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Studies of partial molar volumes of alkylamine in non-electrolyte solvents I. Alkylamines in hydrocarbons at 303.15 and 313.15 K

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Abstract

Apparent molar volumes $V_{\phi,\mathrm{B}}$ of *n*-propylamine, *n*-butylamine, di-*n*-propylamine, di-*n*-butylamine, triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine in cyclohexane and benzene at 303.15 and 313.15 K have been calculated from the densities ρ determined with high precision vibrating tube densimeter. From these data limiting partial molar volume $\bar{V}_{\mathrm{B}}^{\infty}$ and limiting excess partial molar volumes $\bar{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ were estimated. The results are analysed and interpreted in terms of disruption of amine–amine and solute–solvent interactions.

The contribution to partial molar volumes of the methyl, methylene, and primary, secondary and tertiary amine groups at 303.15 and 313.15 K in cyclohexane and benzene solutions have been calculated using simple additive scheme. The results were interpreted in terms of conformational effects present in these molecules. An attempt to find a measure of the contribution of the specific interactions to the partial molar volume of primary, secondary and tertiary amines in benzene was made using Teresawa model, hard sphere theory (HST) and scaled particle theory (SPT). The Flory theory/ERAS model has also been applied to estimate apparent molar volumes. The results agree well in the different approaches used.

Keywords: Alkylamines; Partial molar volume; Group additivity; Hard sphere and scaled particle theories; ERAS model

1. Introduction

We are engaged in systematic studies of thermodynamic and transport properties of solutions involving alkylamine, as they are important organic bases because of their strong electron donating capability. Transport and volumetric properties of binary liquid mixtures have been extensively studied in order to know the nature and extent of various intermolecular interactions existing between different species present in solution [1–9]. Much effort has gone into determination of partial molar volume and transport properties of dilute solutions in non-polar non-interacting solvent [10–17]. These properties can contribute to the comprehension of liquid solutions in numerous ways, some of which will be presented below.

Many investigators [18–25] have applied the widely used additivity rule at 298.15 K, not only to predict new values of partial molar volumes but also to understand the molecular basis of exhibited volumetric behaviour. Information on specific interactions, conformational effects and packing efficiencies can be extracted by the use of such simple relations.

As the hard sphere mixture is the simplest system we can deal with, we have considered this model to describe the main contribution to be considered in partial molar volumes. We used the expression derived by Lee [26] for the partial molar volume of a solute in infinitely dilute hard sphere binary mixtures. The expression was obtained from a very accurate equation of state for hard sphere mixtures [27] and only takes into account the geometrical aspect of partial molar volume. The differences calculated from experimental values were attributed to the non-sphericity of the molecules and to interactions in the solution.

Another approach consists of imagining the partial molar volume $\bar{V}_{\mathrm{B}}^{\infty}$ as derived from the process of making a cavity in a solvent, of a suitable size to accommodate a solute molecule, and then allowing the solute to interact with the solvent. The statistical mechanical scaled particle theory

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(SPT) [28,29] produced an expression for such a volumetric cavity term that has been extensively mentioned in the literature.

A theoretical model based on a statistical mechanical derivation, which accounts for self-association and cross-association in unlike components is Extended Real Associated Solution (ERAS) model due to Heintz et al. [30,31]. It combines the effect of association with non-associative intermolecular interaction occurring in liquid mixtures based on equation of state developed originally by Flory et al. [32]. The ERAS model has subsequently being successfully applied by many investigators to describe the excess thermodynamic properties and apparent molar volumes of associated component in polar and non-polar components [33–40]. In this paper we have also applied the Flory theory/the ERAS model to estimate apparent molar volumes of mono-, di- and tri-*n*-alkylamines in cyclohexane and benzene solutions.

As a part of our systematic studies, in previous papers [41,42] measurements of viscosities of dilute solutions of *n*-propylamine (PA), *n*-butylamine (BA), di-*n*-propylamine (DPA), di-*n*-butylamine (DBA), triethylamine (TEA), tri-*n*-propylamine (TPA), and tri-*n*-butylamine (TBA) in hydrocarbons and chloroalkanes have been reported. As an extension of our studies in this paper we report volumetric properties of PA, BA, DPA, DBA, TEA, TPA, and TBA in cyclohexane and benzene at 303.15 and 313.15 K.

The partial molar properties reported in the literature usually refer to standard conditions of 298.15 K and 1 atm. In this paper the contribution to partial molar volumes of the methyl, methylene, and primary, secondary, and tertiary amine groups at 303.15 and 313.15 K in cyclohexane and benzene solutions and in pure compounds have been calculated using simple additive schemes [25]. The contributions of the specific interactions to partial molar volume of presently investigated amines in benzene were then calculated using Teresawa model [20], hard sphere theory [26] and scaled particle theory [29].

2. Experimental

2.1. Method

Densities ρ at 303.15 and 313.15 K were measured with Anton Paar (60/602) vibrating tube digital densimeter, thermostatted within ±0.01 K using a Heto Birkeroad ultrathermostat. Before each series of measurements the reference samples used for calibration were redistilled degassed water and air. Accurate densities of water and air were taken from literature [43,44]. The details of the methods and techniques used to determine densities ρ have been describe previously [5]. The results of densimeter were further checked by measuring densities of aqueous solutions of triethylamine and the calculated values of partial molar volume of TEA was 120.95 $\text{cm}^3\,\text{mol}^{-1}$ at 298.15 K. Observed partial molar volume was in excellent agreement with the literature value $120.9 \pm 0.1\,\text{cm}^3\,\text{mol}^{-1}$ [45].

All the solutions were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking precautions to minimize the evaporation losses. All the mass measurements were performed on an electronic balance (Mettler AE163, Switzerland) accurate to 0.01 mg. Nine to 10 solutions up to 0.1 mol fraction of each alkylamine in different solvents were prepared. The values of molality and density ρ are accurate to $\pm 1 \times 10^{-4}\,\text{mol}\,\text{kg}^{-1}$ and $\pm 1 \times 10^{-5}\,\text{g}\,\text{cm}^{-3}$, respectively.

2.2. Materials

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. Cyclohexane (Fluka AG) and benzene (Merck, GR) of purity better than 99.5 mol% were used after further purification and drying by standard procedures [46]. The measured values of densities were compared with literature values in Table 1.

3. Results and discussion

The experimentally determined values of densities ρ for dilute solutions of amines in different solvents at different concentrations and at 303.15 and 313.15 K were fitted to polynomial equation of type

$$\rho = A + Bm + Cm^2 \tag{1}$$

The values of A, B, and C coefficients along with standard deviations values (σ) are given in Table 2. The apparent molar volumes $V_{\phi,\text{B}}$ of all solutes were calculated in the usual way

$$V_{\phi,\text{B}} = \frac{M_\text{B}}{\rho} - \left(\frac{\rho - \rho_\text{A}}{\rho\rho_\text{A}}\right)\frac{1000}{m} \tag{2}$$

where M_B is the molar mass of solute (amine) and m the concentration of amine in molality. ρ and ρ_A are the densities of solution and pure solvent, respectively. The values of $V_{\phi,\text{B}}$ are presented in Tables 3 and 4.

The partial molar volume $\bar{V}_\text{B}^\infty$ of amines were obtained by linear extrapolation of the apparent molal volumes to infinite dilution by the least-squares method through the fitting of following equation:

$$V_{\phi,\text{B}} = \bar{V}_\text{B}^\infty + S_\text{v} m \tag{3}$$

The values of coefficients of Eq. (3) are given in Table 5, along with the excess partial molar volumes $\bar{V}_\text{B}^{\text{E},\infty}$ ($\bar{V}_\text{B}^{\text{E},\infty} = \bar{V}_\text{B}^\infty - V_\text{B}^0$) at infinite dilution for each solute in different solvents. The values of $V_{\phi,\text{B}}$, $\bar{V}_\text{B}^\infty$ or $\bar{V}_\text{B}^{\text{E},\infty}$ of alkylamines depend to great extent on the type of solvent used.

Table 1
Comparison of experimental densities ρ with the literature, values of molar volumes V^0, isothermal compressibilities k_T, and hard sphere diameters σ of pure components

Component	Temperature (K)	ρ (g cm^{-3})		V^0 (cm^3 mol^{-1})	k_T (TPa^{-1})	σ^a (Å)
		Obs.	Lit.			
PA	303.15	0.70610	0.70615[b]	83.71	1275[c]	4.771
	313.15	0.69604	0.6960[b]	84.92	1411[c]	4.744
BA	303.15	0.72865	0.72865[d]	100.37	1189[c]	5.167
	313.15	0.71917	0.7182[e] 0.71917[d]	101.70	1288[c]	5.142
DPA	303.15	0.73121	0.73019[f]	138.39	1237[c]	5.849
	313.15	0.72615	0.7216[b]	139.39	1356[c]	5.823
DBA	303.15	0.75228	0.75248[e]	171.80	1078[c]	6.472
	313.15	0.74344	0.74284[g], 0.7431[b]	173.85	1162[c]	6.449
TEA	303.15	0.71844	0.71845[h]	140.85	1493[c]	5.935
	313.15	0.70905	0.7091[b]	142.71	1640[c]	5.912
TPA	303.15	0.74915	0.7497[i]	191.24	1193[c]	6.671
	313.15	0.74041	0.7404[b]	193.50	1290[c]	6.652
TBA	303.15	0.77021	0.7709[b]	240.65	1012[c]	7.357
	313.15	0.76311	0.7612[g] 0.7634[b]	242.89	1095[c]	7.341
Cyclohexane	303.15	0.76910	0.76904[j], 0.76915[l]	190.43	1171[k]	5.37
	313.15	0.75952	0.7595[j]	110.81	1274[k]	5.36
Benzene	303.15	0.86830	0.86829[j]	89.96	1009[m]	5.01
	313.15	0.85759	0.85769[l]	102.85	1085[m]	5.006
Hexane	303.15		0.65034[m]	132.51	1746[m]	5.624
	313.15		0.64109[m]	134.42	1925[m]	5.610
Heptane	303.15		0.67550[m]	148.34	1501[m]	5.968
	313.15		0.66690[m]	150.25	1639[m]	5.958
Octane	303.15		0.69458[m]	164.46	1332[m]	6.285
	313.15		0.68643[m]	166.41	1444[m]	6.274
Nonane	303.15		0.71022[m]	180.59	1217[m]	6.565
	313.15		0.70238[m]	182.60	1310[m]	6.561
Decane	303.15		0.72249[m]	196.94	1134[m]	6.828
	313.15		0.71491[m]	199.02	1218[m]	6.825
Dodecane	303.15		0.73276[m]	213.31	1068[m]	7.074
	313.15		0.72535[m]	215.50	1147[m]	7.071
Undecane	303.15		0.74155[m]	229.70	1020[m]	7.304
	313.15		0.73429[m]	231.97	1091[m]	7.303
Tridecane	303.15		0.74918[m]	246.07	973[m]	7.524
	313.15		0.73429[m]	248.45	1029[m]	7.528
Tetradecane	303.15		0.75562[m]	262.55	938[m]	7.721
	313.15		0.75494[m]	265.02	1000[m]	7.707
Pentadecane	303.15		0.76193[m]	278.79	910[m]	7.927
	313.15		0.75494[m]	281.37	971[m]	7.91
Hexadecane	303.15		0.76621[m]	295.425	887[m]	8.117
	313.15		0.75960[m]	298.114	948[m]	8.107

[a] Derived from Mayer's method using isothermal compressibility and molar volume [47].
[b] Ref. [48].
[c] Ref. [49].
[d] Ref. [50].
[e] Ref. [51].
[f] Ref. [52].
[g] Ref. [53].
[h] Ref. [46].
[i] Ref. [54].
[j] Ref. [55].
[k] Ref. [56].
[l] Ref. [57].
[m] Ref. [58].

Table 2
Empirical parameters in Eq. (1) for amine in cyclohexane and benzene

Solute	Temperature (K)	A (g cm^{-3})	B ($\times 10^2$ g cm^{-3} mol^{-1} kg)	C ($\times 10^3$ g cm^{-3} mol^{-2} kg^2)	σ ($\times 10^5$ g cm^{-3})
Cyclohexane					
PA	303.15	0.76910	−0.67474	0.7061	2.05
	313.15	0.75949	−0.62568	0.5166	1.97
BA	303.15	0.76911	−0.62061	0.8215	2.60
	313.15	0.75949	−0.57469	0.5207	3.05
DPA	303.15	0.76910	−0.57767	0.6755	1.42
	313.15	0.75952	−0.59306	0.7882	1.06
DBA	303.15	0.76906	−0.40774	0.6940	3.31
	313.15	0.75951	−0.37561	0.4419	0.97
TEA	303.15	0.76913	−0.73485	1.0930	1.91
	313.15	0.75952	−0.71359	1.0115	2.60
TPA	303.15	0.76909	−0.42057	0.6938	2.29
	313.15	0.75950	−0.38501	0.5789	1.64
TBA	303.15	0.76907	−0.11822	0.3171	2.07
	313.15	0.75953	−0.12128	0.6254	2.32
Benzene					
PA	303.15	0.86831	−1.22494	0.8026	3.87
	313.15	0.85758	−1.18082	0.7779	0.62
BA	303.15	0.86828	−1.23135	0.9613	2.06
	313.15	0.85758	−1.21341	0.9766	0.62
DPA	303.15	0.86826	−1.70128	1.8738	3.46
	313.15	0.85757	−1.63072	1.6858	1.99
DBA	303.15	0.86828	−1.84423	2.2521	1.54
	313.15	0.85757	−1.74041	2.0243	1.44
TEA	303.15	0.86825	−1.82551	1.7115	2.94
	313.15	0.85756	−1.85450	1.9366	2.40
TPA	303.15	0.86826	−2.08335	2.7024	3.39
	313.15	0.85755	−2.03154	2.7032	3.58
TBA	303.15	0.86824	−2.18327	3.3865	4.41
	313.15	0.85752	−2.11133	3.3661	4.52

3.1. Amine solutions in cyclohexane

The values of excess partial molar volumes $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ are positive for all amine in cyclohexane and decrease in the sequence for different amines: BA > PA > DBA ≈ DPA > TEA ≈ TBA > TPA. The positive values of $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ are due to the reduction in amine–amine interaction and dispersion interaction between amine–cyclohexane, when amines are added to cyclohexane.

The dependence of apparent molar volumes of amines $V_{\phi,\mathrm{B}}$ on molality m i.e. $S_{\mathrm{V}} \neq 0$ of Eq. (3) shows the presence of solute–solute interactions, meaning that in non-infinitely dilute mixtures solute–solute, apart from solute–solvent and solvent–solvent interactions will be present. The slopes for the plots i.e. values of S_{V}, presented in Table 5, are always negative for cyclohexane solutions as a consequence of attractive solute–solute short-range interactions. These results are well supported by large and positive values of excess molar enthalpy and excess molar volumes of amines in cyclohexane [6–8,59–62]. The presence of both dipole–dipole interaction and of H-bonded self-association, in primary and secondary amines and their destruction by the dilution with cyclohexane molecules resulted into larger values of $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ compared to the trialkylamine solutions where only the dipole–dipole interaction exists. It is expected that $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ for PA should be some what larger than that for butylamine as the amine–amine interactions are stronger in PA than that in BA. The values of equimolar H^{E} and V^{E} for propylamine + cyclohexane ($H^{\mathrm{E}} = 1243$ J mol^{-1} [63], $V^{\mathrm{E}} = 0.873$ cm^3 mol^{-1} [60]) are slightly larger than for butylamine + cyclohexane ($H^{\mathrm{E}} = 1131$ J mol^{-1} [63], $V^{\mathrm{E}} = 0.822$ cm^3 mol^{-1} [60]). The observed reverse trend in dilute solution of PA and BA may be attributed to the structural effects.

3.2. Amine solutions in benzene

The values of excess partial molar volumes $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ of the amines in benzene are positive at both the temperatures. However, there is a significant difference in the values of $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ when cyclohexane is replaced by benzene. The $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ decreases in the sequence for different amines: tertiary > secondary > primary. This order is opposite to that observed in case of amine solutions in cyclohexane. The difference in $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ values may be attributed to the benzene–amine specific interactions [14,59,60] and destruction of a local order in benzene molecules due to (π–π) interactions [64].

For solutions involving primary and secondary amines, the values of $\overline{V}_{\mathrm{B}}^{\mathrm{E},\infty}$ are reduced when cyclohexane is replaced by benzene, which definitely indicate presence of specific interactions [14] in solute and solvent. The positive contribution

Table 3
Densities ρ and apparent molar volumes $V_{\phi,\mathrm{B}}$ of amine solution in cyclohexane

	x_B	m (mol kg^{-1})	ρ (g cm^{-3})		$V_{\phi,\mathrm{B}}$ (cm^3 mol^{-1})	
			303.15 K	313.15 K	303.15 K	313.15 K
PA	0.0076	0.0911	0.76847	0.75892	88.63	89.32
	0.0169	0.2040	0.76775	0.75821	88.20	89.11
	0.0282	0.3449	0.76686	0.75738	88.09	88.83
	0.0365	0.4504	0.76622	0.75680	88.00	88.61
	0.0483	0.6032	0.76530	0.75592	87.94	88.59
	0.0570	0.7178	0.76461	0.75527	87.94	88.58
	0.0652	0.8282	0.76397	0.75468	87.91	88.52
	0.0747	0.9588	0.76325	0.75396	87.84	88.53
	0.0859	1.1163	0.76247	0.75315	87.65	88.46
BA	0.0097	0.1159	0.76839	0.75882	105.55	106.86
	0.0197	0.2391	0.76770	0.75812	105.19	106.65
	0.0282	0.3450	0.76710	0.75754	105.17	106.52
	0.0380	0.4699	0.76638	0.75691	105.26	106.29
	0.0471	0.5877	0.76576	0.75630	105.16	106.25
	0.0581	0.7331	0.76498	0.75561	105.16	106.09
	0.0674	0.8587	0.76435	0.75491	105.10	106.25
	0.0724	0.9268	0.76408	0.75462	104.94	106.15
	0.0873	1.1366	0.76314	0.75362	104.78	106.12
DPA	0.0114	0.1367	0.76831	0.75872	141.49	143.53
	0.0213	0.2580	0.76765	0.75803	141.34	143.52
	0.0321	0.3943	0.76694	0.75730	141.23	143.41
	0.0414	0.5132	0.76629	0.75667	141.34	143.40
	0.0509	0.6375	0.76571	0.75607	141.18	143.26
	0.0622	0.7879	0.76496	0.75534	141.21	143.21
	0.0727	0.9314	0.76429	0.75466	141.18	143.19
	0.0811	1.0492	0.76378	0.75417	141.12	143.08
	0.0919	1.2028	0.76313	0.75352	141.06	143.01
DBA	0.0109	0.1314	0.76853	0.75901	175.52	177.02
	0.0204	0.2475	0.76807	0.75859	175.32	176.90
	0.0298	0.3653	0.76762	0.75819	175.24	176.80
	0.0392	0.4844	0.76724	0.75779	174.97	176.77
	0.0493	0.6160	0.76684	0.75736	174.77	176.76
	0.0583	0.7357	0.76646	0.75699	174.72	176.72
	0.0689	0.8799	0.76605	0.75655	174.61	176.72
	0.0797	1.0284	0.76560	0.75611	174.60	176.71
	0.0881	1.1474	0.76527	0.75577	174.57	176.71
TEA	0.0102	0.1226	0.76828	0.75866	143.73	145.55
	0.0192	0.2320	0.76750	0.75793	143.60	145.41
	0.0299	0.3662	0.76658	0.75705	143.58	145.39
	0.0422	0.5236	0.76557	0.75607	143.52	145.31
	0.0498	0.6222	0.76497	0.75548	143.48	145.26
	0.0618	0.7827	0.76404	0.75454	143.44	145.21
	0.0712	0.9102	0.76335	0.75386	143.32	145.09
	0.0799	1.0314	0.76272	0.75322	143.22	145.02
	0.0895	1.1676	0.76205	0.75262	143.09	144.79
	0.0995	1.3125	0.76136	0.75188	142.98	144.78
TPA	0.0109	0.1307	0.76854	0.75899	193.67	195.80
	0.0200	0.2426	0.76811	0.75857	193.43	195.67
	0.0305	0.3738	0.76760	0.75814	193.44	195.39
	0.0406	0.5024	0.76714	0.75771	193.37	195.34
	0.0511	0.6396	0.76665	0.75728	193.37	195.28
	0.0596	0.7526	0.76635	0.75693	193.15	195.26
	0.0693	0.8845	0.76593	0.75656	193.14	195.19
	0.0787	1.0153	0.76554	0.75618	193.10	195.19
	0.0878	1.1444	0.76516	0.75584	193.09	195.15
TBA	0.0103	0.1237	0.76892	0.75938	243.51	246.04
	0.0216	0.2623	0.76875	0.75925	243.36	245.91
	0.0318	0.3900	0.76865	0.75917	243.09	245.71

Table 3 (*Continued*)

x_B	m (mol kg^{-1})	ρ (g cm^{-3})		$V_{\phi,B}$ (cm^3 mol^{-1})	
		303.15 K	313.15 K	303.15 K	313.15 K
0.0402	0.4980	0.76857	0.75909	242.96	245.67
0.0516	0.6463	0.76846	0.75899	242.87	245.63
0.0598	0.7554	0.76838	0.75897	242.84	245.48
0.0709	0.9067	0.76826	0.75892	242.83	245.38
0.0807	1.0431	0.76818	0.75891	242.78	245.25
0.0861	1.1190	0.76814	0.75899	242.75	245.03

due to destruction in H-bonded associated structure in amine is partly counter balanced by benzene–amine (NH–π) specific interactions. In case of solutions of trialkylamine in benzene, the value of $\bar{V}_B^{E,\infty}$ for TEA in benzene is smaller than that for TEA in cyclohexane while there is a very small change in the values of $\bar{V}_B^{E,\infty}$ for TPA and TBA in benzene compared to the TPA and TBA in cyclohexane solutions. It was observed that the excess molar volumes V^E and excess molar enthalpies H^E for benzene + trialkylamine [6–8,59,60,65] were comparatively more positive than the corresponding cyclohexane + trialkylamine systems [6–8,60–62] except V^E for TEA + C_6H_6. For latter mixture reverse is the case. This suggests that except TEA–benzene, the negative-contribution because of trialkylamine–benzene specific interactions is smaller than the positive contributions due to destruction of π–π interactions in the benzene molecules. The specific interaction of benzene is stronger with TEA than that with TPA and TBA. Barbosa and Lampreia [14] in studying partial molar volumes of trialkylamines in benzene also found that TEA behaves differently than other higher trialkylamines.

Transference functions have often been used to clarify the influence of solvent characteristics in thermodynamic quantities. The partial molar volumes at infinite dilution of transference from cyclohexane to benzene, $\Delta\bar{V}_{B,tr}^{\infty}$ ($C_6H_{12} \rightarrow C_6H_6$) calculated as $\bar{V}_B^{\infty}(C_6H_6) - \bar{V}_B^{\infty}(C_6H_{12})$ are included in last column of Table 5. As can be seen, the negative transference volume from cyclohexane to benzene again shows specific interactions between the primary and secondary amine group with benzene [14,60]. In case of tertiary amine, except for TEA, the negative contribution due to specific interactions between the tertiary amine-group with benzene is masked by the positive contribution due to destruction of benzene structure. This graded behaviour is consistent with viscosity of amine solutions in benzene [41].

4. Theories

4.1. Group contributions

The focus has been placed on to estimate contributions of different groups in organic molecules at 298.15 K only [19,24,25]. We have studied amine solutions in cyclohexane and benzene at 303.15 and 313.15 K. Therefore, it is essential first to determine contributions to partial molar volumes of the methyl, methylene, and amine (primary, secondary and tertiary) groups at 303.15 and 313.15 K in cyclohexane and benzene solutions and in pure compounds using simple additive scheme. Different methods have been used to determine alkyl group contributions [20,22–25] in water and organic solvents through the equation

$$\bar{V}_B^{\infty} = A + \Sigma_i n_i B_i + C \tag{4}$$

where B_i is the contribution of the ith group, which appears n_i times in the solute molecule, A is a constant covolume term, and C is a correction term for polyfunctional compounds and peculiar structures. Yoshimura et al. [22,23] and Nishimura et al. [24] have demonstrated that A is equal to $\kappa_T RT$ due to motion of the molecules along the translational degrees of freedom, where κ_T is the isothermal compressibility of the solvent. C for present amines is zero. In order to obtain alkyl and amine group contributions at 303.15 and 313.15 K, partial molar volume for n-alkane and alkylamine in cyclohexane and benzene and molar volumes of pure n-alkane and alkylamine at corresponding temperatures are needed. In absence of direct partial molar volume data at 303.15 and 313.15 K for n-alkane in cyclohexane and benzene, partial molar volume for n-alkane in cyclohexane and benzene at 303.15 and 313.15 K has been determined from the very accurate excess molar volumes data of binary mixtures of homologous series of n-alkane with cyclohexane [66,67] and benzene [68]. The linear dependence of partial molar volume on the number of carbon atoms n_C, for the n-alkane homologous series in cyclohexane and benzene at 303.15 and 313.15 K, allowed us to identify the slopes, b, of Eq. (5) with the contribution of the –CH_2 group, and the intercepts, a, with the combination of group contributions as shown in Eq. (6)

$$\bar{V}_B^{\infty} = a + bn_C \tag{5}$$

$$a_{HC} = -2\bar{V}_{CH_2}^{\infty} + 2\bar{V}_{CH_3}^{\infty} + \kappa_T RT \tag{6}$$

For –NH_2, >NH and >N– groups following expression were used:

$$a_{PA} = -\bar{V}_{CH_2}^{\infty} + \bar{V}_{CH_3}^{\infty} + \bar{V}_{NH_2}^{\infty} + \kappa_T RT \tag{7}$$

$$a_{SA} = -2\bar{V}_{CH_2}^{\infty} + 2\bar{V}_{CH_3}^{\infty} + \bar{V}_{NH}^{\infty} + \kappa_T RT \tag{8}$$

$$a_{TA} = -3\bar{V}_{CH_2}^{\infty} + 3\bar{V}_{CH_3}^{\infty} + \bar{V}_{N}^{\infty} + \kappa_T RT \tag{9}$$

Table 4
Densities ρ and apparent molar volumes $V_{\phi,\mathrm{B}}$ of amine solution in benzene

	x_B	m (mol kg^{-1})	ρ (g cm^{-3})		$V_{\phi,\mathrm{B}}$ (cm^3 mol^{-1})	
			303.15 K	313.15 K	303.15 K	313.15 K
PA	0.0079	0.1015	0.86707	0.85639	84.26	85.11
	0.0186	0.2432	0.86541	0.85475	84.12	85.09
	0.0280	0.3681	0.86391	0.85334	84.32	85.04
	0.0366	0.4869	0.86258	0.85202	84.21	85.03
	0.0470	0.6309	0.86086	0.85044	84.44	85.04
	0.0579	0.7868	0.85918	0.84878	84.34	85.02
	0.0659	0.9025	0.85786	0.84756	84.43	85.03
	0.0759	1.0519	0.85637	0.84603	84.28	85.01
	0.0844	1.1795	0.85497	0.84473	84.36	85.03
BA	0.0094	0.1209	0.86680	0.85612	100.86	101.99
	0.0195	0.2544	0.86519	0.85455	100.81	101.90
	0.0284	0.3744	0.86377	0.85317	100.81	101.86
	0.0380	0.5054	0.86230	0.85170	100.67	101.83
	0.0480	0.6454	0.86074	0.85016	100.65	101.82
	0.0588	0.8000	0.85906	0.84850	100.62	101.81
	0.0669	0.9178	0.85780	0.84727	100.63	101.80
	0.0764	1.0593	0.85632	0.84582	100.62	101.79
	0.0859	1.2024	0.85484	0.84440	100.64	101.77
DPA	0.0105	0.1359	0.86597	0.85538	139.65	140.46
	0.0207	0.2709	0.86374	0.85326	139.60	140.44
	0.0306	0.4041	0.86167	0.85124	139.36	140.40
	0.0390	0.5190	0.85991	0.84955	139.33	140.37
	0.0508	0.6849	0.85750	0.84719	139.18	140.34
	0.0614	0.8372	0.85536	0.84511	139.11	140.30
	0.0723	0.9980	0.85317	0.84300	139.07	140.26
	0.0812	1.1315	0.85142	0.84129	139.03	140.25
	0.0917	1.2926	0.84936	0.83928	139.00	140.25
DBA	0.0108	0.1394	0.86575	0.85517	173.63	174.82
	0.0201	0.2624	0.86358	0.85313	173.66	174.74
	0.0300	0.3950	0.86133	0.85100	173.65	174.74
	0.0390	0.5185	0.85932	0.84909	173.62	174.73
	0.0487	0.6547	0.85718	0.84705	173.60	174.75
	0.0593	0.8069	0.85488	0.84485	173.60	174.78
	0.0689	0.9463	0.85286	0.84292	173.58	174.78
	0.0797	1.1076	0.85062	0.84079	173.56	174.76
	0.0892	1.2533	0.84869	0.83892	173.53	174.77
TEA	0.0102	0.1324	0.86585	0.85514	141.28	143.57
	0.0209	0.2734	0.86338	0.85262	141.11	143.54
	0.0311	0.4113	0.86103	0.85024	141.10	143.52
	0.0395	0.5272	0.85907	0.84831	141.21	143.48
	0.0501	0.6747	0.85675	0.84593	141.08	143.44
	0.0618	0.8435	0.85410	0.84331	141.15	143.40
	0.0712	0.9819	0.85195	0.84123	141.26	143.38
	0.0804	1.1194	0.85000	0.83927	141.18	143.31
	0.0919	1.2958	0.84745	0.83679	141.25	143.30
	0.1000	1.4217	0.84576	0.83508	141.22	143.28
TPA	0.0104	0.1344	0.86550	0.85485	193.25	195.40
	0.0206	0.2694	0.86282	0.85224	193.20	195.29
	0.0307	0.4051	0.86021	0.84971	193.29	195.30
	0.0402	0.5369	0.85787	0.84743	193.09	195.11
	0.0497	0.6702	0.85554	0.84518	193.09	195.06
	0.0596	0.8111	0.85315	0.84285	193.14	195.12
	0.0693	0.9537	0.85088	0.84066	193.10	195.05
	0.0788	1.0955	0.84869	0.83855	193.10	195.02
	0.0889	1.2496	0.84642	0.83635	193.09	195.00
TBA	0.0102	0.1316	0.86538	0.85476	243.71	246.18
	0.0206	0.2690	0.86254	0.85203	243.48	245.83
	0.0302	0.3987	0.86005	0.84961	243.22	245.63

Table 4 (*Continued*)

x_B	m (mol kg^{-1})	ρ (g cm^{-3})		$V_{\phi,B}$ (cm^3 mol^{-1})	
		303.15 K	313.15 K	303.15 K	313.15 K
0.0404	0.5395	0.85748	0.84712	243.09	245.51
0.0499	0.6721	0.85512	0.84487	243.16	245.50
0.0596	0.8108	0.85277	0.84265	243.22	245.46
0.0698	0.9603	0.85040	0.84038	243.20	245.42
0.0796	1.1070	0.84822	0.83828	243.14	245.37
0.0874	1.2266	0.84653	0.83665	243.10	245.33

Subscripts HC, PA, SA, and TA stand for alkane hydrocarbon, primary amine, secondary amine and tertiary amine. The group contributions as presented in Table 6 were determined by a least-square fitting of experimental data to Eq. (6) and using expressions (6)–(9) as described by Lampreia and Barbosa [15]. The values of κ_T used were taken from literature [49,56]. In order to verify our present method we have also obtained $\bar{V}^{\infty}_{CH_3}$ and $\bar{V}^{\infty}_{CH_2}$ group contributions at 298.15 K and compared with the literature data [14,22,69]. The agreement between present values and literature values is very good. In order to compare the contributions of $\bar{V}^{\infty}_{CH_3}$ and $\bar{V}^{\infty}_{CH_2}$ groups in pure compounds and in cyclohexane and benzene solutions, the contributions of $\bar{V}^{\infty}_{CH_3}$ and $\bar{V}^{\infty}_{CH_2}$ groups in pure compounds were determined from liquid molar volumes at corresponding temperatures taken from literature [49,56].

It can be seen from Table 6, the values of contributions of $\bar{V}^{\infty}_{CH_3}$ and $\bar{V}^{\infty}_{CH_2}$ to partial molar volumes are relatively less sensitive with the type of solvent, while for $\bar{V}^{\infty}_{NH_2}$, $\bar{V}^{\infty}_{>NH}$, and $\bar{V}^{\infty}_{>N-}$ they are highly sensitive to type of solvent. The values of $\bar{V}^{\infty}_{NH_2}$, $\bar{V}^{\infty}_{>NH}$, and $\bar{V}^{\infty}_{>N-}$ are highest in cyclohexane solvent and some what reduced in benzene. Table 7 compares the observed $\bar{V}^{\infty}_B$ with calculated, by using group contributions given in Table 6.

4.2. Terasawa model

According to Terasawa et al. [20] 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 1 mol of solute B to

Table 5
Partial molar volume $\bar{V}^{\infty}_B$, coefficient S_V and standard deviation σ of Eq. (3) for apparent molar volume of amines $V_{\phi,B}$ along with limiting value of excess partial molar volume $\bar{V}^{E,\infty}_B$ and volume of transference from cyclohexane to benzene $\Delta\bar{V}^{\infty}_{B,tr}$

Solute	Temperature (K)	$\bar{V}^{\infty}_B$ (cm^3 mol^{-1})	S_v (cm^3 kg mol^{-2})	σ (cm^3 mol^{-1})	$\bar{V}^{E,\infty}_B$ (cm^{-3} mol^{-1})	$\Delta\bar{V}^{\infty}_{B,tr}$ (cm^{-3} mol^{-1})
Cyclohexane						
PA	303.15	88.44	−0.71	0.13	4.74	
	313.15	89.18	−0.76	0.15	4.28	
BA	303.15	105.48	−0.55	0.11	5.11	
	313.15	106.77	−0.69	0.13	5.09	
DPA	303.15	141.45	−0.33	0.06	3.07	
	313.15	143.62	−0.51	0.03	3.41	
DBA	303.15	175.53	−0.96	0.12	3.74	
	313.15	176.95	−0.26	0.06	3.10	
TEA	303.15	143.81	−0.58	0.06	2.98	
	313.15	145.63	−0.64	0.06	2.94	
TPA	303.15	193.65	−0.54	0.07	2.42	
	313.15	195.73	−0.59	0.10	2.25	
TBA	303.15	243.46	−0.71	0.12	2.83	
	313.15	246.14	−0.89	0.07	3.34	
Benzene						
PA	303.15	84.21	0.15	0.09	0.49	−4.25
	313.15	85.09	−0.07	0.02	0.17	−4.11
BA	303.15	100.85	−0.23	0.05	0.48	−4.63
	313.15	101.95	−0.16	0.03	0.25	−4.84
DPA	303.15	139.66	−0.58	0.07	1.29	−1.78
	313.15	140.48	−0.20	0.01	0.27	−3.14
DBA	303.15	173.67	−0.10	0.02	1.87	−1.87
	313.15	174.76	0.00	0.03	0.90	−2.20
TEA	303.15	141.15	0.04	0.07	0.30	−2.68
	313.15	143.61	−0.21	0.01	0.90	−2.04
TPA	303.15	193.25	−0.15	0.06	2.02	−0.40
	313.15	195.38	−0.34	0.06	1.90	−0.35
TBA	303.15	243.53	−0.40	0.14	2.90	0.07
	313.15	246.01	−0.63	0.13	3.21	−0.13

Table 6
Average group contribution to partial molar volume in neat components[a], cyclohexane and benzene

	Temperature (K)	$\bar{V}^{\infty}_{CH_3}$ (cm^3 mol^{-1})	$\bar{V}^{\infty}_{CH_2}$ (cm^3 mol^{-1})	$\bar{V}^{\infty}_{NH_2}$ (cm^3 mol^{-1})	$\bar{V}^{\infty}_{>NH}$ (cm^3 mol^{-1})	$\bar{V}^{\infty}_{>N-}$ (cm^3 mol^{-1})
Pure components	298.15	30.81	16.52	16.02	6.29	−3.42
	303.15	31.02	16.63	16.29	6.79	−4.47
	313.15	31.45	16.74	16.89	7.74	−4.99
	298.15[b]	31.5 ± 0.2	16.45			
	298.15[c]	31.5 ± 0.2	16.51			
Cyclohexane	298.15	31.67	16.64	21.67	9.38	−4.28
	298.15[d]	33.80	15.76			
	303.15	31.99	16.66	20.33	8.33	−5.28
	313.15	32.54	16.72	20.29	8.27	−5.41
Benzene	298.15	32.07	16.77	18.18	6.75	−6.20
	298.15[e]	33.3 ± 0.2	16.82 ± 0.02		4.6 ± 0.3	−8.3 ± 0.3
	303.15	32.32	16.82	15.64	5.20	−7.75
	313.15	32.50	16.99	15.46	4.61	−7.30

[a] Data of pure alkane, primary, secondary and tertiary amines were considered.
[b] Ref. [22].
[c] Refs. [14,69].
[d] Ref. [13] uncorrected for translational motion of solute.
[e] Ref. [14].

solvent)

$$\bar{V}^{\infty}_{B} = V_{W,B} + \bar{V}_{void,B} \tag{10}$$

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. $\bar{V}_{void,B}$ is a measure of the volume of the empty spaces or of the interstices between the solute molecular surface and the solvent molecules, and contains all the effects due to solute–solvent interactions. Several procedures have been used to calculate the intrinsic volumes, above all those of Bondi [70] and Edward [71]. Recently, Lepori and Gianni [25] in the frame work of a group contributions to the intrinsic volume, which over comes some inconsistencies in Bondi's formulations and yield better representation of $V_{W,B}$ volumes of organic compounds. The intrinsic volumes of the solutes calculated using Lepori and Gianni's method are reported in Table 8 together with the $\bar{V}_{void,B}$ values obtained by Eq. (10). As can be seen, $\bar{V}_{void,B}$ 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 $\tilde{V}_{void,B} = \bar{V}_{viod,B}/V_{W,B}$ for common amine decreases in the order: cyclohexane > benzene, except in case of tripropylamine and tributylamine. For latter two tertiary amines values of $\tilde{V}_{void,B}$ are almost identical. According to Patterson and Delmas [72], the changes in volumetric properties depend upon (i) a free volume contribution, (ii) an internal pressure contribution and (iii) an interactional contribution. As explained earlier, in case of these tertiary amines, the specific interactions between the tertiary amine-group with

Table 7
Comparison of experimental and calculated partial molar volume $\bar{V}^{\infty}_{B}$ (cm^3 mol^{-1}) of amines from group contribution parameters given in Table 6

Solute	$\bar{V}^{\infty}_{B}$ at 303.15 K			$\bar{V}^{\infty}_{B}$ at 313.15 K		
	Exp.	Cal.	Dif.	Exp.	Cal.	Dif.
Cyclohexane						
$C_3H_7NH_2$	88.44	88.59	−0.15	89.18	89.62	−0.44
$C_4H_9NH_2$	105.48	105.25	0.23	106.77	106.34	0.43
$(C_3H_7)_2NH$	141.45	141.90	−0.45	143.62	143.58	0.04
$(C_4H_9)_2NH$	175.53	175.22	0.31	176.95	177.02	−0.07
$(C_2H_5)_3N$	143.81	143.62	0.19	145.63	145.72	−0.09
$(C_3H_7)_3N$	193.65	193.60	0.05	195.73	195.88	−0.15
$(C_4H_9)_3N$	243.46	243.58	−0.12	246.14	246.04	0.10
Benzene						
$C_3H_7NH_2$	84.21	84.14	0.07	85.09	85.00	0.09
$C_4H_9NH_2$	100.85	100.96	−0.11	101.95	101.99	−0.04
$(C_3H_7)_2NH$	139.66	139.66	0.00	140.48	140.63	−0.52
$(C_4H_9)_2NH$	173.67	173.30	0.37	174.76	174.61	0.15
$(C_2H_5)_3N$	141.15	142.21	−1.06	143.61	144.23	−0.62
$(C_3H_7)_3N$	193.25	192.67	0.58	195.38	195.20	0.18
$(C_4H_9)_3N$	243.53	243.13	0.40	246.01	246.17	−0.16

Table 8
Intrinsic van der Waals volumes ($V_{W,B}$) and void volumes ($\bar{V}_{void,B}$) of amines in cyclohexane and benzene at 303.15 K

Solutes	$V_{W,B}$ ($cm^3\,mol^{-1}$)	$\bar{V}_{void,B}$ ($cm^3\,mol^{-1}$)	
		C_6H_{12}	C_6H_6
$C_3H_7NH_2$	44.37	44.07	39.84
$C_4H_9NH_2$	54.46	51.02	46.39
$(C_3H_7)_2NH$	74.96	66.49	64.70
$(C_4H_9)_2NH$	95.14	80.39	78.53
$(C_2H_5)_3N$	75.21	68.60	66.06
$(C_3H_7)_3N$	105.48	88.17	87.77
$(C_4H_9)_3N$	135.75	107.71	107.78

benzene are masked by the destruction of benzene structure. It seems that for these two-amine solutions in cyclohexane and benzene, the net volumetric changes at infinite dilutions are almost identical.

4.3. The scaled particle theory

Using the scaled particle theory [28] one can derive in a similar way to Terasawa model, a comparative measure of the specific interactions from a different conception of the separation of the various contributions to $\bar{V}^{\infty}$. The SPT expression for $\bar{V}^{\infty}$ is

$$\bar{V}^{\infty} = \bar{V}_{cav} + \Delta\bar{V}_i + k_T RT \tag{11}$$

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 $k_T RT$ changes of standard state between the gas and solution. Application of this to amines and hydrocarbons with the same $\bar{V}_{cav}$, and subsequent substraction leads to

$$\bar{I}_{S-S} = \bar{V}_B^{\infty} - \bar{V}_{HC}^{\infty} = \Delta\bar{V}_{i,B} - \Delta\bar{V}_{i,HC} \tag{12}$$

$$\Delta\bar{I}_{S-S,tr} = \bar{I}_{S-S}(C_6H_6) - \bar{I}_{S-S}(C_6H_{12}) \tag{13}$$

$\bar{I}_{S-S}$ is a new interaction parameter and $\Delta\bar{I}_{S-S,tr}$ represent interaction parameter of transference from cyclohexane to benzene. In order to obtain this interaction contribution it is necessary to calculate $\bar{V}_{cav}$ for the amine and hydrocarbon molecules under consideration.

From SPT, $\bar{V}_{cav}$ is a known function of temperature, molar volume, isothermal compressibility, hard sphere diameter of a solvent and solute σ_A and σ_B

$$\bar{V}_{cav} = 0.3153\sigma_B^3 + A\sigma_B^2 + B\sigma_B + C \tag{14}$$

where

$$A = \frac{3k_T RT(y + 2y^2)}{(1-y)^3\sigma_A^2} \tag{15}$$

$$B = \frac{3k_T RTy}{(1-y)^2\sigma_A} \tag{16}$$

$$C = \frac{k_T RTy}{1-y} \tag{17}$$

where y is defied as

$$y = \frac{N_A\pi\sigma_A^3}{6V} \tag{18}$$

y is the volume occupied by 1 mol of hard-sphere solvent molecules to the molar volume of the solvent.

To consider the scaled particle theory, the hard sphere diameters for the solvent and solute σ_A and σ_B are required. As can be seen from the above expressions (14)–(18), $\bar{V}_{cav}$ is extremely sensitive to the choice of σ_A; in fact, it appears as the sixth power of this parameter. As per the theory σ has a very precise physical meaning and can be determined from independent measurements such as viscosities, second virial coefficient, compressibilities, surface tensions and solubilities. Different sets of molecular diameters are not in agreement, thus leading to very different $\bar{V}_{cav}$ and $\Delta\bar{V}_i$ values. As suggested by Barbosa and Lampreia [14], from extensive data analysis, that σ derived from Mayer's method [48] using molar volume V and isothermal compressibility k_T are consistent with the SPT model. Hence, we have derived σ from molar volumes V^0 and isothermal compressibilities k_T [49,56,58] at 303.15 and 313.15 K using Mayer's method [48]. The results are included in last column of Table 1. $\bar{V}_{cav}$ for the amines under study in different solvents were then calculated and $\Delta\bar{V}_i$ derived. Table 9 shows $\bar{V}_{cav}$, $\Delta\bar{V}_{i,B}$, and $\Delta\bar{V}_{i,HC}$, $\bar{I}_{S-S}$ and $\Delta\bar{I}_{S-S,tr}$ for amines under study. The uncertainty in $\bar{V}_{cav}$ calculation 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. In present case it is observed the $\bar{V}_{cav}$ for common amine decreases in the sequence cyclohexane > benzene and increases with temperature. The interaction parameters $\bar{I}_{S-S}$ and $\Delta\bar{I}_{S-S,tr}$ will be discussed jointly with corresponding parameter presented in next section through hard sphere theory.

4.4. The hard sphere theory

Klapper [73] pointed out for a spherical and non-polar solute, the geometrical packing effect is entirely responsible for its volumetric behaviour in solution. In case of hard sphere mixtures, an exact expression for $\bar{V}_B^{\infty}$(HS) has been derived by Lee [26]. Lampreia and Barbosa [15] found its usefulness to estimate contribution of specific solute–solvent interaction to partial molar volume. The expression for limiting partial molar volume of hard sphere mixture [15] is

$$\frac{\bar{V}_B^{\infty}(\mathrm{HS})}{V_A^*} = C\left[\left(\frac{\sigma_B}{\sigma_A}\right)^3 + 3\alpha\left(\frac{\sigma_B}{\sigma_A}\right)^2 + 3\alpha\beta\left(\frac{\sigma_B}{\sigma_A}\right) + \alpha\beta\gamma\right] \tag{19}$$

$$\alpha = \frac{1-y}{1+2y} \tag{20}$$

Table 9
The SPT cavity and interaction contribution to partial molar volumes of amines in cyclohexane and benzene

Solute	Temperature (K)	$\bar{V}_{\mathrm{cav}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$\Delta\bar{V}_{i,\mathrm{B}}$[a] ($\mathrm{cm^3\,mol^{-1}}$)	$\Delta\bar{V}_{i,\mathrm{HC}}$[b] ($\mathrm{cm^3\,mol^{-1}}$)	$\bar{I}_{\mathrm{S-S}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$\Delta\bar{I}_{\mathrm{S-S,tr}}$ ($\mathrm{cm^3\,mol^{-1}}$)
Cyclohexane						
PA	303.15	82.69	2.80	12.73	−9.93	
	313.15	84.64	1.22	12.55	−11.33	
BA	303.15	98.88	3.65	11.47	−7.82	
	313.15	101.19	2.26	10.65	−8.39	
DPA	303.15	131.54	6.95	9.25	−2.30	
	313.15	134.33	5.97	7.34	−1.37	
DBA	303.15	165.69	6.89	7.38	−0.49	
	313.15	170.60	3.03	4.48	−1.45	
TEA	303.15	136.12	4.73	8.97	−4.24	
	313.15	139.13	3.17	5.25	−2.08	
TPA	303.15	179.69	11.01	6.74	4.27	
	313.15	183.64	8.78	3.88	4.90	
TBA	303.15	227.93	12.58	5.17	7.41	
	313.15	232.83	9.99	2.82	7.17	
Benzene						
PA	303.15	79.31	2.36	18.37	−16.01	−6.08
	313.15	80.86	1.41	16.33	−14.92	−3.59
BA	303.15	95.09	3.22	18.10	−14.88	−7.06
	313.15	96.94	2.18	15.50	−13.32	−4.93
DPA	303.15	126.98	10.13	17.87	−7.74	−5.44
	313.15	129.21	8.44	14.20	−5.76	−4.37
DBA	303.15	160.39	10.74	18.06	−7.32	−5.95
	313.15	164.62	7.04	13.80	−6.76	−5.39
TEA	303.15	131.45	7.15	17.87	−10.72	−7.02
	313.15	134.38	6.28	12.55	−9.27	−7.19
TPA	303.15	174.10	16.61	18.27	−1.66	−3.06
	313.15	177.35	15.20	13.91	−1.39	−3.51
TBA	303.15	221.40	19.59	19.57	−0.02	−7.39
	313.15	225.48	17.70	15.25	−2.45	−4.73

$$\beta = \frac{1-y}{1+2y-hy^2} \tag{21}$$

$$\gamma = \frac{1-y}{y} \tag{22}$$

$$C = (1+3\alpha+3\alpha\beta+\alpha\beta\gamma)^{-1} \tag{23}$$

σ_{A} and σ_{B} are the hard sphere diameters of the solvent and solute respectively, y is the average packing density of the pure solvent ($y = N_{\mathrm{A}}\pi\sigma_{\mathrm{A}}^3/6V_{\mathrm{A}}^*$) 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 $\bar{V}_{\mathrm{B}}^{\infty}(\mathrm{HS})$ of size and packing density of the solvent, Eq. (19) can be transferred into

$$\frac{\bar{V}_{\mathrm{B}}^{\infty}(\mathrm{HS})}{V_{\mathrm{B}}(\mathrm{HS})} = \frac{C}{y}\left[1+3\alpha\left(\frac{\sigma_{\mathrm{A}}}{\sigma_{\mathrm{B}}}\right)+3\alpha\beta\left(\frac{\sigma_{\mathrm{A}}}{\sigma_{\mathrm{B}}}\right)^2+\alpha\beta\gamma\left(\frac{\sigma_{\mathrm{A}}}{\sigma_{\mathrm{B}}}\right)^3\right] \tag{24}$$

where $V_{\mathrm{B}}(\mathrm{HS}) = N_{\mathrm{A}}\pi\sigma_{\mathrm{B}}^3/6$ is the molar hard sphere volume of solute B.

The difference between experimental and HS model $\bar{V}_{\mathrm{B}}^{\infty}(\mathrm{HS})$ values, $\Delta\bar{V}_{\mathrm{B}}^{\infty}(\mathrm{HS}) = \bar{V}_{\mathrm{B}}^{\infty}(\mathrm{exp}) - \bar{V}_{\mathrm{B}}^{\infty}(\mathrm{HS})$ were considered corrective terms arising from non-spherical shape of the solute molecules and from molecular interactions present in solution.

As suggested by Lampreia and Barbosa [15], one can assume that interactions acting in the systems studied are composed of two contributions: one caused by the amine group and another due to aliphatic part of the molecule. As a common procedure [14], linear hydrocarbons were selected as reference molecules to separate the effects on volume of the two types of interactions. To obtain the contribution of interactions to limiting partial molar volume Barbosa and Lampreia [14] defined the quantity $\bar{R}_{\mathrm{S-S}}$ by

$$\bar{R}_{\mathrm{S-S}} = \Delta\bar{V}_{i,\mathrm{B}}^{\infty}(\mathrm{HS}) - \Delta\bar{V}_{i,\mathrm{HC}}^{\infty}(\mathrm{HS}) \tag{25}$$

where $\Delta\bar{V}_{i,\mathrm{HC}}^{\infty}(\mathrm{HS})$ is the corrective term, for the linear hydrocarbon with the same $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}}$ as the amine considered. The required values of $\bar{V}_{\mathrm{B}}^{\infty}(\mathrm{exp})$ for the hydrocarbons were estimated from a linear relation $\bar{V}_{\mathrm{B}}^{\infty}$ versus V_{w} for these compounds in cyclohexane and benzene. Contributions to the limiting partial molar volume of transference from cyclohexane to benzene were estimated as

$$\Delta\bar{R}_{\mathrm{S-S,tr}} = \bar{R}_{\mathrm{S-S}}(C_6H_6) - \bar{R}_{\mathrm{S-S}}(C_6H_{12}) \tag{26}$$

Table 10
Reference volume and interaction contribution to the limiting partial molar volumes of amines in cyclohexane and benzene

Compound	Temperature (K)	$\bar{V}_{\mathrm{B}}^{\infty}$(HS) ($\mathrm{cm^3\,mol^{-1}}$)	$\Delta\bar{V}_{i,\mathrm{B}}^{\infty}$(HS) ($\mathrm{cm^3\,mol^{-1}}$)	$\Delta\bar{V}_{i,\mathrm{HC}}^{\infty}$(HS) ($\mathrm{cm^3\,mol^{-1}}$)	$\bar{R}_{\mathrm{S-S}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$\Delta\bar{R}_{\mathrm{S-S,tr}}$ ($\mathrm{cm^3\,mol^{-1}}$)
Cyclohexane						
PA	303.15	84.80	3.64	9.73	−6.09	
	313.15	85.29	3.90	11.65	−7.76	
BA	303.15	100.64	4.84	10.20	−5.36	
	313.15	101.24	5.53	12.42	−6.89	
DPA	303.15	132.60	8.85	11.39	−2.54	
	313.15	133.20	10.42	14.42	−4.00	
DBA	303.15	167.37	8.16	9.24	−1.08	
	313.15	168.20	8.75	12.85	−4.10	
TEA	303.15	137.07	6.74	7.32	−0.58	
	313.15	137.83	7.79	6.56	1.12	
TPA	303.15	179.68	13.97	13.65	0.32	
	313.15	180.79	14.94	17.39	−2.45	
TBA	303.15	226.85	16.61	15.42	1.19	
	313.15	228.32	17.82	20.01	−2.19	
Benzene						
PA	303.15	80.87	3.34	14.11	−10.77	−4.68
	313.15	81.09	3.61	15.72	−12.11	−4.35
BA	303.15	96.30	4.55	15.93	−11.38	−6.02
	313.15	96.60	5.35	17.20	−11.85	−4.96
DPA	303.15	127.48	12.18	19.81	−7.63	−5.09
	313.15	127.74	12.74	20.58	−7.84	−3.84
DBA	303.15	161.48	12.19	20.32	−8.13	−7.05
	313.15	161.93	12.84	20.37	−7.54	−3.44
TEA	303.15	131.85	9.30	15.87	−6.57	−6.52
	313.15	132.26	11.21	15.45	−6.57	−4.24
TPA	303.15	173.53	19.72	25.95	−6.23	−6.55
	313.15	174.23	21.15	25.48	−4.33	−1.88
TBA	303.15	219.76	23.77	31.49	−7.72	−8.91
	313.15	220.76	25.25	29.92	−4.67	−2.48

The values of $\bar{V}_{\mathrm{B}}^{\infty}$(HS), $\Delta\bar{V}_{i,\mathrm{B}}^{\infty}$(HS), $\Delta\bar{V}_{i,\mathrm{HC}}^{\infty}$(HS), $\bar{R}_{\mathrm{S-S}}$, and $\Delta\bar{R}_{\mathrm{S-S,tr}}$ for HST are listed in Table 10.

Now we shall discuss the importance of sign and magnitude of interaction parameters $\bar{I}_{\mathrm{S-S}}$ and $\Delta\bar{I}_{\mathrm{S-S,tr}}$ from the SPT and $\bar{R}_{\mathrm{S-S}}$ and $\Delta\bar{R}_{\mathrm{S-S,tr}}$ from the HST to shed light on the specific interactions. It is interesting to compare $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ obtained from the SPT and the HST, both the values show similar trend, however, quantitative agreement is not so good.

It is proposed by Barbosa and Lampreia [14,15] through analysis of results of amine solutions in benzene and methanol that the values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ represent specific interactions between solute and solvent. They found magnitude of negative values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ decreases in the order: secondary amine > tertiary amine in benzene and the values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ are twice in methanol than that in the benzene. From these results they concluded that the negative values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ represent the strength of specific interactions.

In the present study in addition to the benzene solutions of amines, we have also analysed partial molar volume data in cyclohexane. Except for some trialkylamines, the values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ are also found to be negative in cyclohexane solutions. According to the suggestions of Barbosa and Lampreia, the observed negative values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ point towards the existence of specific interactions in amines and cyclohexane. This is untrue, since no specific interactions between amine and cyclohexane exists. On the contrary there is a reduction in the dipolar order by adding the cyclohexane molecules to amines. The negative values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ may be related to the non-spherical shape of the molecules. Hence, the more negative values of interaction parameters $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$ in benzene, with reference to cyclohexane solutions may be said to represent specific interactions between amine and benzene, as found by the partial molar volumes at infinite dilution of transference $\Delta\bar{V}_{\mathrm{B,tr}}^{\infty}$ from cyclohexane to benzene. Thus, to obtain specific interactions, it would be better to analyse $\Delta\bar{I}_{\mathrm{S-S,tr}}$ and $\Delta\bar{R}_{\mathrm{S-S,tr}}$ of transference from cyclohexane to benzene or to any other solvent. The negative values of $\Delta\bar{I}_{\mathrm{S-S,tr}}$ and $\Delta\bar{R}_{\mathrm{S-S,tr}}$ represent specific interactions instead of negative values of $\bar{I}_{\mathrm{S-S}}$ and $\bar{R}_{\mathrm{S-S}}$.

4.5. The Flory theory and the ERAS model

The assumption made in frame-work of the ERAS model [30,31] include the self-association of amines (B) according to the following reaction scheme:

$$\mathrm{B}_n + \mathrm{B} \overset{K_{\mathrm{B}}}{\longleftrightarrow} \mathrm{B}_{n+1} \qquad (27)$$

The cross-association between B and A (benzene) molecules is represented by

$$B_n + A \overset{K_{AB}}{\longleftrightarrow} AB_n \tag{28}$$

where n is the degree of self-association, ranging from 1 to ∞. The association constants K_i (i = B, AB) are assumed to be independent of the chain length. Their temperature dependence is given by

$$K_i = K_0 \exp\left[-\left(\frac{\Delta h_i^*}{R}\right)\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{29}$$

where K_0 is the equilibrium constant at the standard temperature T_0 (298.15 K), R the gas constant and Δh_i^* the enthalpy for the reactions given by Eqs. (27) and (28), which corresponds to the hydrogen bond energy. These reactions are also characterized by the volume change Δv_i^*, related to the formation of the linear chains.

The essential property of the EARS-model is that the excess functions H^E and V^E are split into a chemical and a physical contribution. The expressions for excess molar volumes V^E of the ERAS model extended to the two-block approach of cross association [74] are given by [31,35]

$$V^E_{\text{chem}} = \tilde{V}_M \left[x_B K_B \, \Delta v_B^*(\phi_{B1} - \phi^0_{B1}) + x_B K_{AB}\, \Delta v^*_{AB} \left\{\frac{\phi_{A1}(1-K_B\phi_{B1})}{(V_A/V_B)+K_{AB}\phi_{A1}}\right\}\right] \tag{30}$$

$$V^E_{\text{phy}} = (x_A V_A^* + x_B V_B^*)(\tilde{V}_M - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B) \tag{31}$$

$$V^E_{\text{ERAS}} = V^E_{\text{chem}} + V^E_{\text{phy}} \tag{32}$$

Δh^*_{AB} is hydrogen bond energy from the cross association. ϕ_{A1} is hard core volume fraction of benzene and ϕ_{B1} is the hard core volume fraction of the monomeric amine in the mixture. They have been calculated numerically from the solution of the following coupled equations:

$$\phi_A = \phi_{A1}\left[1 + \frac{K_{AB}\phi_{B1}}{1-K_B\phi_{B1}}\right] \tag{33}$$

$$\phi_B = \frac{\phi_{B1}}{(1-K_B\phi_{B1})^2}\left[1 + \frac{V_B K_{AB}\phi_{A1}}{V_A}\right] \tag{34}$$

The apparent molar volume of alkylamine in cyclohexane and benzene are obtained through [33]

$$V_{\phi,B} = \frac{V^E_{\text{ERAS}} + x_B V^0_B}{x_B} \tag{35}$$

and hence, the physical and chemical contribution to apparent volume is given by

$$V^E_{\phi,B,\text{phy}} = \left(\frac{x_A V_A^*}{x_B} + V_B^*\right)[\tilde{V}_m - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B] \tag{36}$$

$$V^E_{\phi,B,\text{chem}} = \tilde{V}_m \left[K_B \, \Delta v_B^*(\phi_{B1} - \phi^0_{B1}) + K_A \, \Delta v^*_{AB} \frac{\phi_{A1}(1-K_B\phi_{B1})}{(V_A/V_B)+K_{AB}\phi_{A1}}\right] \tag{37}$$

and excess apparent molar volumes and apparent molar volumes are obtained as

$$V^E_{\phi,B} = V^E_{\phi,B,\text{phy}} + V^E_{\phi,B,\text{chem}} \tag{38}$$

$$V_{\phi,B} = V^0_B + V^E_{\phi,B,\text{phy}} + V^E_{\phi,B,\text{chem}} \tag{39}$$

and at the limit of infinite dilution V^E and x_B becomes zero, then

$$\bar{V}^{\infty,E}_{B,\text{chem}} = -\tilde{V}_B\left[K_A\,\Delta v_A \phi_{A1} - \frac{K_{AB}\,\Delta v_{AB}}{V^0_B/V^0_A + K_{AB}}\right] \tag{40}$$

$$\bar{V}^{\infty,E}_{B,\text{phy}} = V_A^*\left[\frac{P_A^*\tilde{T}_B^*}{P_B^*}\left(\frac{\tilde{T}_A}{\tilde{T}_B} - 1 + \frac{X_{AB}}{P_A^*}\right) \times \left(\frac{3\tilde{V}_B^2}{1-4\tilde{V}_B\tilde{T}_B}\right) + \tilde{V}_B - \tilde{V}_A\right] \tag{41}$$

add infinity to

$$\bar{V}^{\infty,E}_{B,\text{thr}} = \bar{V}^{\infty,E}_{B,\text{chem}} + \bar{V}^{\infty,E}_{B,\text{phy}} \tag{42}$$

The ERAS model expressions from (30) to (42) are applicable to alkylamine solutions in benzene. Further, the above expressions for the ERAS model with K_A and K_{AB} equal to zero reduce to the original Flory theory [32,75] and are applicable to trialkylamine solutions in cyclohexane. When the cross parameters K_{AB}, Δh^*_{AB}, and Δv^*_{AB} are zero but K_B, Δh^*_B, and Δv^*_B are non-zero in theoretical equations (30)–(42), then the ERAS model is applicable to the solutions of primary and secondary amines in cyclohexane.

Properties of pure components such as: molar volume V^0, thermal expansion coefficient α, isothermal compressibility κ_T, and surface to volume ratio S, equilibrium constants K, characteristic volume V^*, characteristic pressure P^*, the values of Δh^* and Δv^* for the pure components needed for application of the Flory theory and the ERAS model are summarized in Tables 1 and 11. ERAS parameters: characteristic volume V^*, characteristic pressure P^*, and the values of Δh^* and Δv^* for PA and BA were obtained from molar volume V^0, thermal expansion coefficient α, isothermal compressibility κ_T of PA and BA and experimental equimolar H^E [63] and V^E [60] of PA + C_6H_{12} and PA + C_6H_{12} mixtures.

4.5.1. Alkylamine solutions in cyclohexane

Since there is no cross-association between alkylamine and cyclohexane, the values of cross parameters K_{AB}, Δh^*_{AB} and Δv^*_{AB} are zero in theoretical equations (30)–(42). The only adjustable parameter required is the Flory interaction parameter X_{AB}. For trialkylamine solutions, compatible values of X_{AB} were obtained through the Flory theory by adjusting to experimental equimolar H^E. In case of primary amine

Table 11
Thermal expansion coefficient α, equilibrium constant K, reduction parameters V^* and P^*, surface to volume ratio S, enthalpy and volume of hydrogen bonding Δh^* and Δv^* for pure components

Compound	α (kK^{-1})	K	V^* (cm^3 mol^{-1})	P^* (J cm^{-3})	S (Å^{-1})	Δh^* (kJ mol^{-1})	Δv^* cm^3 mol^{-1}
C_6H_{12}	1.233[a]	0	84.33[a]	534[a]	1.315[b]	0	0
C_6H_6	1.233[a]	0	69.33[a]	623[a]	1.243[b]	0	0
PA	1.387[c]	1.52[d]	65.63	424	1.469[b]	−15.0[e]	−5.3[e]
BA	1.318[c]	0.87[f]	79.12	447	1.441[b]	−15.5[e]	−5.3[e]
DPA	1.216[c]	0.52[g]	107.89[c]	466[c]	1.412[b]	−7.5[c]	−4.2[c]
DBA	1.066[c]	0.15[h]	136.34[c]	467[c]	1.377[b]	−6.5[c]	−3.4[c]
TEA	1.355[c]	0	106.61[c]	475[c]	1.399[b]	0	0
TPA	1.078[c]	0	150.80[c]	439[c]	1.377[b]	0	0
TBA	0.914[c]	0	195.11[c]	414[c]	1.364[b]	0	0

[a] Ref. [76].
[b] Ref. [69].
[c] Ref. [49].
[d] Ref. [40].
[e] Obtained from H^E [63] and V^E [60] of PA + C_6H_{12} and BA + C_6H_{12} by ERAS model.
[f] Ref. [31].
[g] Ref. [77].
[h] Ref. [78].

solutions, optimum values of X_{AB} were estimated by simultaneously adjusting equimolar H^E and V^E. Since, we could not find H^E data in the literature for the mixtures of DPA and DBA with C_6H_{12}, for these latter solutions X_{AB} was estimated from the equimolar V^E values by the ERAS model. The values of interaction parameter X_{AB} are given in Table 12. The experimental and theoretical values of equimolar H^E and V^E are also included in Table 12. The values of X_{AB} are in the range from 6.1 to 7.9 J cm^{-3} for trialkylamine in cyclohexane, while from 11.0 to 19.5 J cm^{-3} for primary and secondary amines in cyclohexane.

The results of calculated excess apparent molar volume and their comparison with the experimental data are shown graphically in Fig. 1. The limiting values of partial molar volumes $\bar{V}_B^{\infty}$ and excess partial molar volumes $\bar{V}_B^{E,\infty}$ along with the physical $\bar{V}_{B,\text{phy}}^{\infty,E}$ and chemical $\bar{V}_{B,\text{chem}}^{\infty,E}$ contributions to $\bar{V}_B^{E,\infty}$ are summarized in Table 13.

Table 12
Flory and ERAS parameters and comparison of equimolar experimental and theoretical excess molar enthalpy and excess molar volume for amine solutions in cyclohexane and benzene

Solute	X_{AB} (J cm^{-3})	K_{AB}	Δh_{AB} (kJ mol^{-1})	Δv_{AB} (cm^3 mol^{-1})	H^E (J mol^{-1})		V^E (cm^3 mol^{-1})	
					Expt.	Ther.	Expt.	Ther.
Cyclohexane								
PA	18.0	0	0	0	1242[b]	1244	0.873[c]	0.866
BA	19.5	0	0	0	1131[b]	1154	0.822[c]	0.834
DPA	11.0	0	0	0			0.502[c]	0.497
DBA	16.0	0	0	0			0.529[c]	0.525
TEA	7.9	0	0	0	226[d]	224	0.264[c]	0.137
TPA	6.7	0	0	0	221[d]	222	0.362[c]	0.328
TBA	6.1	0	0	0	158[d]	158	0.390[c]	0.461
Benzene								
PA	6.0	0.65	−10.1	−6.0	594[e]	597	0.190[c]	0.186
BA	6.0	0.31	−9.5	−6.1	584[e]	588	0.283[c]	0.281
DPA	11.0	0.20	−5.0	−6.8	370[a]	376	0.136[c]	0.139
DBA	16.0	0.10	−5.0	−7.9	408[f]	403	0.318[c]	0.316
TEA	16.0	0.13	−3.0	−3.6	327[g]	326	0.005[c]	0.033
TPA	25.0	0.13	−3.3	−6.0	543[h]	545	0.440[c]	0.445
TBA	30.0	0.13	−3.0	−12.2	775[h]	781	0.551[c]	0.561

[a] Interpolated from diethylamine and dibutylamine H^E data [59,80].
[b] Ref. [63].
[c] Ref. [60].
[d] Ref. [62].
[e] Ref. [79].
[f] Ref. [80].
[g] Ref. [59].
[h] Ref. [65].

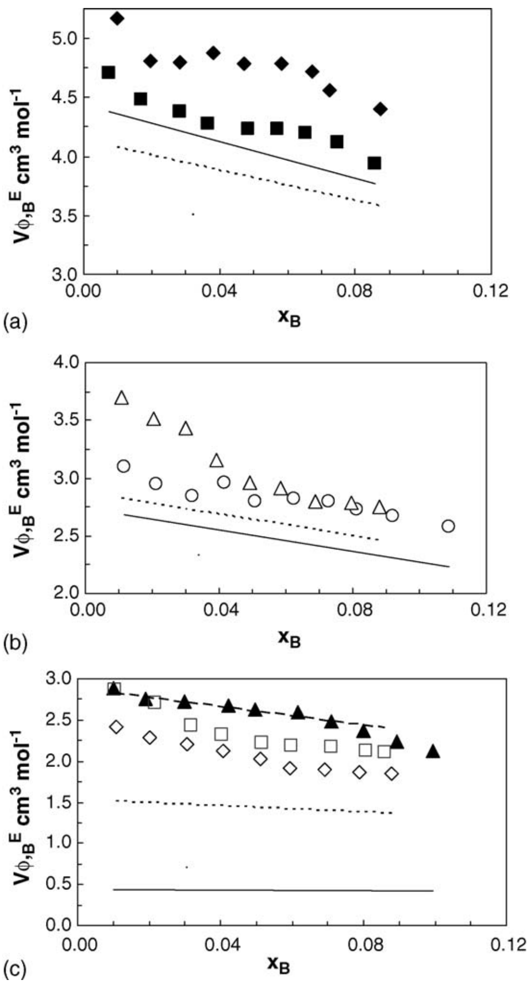

Fig. 1. Comparison of excess apparent molar volumes of (a) PA: expt. (■), ERAS (—); BA: expt. (⧫), ERAS (- - -), (b) DPA: expt. (○), ERAS (—); DBA: expt. (△), ERAS (- - -), (c) TEA: expt. (▲), Flory (—); TPA: expt. (◇), Flory (- - -) and TBA: expt. (□), Flory (- - -); in C_6H_{12} at 303.15 K.

There is no self-association in trialkylamine where as primary and secondary amine molecules are self-associated through the hydrogen bonds. Accordingly, for solutions of trialkylamine in cyclohexane, there is only physical contribution to $\bar{V}_B^{E,\infty}$ while for the solutions of primary and secondary amines in cyclohexane, both the physical as well as chemical contributions contribute to net $\bar{V}_B^{E,\infty}$.

The values of standard deviations σ between experimental and theoretical apparent molar volumes are in the range from 0.26 to 2.51 cm^3 mol^{-1} (Table 13). Except for BA and TEA solutions, the description of the apparent molar volumes by the Flory theory/ERAS model is quite reasonable. In case of TEA with C_6H_{12}, the apparent molar volume as well as the equimolar excess molar volumes predicted by the Flory theory was lower than the experimental results (Tables 12 and 13). Similar results were obtained from the Flory theory when applied to trialkylamine + cyclohexane mixtures by Phuong-Nguyen et al. [62] and Oswal and Patel [6]. The difference between experimental and theoretical values decreased as size of trialkylamine was increased. Such behaviour may be attributed to dipolar association of trialkylamine [6,56] which cannot be accounted by the Flory theory.

4.5.2. Alkylamine solutions in benzene

It is known that there exist weak specific interactions between alkylamine + benzene, which are accounted by cross parameters K_{AB}, Δh^*_{AB} and Δv^*_{AB} in the ERAS model. The values of unknown interaction parameter X_{AB} and cross parameters K_{AB}, Δh^*_{AB} and Δv^*_{AB} can be determined by simultaneously adjusting the theoretical expressions of the ERAS model to the experimental H^E and V^E data. There can be several sets of these parameters. The optimum values of cross parameters can be obtained to give minimum deviations for H^E and V^E data. In the present study we have obtained optimum values of X_{AB}, K_{AB}, Δh^*_{AB}, and Δv^*_{AB}

Table 13
Comparison of experimental and theoretical (Flory/ERAS) partial molar volumes and values of chemical and physical contributions to net excess partial molar volumes of alkylamines in cyclohexane and benzene

Solute	$\bar{V}^{\infty}_{B,thr}$ (cm^3 mol^{-1})	$\bar{V}^{\infty}_{B,expt}$ (cm^3 mol^{-1})	σ[a] (cm^3 mol^{-1})	$\bar{V}^{\infty,E}_{B,chem}$ (cm^3 mol^{-1})	$\bar{V}^{\infty,E}_{B,phy}$ (cm^3 mol^{-1})	$\bar{V}^{\infty,E}_{B,thr}$ (cm^3 mol^{-1})
Cyclohexane						
PA	88.18	88.44	0.26	3.12	1.34	4.46
BA	104.53	105.48	0.94	2.46	1.69	4.15
DPA	141.13	141.45	0.36	1.49	1.25	2.74
DBA	174.69	175.53	0.52	0.25	2.36	2.88
TEA	141.19	143.81	2.51	0.0	0.43	0.43
TPA	192.78	193.65	0.64	0.0	1.54	1.54
TBA	243.54	243.46	0.28	0.0	2.89	2.89
Benzene						
PA	84.63	84.21	0.28	0.19	0.73	0.92
BA	101.76	100.85	0.95	0.44	0.94	1.38
DPA	139.02	139.66	0.35	−0.67	1.30	0.63
DBA	173.44	173.67	0.29	−1.13	2.75	1.63
TEA	140.66	141.15	0.49	−0.79	0.69	−0.10
TPA	193.66	193.25	0.32	−1.69	4.10	2.41
TBA	244.47	243.53	0.81	−4.08	7.91	3.82

[a] Here σ represents standard deviation between observed apparent molar volumes and theoretical values over the range of composition studied.

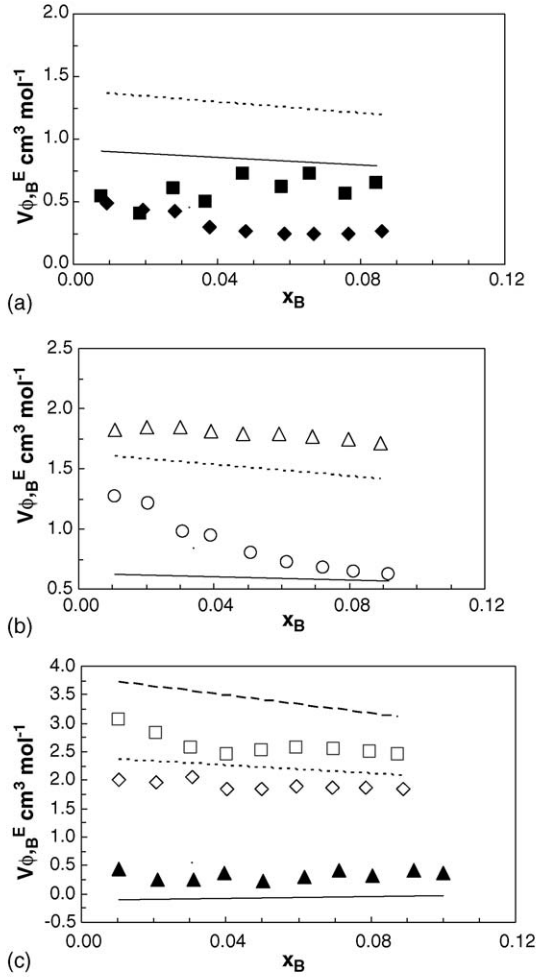

Fig. 2. Comparison of excess apparent molar volumes of (a) PA: expt. (■), ERAS (—); BA: expt. (♦), ERAS (- - -), (b) DPA: expt. (○), ERAS (—); DBA: expt. (△), ERAS (- - -), (c) TEA: expt. (▲), ERAS (—); TPA: expt. (◇), ERAS (- - -) and TBA: expt. (□), ERAS (– – –); in C_6H_6 at 303.15 K.

for alkylamine + benzene by simultaneously adjusting the theoretical expressions of the ERAS model to experimental equimolar H^E and V^E. The values of X_{AB}, K_{AB}, Δh^*_{AB}, and Δv^*_{AB} are given in Table 12. The values of X_{AB}, K_{AB}, Δh^*_{AB} and Δv^*_{AB} are in the ranges from 6 to 30 J cm^{-3}, 0.10 to 0.65, −3.0 to −10.1 kJ mol^{-1} and −3.6 to −12.2 cm^3 mol^{-1} for alkylamine in benzene. The small values of cross-parameters K_{AB} and Δh^*_{AB} are consistent with weak-specific interactions.

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 $\overline{V}_B^{\infty}$ and excess partial molar volumes $\overline{V}_B^{E,\infty}$ along with physical and chemical contribution to $\overline{V}_B^{E,\infty}$ are given in Table 13. The values of σ (Table 13) for present solutions are in the range from 0.28 to 0.95 cm^3 mol^{-1}. Except for butylamine solutions, the description of the apparent molar volume by the ERAS model is quite reasonable.

5. Conclusions

(i) The partial molar volumes and excess partial molar volumes of amines in cyclohexane are more than that in benzene indicating specific interactions between benzene and amine molecules.

(ii) The partial molar volumes at infinite dilution of transference from cyclohexane to benzene, $\Delta\overline{V}^{\infty}_{B,tr}$ ($C_6H_{12} \rightarrow C_6H_6$) are negative.

(iii) The values of group contributions of NH_2, NH, and N in cyclohexane and benzene are 20.33, 8.33, −5.28 cm^3 mol^{-1} and 15.64, 5.20, −7.75 cm^3 mol^{-1}, at 303.15 K, respectively.

(iv) The scaled particle theory and the hard sphere theory provide insight into molecular structure of solute and its interaction with solvent.

(v) Except for triethylamine and butylamine solutions in cyclohexane, and butylamine solutions in benzene the Flory theory and the ERAS model had described partial molar volume of investigated amine solutions quite well.

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