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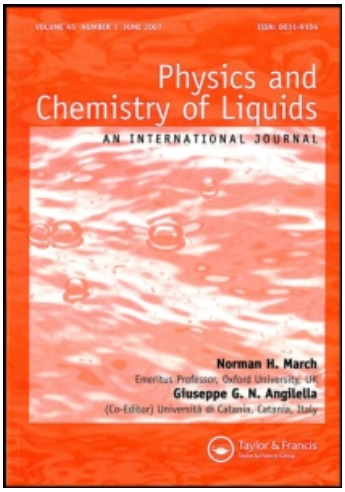

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Determination of the excess molar and partial molar volumes of the constituents in the binary mixtures with tri-ethylamine

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Determination of the excess molar and partial molar volumes of the constituents in the binary mixtures with tri-ethylamine

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The excess molar volume and excess partial molar volumes of binary mixtures of tri-ethylamine with toluene (Tn), ethylbenzene (Ebz) and n-propylbenzene (n-PBz) have been calculated using the MS-Excel method. The excess molar volumes have been found to be negative throughout the entire range of composition. The temperature effects are found to be insignificant, so the mixtures may be termed regular mixtures of Hildebrand.

Keywords: Tri-ethylamine; Excess molar volumes; Regular Hildebrand mixtures

1. Introduction

The excess molar volume of a binary mixture can be expressed in terms of one of the mole fractions $x = x_1$ as its polynomial, viz.,

$$V^{\mathrm{E}}(x) = \sum_{0}^{n} c_i x_i \tag{1}$$

$$\text{as } V^{\mathrm{E}}(x) = 0, \quad \text{when} \quad x = 0,\ 1;$$

$$\text{we have } c_0 = 0, \quad \text{and} \quad \sum_{0}^{n} c_i = 0$$

Hence, for a quadratic mixture ($n = 2$), it is observed that,

$$c_1 = -c_2 = c \text{ (say)}$$

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Hence,

$$V^{E}(x) = c(x - x^2) \tag{2}$$

$$V^{E}(x) = c(1 - 2x) \tag{3}$$

The excess partial molar volumes of the components can be calculated [1] as

$$\begin{aligned}\overline{V}_1^{E}(x) &= V^{E}(x) + (1 - x)V^{E}(x) \\ &= c(1 - x)^2\end{aligned} \tag{4}$$

and similarly,

$$\overline{V}_2^{E}(x) = cx^2 \tag{5}$$

The same expressions result from the Redlich–Kister equation [2].

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2. Experimental

2.1. *Materials*

Try-ethylamine, toluene, ethyl benzene and propyl benzene (Aldrich > 90%) purity were used. The densities of the liquids were measured and compared with the literature [3] values (table 1).

2.2. *Mixture preparation*

All mixtures were prepared by mixing weighed amount of pure liquids in airtight narrow-mouthed Stoppard bottles. Special precautions were taken to prevent evaporation and introduction of moisture into the samples.

2.3. *Method*

Three times distilled water was used for calibration of the pycnometer. An analytical balance within an accuracy of 0.1 mg was used.

The temperature was controlled by a thermostatic bath (water) fluctuating to ±0.05°C. The densities of a series of binary mixtures of TEA with Tn, Ebz

Table 1. The density of pure liquids.

		Density	
Liquids	Temperature (K)	Obs.	Lit.
TEA	303.15	0.7184	0.7184[b]
Tn	308.15	0.8527	0.8531[a]
Ebz	308.15	0.8443	0.8438[a]
PBz	308.15	0.8493	0.8494[a]

[a] Subha, M.C.S. and Rao, S.B. (1988), *J. Chem. Eng. Data*, **33**, 401.
[b] Oswal, S.L. and Rao, A.V. (1985), *Indian J. Chem.*, **24A**, 1026.

Table 2. The excess molar volumes of binary mixtures of TEA at different temperatures.

Mole fraction of TEA (x)	$-V^E$ (cm^3 mol^{-1})				
	30°C	35°C	40°C	45°C	50°C
(i) TEA + Tn					
0.1294	0.1532	0.2064	0.1681	0.1590	0.1193
0.1962	0.2024	0.1866	0.2170	0.2092	0.2262
0.2805	0.3263	0.3271	0.3271	0.2912	0.3092
0.4012	0.3106	0.3039	0.3056	0.2992	0.3168
0.5004	0.3086	0.2981	0.3142	0.3074	0.3241
0.6001	0.2958	0.3146	0.2783	0.2704	0.2675
0.6996	0.3332	0.3143	0.3271	0.3361	0.3495
0.7999	0.1875	0.1800	0.2257	0.1948	0.2038
0.9000	0.1402	0.1082	0.1130	0.1165	0.1414
(ii) TEA + EtBz					
0.1011	0.1705	0.1726	0.1563	0.1623	0.1571
0.2019	0.2780	0.2963	0.2924	0.3194	0.2756
0.2635	0.3371	0.3403	0.3592	0.3573	0.3498
0.4031	0.4165	0.4101	0.4200	0.4053	0.4241
0.5063	0.4469	0.4311	0.4412	0.4455	0.4885
0.6050	0.5126	0.4776	0.4964	0.4848	0.5524
0.7008	0.3631	0.3407	0.3653	0.3523	0.4053
0.7796	0.4737	0.4313	0.4442	0.1852	0.4706
0.8969	0.2531	0.2024	0.2194	0.1837	0.2041
(iii) TEA + nPBz					
0.1474	0.2080	0.2158	0.2071	0.2181	0.2039
0.2021	0.2772	0.2878	0.2879	0.2679	0.3211
0.2563	0.3872	0.4008	0.3928	0.3942	0.3681
0.4040	0.4446	0.4453	0.4942	0.5038	0.4814
0.5007	0.5185	0.5580	0.5673	0.5634	0.5917
0.6012	0.4710	0.4573	0.4782	0.1953	0.4794
0.7021	0.4131	0.3808	0.3942	0.3944	0.4279
0.8011	0.3798	0.3659	0.3710	0.3927	0.3785
0.8997	0.2388	0.1646	0.2167	0.1586	0.1716

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and n-PBz at 30, 35, 40 and 50°C were used to calculate the excess molar volumes using the following equation:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{d_{mix}} - (x_1 V_1^0 + x_2 V_2^0) \quad (6)$$

where, d, V, x and M are density, molar volume, mole fraction and molar mass respectively.

The excess molar values are shown in table 2.

These data on MS-Excel treatment with $n = 2$ yield the following values of R^2 and c. Higher values of 'n' do not yield improved values of R^2. On the other hand the higher co-efficient with $n > 2$ are very large indicating erroneous results. Hence the value of 'n' was restricted to 2.

3. Results and discussion

As c does not change appreciably with temperature (table 3), the mixtures can be viewed as regular Hilderbrand mixtures [4]. It may be observed that the excess

molar volumes of TEA with Tn/EBz/n-PBz are negative in magnitude while those of TBA with the same constituents are positive, as is the case for a mixture of TEA with benzene [5]. The excess partial molar volumes, V^{E} depend on the value of c only. Results calculated on the average value of c are given below (table 3).

The partial molar volumes of the constituents can be derived by using the following equation:

$$\overline{V}_i = V_i^0 + \overline{V}_i^E \tag{7}$$

The results are shown in figures 1 and 2, and table 4.

The negative V^{E} values of the three binary mixtures (table 2) are in the order TEA + Tn < TEA + EBz < TEA + n-PBz. Such a trend in V^{E} values may be the resultant contribution of several factors which can be classified as physical, chemical and geometrical interactions [6]. The physical interactions result mainly from the dispersion type or unfavorable interaction between the unlike molecules TEA and non polar aromatic hydrocarbons giving positive contribution to V^{E}. The chemical or specific interactions involve in the formation or breaking of the H-bonds or both, and other complex forming interactions. Geometrical or structural effects occurring from interstitial accommodation partially or fully of the substituent attached

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Table 3. The values of R^2 and c for binary mixtures of TEA.

	TEA + Tn		TEA + EBz		TEA + n-PBz	
Temperature (°C)	R^2	c	R^2	c	R^2	c
30	0.95	−1.32	0.91	−1.85	0.97	−1.98
35	0.95	−1.32	0.91	−1.85	0.97	−2.02
40	0.95	−1.31	0.94	−1.87	0.97	−2.10
45	0.95	−1.27	0.93	−1.73	0.96	−2.16
50	0.93	−1.35	0.94	−2.00	0.97	−2.16

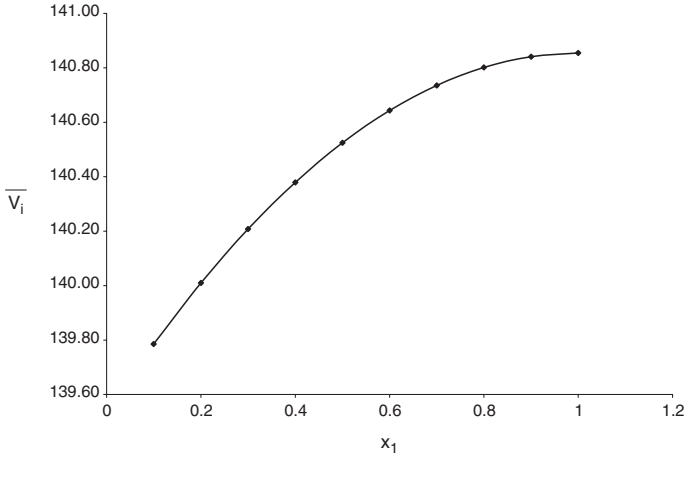

Figure 1. Partial molar volume of TEA at 30°C.

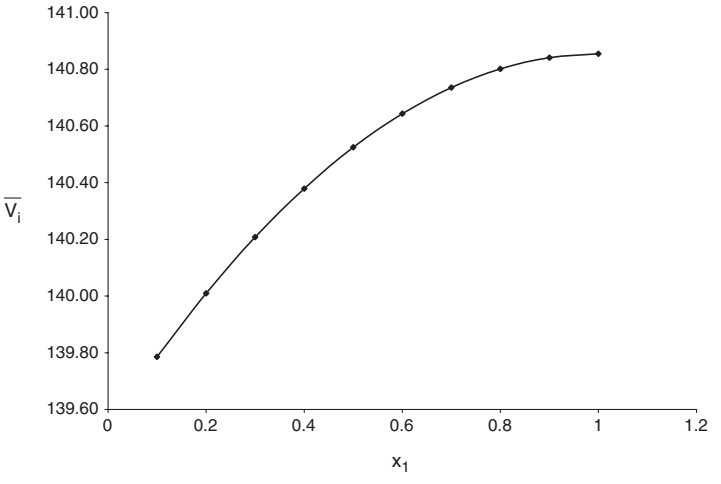

Figure 2. Partial molar volume of Tn at 30°C.

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Table 4. Excess partial molar volumes of TEA, Tn, EBz and n-PBz at 30°C.

TEA + Tn			TEA + EBz			TEA + n-PBz		
x_1	$\overline{V}_1^E$	$\overline{V}_2^E$	x_1	$\overline{V}_1^E$	$\overline{V}_2^E$	x_1	$\overline{V}_1^E$	$\overline{V}_2^E$
0.1	−1.069443	−0.013203	0.1	−1.498500	−0.018500	0.1	−1.701000	−0.021000
0.2	−0.844992	−0.052812	0.2	−1.184000	−0.074000	0.2	−1.344000	−0.084000
0.3	−0.646947	−0.118827	0.3	−0.906500	−0.166500	0.3	−1.029000	−0.189000
0.4	−0.475308	−0.211248	0.4	−0.666000	−0.296000	0.4	−0.756000	−0.336000
0.5	−0.330075	−0.330075	0.5	−0.462500	−0.462500	0.5	−0.525000	−0.525000
0.6	−0.211248	−0.475308	0.6	−0.296000	−0.666000	0.6	−0.336000	−0.756000
0.7	−0.118827	−0.646947	0.7	−0.166500	−0.906500	0.7	−0.189000	−1.029000
0.8	−0.052812	−0.844992	0.8	−0.074000	−1.184000	0.8	−0.084000	−1.344000
0.9	−0.013203	−1.069443	0.9	−0.018500	−1.498500	0.9	−0.021000	−1.701000
1	0.000000	−1.320300	1	0.000000	−1.850000	1	0.000000	−2.100000

to benzene ring of the aromatic hydrocarbons into the void space of the associated component TEA. The larger the chain of the substituent more is its inclusion thereby resulting in greater net contraction in the total volume of the mixtures (table 2).

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