# Study of Intermolecular Interactions of Binary Mixture of sec- and tert-Amines with Alkanols $\left(\mathrm{C}_{1}-\mathrm{C}_{3}\right)$ : Refractive Indices 

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#### Abstract

In this work, the refractive indices ( $n_{\mathrm{D}}$ ) of binary mixture of diisopropylamine (DIPA) and tributylamine (TBA) (as sec- and tert-amines) with alkanol (methanol, ethanol, 1-propanol, 2-propanol) were measured from 298.15 K to 318.15 K . The sec-and tert-amines were selected to study the effect of branching at $N$-atom of amine on intermolecular interactions with alkanols having different chain length. It was found that the TBA interacts strongly with alkanol in comparison to DIPA due to steric hindrance offered by isopropyl group at $N$ atom. Various mixing rules were applied to evaluate the refractive index compared well with the experimental refractive indices data for the present binary mixtures. The experimental refractive indices was also fitted to Redlich-Kister polynomial.


Keywords: Intermolecular interactions, $\mathrm{CO}_{2}$ absorbent, Amines, Refractive index, Alkanols.

## INTRODUCTION

Increased greenhouse gas emissions due to continuous discharge of industrial pollutants in the atmosphere are causing significant threat to the climate change (now referred to as climate crisis) [1-4]. The Inter-Governmental Panel on Climate Change (IPCC) reports shows that greenhouse gas emissions will increase global temperature from 1.1 to $6.4^{\circ} \mathrm{C}$ at the average [4-6]. Now days, the solvent based capturing of $\mathrm{CO}_{2}$ is the most commercial technology for carbon emission reduction [6-9]. Therefore, the researchers are constantly in search of a novel solvent to capture out $\mathrm{CO}_{2}$. Basically, the alkylamines are regarded as the organic bases due to their strong capability to donate electrons where the primary and secondary amines are considered as the self-associated molecules and tertiary amines are considered as the weakly polar molecule. Amines are well known solvent for capturing of $\mathrm{CO}_{2}$ [10]. Due to $\mathrm{H}-$ bonding capability of the $-\mathrm{NH}_{2}$ with that of alcohols it leads to association of the components [11-19]. The reason for choosing the alcohol as other component with amine is to increase the solubility of amine. Alkanols are important compounds in both industries and in the synthesis of several organic compounds [20-22].

Thermodynamic properties are very important to interpret the intermolecular interactions in between constituting components [23-25]. The dependency of volume, acoustic or optical properties of multicomponent mixtures on concentration or temperature is a useful indicator for reality of significant effects resulting due to intermolecular interactions [26-29]. The value of refractive index is used for theoretical purpose because it gives information about the electronic arrangement of different ions and the molecules in the liquid. The refractive index $\left(n_{\mathrm{D}}\right)$ is related to the speed of light that is affected by density of medium which in turn depends on specific interactions between the constituting molecules of binary mixture [30-33]. Thus denser the medium slower would be the speed of light that results in increase of refractive index of mixture. In this article, to understand the interactional behaviour between unlike molecules in diisopropylamine (DIPA) or tributylamine (TBA) (1) + methanol or ethanol or propanol isomers (2) mixtures in the temperature range (298.15-318.15) K at the interval of 10 K and at ambient pressure have been studied. The data were also fitted to Redlich-Kister polynomial. Various mixing rules were used to evaluate the for these mixtures from pure component data. No data is available in the literature which is having the compatibility equivalent to these binary liquid mixtures.

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## EXPERIMENTAL

Diisopropylamine (DIPA), tributylamine (TBA) and alkanols having purity $>99 \%$ were purchased from Central Drug House (CDH, India) and Fisher, respectively. All the purchased chemicals were purified by standard procedure [34]. Diisopropylamine was mixed with calcium hydride and then boiled for $2-3 \mathrm{~h}$. For purification of tributylamine, the sample was shaken with one-half its volume of KOH then it was filtered and then distilled from sodium into a flask with a distillation side arm. Methanol was distilled by refluxing for 20 h over 25 g of magnesium and again refluxed for 20 h over silver nitrate avoiding the contact of the solvent from atmospheric moisture and carbon dioxide. After distillation, the solvent was shaken for about 20 h with activated alumina and then filtered through a sintered glass funnel into a pot containing 1 atm of pure nitrogen. Ethanol was refluxed over slaked lime. During the process of refluxing, calcium oxide was changed once in the time interval of 24 h of refluxing. 1-Propanol was refluxed over slaked lime for about 5 h and then distilled through a column followed by redistillation with a stream of hydrogen. For purification of 2propanol, distillation of solvent was done over freshly burned lime through an efficient column. It was then shaked for 2 days with copper sulphate and then fractional distilled until it's boiling point remains constant.

All the distilled chemicals were stored in amber coloured glass bottles over activated molecular sieves (4A) for at least 48 h before use. These were filtered with the help of Whatman filter paper before experimental measurements. After keeping on molecular sieves, the purity levels of all pure chemicals was confirmed with gas chromatograph (Hewlett-Packard, 5890 Series II) having a thermal conductivity detector and column packed with Porapak Q. The analysis conditions of the gas chromatograph were: a detector temperature of $140^{\circ} \mathrm{C}$, a column temperature of $30^{\circ} \mathrm{C}$ and carrier gas (helium) total flow rate of $75 \mathrm{~mL} \mathrm{~min}^{-1}$. It was found better than stated purity as 0.994 mass fraction of TBA, 0.995 mass fraction of DIPA, 0.996 mass fraction of methanol, 0.993 mass fraction of ethanol, 0.995 mass fraction of 1 -propanol and 0.996 mass fraction of 2 propanol), respectively as shown in Table-1. The purities of the
compounds were confirmed by measuring their densities ( $\rho$ ) and refractive index $\left(n_{\mathrm{D}}\right)$ at 298.15 K and then compared their values from literature (Table-1).

The densities $(\rho)$ and refractive index $\left(n_{\mathrm{D}}\right)$ were measured with vibrating tube densimeter (Anton Paar DSA-5000) and refractometer (Abbemat-200) with an uncertainty of $5 \times 10^{-3}$ $\mathrm{kg} \mathrm{m}^{-3}$ and $1 \times 10^{-4}$, respectively, having temperature controlled within $\pm 0.01 \mathrm{~K}$ and measured data for mixtures are reported in Table-2. The samples were prepared by mixing pure components at different proportions, which was then converted into mole fraction. All the molar quantities used in the experiments are based on the IUPAC relative atomic mass table. The weighing balance (OHAUS, AR224CN) with precision of $\pm 0.1 \mathrm{mg}$ was used to prepare mixtures.

## RESULTS AND DISCUSSION

The deviation in refractive index $(\Delta n)$ values were calculated as:

$$
\begin{equation*}
\Delta n=n_{\mathrm{D}}-\sum_{i=1}^{2} x_{i} n_{\mathrm{D} i} \tag{1}
\end{equation*}
$$

Experimental $n_{\mathrm{D}}$ and $\Delta n$ data of binary mixture are given in Table-2. The experimental data along with polynomial fitted values are shown in Figs. 1 and 2.

$$
\begin{equation*}
\Delta n=x_{1}\left(1-x_{1}\right)\left(\sum_{n=1}^{4} A^{(j)}\left(2 x_{1}-1\right)^{(j-1)}\right) \tag{2}
\end{equation*}
$$

The adjustable parameters $A^{(j)}$ along with standard deviations $\sigma(\Delta n)$ are shown in Table-3. From Figs. 1 and 2, it is observed that the $\Delta n$ values for both the amines are positive while in case of DIPA, it follow the sequence: methanol $>$ ethanol $>1$ propanol $>2$-propanol, while for TBA, the order is: methanol $>$ ethanol $>2$-propanol $>1$-propanol. The positive behaviour of $\Delta n$ values is due to specific interaction of hydrogen bonding between hydroxyl hydrogen $\left(\mathrm{OH}^{-}\right)$of alkanol and $\mathrm{NH}_{2}$ group of amines. The amine have lone pair of electron in $p$-orbital, which are easily available to interact with the acidic $\mathrm{H}^{+}$of hydroxyl group of alkanol [39-41]. As hydrogen bonding increases due to interaction between amine and alcohol the speed of light

TABLE-1
PURITIES, MEASURED DENSITIES ( $\rho$ ) AND REFRACTIVE INDICES ( $n_{\mathrm{D}}$ ) OF THE PURE COMPOUNDS

| Compound | Temp. (K) | $\rho\left(\mathrm{g} \mathrm{cm}^{3}\right)$ |  | $n_{\text {D }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | This work | Literature | This work | Literature |
| DIPA | 298.15 | 0.714740 | 0.714800 [35] | 1.3919 | 1.3921 [35] |
|  | 308.15 | 0.705021 | 0.705180 [35] | 1.3843 | 1.3857 [35] |
|  | 318.15 | 0.695480 | 0.695590 [35] | 1.3789 | 1.3799 [35] |
| TBA | 298.15 | 0.773872 | 0.773910 [35] | 1.4269 | 1.4268 [35] |
|  |  |  | 0.773283 [36] |  | 1.4272 [36] |
|  | 308.15 | 0.766519 | 0.766950 [35] | 1.4225 | 1.4232 [35] |
|  | 318.15 | 0.759655 | 0.759740 [35] | 1.4182 | 1.4189 [35] |
| Methanol | 298.15 | 0.786664 | 0.786600 [37] | 1.3284 | 1.3278 [37] |
|  |  |  | 0.786660 [38] |  |  |
| Ethanol | 298.15 | 0.784638 | 0.785100 [37] | 1.3609 | 1.3605 [37] |
|  |  |  | 0.784970 [38] |  |  |
| 1-Propanol | 298.15 | 0.798286 | 0.799500 [37] | 1.3837 | 1.3831 [37] |
|  |  |  | 0.799580 [38] |  |  |
| 2-Propanol | 298.15 | 0.781355 | 0.781230 [38] | 1.3755 |  |

TABLE-2
REFRACTIVE INDEX $\left(n_{\mathrm{D}}\right)$ AND DEVIATION IN REFRACTIVE INDEX ( $\Delta n$ ) FOR THE BINARY SYSTEMS AT DIFFERENT TEMPERATURES

| $x_{1}$ | 298.15 K |  | 308.15 K |  | 318.15 K |  | $x_{1}$ | 298.15 K |  | 308.15 K |  | 318.15 K |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $n_{\text {D }}$ | $\Delta n$ | $n_{\text {D }}$ | $\Delta n$ | $n_{\text {D }}$ | $\Delta n$ |  | $n_{\text {D }}$ | $\Delta n$ | $n_{\text {D }}$ | $\Delta n$ | $n_{\text {D }}$ | $\Delta n$ |
| DIPA (1) + Methanol (2) |  |  |  |  |  |  | DIPA (1) + Ethanol (2) |  |  |  |  |  |  |
| 0.1158 | 1.3550 | 0.0195 | 1.3520 | 0.0206 | . 348 | . 021 | 1086 | 1.372 | 0.0076 | 1.3684 | 0.0076 | . 36 | 0.0075 |
| 0.1940 | 1.3680 | 0.0275 | 1.3645 | 0.0284 | 1.3604 | 0.0281 | 0.2152 | 1.3809 | 0.0126 | 1.3761 | 0.0124 | 1.3719 | 0.0125 |
| 0.2534 | 1.3749 | 0.0306 | 1.3709 | 0.0312 | 1.3665 | 0.0308 | 0.2572 | 1.3836 | 0.0140 | 1.3785 | 0.0137 | 1.3739 | 0.0135 |
| 0.3001 | 1.3790 | 0.0318 | 1.3746 | 0.0321 | 1.3701 | 0.0317 | 0.3033 | 1.3857 | 0.0147 | 1.3809 | 0.0149 | 1.3764 | 0.0148 |
| 0.3540 | 1.3830 | 0.0323 | 1.3783 | 0.0326 | 1.3733 | 0.0318 | 0.3541 | 1.3881 | 0.0156 | 1.3828 | 0.0155 | 1.3782 | 0.0154 |
| 0.4168 | 1.3862 | 0.0315 | 1.3809 | 0.0314 | 1.3760 | 0.0309 | 0.4103 | 1.3898 | 0.0156 | 1.3848 | 0.0160 | 1.3798 | 0.0156 |
| 0.4523 | 1.3874 | 0.0305 | 1.3825 | 0.0309 | 1.3772 | 0.0300 | 0.4566 | 1.3908 | 0.0152 | 1.3854 | 0.0154 | 1.3809 | 0.0155 |
| 0.5118 | 1.3892 | 0.0284 | 1.3839 | 0.0288 | 1.3788 | 0.0281 | 0.5069 | 1.3916 | 0.0145 | 1.3862 | 0.0149 | 1.3817 | 0.0151 |
| 0.5562 | 1.3902 | 0.0266 | 1.3849 | 0.0271 | 1.3796 | 0.0264 | 0.5429 | 1.3919 | 0.0137 | 1.3866 | 0.0143 | 1.3820 | 0.0145 |
| 0.6053 | 1.3905 | 0.0238 | 1.3855 | 0.0248 | 1.3804 | 0.0243 | 0.6012 | 1.3918 | 0.0119 | 1.3866 | 0.0128 | 1.3828 | 0.0138 |
| 0.6596 | 1.3909 | 0.0207 | 1.3861 | 0.0222 | 1.3810 | 0.0217 | 0.6432 | 1.3917 | 0.0105 | 1.3866 | 0.0117 | 1.3827 | 0.0127 |
| 0.7201 | 1.3911 | 0.0171 | 1.3865 | 0.0189 | 1.3813 | 0.0186 | 0.7116 | 1.3918 | 0.0085 | 1.3866 | 0.0099 | 1.3825 | 0.0108 |
| 0.7531 | 1.3916 | 0.0155 | 1.3862 | 0.0167 | 1.3814 | 0.0168 | 0.7612 | 1.3912 | 0.0065 | 1.3867 | 0.0087 | 1.3827 | 0.0097 |
| 0.8251 | 1.3915 | 0.0107 | 1.3863 | 0.0125 | 1.3812 | 0.0124 | 0.8143 | 1.3911 | 0.0047 | 1.3863 | 0.0069 | 1.3826 | 0.0083 |
| 0.9067 | 1.3914 | 0.0054 | 1.3860 | 0.0072 | 1.3805 | 0.0069 | 0.9018 | 1.3915 | 0.0026 | 1.3854 | 0.0037 | 1.3812 | 0.0047 |
| DIPA (1) + 1-Propanol (2) |  |  |  |  |  |  | DIPA (1) + 2-Propanol (2) |  |  |  |  |  |  |
| 0.1073 | 1.3895 | 0.0059 | 1.3848 | 0.0059 | 1.380 | . 005 | . 1004 | 1.3810 | 0.0043 | 1.3761 | 0.0041 | 1.3714 | 0.0041 |
| 0.1544 | 1.3913 | 0.0072 | 1.3864 | 0.0072 | 1.3816 | 0.0068 | 0.1983 | 1.3850 | 0.0067 | 1.3802 | 0.0069 | 1.3748 | 0.0062 |
| 0.2051 | 1.3934 | 0.0088 | 1.3885 | 0.0089 | 1.3829 | 0.0078 | 0.2588 | 1.3870 | 0.0076 | 1.3818 | 0.0077 | 1.3763 | 0.0070 |
| 0.2487 | 1.3947 | 0.0097 | 1.3896 | 0.0098 | 1.3836 | 0.0083 | 0.3002 | 1.3876 | 0.0076 | 1.3826 | 0.0079 | 1.3772 | 0.0073 |
| 0.3075 | 1.3960 | 0.0105 | 1.3906 | 0.0105 | 1.3844 | 0.0088 | 0.3505 | 1.3885 | 0.0076 | 1.3836 | 0.0082 | 1.3782 | 0.0076 |
| 0.3452 | 1.3964 | 0.0105 | 1.3909 | 0.0105 | 1.3847 | 0.0090 | 0.4044 | 1.3896 | 0.0078 | 1.3845 | 0.0083 | 1.3791 | 0.0078 |
| 0.3988 | 1.3965 | 0.0101 | 1.3911 | 0.0104 | 1.3851 | 0.0091 | 0.4474 | 1.3902 | 0.0076 | 1.3853 | 0.0086 | 1.3797 | 0.0079 |
| 0.4565 | 1.3967 | 0.0098 | 1.3916 | 0.0106 | 1.3854 | 0.0091 | 0.5084 | 1.3916 | 0.0080 | 1.3859 | 0.0083 | 1.3804 | 0.0078 |
| 0.5026 | 1.3969 | 0.0096 | 1.3912 | 0.0099 | 1.3855 | 0.0090 | 0.5574 | 1.3923 | 0.0079 | 1.3865 | 0.0083 | 1.3808 | 0.0076 |
| 0.5516 | 1.3968 | 0.0090 | 1.3908 | 0.0092 | 1.3855 | 0.0087 | 0.6092 | 1.3920 | 0.0068 | 1.3869 | 0.0079 | 1.3811 | 0.0072 |
| 0.6037 | 1.3959 | 0.0076 | 1.3909 | 0.0090 | 1.3853 | 0.0083 | 0.6456 | 1.3926 | 0.0067 | 1.3868 | 0.0073 | 1.3812 | 0.0068 |
| 0.6591 | 1.3953 | 0.0065 | 1.3906 | 0.0083 | 1.3850 | 0.0077 | 0.7029 | 1.3923 | 0.0054 | 1.3868 | 0.0066 | 1.3811 | 0.0061 |
| 0.6981 | 1.3947 | 0.0056 | 1.3898 | 0.0073 | 1.3846 | 0.0072 | 0.8070 | 1.3918 | 0.0032 | 1.3860 | 0.0043 | 1.3805 | 0.0041 |
| 0.8034 | 1.3938 | 0.0037 | 1.3888 | 0.0056 | 1.3831 | 0.0051 | 0.8520 | 1.3917 | 0.0023 | 1.3858 | 0.0036 | 1.3800 | 0.0030 |
| 0.8969 | 1.3928 | 0.0018 | 1.3870 | 0.0034 | 1.3812 | 0.0028 | 0.8990 | 1.3915 | 0.0013 | 1.3853 | 0.0024 | 1.3796 | 0.0020 |
| TBA (1) + Methanol (2) |  |  |  |  |  |  | TBA (1) + Ethanol (2) |  |  |  |  |  |  |
| 0.1093 | 1.3938 | 0.0538 | 1.3887 | 0.0529 | 1.3723 | 0408 | . 1034 | 1.4220 | 0.0144 | 1.3786 | 0.0149 | 1.3748 | 0.0153 |
| 0.2027 | 1.4169 | 0.0678 | 1.4120 | . 0671 | 1.3974 | 0.0568 | 0.1456 | 1.4421 | 0.0180 | 1.3850 | 0.0185 | 1.3814 | 0.0191 |
| 0.2560 | 1.4227 | 0.0684 | 1.4180 | 0.0679 | 1.4061 | 0.0604 | 0.2099 | 1.4462 | 0.0217 | 1.3928 | 0.0222 | 1.3893 | 0.0228 |
| 0.3035 | 1.4252 | 0.0662 | 1.4206 | 0.0659 | 1.4114 | 0.0610 | 0.2529 | 1.4472 | 0.0233 | 1.3971 | 0.0236 | 1.3936 | 0.0242 |
| 0.3620 | 1.4262 | 0.0616 | 1.4218 | 0.0614 | 1.4153 | 0.0593 | 0.3036 | 1.4464 | 0.0242 | 1.4013 | 0.0244 | 1.3976 | 0.0250 |
| 0.4040 | 1.4263 | 0.0575 | 1.4219 | 0.057 | 1.4169 | 0.0567 | 0.3531 | 1.4451 | 0.0245 | 1.4047 | 0.0246 | 1.4009 | 0.0250 |
| 0.4528 | 1.4260 | 0.0525 | 1.4216 | 0.0524 | 1.4177 | 0.0528 | 0.3986 | 1.4433 | 0.0242 | 1.4074 | 0.0243 | 1.4033 | 0.0245 |
| 0.5101 | 1.4257 | 0.0466 | 1.4212 | 0.0464 | 1.4178 | 0.0473 | 0.4508 | 1.4412 | 0.0235 | 1.4101 | 0.0236 | 1.4057 | 0.0234 |
| 0.5541 | 1.4255 | 0.0421 | 1.4210 | 0.0419 | 1.4175 | 0.0428 | 0.4951 | 1.4396 | 0.0225 | 1.4120 | 0.0226 | 1.4074 | 0.0223 |
| 0.6040 | 1.4255 | 0.0372 | 1.4210 | 0.0370 | 1.4170 | 0.0374 | 0.5448 | 1.4380 | 0.0211 | 1.4139 | 0.0213 | 1.4091 | 0.0207 |
| 0.6609 | 1.4255 | 0.0317 | 1.4210 | 0.0315 | 1.4165 | 0.0313 | 0.6010 | 1.4363 | 0.0192 | 1.4158 | 0.0195 | 1.4108 | 0.0187 |
| 0.6925 | 1.4256 | 0.0287 | 1.4210 | 0.0285 | 1.4163 | 0.0280 | 0.6648 | 1.4353 | 0.0166 | 1.4175 | 0.0170 | 1.4125 | 0.0162 |
| 0.7264 | 1.4256 | 0.0254 | 1.4211 | 0.0252 | 1.4161 | 0.0245 | 0.7126 | 1.4343 | 0.0145 | 1.4185 | 0.0148 | 1.4136 | 0.0142 |
| 0.8027 | 1.4254 | 0.0178 | 1.4211 | 0.0178 | 1.4161 | 0.0171 | 0.7934 | 1.4317 | 0.0106 | 1.4198 | 0.0108 | 1.4153 | 0.0106 |
| 0.8925 | 1.4251 | 0.0087 | 1.4209 | 0.0089 | 1.4168 | 0.0091 | 0.9232 | 1.4285 | 0.0038 | 1.4213 | 0.0038 | 1.4173 | 0.0042 |
| TBA (1) + 1-Propanol (2) |  |  |  |  |  |  | TBA (1) + 2-Propanol (2) |  |  |  |  |  |  |
| 0.1089 | 1.3966 | 0.0087 | 1.3919 | 0.0082 | 1.3882 | 0.0087 | 0.0562 | 1.3770 | -0.0014 | 1.3730 | -0.0009 | 1.3673 | -0.0021 |
| 0.2045 | 1.4055 | 0.0135 | 1.4009 | 0.0130 | 1.3969 | 0.0133 | 0.1175 | 1.3827 | 0.0011 | 1.3789 | 0.0018 | 1.3729 | 0.0003 |
| 0.2539 | 1.4092 | 0.0150 | 1.4047 | 0.0147 | 1.4005 | 0.0147 | 0.1499 | 1.3867 | 0.0035 | 1.3829 | 0.0042 | 1.3769 | 0.0027 |
| 0.3026 | 1.4123 | 0.0160 | 1.4078 | 0.0157 | 1.4035 | 0.0156 | 0.1897 | 1.3920 | 0.0068 | 1.3882 | 0.0074 | 1.3824 | 0.0061 |
| 0.3584 | 1.4152 | 0.0165 | 1.4108 | 0.0162 | 1.4063 | 0.0160 | 0.2240 | 1.3968 | 0.0098 | 1.3928 | 0.0103 | 1.3873 | 0.0092 |
| 0.4003 | 1.4170 | 0.0164 | 1.4126 | 0.0162 | 1.4081 | 0.0159 | 0.2648 | 1.4022 | 0.0132 | 1.3982 | 0.0136 | 1.3930 | 0.0128 |
| 0.4469 | 1.4187 | 0.0161 | 1.4142 | 0.0158 | 1.4097 | 0.0155 | 0.3035 | 1.4071 | 0.0161 | 1.4030 | 0.0164 | 1.3980 | 0.0159 |
| 0.4987 | 1.4202 | 0.0153 | 1.4156 | 0.0150 | 1.4112 | 0.0148 | 0.3493 | 1.4122 | 0.0188 | 1.4079 | 0.0190 | 1.4033 | 0.0188 |
| 0.5569 | 1.4215 | 0.0141 | 1.4168 | 0.0137 | 1.4125 | 0.0135 | 0.4040 | 1.4171 | 0.0209 | 1.4128 | 0.0210 | 1.4085 | 0.0211 |
| 0.6053 | 1.4224 | 0.0129 | 1.4176 | 0.0123 | 1.4133 | 0.0123 | 0.4528 | 1.4205 | 0.0218 | 1.4160 | 0.0218 | 1.4120 | 0.0221 |
| 0.6587 | 1.4231 | 0.0113 | 1.4183 | 0.0107 | 1.4140 | 0.0107 | 0.4899 | 1.4224 | 0.0218 | 1.4179 | 0.0217 | 1.4139 | 0.0221 |
| 0.6973 | 1.4236 | 0.0101 | 1.4187 | 0.0094 | 1.4144 | 0.0094 | 0.5541 | 1.4246 | 0.0207 | 1.4201 | 0.0206 | 1.4161 | 0.0210 |
| 0.7606 | 1.4243 | 0.0080 | 1.4194 | 0.0074 | 1.4151 | 0.0073 | 0.6040 | 1.4255 | 0.0190 | 1.4210 | 0.0189 | 1.4169 | 0.0192 |
| 0.8067 | 1.4247 | 0.0064 | 1.4199 | 0.0059 | 1.4155 | 0.0057 | 0.6925 | 1.4260 | 0.0151 | 1.4216 | 0.0150 | 1.4173 | 0.0151 |
| 0.9104 | 1.4257 | 0.0029 | 1.4212 | 0.0027 | 1.4166 | 0.0024 | 0.8457 | 1.4265 | 0.0077 | 1.4221 | 0.0076 | 1.4176 | 0.0075 |



Fig. 1. Deviation in refractive index as a function of mole fraction of DIPA $\left(x_{1}\right)$. Symbols represent experimental values and lines represent values calculated from Redlich-Kister equation
decreases due to this refractive index increases. Due to small size of methanol its interaction with the amine is more, which results into stronger hydrogen bonding between the two components, as the chain length increased and shifts towards ethanol due to increase in carbon atomic hydrophobic part increases, which results a decrease in the interaction between the two components and hence speed of light increases in comparison to methanol which in turn results in decrease in refractive indices. It can be seen from Figs. 1 and 2 that the $\Delta n$ values goes on decreasing with increase in chain length of alkanol molecules [39]. This may be due to decrease in acidity of $\mathrm{OH}^{-}$owing to addition of alkyl group which in turn decrease the specific interaction between the component molecules. The $\Delta n$ values are higher for TBA in comparison to DIPA (Figs. 1 and 2),


Fig. 2. Deviation in refractive index as a function of mole fraction of TBA $\left(x_{1}\right)$. Symbols represent experimental values and lines represent values calculated from Redlich-Kister equation
which may be owing to greater steric hindrance offered by branching of isopropyl group at nitrogen atom of DIPA in comparison to TBA. In this article, the effect of temperature on $n_{\mathrm{D}}$ was also investigated but as can be seen from Figs. 1 and 2 , there is no significant effect of temperature on values for present systems.

The $n_{\mathrm{D}}$ data were estimated by employing the following mixing relation and also compared in terms of standard deviation $(\sigma)$ at all temperatures (Table-4):

Arago-Biot (A-B):

$$
\begin{equation*}
n_{\mathrm{D}}=n_{\mathrm{D} 1} \phi_{1}+n_{\mathrm{D} 2} \phi_{2} \tag{3}
\end{equation*}
$$

Gladstone-Dale (G-D):

$$
\begin{equation*}
n_{\mathrm{D}}-1=\left(n_{\mathrm{D} 1}-1\right) \phi_{1}+\left(n_{\mathrm{D} 2}-1\right) \phi_{2} \tag{4}
\end{equation*}
$$

Lorentz-Lorenz (L-L):

$$
\begin{equation*}
\frac{n_{\mathrm{D}}^{2}-1}{n_{\mathrm{D}}^{2}+2}=\left(\frac{n_{\mathrm{D} 1}^{2}-1}{n_{\mathrm{D}}^{2}+2}\right) \phi_{1}+\left(\frac{n_{\mathrm{D} 2}^{2}-1}{n_{\mathrm{D}}^{2}+2}\right) \phi_{2} \tag{5}
\end{equation*}
$$

Heller (H):

$$
\begin{equation*}
\frac{n_{\mathrm{D}}-1}{n_{\mathrm{D}}}=\frac{3}{2}\left(\frac{\left(n_{\mathrm{D} 2} / n_{\mathrm{D} 1}\right)^{2}-1}{\left(n_{\mathrm{D} 2} / n_{\mathrm{D} 1}\right)^{2}+2}\right) \phi_{2} \tag{6}
\end{equation*}
$$

| TABLE-3 <br> ADJUSTABLE PARAMETERS OF REDLICH-KISTER EQUATION [A $\left.{ }^{(i)}(i=1-4)\right]$ AND CORRESPONDING STANDARD DEVIATION $[\sigma(\Delta n)]$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Temp. (K) | $A^{(1)}$ | $A^{(2)}$ | $A^{(3)}$ | $A^{(4)}$ | $\sigma(\Delta n)$ |
| DIPA (1) + <br> Methanol (2) | 298.15 | 0.1157 | -0.0797 | 0.0254 | -0.0022 | 0.0002 |
|  | 308.15 | 0.1170 | -0.0724 | 0.0451 | -0.0075 | 0.0002 |
|  | 318.15 | 0.1140 | -0.0685 | 0.0517 | -0.0193 | 0.0006 |
| DIPA (1) + <br> Ethanol (2) | 298.15 | 0.0579 | -0.0384 | -0.0099 | 0.0104 | 0.0002 |
|  | 308.15 | 0.0598 | -0.0293 | 0.0006 | 0.0135 | 0.0002 |
|  | 318.15 | 0.0603 | -0.0227 | 0.0097 | 0.0155 | 0.0004 |
| $\underset{\text { 1-Propanol (2) }}{\text { DIPA (1) }}$ | 298.15 | 0.0377 | -0.0271 | 0.0026 | 0.0032 | 0.0002 |
|  | 308.15 | 0.0400 | -0.0176 | 0.0141 | 0.0043 | 0.0002 |
|  | 318.15 | 0.0359 | -0.0072 | 0.0122 | -0.0160 | 0.0004 |
| $\underset{\text { 2-Propanol (2) }}{\text { DIPA (1) }}$ | 298.15 | 0.0312 | -0.0076 | 0.0006 | -0.0245 | 0.0002 |
|  | 308.15 | 0.0338 | -0.0061 | 0.0050 | -0.0123 | 0.0002 |
|  | 318.15 | 0.0314 | -0.0047 | 0.0034 | -0.0160 | 0.0002 |
| TBA (1) + <br> Methanol (2) | 298.15 | 0.1903 | -0.2058 | 0.2154 | -0.1458 | 0.0000 |
|  | 308.15 | 0.1898 | -0.2072 | 0.2105 | -0.1324 | 0.0000 |
|  | 318.15 | 0.1934 | -0.1989 | 0.1048 | -0.0140 | 0.0000 |
| TBA (1) + Ethanol (2) | 298.15 | 0.0894 | -0.0514 | 0.0252 | -0.0173 | 0.0000 |
|  | 308.15 | 0.0901 | -0.0493 | 0.0295 | -0.0260 | 0.0000 |
|  | 318.15 | 0.0885 | -0.0590 | 0.0378 | -0.0115 | 0.0000 |
| $\underset{\text { 1-Propanol (2) }}{\text { TBA }}$ | 298.15 | 0.0612 | -0.0357 | 0.0035 | 0.0028 | 0.0000 |
|  | 308.15 | 0.0599 | -0.0394 | -0.0019 | 0.0114 | 0.0000 |
|  | 318.15 | 0.0590 | -0.0365 | 0.0019 | -0.0021 | 0.0000 |
| $\underset{\text { 2-Propanol (2) }}{\text { TBA (1) }}$ | 298.15 | 0.0869 | -0.0207 | -0.0891 | 0.0883 | 0.0000 |
|  | 308.15 | 0.0866 | -0.0222 | -0.0840 | 0.0822 | 0.0000 |
|  | 318.15 | 0.0882 | -0.0206 | -0.1001 | 0.0949 | 0.0000 |

TABLE-4
STANDARD DEVIATION OF CALCULATED VALUES OF REFRACTIVE INDEX USING VARIOUS CORRELATIONS

| Binary system | Temp. (K) | AB | GD | LL | Weiner | Heller | Newton | Eyring |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| DIPA (1) + | 298.15 | 0.0111 | 0.0111 | 0.0114 | 0.0100 | 0.0113 | 0.0108 | 0.0113 |
|  | 308.15 | 0.0130 | 0.0130 | 0.0132 | 0.0120 | 0.0131 | 0.0127 | 0.0131 |
|  | 318.15 | 0.0141 | 0.0141 | 0.0141 | 0.0141 | 0.0141 | 0.0142 | 0.0141 |
| DIPA (1) + | 298.15 | 0.0078 | 0.0078 | 0.0079 | 0.0075 | 0.0078 | 0.0077 | 0.0078 |
|  | 308.15 | 0.0091 | 0.0091 | 0.0091 | 0.0088 | 0.0091 | 0.0090 | 0.0091 |
|  | 318.15 | 0.0099 | 0.0099 | 0.0099 | 0.0098 | 0.0099 | 0.0099 | 0.0098 |
| DIPA (1) + | 298.15 | 0.0081 | 0.0081 | 0.0081 | 0.0081 | 0.0081 | 0.0081 | 0.0081 |
|  | 308.15 | 0.0092 | 0.0092 | 0.0092 | 0.0092 | 0.0092 | 0.0092 | 0.0092 |
|  | 318.15 | 0.0099 | 0.0098 | 0.0099 | 0.0099 | 0.0098 | 0.0099 | 0.0098 |
| DIPA (1) + | 298.15 | 0.0051 | 0.0051 | 0.0051 | 0.0050 | 0.0051 | 0.0051 | 0.0051 |
|  | 308.15 | 0.0062 | 0.0062 | 0.0062 | 0.0061 | 0.0062 | 0.0062 | 0.0062 |
|  | 318.15 | 0.0071 | 0.0071 | 0.0071 | 0.0071 | 0.0071 | 0.0071 | 0.0071 |
| TBA (1) + | 298.15 | 0.0190 | 0.0190 | 0.0196 | 0.0171 | 0.0193 | 0.0184 | 0.0193 |
|  | 308.15 | 0.0180 | 0.0180 | 0.0186 | 0.0163 | 0.0183 | 0.0175 | 0.0183 |
|  | 318.15 | 0.0144 | 0.0144 | 0.0149 | 0.0129 | 0.0146 | 0.0139 | 0.0147 |
| TBA (1) + | 298.15 | 0.0373 | 0.0373 | 0.0376 | 0.0360 | 0.0375 | 0.0370 | 0.0375 |
|  | 308.15 | 0.0021 | 0.0021 | 0.0024 | 0.0019 | 0.0023 | 0.0019 | 0.0023 |
|  | 318.15 | 0.0114 | 0.0114 | 0.0118 | 0.0080 | 0.0118 | 0.0110 | 0.0116 |
| TBA (1) + 1- | 298.15 | 0.0034 | 0.0034 | 0.0035 | 0.0030 | 0.0035 | 0.0033 | 0.0035 |
|  | 308.15 | 0.0029 | 0.0029 | 0.0031 | 0.0025 | 0.0030 | 0.0028 | 0.0030 |
|  | 318.15 | 0.0029 | 0.0029 | 0.0030 | 0.0025 | 0.0029 | 0.0027 | 0.0029 |
| TBA (1) + 2- | 298.15 | 0.0069 | 0.0069 | 0.0069 | 0.0072 | 0.0069 | 0.0068 | 0.0069 |
| Propanol (2) | 308.15 | 0.0230 | 0.0230 | 0.0231 | 0.0236 | 0.0230 | 0.0229 | 0.0230 |
|  | 318.15 | 0.0128 | 0.0128 | 0.0130 | 0.0123 | 0.0129 | 0.0127 | 0.0129 |

Weiner (W):

$$
\begin{equation*}
\frac{n_{\mathrm{D}}^{2}-n_{\mathrm{D} 1}^{2}}{n_{\mathrm{D}}^{2}+2 n_{\mathrm{D} 2}^{2}}=\left(\frac{n_{\mathrm{D} 2}^{2}-n_{\mathrm{D} 1}^{2}}{n_{\mathrm{D} 2}^{2}+2 n_{\mathrm{D} 2}^{2}}\right) \phi_{2} \tag{7}
\end{equation*}
$$

Newton (Nw):

$$
\begin{equation*}
n_{\mathrm{D}}^{2}-1=\left(n_{\mathrm{D} 1}^{2}-1\right) \phi_{1}+\left(n_{\mathrm{D} 2}^{2}-1\right) \phi_{2} \tag{8}
\end{equation*}
$$

Eyring and John (E-J):

$$
\begin{equation*}
n_{\mathrm{D}}=n_{\mathrm{D} 1} \phi_{1}^{2}+2\left(n_{\mathrm{D} 1} n_{\mathrm{D} 2}\right)^{1 / 2} \phi_{1} \phi_{2}+n_{\mathrm{D} 2} \phi_{2}^{2} \tag{9}
\end{equation*}
$$

In these equations, $n_{\mathrm{D}}, n_{\mathrm{D} 1}$ and $n_{\mathrm{D} 2}$ represent the refractive index of mixture and pure compound, respectively. From Table-4, it can be seen that these mixing rules have good results for all these binary mixtures.

## Conclusion

In this work, alkanols (methanol, ethanol, 1-propanol, 2-propanol) were selected as second component with amine (sec- and tert-amines) due to its hydrogen bonding capability with amine which in turn increase the solubility of amine. The refractive indices ( $n_{\mathrm{D}}$ ) of binary mixture of sec-and tert-amines as diisopropylamine (DIPA) and tributylamine (TBA) (1), respectively, with alkanol (2) from (298.15-318.15) K at the interval of 10 K and at ambient pressure. The $n_{\mathrm{D}}$ values for both amines were positive and in case of DIPA, it follows the sequence: methanol $>$ ethanol $>$ 1-propanol $>2$-propanol, whereas in case of TBA it follows the sequence methanol $>$ ethanol > 2-propanol $>$ 1-propanol. The positive behaviour of $n_{\mathrm{D}}$ values is due to specific interaction of hydrogen bonding between hydroxyl $\left(\mathrm{OH}^{-}\right)$group of alkanol and $\mathrm{NH}_{2}$ group of amines. It was found that the TBA is more interactive with alkanol in comparison to DIPA due to steric hindrance of isopropyl group at N atom. All mixing rules predicted the refractive index very well for all the binary mixtures.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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