Studies of partial molar volumes of alkylamines in non-electrolyte solvents. 
V – Alkylamines in toluene at 303.15 K

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Apparent molar volumes, \( V_{\text{app},B} \), of \( n \)-propylamine, \( n \)-butylamine, di-\( n \)-propylamine, di-\( n \)-butylamine, triethylamine, tri-\( n \)-propylamine, and tri-\( n \)-butylamine in toluene at 303.15 K have been determined with high precision vibrating tube Anton Paar densimeter. The limiting partial molar volumes \( \bar{V}_{B}^{\infty} \) and limiting excess partial molar volumes \( \bar{V}_{B}^{E,\infty} \) are analysed and interpreted in terms of solute-solvent interactions and structural effects of the molecules. An attempt has been made to find a measure of the contribution of the specific interactions to the partial molar volumes of primary, secondary and tertiary amines in toluene using Terasawa model, scaled particle theory and hard sphere theory. The ERAS model has also been applied to estimate the apparent molar volumes and excess apparent molar volumes of alkylamines in toluene solutions.

\textbf{Keywords}: Solution chemistry, Thermodynamics, Hard sphere theory, Scaled particle theory, ERAS model, Partial molar volumes, Alkylamines, Toluene

Partial molar properties of dilute solutions provide information about the molecular interactions between solute-solute and solute-solvent interactions, and can be used for the development of molecular models for describing the thermodynamic behaviour of solutions. The partial molar volumes depend upon molecular size, shape, interactions and structural effects of different components. It is of interest and significance to study the partial molar volumes of alkylamines in different types of solvents to extract information on specific interactions, conformational effects and packing efficiencies. Systematic investigations of thermodynamic and transport properties of solutions involving important organic bases, viz., primary, secondary and tertiary alkylamines, in polar and non-polar solvents are being carried out in our laboratories. In previous papers\textsuperscript{1-4} partial molar volumes of dilute solutions of propylamine (\( \text{C}_3\text{H}_7\text{NH}_2 \)), \( n \)-butylamine (\( \text{C}_4\text{H}_9\text{NH}_2 \)), di-\( n \)-propylamine (\( \text{C}_6\text{H}_{13}\text{NH} \)), di-\( n \)-butylamine (\( \text{C}_8\text{H}_{17}\text{NH} \)), triethylamine (\( \text{C}_6\text{H}_{14}\text{N} \)), tri-\( n \)-propylamine (\( \text{C}_9\text{H}_{19}\text{N} \)), and tri-\( n \)-butylamine (\( \text{C}_{10}\text{H}_{21}\text{N} \)) in cyclohexane, benzene, tetrachloromethane, trichloromethane, 1-butanol, 2-butanol, 1,4-dioxane and oxalane have been reported. The results of \( \bar{V}_{B}^{E,\infty} \) of alkylamines in benzene were attributed to the existence of benzene-amine specific interactions and destruction of a local order in benzene molecules due to (\( \pi \)-\( \pi \)) interactions. Toluene molecules possess a small dipole moment, which may results in additional weak dipole-dipole interactions along with the \( \pi \)-\( n \) and \( \pi \)-\( \pi \) interactions\textsuperscript{5}. In continuation of these studies, we report herein studies of the volumetric properties of dilute solutions of seven alkylamines in toluene solutions.

The contribution to partial molar volumes of the methyl, methylene, and primary, secondary, and tertiary amine groups at 303.15 K in toluene solutions has been calculated using simple additive schemes.\textsuperscript{6,7} Information on specific interactions, conformational effects and packing efficiencies can be extracted using Terasawa model\textsuperscript{8}, scaled particle theory\textsuperscript{9}, hard sphere theory\textsuperscript{10} and the ERAS model.\textsuperscript{11,12}

\textbf{Materials and Methods}

Densities at 303.15 K were measured with Anton Paar densimeter (model DMA 60/602) with thermostatted bath controlled to \( \pm 0.01 \) K. The details of the method and technique used to determine density have been described previously.\textsuperscript{1,13} All the solutions were prepared by mixing known masses of pure liquids in air tight, narrow-mouth
ground stoppered bottles taking due precautions to minimize the evaporation losses. Dilute solutions up to 0.1 mole fraction of each alkylamine in both the solvents were prepared. The values of molality, \(m\), mole fraction, \(x_B\), and density, \(\rho\), are accurate to \(\pm 1 \times 10^{-4} \text{ mol kg}^{-1}\), \(\pm 1 \times 10^{-4}\) and \(\pm 2 \times 10^{-5} \text{ g cm}^{-3}\), respectively.

\(n\)-Propylamine (Merck, Schuchardt), \(n\)-butylamine (Fluka AG), di-\(n\)-propylamine (Fluka AG), di-\(n\)-butylamine (Fluka AG), triethylamine (Sisco, extra pure), tri-\(n\)-propylamine (Fluka AG), and tri-\(n\)-butylamine (SRL, Bombay), of purity better than 99.0 mol % were refluxed over Na metal and distilled twice fractionally before use. Toluene (\(C_6H_5CH_3\), Galaxo AR) of purity better than 99.5 mol % was used after further purification and drying by standard procedures.\(^{14}\) Toluene was shaken repeatedly with conc. sulphuric acid until free from thiophene, washed first with aqueous sodium carbonate and then with water, dried over \(P_2O_5\) and fractionally distilled. Immediately before use, the samples were dried over a molecular sieve (0.4 nm, Fluka) and fractionally distilled twice. The purity of all the liquid samples was checked by gas-liquid chromatography and by comparing measured normal boiling points. The measured values of densities were compared with literature values in Table 1.

### Results and Discussion

The experimentally determined values of densities \(\rho\) for dilute solutions of seven alkylamines in toluene at different concentrations and at 303.15 K were fitted to polynomial equation of type Eq. (1),

\[
\rho = A + Bm + Cm^2 + Dm^3 \quad \text{...}(1)
\]

The values of \(A\), \(B\), \(C\) and \(D\) coefficients along with standard deviations values \((\sigma)\) are given in Table 2. The apparent molar volumes \(\varphi_{B}V\) of all the solutes were calculated in the usual way,

\[
\varphi_{B}V = \frac{M_B}{\rho} \left( \frac{\rho - \rho_A}{\rho \rho_A} \right) \frac{1000}{m} \quad \text{...}(2)
\]

where \(M_B\) is molar mass of solute (amine) and \(m\) is concentration of amine in molality. \(\rho\) and \(\rho_A\) are densities of solution and pure solvent, respectively. The values of \(\rho\) and \(\varphi_{B}V\) are presented in Table 3.

The limiting partial molar volume of amines \(\varphi_{B}V\) was obtained by the least-squares method through the fitting of Eq. (3).

\[
\varphi_{B}V = \varphi_{B,\infty} + S_m m \quad \text{...}(3)
\]

The values of coefficients of Eq. (3) are given in Table 4, which includes the excess partial molar volumes at infinite dilution \(\varphi_{B,\infty} (\varphi_{B,\infty} = \varphi_{B}V - \varphi_{B}V)\)

### Table 1 — Densities (\(\rho\)), molar volumes (\(V_{o}\)), isothermal compressibilities (\(k_T\)) and hard sphere diameters (\(\sigma\)) of pure components at 303.15 K

<table>
<thead>
<tr>
<th>Comp. (C_3H_7NH_2)</th>
<th>Expt. (\rho) (g cm(^{-3}))</th>
<th>Lit. (\rho) (g cm(^{-3}))</th>
<th>(V_{o}) (cm(^3) mol(^{-1}))</th>
<th>(k_T) (TPa(^{-1}))</th>
<th>(\sigma) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_3H_7NH_2)</td>
<td>0.70610</td>
<td>0.70615</td>
<td>83.71</td>
<td>1275(^{17})</td>
<td>4.76</td>
</tr>
<tr>
<td>(C_4H_9NH_2)</td>
<td>0.72865</td>
<td>0.72848</td>
<td>100.37</td>
<td>1189(^{17})</td>
<td>5.17</td>
</tr>
<tr>
<td>((C_3H_7)_2NH)</td>
<td>0.73121</td>
<td>0.73019(^{17})</td>
<td>138.39</td>
<td>1237(^{17})</td>
<td>5.88</td>
</tr>
<tr>
<td>((C_4H_9)_2NH)</td>
<td>0.75228</td>
<td>0.75248(^{17})</td>
<td>171.80</td>
<td>1078(^{17})</td>
<td>6.48</td>
</tr>
<tr>
<td>((C_2H_5)_3N)</td>
<td>0.71844</td>
<td>0.7185(^{17})</td>
<td>140.85</td>
<td>1493(^{17})</td>
<td>5.91</td>
</tr>
<tr>
<td>((C_3H_7)_3N)</td>
<td>0.74915</td>
<td>0.74848(^{16})</td>
<td>191.24</td>
<td>1193(^{17})</td>
<td>6.72</td>
</tr>
<tr>
<td>((C_4H_9)_3N)</td>
<td>0.77021</td>
<td>0.7701(^{12})</td>
<td>240.65</td>
<td>1012(^{17})</td>
<td>7.44</td>
</tr>
<tr>
<td>(C_6H_5CH_3)</td>
<td>0.85753</td>
<td>0.85754(^{14})</td>
<td>107.45</td>
<td>952(^{24})</td>
<td>5.41</td>
</tr>
</tbody>
</table>

\(\rho\) values of \(\sigma\) were derived from Mayer’s method using isothermal compressibility and molar volume\(^{15}\).

### Table 2 — Empirical parameters \(^a\) in Eq. (1) for amine in toluene

<table>
<thead>
<tr>
<th>Solute</th>
<th>(A) (g cm(^{-3}))</th>
<th>(B\times10^2) (g cm(^{-3}) mol(^{-1}) kg)</th>
<th>(C\times10^4) (g cm(^{-3}) mol(^{-2}) kg(^2))</th>
<th>(D\times10^5) (g cm(^{-3}) mol(^{-3}) kg(^3))</th>
<th>(\sigma\times10^5) (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_3H_7NH_2)</td>
<td>0.85753</td>
<td>-1.09478</td>
<td>0.72489</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>(C_4H_9NH_2)</td>
<td>0.85753</td>
<td>-1.12624</td>
<td>0.81709</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>((C_3H_7)_2NH)</td>
<td>0.85753</td>
<td>-1.42433</td>
<td>1.31769</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>((C_4H_9)_2NH)</td>
<td>0.85753</td>
<td>-1.52594</td>
<td>2.10400</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>((C_2H_5)_3N)</td>
<td>0.85753</td>
<td>-1.60250</td>
<td>1.77147</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>((C_3H_7)_3N)</td>
<td>0.85753</td>
<td>-1.77906</td>
<td>2.75327</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>((C_4H_9)_3N)</td>
<td>0.85753</td>
<td>-1.8782</td>
<td>3.71425</td>
<td>0.59</td>
<td></td>
</tr>
</tbody>
</table>
and the partial molar volumes at infinite dilution of transfer of solute from cyclohexane \((\text{C}_6\text{H}_{12})\) to toluene \((\text{C}_7\text{H}_8)\), \(\Delta V^\infty_{\phi,\text{tr}}\) \((\text{C}_6\text{H}_{12} \rightarrow \text{C}_7\text{H}_8)\) calculated as \(\{V^\infty_{\phi} (\text{C}_7\text{H}_8) - V^\infty_{\phi} (\text{C}_6\text{H}_{12})\}\).

The dependence of \(V^\phi_{\phi,\text{tr}}\) on \(m\) is shown in Fig. 1.

The values of \(V^\phi_{\phi,\text{tr}}, V^\infty_{\phi}\) or \(V^{E,\infty}_{\phi}\) of amines depend to a great extent on the type and polarity of solute and solvent used. The values of excess partial molar volumes of amine solution in toluene at 303.15 K are listed in Table 3.

### Table 3 — Apparent molar volumes of amine solution in toluene at 303.15 K

<table>
<thead>
<tr>
<th>Solute</th>
<th>(m) (mol kg(^{-1}))</th>
<th>(x_B)</th>
<th>(\rho) (g cm(^{-3}))</th>
<th>(V^\phi_{\phi,\text{tr}}) (cm(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>0.1463</td>
<td>0.0133</td>
<td>0.85695</td>
<td>83.77</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>0.1997</td>
<td>0.0181</td>
<td>0.85537</td>
<td>83.85</td>
</tr>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>0.3727</td>
<td>0.0364</td>
<td>0.85317</td>
<td>83.82</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>0.5634</td>
<td>0.0494</td>
<td>0.85159</td>
<td>83.85</td>
</tr>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>0.7258</td>
<td>0.0627</td>
<td>0.84997</td>
<td>83.84</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>0.8229</td>
<td>0.0705</td>
<td>0.84801</td>
<td>83.84</td>
</tr>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>0.9299</td>
<td>0.0789</td>
<td>0.84708</td>
<td>83.83</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>0.9735</td>
<td>0.0823</td>
<td>0.84676</td>
<td>83.83</td>
</tr>
</tbody>
</table>

### Table 4 — Coefficients and standard deviations of Eq. (3) for apparent molar volumes of amines in toluene along with limiting values of excess partial molar volume and volume of transfer from cyclohexane to toluene

<table>
<thead>
<tr>
<th>Solute</th>
<th>(\bar{V}^\infty_{\phi}) (cm(^3) mol(^{-1}))</th>
<th>(S_v) (cm(^3) kg mol(^{-2}))</th>
<th>(\sigma) (cm(^3) mol(^{-1}))</th>
<th>(\bar{V}^{E,\infty}_{\phi}) (cm(^3) mol(^{-1}))</th>
<th>(\Delta \bar{V}^\infty_{\phi,\text{tr}}) (cm(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>83.82</td>
<td>0.03</td>
<td>0.02</td>
<td>0.10</td>
<td>-4.47</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>100.65</td>
<td>0.08</td>
<td>0.03</td>
<td>0.27</td>
<td>-4.87</td>
</tr>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>137.43</td>
<td>0.23</td>
<td>0.04</td>
<td>-0.96</td>
<td>-4.47</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>171.47</td>
<td>0.06</td>
<td>0.04</td>
<td>-3.93</td>
<td>-4.47</td>
</tr>
<tr>
<td>((\text{C}_3\text{H}_7)\text{NH}_2)</td>
<td>191.30</td>
<td>0.04</td>
<td>0.02</td>
<td>-1.02</td>
<td>-4.47</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_9\text{NH}_2)</td>
<td>241.44</td>
<td>-0.07</td>
<td>0.03</td>
<td>0.79</td>
<td>-4.47</td>
</tr>
</tbody>
</table>
volumes \( \bar{V}_{E}^{\infty} \) in toluene decrease in the following sequence for different amines: BA > PA; DBA > DPA; TBA > TPA > TEA.

The values of \( \bar{V}, \bar{\phi}, \bar{E}, \bar{\phi}^{\infty}, \bar{E}^{\infty} \) of corresponding amine solutions in toluene are always lower than that found in cyclohexane and benzene. Further, values of transfer volumes from cyclohexane to toluene as compared with the cyclohexane to benzene are more negative. As already pointed out, to a first approximation the limiting value of excess partial molar volume, \( \bar{E}^{\infty} \), in dilute alkylamine-cyclohexane solutions, is a sum of the contributions as a result of destruction of dipolar order in amine (\( \mu \) for amines 0.78 to 1.37 D) and breaking of H-bonding in primary and secondary amines. The difference in the values of \( \bar{E}^{\infty} \) between cyclohexane and toluene is attributed to the additional specific interactions between amine and toluene molecules to the interactions present in alkylamine-cyclohexane solutions.

The difference in volumetric behaviour between benzene and toluene is a result of substitutions of methyl group in benzene, resulting a small dipole moment (\( \mu = 0.45 \) D) in toluene. Thus, in addition to (i) breaking of amine structure either through dipolar order and/or H-bonding and (ii) (n-\( \pi \)) amine-toluene specific interactions, there exists (iii) enhance dipole-dipole or dipole induced dipole interactions. It is a known fact that the additional dipole-dipole interactions contribute to negative values of \( \bar{E}^{E} \). Therefore, overall values of \( \bar{E}^{E} \) for alkylamine in toluene are less than that for corresponding alkylamine in benzene.

**Group contributions**

The values of group contributions give information regarding structural effects and interactions. We have determined group contributions of the methyl, methylene, and amine (primary, secondary and tertiary) to the partial molar volumes at 303.15 K in toluene solution using simple additive scheme. The linear dependence of partial molar volume on the number of carbon atoms, \( n_C \), for the \( n \)-alkane homologous series in toluene at 303.15 K, allowed us to identify the slopes, \( b \), of Eq. (4) with the contribution of the -CH\(_2\) group, and the intercepts, \( a \), with the combination of group contributions as shown in Eq. (5).

\[
\bar{V}_{E}^{\infty} = a + b n_C \quad \text{...(4)}
\]

\[
a_{HC} = -2 \bar{V}_{CH_2}^{\infty} + 2 \bar{V}_{CH_3}^{\infty} + \kappa_T RT \quad \text{...(5)}
\]

For -NH\(_2\), >NH and >N- groups, the following expression were used:

\[
a_{PA} = -2 \bar{V}_{CH_2}^{\infty} + \bar{V}_{CH_3}^{\infty} + \bar{V}_{NH}^{\infty} + \kappa_T RT \quad \text{...(6)}
\]

\[
a_{SA} = -2 \bar{V}_{CH_2}^{\infty} + 2 \bar{V}_{CH_3}^{\infty} + \bar{V}_{NH}^{\infty} + \kappa_T RT \quad \text{...(7)}
\]

\[
a_{TA} = -3 \bar{V}_{CH_2}^{\infty} + 3 \bar{V}_{CH_3}^{\infty} + \bar{V}_{N}^{\infty} + \kappa_T RT \quad \text{...(8)}
\]

Subscripts HC, PA, SA, and TA stand for alkane hydrocarbon, primary amine, secondary amine and tertiary amine respectively. The partial molar volumes for \( n \)-alkane in toluene needed were determined from the very accurate excess molar volumes, \( V_m^E \) data of binary mixtures of homologous series of \( n \)-alkane in the toluene. The group contributions as presented in Table 5 were determined by a least-squares fitting of experimental data using expressions (5)-(8) as described by Lampreia and Barbosa. The values of \( \kappa_T \) used were taken from literature.

It can be seen from Table 5, that the values of contributions of \( \bar{V}_{CH_2}^{\infty} \) to partial molar volumes are relatively less sensitive to the type of solvent, while for \( \bar{V}_{NH}^{\infty}, \bar{V}_{NH}^{\infty}, \) and \( \bar{V}_{N}^{\infty} \) they are highly sensitive to the solvent type. The average values of -NH\(_2\), >NH, and >N- in toluene are slightly higher than their Bondi’s van der Waals volumes (in neat liquids) and benzene but are less than their corresponding contributions in cyclohexane solvent.
Table 6 compares the observed $\bar{V}_B^\infty$ with calculated value, by using group contributions given in Table 5.

Terasawa model

According to Terasawa et al. the partial molar volume of a solute B is composed of two contributions, i.e., the van der Waals volumes, $V_{W,B}$, and the void partial molar volumes (the actual void created by addition of one mole of solute B to solvent),

$$\bar{V}_B^\infty = V_{W,B} + \bar{V}_{\text{void},B}$$  \(\text{...(9)}\)

where the intrinsic volume, $V_{W,B}$, is approximated by the van der Waals volumes. Usually, $V_{W,B}$ is intended as the volume actually occupied by solute molecules, i.e., it is impenetrable for the solvent molecules. $V_{\text{void}}$ is a measure of the volume of the empty spaces or of the interstices between the solute molecule surface and the solvent molecules, and contains all the effects due to solute-solvent interactions. The intrinsic volumes of the solutes calculated using Lepori and Gianni’s method are reported in Table 6 together with the $\bar{V}_{\text{void},B}$ values obtained by Eq. (9). As can be seen, $\bar{V}_{\text{void},B}$ values are spread differently according to solute molecules, the range width being maximum for primary amine and the minimum for tertiary amine. The reduced void volumes $\bar{V}_{\text{void},B}$ in pure liquid state lies in between cyclohexane and aromatic hydrocarbon solvents. The lower values of $\bar{V}_{\text{void},B}$ indicate enhanced specific interactions between the amines and aromatic hydrocarbon. The interactions may be considered as of n-$\pi$ and dipole-dipole between amines and toluene.

The scaled particle theory

Reiss et al. developed a statistical mechanical theory of fluids based upon the properties of the exact radial distribution functions which yields an approximate expression for the reversible work required to introduce a spherical particle into a fluid of spherical particles. If the solution is sufficiently dilute to ignore solute-solute interactions, then the reversible work of adding a solute molecule to the solution is equivalent to that of adding it to the pure solvent. It is convenient to consider the process of
introducing the solute molecule in to the solvent as consisting of two steps: (i) the creation of cavity in the solvent of suitable size to accommodate the solute molecule, and, (ii) the introduction into the cavity of a solute molecule, which interacts with the solvent according to a pair-wise potential. The SPT expression for $\bar{V}_B^\infty$ is, given in Eq. (10)

$$\bar{V}_B^\infty = \bar{V}_{cav} + \Delta \bar{V}_i + k_T RT$$  \hspace{1cm} \text{(10)}$$

where $\bar{V}_{cav}$ is the partial molal volumes associated with cavity formation, $\Delta \bar{V}_i$ is the partial molal volume contribution from solute-solvent interactions, and $k_T RT$ the changes of standard state between the gas and solution. Application of Eq. (11) to amines and hydrocarbons with the same $\bar{V}_{cav}$ of the amines and subsequent subtraction leads to Eq. (11),

$$\bar{V}_{S-S} = \bar{V}_B^\infty - \bar{V}_{HC}^\infty$$  \hspace{1cm} \text{(11)}$$

where $\bar{V}_{S-S}$ is a new interaction parameter. In order to obtain this interaction contribution it is necessary to calculate $\bar{V}_{cav}$ for the amine and hydrocarbon molecules under consideration.

As per the SPT, $\bar{V}_{cav}$ is a known function of temperature, molar volume, isothermal compressibility, hard sphere diameter of a solvent and solute $\sigma_A$ and $\sigma_B$. It is given by Eq. (12),

$$\bar{V}_{cav} = 0.3153 \sigma_B^3 + A \sigma_B^2 + B \sigma_B + C$$  \hspace{1cm} \text{(12)}$$

where

$$A = 3k_T RT(y + 2y^2)/(1 - y)^3 \sigma_A^3$$  \hspace{1cm} \text{(13)}$$

and $y$ is defined as

$$y = N_A \pi \sigma_A^3/6V_A$$  \hspace{1cm} \text{(16)}$$

Here, $y$ is the ratio of volume occupied by one mole of hard sphere solvent molecules to the molar volume of the solvent.

The required values of $\sigma$, derived from molar volumes $V$ and isothermal compressibilities $k_T$ at 303.15 K using Mayer’s method are included in the last column of Table 1. $\bar{V}_{cav}$ for the amines under study in toluene were then calculated and $\Delta \bar{V}_i$ derived. Table 7 shows $\bar{V}_{cav}$, $\Delta \bar{V}_{i,B}$ and $\Delta \bar{V}_{i,HC}$ for amines under study. The uncertainty in $\bar{V}_{cav}$ is generally of the order of 2 cm$^3$ mol$^{-1}$. The size of cavity, $\bar{V}_{cav}$, depends upon solute-solvent interaction, volume and compressibility of solvent. The interaction parameters, $\bar{V}_{S-S}$, will be discussed jointly with the corresponding parameter presented in next section through hard sphere theory.

The hard sphere theory

Despite the geometrical nature of concept of volume it is not possible to calculate partial molar volume directly from simple geometrical consideration. Klapper$^{35}$ pointed out that for a spherical and non-polar solute, the geometrical packing effect is entirely responsible for its volumetric behaviour in solution. In the case of hard sphere mixtures, an exact expression for $\bar{V}_B^\infty(HS)$ has been derived by Lee.$^{10}$ It’s usefulness to estimate contribution of specific solute-solvent interaction to the partial molar volume has been demonstrated by

$$B = 3k_T RTy/(1 - y)^2 \sigma_A$$  \hspace{1cm} \text{(14)}$$

$$C = k_T RTy/(1 - y)$$  \hspace{1cm} \text{(15)}$$

$$y = N_A \pi \sigma_A^3/6V_A$$  \hspace{1cm} \text{(16)}$$

Table 7 — SPT and HST results and interaction contributions to limiting partial molar volumes of amines in toluene at 303.15 K

<table>
<thead>
<tr>
<th>Solute</th>
<th>SPT results</th>
<th>HST results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{V}_{cav}$</td>
<td>$\Delta \bar{V}_{i,B}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{NH}_2$</td>
<td>79.3</td>
<td>2.1</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7\text{NH}_2$</td>
<td>95.7</td>
<td>2.6</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)\text{NH}_2$</td>
<td>129.2</td>
<td>5.9</td>
</tr>
<tr>
<td>$(\text{C}_3\text{H}_7)\text{NH}_2$</td>
<td>162.9</td>
<td>6.2</td>
</tr>
<tr>
<td>$(\text{C}_3\text{H}_7)\text{NH}_2$</td>
<td>130.7</td>
<td>6.7</td>
</tr>
<tr>
<td>$(\text{C}_4\text{H}_9)\text{NH}_2$</td>
<td>177.9</td>
<td>11.0</td>
</tr>
<tr>
<td>$(\text{C}_4\text{H}_9)\text{NH}_2$</td>
<td>228.5</td>
<td>10.6</td>
</tr>
</tbody>
</table>

$^*$ $\bar{V}_{i,HC}^\infty$ stands for partial molar volumes for hydrocarbons with the same van der Waals volume or hard-sphere diameter as that of amine.
Lampreia and Barbosa. The expression for limiting partial molar volume of hard-sphere divided by the molar volume of the solvent mixture is given by Eqs (17) – (21),

\[ \bar{V}_B^{\infty} (HS)/V_A^{\infty} = C[(\sigma_B/\sigma_A)^3 + 3\alpha(\sigma_B/\sigma_A)^2 + 3\alpha\beta(\sigma_B/\sigma_A) + \alpha\beta\gamma] \quad ... (17) \]

\[ \alpha = (1 - y)/(1 + 2y) \quad ... (18) \]

\[ \beta = (1 - y)/(1 + 2y - h^2) \quad ... (19) \]

\[ \gamma = (1 - y)/y \quad ... (20) \]

\[ C = (1 + 3\alpha + 3\alpha\beta + \alpha\beta\gamma)^{-1} \quad ... (21) \]

where \( \sigma_A \) and \( \sigma_B \) are the hard sphere diameters of the solvent and solute respectively, \( y \) is the average packing density of the pure solvent \( (y = N_d\pi\sigma_A^3/6V_A^{\infty}) \) and \( h \) is a parameter varying between 0 and 3, depending on how the equation of state derived. Apparently, the more exact equation is obtained with \( h = 1 \).

In order to clarify the influence upon \( \bar{V}_B^{\infty} (HS) \) of size and packing density of the solvent, Eq. (17) can be transferred into Eq. (22),

\[ \bar{V}_B^{\infty} (HS)/V_B^{\infty} (HS) = C/y[1 + 3\alpha(\sigma_A/\sigma_B) + 3\alpha\beta(\sigma_A/\sigma_B)^2 + \alpha\beta\gamma(\sigma_A/\sigma_B)^3] \quad ... (22) \]

where \( V_B^{\infty} (HS) = N_d\pi\sigma_B^3/6 \) is the molar hard sphere volume of solute B.

The differences between experimental and HS models, \( \bar{V}_B^{\infty} (HS) \) values, i.e., \( \Delta \bar{V}_B^{\infty} (HS) = \bar{V}_B^{\infty} \text{(exp)} - \bar{V}_B^{\infty} (HS) \) are considered as corrective terms arising from non-spherical shape of the solute molecules and from molecular interactions present in solution. One can assume that interactions in the systems studied are composed of two contributions: one caused by the amine group, and, another due to the aliphatic part of the molecule. As a common procedure \( \alpha \) linear hydrocarbons were selected as reference molecules to separate the effects on volume on the two types of interactions. To obtain the contribution of interactions to limiting partial molar volume Barbosa and Lampreia defined the quantity \( \bar{R}_{S-S}^{\infty} \) by Eq. (23),

\[ \bar{R}_{S-S}^{\infty} = \Delta \bar{V}_B^{\infty} (HS) - \Delta \bar{V}_B^{\infty} (HS) \quad ... (23) \]

where \( \Delta \bar{V}_B^{\infty} (HS) \) is the corrective term, for the linear hydrocarbon with the same \( \sigma_A/\sigma_B \) as the amine under consideration. The required values of \( \bar{V}_B^{\infty} \text{(exp)} \) for the hydrocarbons were estimated from a linear relation \( \bar{V}_B^{\infty} \) versus \( V_A \) for these compounds in toluene. The values of \( \bar{V}_B^{\infty} (HS) \), \( \Delta \bar{V}_B^{\infty} (HS) \), \( \Delta \bar{V}_{T HCI}^{\infty} (HS) \) and \( \bar{R}_{S-S}^{\infty} \) for HST are listed in Table 7.

We shall now compare the values of interaction parameters, \( I_{S-S} \), from the SPT and \( \bar{R}_{S-S}^{\infty} \) from the HST and discuss the importance of sign and magnitude to shed light on the specific interactions. There is excellent agreement in the values of interaction parameters \( I_{S-S} \) and \( \bar{R}_{S-S}^{\infty} \) from both the approaches. The fact that these numbers were obtained from such different approaches gives support to both. It has been observed that the sign and magnitude of \( I_{S-S} \) and \( \bar{R}_{S-S}^{\infty} \) values provides quantitative information about the effects on volume produced by specific interactions between solute and solvent. The negative values of \( I_{S-S} \) and \( \bar{R}_{S-S}^{\infty} \) (Table 7) observed for all the amines indicate that the contribution to \( \bar{V}_B^{\infty} \) of the amines group interaction is always smaller than the corresponding contribution of hydrocarbons in toluene and can be a result of amine-toluene specific interactions. In the present study the magnitude of negative values of \( I_{S-S} \) and \( \bar{R}_{S-S}^{\infty} \) for amines in toluene decreases in the order primary > secondary > tertiary, indicating the extent of specific interaction.

The ERAS model

The ERAS model has been utilized to interpret quantitatively the thermodynamic properties of mixtures formed from non-associating but active component (toluene, A) or and other weakly polar (amine, B) component. In addition, cross association (AB) in the mixture can also be accounted for. The ERAS model combines the linear-chain association model with Flory’s equation of state. The details of the ERAS model and its successful application to excess thermodynamic properties are given elsewhere. The model has also been utilized to estimate apparent or partial molar volumes of alkanols in alkanes, di-n-butylamine in haloalkanes and...
n-alkylamines in cyclohexane, benzene, 1,4-dioxane, and oxolane.1,4 We shall examine the ERAS model to analyse volumetric properties of alkylamines solutions in toluene. Herein we shall present only those results which are relevant to the amine solutions in toluene. In the framework of the ERAS model, the thermodynamic excess properties of binary mixtures can be expressed as the addition of a physical and a chemical contribution. The expressions for calculating the physical contributions $H_{\text{phy}}^E$, $V_{\text{phy}}^E$, and $V_{\phi, B, \text{phy}}^E$ are given in Eqs (24) – (26).

\[
H_{\text{phy}}^E = \phi_A V_A^* + \phi_B V_B^* \left( \frac{\mu_A P_A^*}{V_A} + \frac{\mu_B P_B^*}{V_B} - \frac{P^*}{V_m} \right) \tag{24}
\]

\[
V_{\text{phy}}^E = (\phi_A V_A^* + \phi_B V_B^*) \left( \tilde{V}_M - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B \right) \tag{25}
\]

\[
V_{\phi, B, \text{phy}}^E = (\phi_A V_A^* + \phi_B V_B^*) \left[ \tilde{V}_m - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B \right] \tag{26}
\]

The expressions for chemical contributions1,41, $H_{\text{chem}}^E$, $V_{\text{chem}}^E$, and $V_{\phi, B, \text{chem}}^E$ are given by Eqs (27)- (29).

\[
H_{\text{chem}}^E = \phi_B V_B^* \left( \frac{\mu_B P_B^*}{V_B} \right) + \phi_B K_{AB} \Delta h^*_{AB} \left( \frac{\phi_B - \phi_B^o}{V_m} \right) \tag{27}
\]

\[
V_{\phi, B, \text{chem}}^E = -\phi_B \left[ K_{AB} \Delta V_B \phi_B \frac{1}{V_B} + \frac{K_{AB} \Delta V_{AB}}{V_B} \phi_B \frac{1}{V_B} \right] \tag{32}
\]

\[
V_{\phi, E}^E = \phi_B \left[ \left( \frac{P^*_B \tilde{T}_B}{T_B} \right)^2 \left( 1 - 4 \frac{V_B}{T_B} \right) \right] \tag{33}
\]
adds infinity to

$$\bar{V}_{B,\text{thr}}^{\sigma,E} = \bar{V}_{B,\text{chem}}^{\sigma,E} + \bar{V}_{B,\text{phy}}^{\sigma,E}$$

...(34)

In the ERAS model notations, $\phi_{B1}$ and $\phi_{B1}^o$ are the hard core volume fractions of the monomeric species B in the solution and monomeric species in pure component B, respectively. $K_B$, $\Delta h_{B*}$, and $\Delta v_{B*}$ are respectively the association constants for linear association, hydrogen bond energy, and reaction volume for H-bond formation for B. The required pure component properties and the ERAS parameters are summarized in Table 8.

The existence of enhanced specific interactions in primary, secondary and tertiary amine with toluene has been accounted by the cross-parameters $K_{AB}$ (the cross-association constant), $\Delta h_{AB}^*$ (the association energy per mole of hydrogen bonds due cross association) and $\Delta v_{AB}^*$ (the reaction volume per mole of hydrogen bonds due to cross-association) in the ERAS model. The optimum values of parameters $K_{AB}$, $\Delta h_{AB}^*$ and $\Delta v_{AB}^*$ were simultaneously adjusted to the experimental $H_m^E$ and $V_m^E$ data for a certain value of the Flory’s contact interaction parameter $X_{AB}$. More details are given elsewhere. The experimental and theoretical values of equimolar $H_m^E$ and $V_m^E$ are also included in Table 9.

The results of calculated excess apparent molar volume and their comparison with the experimental data are shown graphically in Fig. 2. The limiting values of partial molar volumes $\bar{V}_B^{\sigma}$ and excess partial molar volumes $\bar{V}_B^{E,\sigma}$ along with the physical

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\bar{V}_{B,\text{thr}}^{\sigma}$ (cm$^3$ mol$^{-1}$)</th>
<th>$\bar{V}_{B,\text{exp}}^{\sigma}$ (cm$^3$ mol$^{-1}$)</th>
<th>$\sigma$ (cm$^3$ mol$^{-1}$)</th>
<th>$\bar{V}_{B,\text{chem}}^{\sigma,E}$ (cm$^3$ mol$^{-1}$)</th>
<th>$\bar{V}_{B,\text{phy}}^{E,\sigma}$ (cm$^3$ mol$^{-1}$)</th>
<th>$\bar{V}_{B,\text{thr}}^{E,\sigma}$ (cm$^3$ mol$^{-1}$)</th>
<th>$\bar{V}_{B,\text{exp}}^{E,\sigma}$ (cm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_7$NH$_2$</td>
<td>84.33</td>
<td>83.82</td>
<td>0.45</td>
<td>0.35</td>
<td>0.27</td>
<td>0.62</td>
<td>0.10</td>
</tr>
<tr>
<td>C$_4$H$_9$NH$_2$</td>
<td>100.14</td>
<td>100.65</td>
<td>0.37</td>
<td>0.84</td>
<td>-0.08</td>
<td>0.76</td>
<td>0.27</td>
</tr>
<tr>
<td>(C$_3$H$_7$)$_2$NH</td>
<td>137.79</td>
<td>137.43</td>
<td>0.27</td>
<td>-1.13</td>
<td>0.53</td>
<td>-0.59</td>
<td>-0.96</td>
</tr>
<tr>
<td>(C$_4$H$_9$)$_2$NH</td>
<td>171.75</td>
<td>171.47</td>
<td>0.25</td>
<td>-1.25</td>
<td>1.18</td>
<td>-0.07</td>
<td>-0.33</td>
</tr>
<tr>
<td>(C$_3$H$_7$)$_3$N</td>
<td>139.72</td>
<td>139.84</td>
<td>0.11</td>
<td>-0.70</td>
<td>-0.34</td>
<td>-1.04</td>
<td>-1.02</td>
</tr>
<tr>
<td>(C$_4$H$_9$)$_3$N</td>
<td>191.55</td>
<td>191.30</td>
<td>0.20</td>
<td>-0.83</td>
<td>1.13</td>
<td>0.29</td>
<td>0.06</td>
</tr>
<tr>
<td>(C$_4$H$_9$)$_3$N</td>
<td>241.83</td>
<td>241.44</td>
<td>0.32</td>
<td>-1.72</td>
<td>2.89</td>
<td>1.18</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Here $\sigma$ represents standard deviation between observed apparent molar volumes and theoretical values over the range of composition studied.
and chemical \( \bar{V}_{\text{B, phys}}^{E, \infty} \) and chemical \( \bar{V}_{\text{B, chem}}^{E, \infty} \) contributions to \( \bar{V}_{\text{B}}^{E, \infty} \) are summarized in Table 10. It can be seen from Fig. 2 that the ERAS model is quite successful in predicting pattern for dependence of excess apparent molar volume on composition for the studied seven amines in toluene.

**Conclusions**

The partial molar volumes \( \bar{V}_{\text{B}}^{E, \infty} \) and excess partial molar volumes \( \bar{V}_{\text{B}}^{E, \infty} \) of seven primary, secondary and tertiary amines were determined from precise experimental densities of alkylamine solutions in toluene at 303.15 K. The values of excess partial molar volumes \( \bar{V}_{\text{B}}^{E, \infty} \) increase with the increase in chain length of alkyl group in primary, secondary and tertiary amines. There exist additional specific interactions between amine and toluene as compared to amine-cyclohexane interactions. The values of group contributions of >NH, >NH and >N- in toluene at 303.15 K are 16.56, 5.50, -6.27 cm³ mol⁻¹, respectively.

Using the scaled particle and the hard-sphere theories, the contribution of specific interaction amine-toluene in primary, secondary and tertiary amines to the partial molar volume was determined. The results agree well in the two different approaches used. The ERAS model was used to predict \( \bar{V}_{\text{B}}^{E, \infty} \) and \( \bar{V}_{\text{B}}^{E, \infty} \) of primary, secondary and tertiary amines in toluene and the agreement between model and experimental values is almost quantitative.

**References**