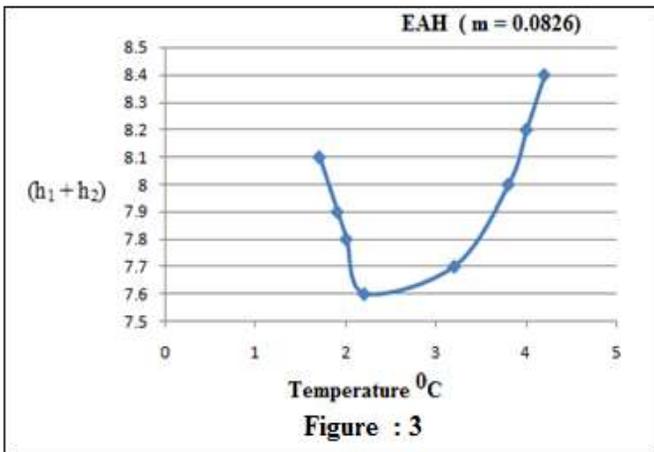
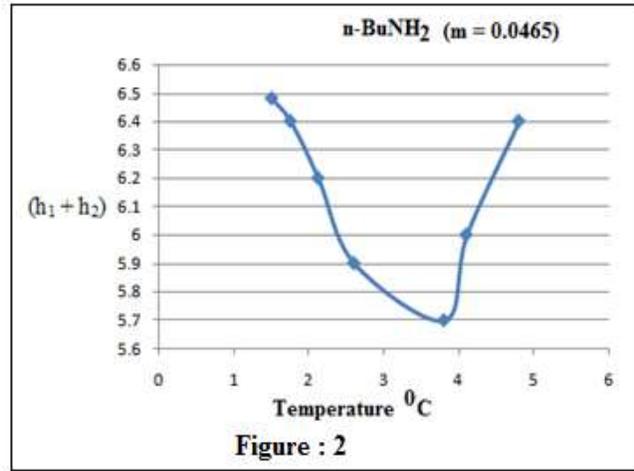
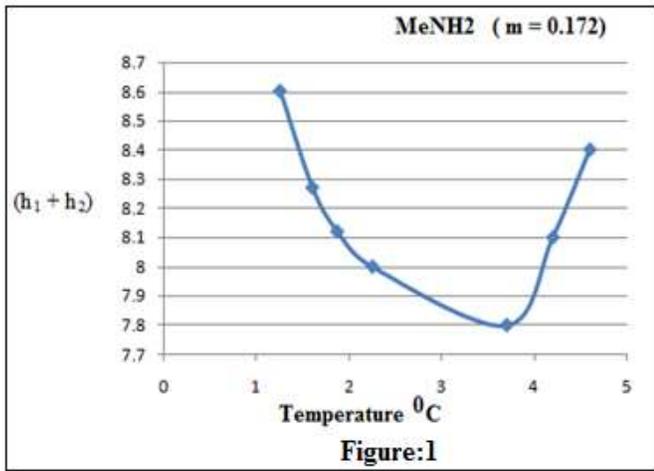


Table – III: TMD Measurement of Methyl amine

m	x x 10 <sup>4</sup>	α	m <sub>ion</sub>	m <sub>mole</sub>	x <sup>ion</sup> x 10 <sup>4</sup>	x <sub>mole</sub> x 10 <sup>4</sup>	θ <sub>ion</sub>	θ <sup>obs</sup>	θ <sub>id</sub>	θ <sup>Obs</sup> <sub>str</sub>
0.02504	4.141	0.1285	0.003217	0.02182	0.5793	3.9292	-0.0371	-0.1280	-0.1083	-0.226
0.0382	6.842	0.1042	0.003980	0.03422	0.7165	6.1606	-0.0459	-0.1409	-0.1651	0.0243
0.0457	8.208	0.0970	0.004433	0.04126	0.7979	7.4272	-0.05115	-0.1601	-0.1992	0.0391
0.0562	10.078	0.0856	0.004812	0.05138	0.8660	9.2470	-0.05551	-0.1720	-0.2481	0.07613
0.0862	15.468	0.0725	0.006249	0.07995	1.1240	14.381	-0.07205	-0.2466	-0.3859	0.1362
0.116	20.67	0.0644	0.007470	0.1085	1.3430	19.506	-0.08608	-0.3141	-0.5236	0.2095
0.145	25.874	0.0584	0.008468	0.1365	1.5213	24.522	-0.09743	-0.3540	-0.6582	0.3042
0.174	30.890	0.0505	0.008787	0.1652	1.5780	29.668	-0.1011	-0.3980	-0.7977	0.3992

Table – IV: TMD Measurement of Ethyl amine

m	x x 10 <sup>4</sup>	α	m <sub>ion</sub>	m <sub>mole</sub>	x <sup>ion</sup> x 10 <sup>4</sup>	x <sub>mole</sub> x 10 <sup>4</sup>	θ <sub>ion</sub>	θ <sup>obs</sup>	θ <sub>id</sub>	θ <sup>Obs</sup> <sub>str</sub>
0.0288	5.04	0.1140	0.00320	0.0255	0.5952	4.628	-0.04534	-0.1577	-0.1680	0.0144
0.0427	7.78	0.0952	0.00406	0.0386	0.7365	7.0485	-0.05608	-0.1993	-0.2559	0.0566
0.0662	11.82	0.0772	0.00511	0.06109	0.9195	11.832	-0.07003	-0.2525	-0.4026	0.1581
0.0885	15.83	0.0674	0.00595	0.08253	1.0821	14.959	-0.0823	-0.3040	-0.5445	0.2305
0.115	20.58	0.0606	0.00697	0.1080	1.268	19.551	-0.09662	-0.4090	-0.7110	0.3020
0.1395	24.80	0.0555	0.00774	0.1713	1.402	23.858	-0.1068	-0.4990	-0.8675	0.3675
0.1614	28.56	0.0502	0.00810	0.1533	1.467	27.760	-0.1118	-0.5830	-1.0083	0.4250

Table – V: TMD Measurement of n- Butyl amine

m	x x 10 <sup>4</sup>	α	m <sub>ion</sub>	m <sub>mole</sub>	x <sup>ion</sup> x 10 <sup>4</sup>	x <sub>mole</sub> x 10 <sup>4</sup>	θ <sub>ion</sub>	θ <sup>obs</sup>	θ <sub>id</sub>	θ <sub>str</sub> <sup>Obs</sup>
0.0282	5.077	0.1306	0.003683	0.0245	0.6632	4.415	-0.0596	-0.2094	-0.2564	0.0490
0.0467	8.371	0.1021	0.004763	0.04193	0.8583	7.548	-0.07344	-0.3024	-0.4188	0.1164
0.0686	12.30	0.0808	0.005955	0.06264	1.0716	11273	-0.09162	-0.3625	-0.6125	0.2500
0.0819	15.77	0.0744	0.006093	0.07581	1.0962	13.638	-0.09382	-0.4683	-0.7853	0.3173
0.119	21.21	0.0614	0.007306	0.1117	1.3127	20.008	-0.1123	-0.6055	-1.0562	0.4507
0.134	23.72	0.0532	0.007812	0.1262	1.404	22.684	-0.1201	-0.6731	-1.1812	0.5061

Table – VI: TMD Measurement of t- Butyl Amine

m	x x 10 <sup>4</sup>	α	m <sub>ion</sub>	m <sub>mole</sub>	x <sup>ion</sup> x 10 <sup>4</sup>	x <sub>mole</sub> x 10 <sup>4</sup>	θ <sub>ion</sub>	θ <sup>obs</sup>	θ <sub>id</sub>	θ <sub>str</sub> <sup>Obs</sup>
0.0234	4.212	0.1462	0.003421	0.01998	0.6159	3.598	-0.0581	-0.2138	0.2048	-0.0090
0.0366	6.33	0.1078	0.00394	0.03265	0.7094	5.879	-0.06702	-0.3080	0.3351	0.0271
0.0548	9.83	0.0970	0.005359	0.04944	0.9641	8.899	-0.09100	-0.4207	0.5054	0.0857
0.0780	13.99	0.0788	0.006146	0.7185	10.975	12.930	-0.1035	-0.5224	0.7327	0.2103
0.1030	18.34	0.0656	0.006757	0.09624	1.205	17.309	-0.1137	-0.6520	0.9833	0.3313
0.1240	22.11	0.0572	0.007093	0.1169	1.2765	21.018	-0.1205	-0.7355	1.1949	0.4594

### III. RESULT AND DISCUSSION:

In this work measurements of TMD for four amines MeNH<sub>2</sub>, EtNH<sub>2</sub>, n- BuNH<sub>2</sub>, and t-BuNH<sub>2</sub> were made. The measurement for EtNH<sub>2</sub> and t-BuNH<sub>2</sub> were carried out for the first time. The plot of Δθ<sup>obs</sup> vs. x<sub>2</sub> are shown in figure 6 (a), (b), (c) and (d). The results show that all amines lower the TMD at all concentrations. In this respect they differ from alcohols (except n-BuOH) which are known to increase TMD [10,11] at least at low concentrations (figure- 5) where Δθ<sup>obs</sup> is not linear with concentrations. However the corresponding amines do show a linear behavior which shows subtle difference in the manner of interaction between amine and water as compared to alcohols and water. Further the extent of lowering of TMD increases with increase in chain length i. e. size of alkyl group. This ability is more in t-BuNH<sub>2</sub> than isomeric n-BuNH<sub>2</sub>. According to usual practice is now more pertinent to calculate the Δθ<sub>str</sub> values and examine the concentration dependence of Δθ<sub>str</sub>/x<sub>2</sub>. Δθ<sub>str</sub> was calculated from equation Δθ<sup>obs</sup> = Δθ<sub>id</sub> + Δθ<sub>str</sub>. The required value of α for MeNH<sub>2</sub> [9] and EtNH<sub>2</sub> [12] were computed from the density data taken from literature. Value of n-BuNH<sub>2</sub> (1.32 x 10<sup>-3</sup> deg<sup>-1</sup>) used by Wada and Umeda [13-14] were found to have been computed by using density data around room temperature and above and were hence regarded as not quite reliable for computing Δθ<sub>str</sub>. In order to evaluate α reliability for the present purpose, it is necessary to have a densities of n-BuNH<sub>2</sub> and t-BuNH<sub>2</sub> in the range of 0- 10<sup>0</sup>C, which were not available in literature. These are measured by us using pure freshly distilled amines and using a density bottle of 25 ml capacity. The cryostat MK-70 adjusted to various temperatures between 0 and 10<sup>0</sup>C was used for this purpose. The table VII A & B shows the densities data used to determine the α values for pure liquid amines.

$$\Delta \theta = \frac{-x}{1-x} \frac{\alpha_2}{2\alpha_1} \frac{v_2^0}{v_1^*} \frac{-dv_x^M / dt}{2(1-x) \alpha_1 v_1^*}$$

Further, WADA and UMEDA [22] have shown that values calculated by using the equation, (v<sub>1</sub><sup>\*</sup> is the molar volume of water at 398 <sup>0</sup>C) obey the following empirical relation for non-electrolyte. Δθ<sub>str</sub> = ax<sub>2</sub> + bx<sub>2</sub><sup>2</sup>, where 'a' and 'b' are constants which depend upon the nature of solute and can be obtained as intercept and slope of the plot Δθ<sub>str</sub> / x<sub>2</sub> Vs. x<sub>2</sub>. Using this relation WADA and UMEDA determine the 'a' value for MeNH<sub>2</sub>, n- BuNH<sub>2</sub> and number of organic compounds including alcohols etc. The curves for alcohols are found to be linear and extrapolations give positive values of 'a' parameter. However, though they have given positive value for 'a' of MeNH<sub>2</sub> and n-BuNH<sub>2</sub>, on plotting their results of Δθ<sub>str</sub> / x<sub>2</sub> for these, we find that the point at lower concentration tend to curve down. This fact has apparently been overlooked by then in the extrapolation of these curves. We have plotted our results of Δθ<sub>str</sub> / x<sub>2</sub> Vs. x<sub>2</sub> for both methyl and n- butyl amine where the measurements were made at still lower concentration and compared with the results of WADA and UMEDA.

Table – VII (A): Density data used to determine  $\alpha$  for MeNH<sub>2</sub> and EtNH<sub>2</sub>

MeNH <sub>2</sub> *		$\alpha$ deg <sup>-1</sup>	** EtNH <sub>2</sub>		$\alpha$ deg <sup>-1</sup>
t <sup>0</sup> C	d	1.65x13 <sup>-3</sup>	t <sup>0</sup> C	d	1.60 x13 <sup>-3</sup>
-10.0	0.697		-10.6	0.7186	
0.0	0.687		0.0	0.7057	
+10.0	0.675		10.10	0.6949	
*Ref : 5			**Ref : 12		

Table- VII(B) : Density Measurements for n-BuNH<sub>2</sub> and t-BuNH<sub>2</sub> around TMD in the present work

n-BuNH <sub>2</sub>		$\alpha$ deg <sup>-1</sup>	t-BuNH <sub>2</sub>		$\alpha$ deg <sup>-1</sup>
t <sup>0</sup> C	d	1.465 x13 <sup>-3</sup>	t <sup>0</sup> C	d	1.574 x13 <sup>-3</sup>
2.2	0.7556		1.9	0.7136	
3.8	0.7528		4.0	0.7114	
6.0	0.7514		7.9	0.7069	
			9.9	0.7047	

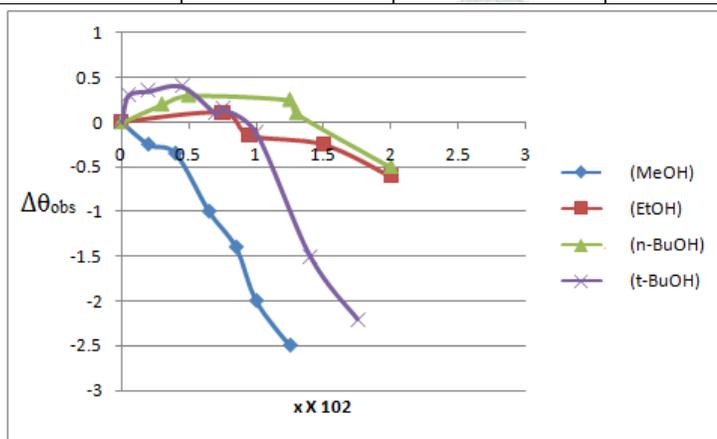


Figure : 5

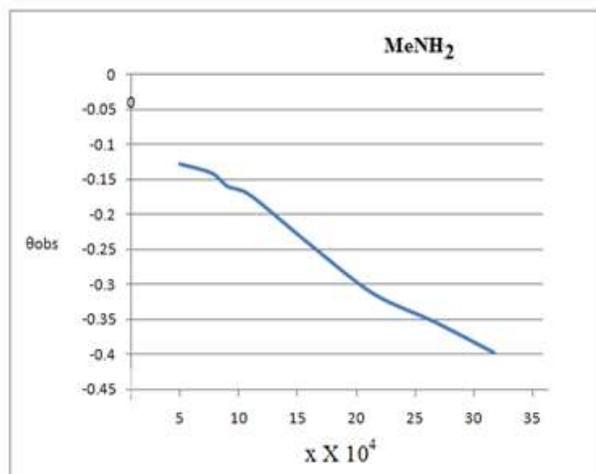


Figure. 6(a)

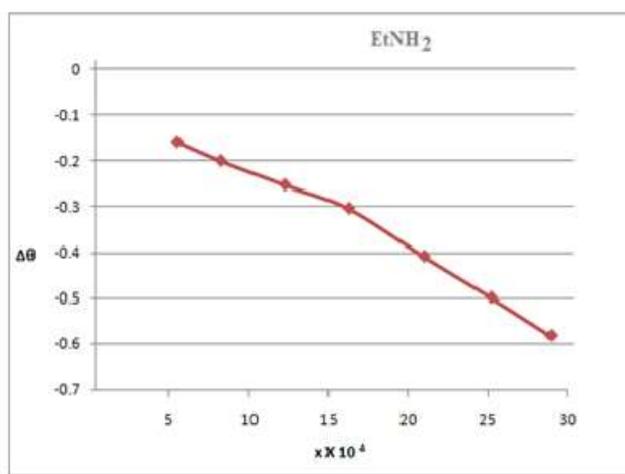


Figure 6(b)

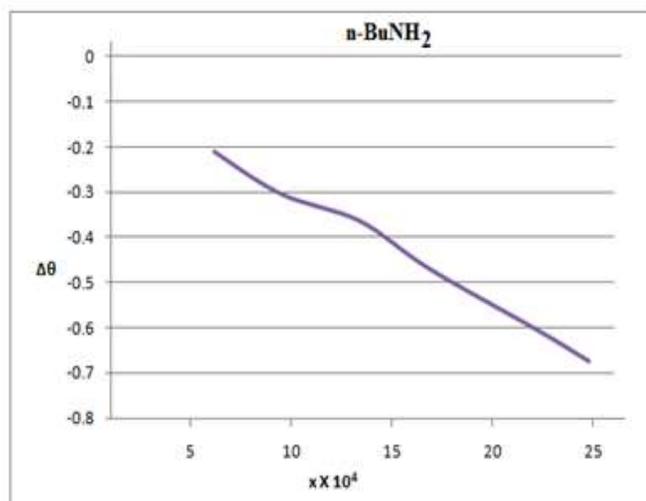


Figure 6 (c)

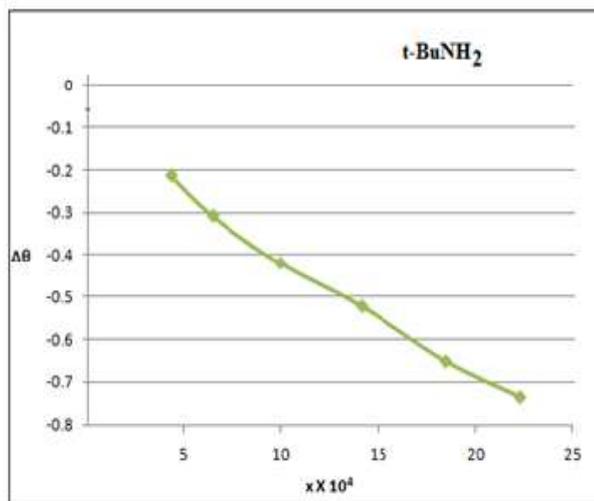


Figure 6 (d)

#### IV. CONCLUSION:

The TMD results on the four amines MeNH<sub>2</sub>, EtNH<sub>2</sub>, n-BuNH<sub>2</sub> and t-BuNH<sub>2</sub> after duly correcting for the hydrolysis exhibit an altogether new behavior indicating positive 'b' value as against negative values so far reported. Moreover the 'a' values are positive and smaller for n-BuNH<sub>2</sub> and t-BuNH<sub>2</sub> and even tends to assume large negative values of MeNH<sub>2</sub> and EtNH<sub>2</sub>.

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