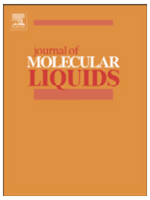
Journal of Molecular Liquids 162 (2011) 26–32

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



Volumetric properties of some binary liquid systems: n-Heptane + Aromatic hydrocarbons between 303.15 and 323.15 K

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A R T I C L E I N F O

Article history:
Received 12 January 2011
Received in revised form 9 May 2011
Accepted 24 May 2011
Available online 12 June 2011

Keywords:
Density
Excess molar volume
Partial molar volume
Excess thermal expansivity
Aromatic hydrocarbon

A B S T R A C T

Densities, ρ, have been measured for the binary systems of n-heptane + toluene, + o-xylene and + mesitylene in the whole range of composition between 303.15 and 323.15 K at an interval of 5 K. From measured, ρ, excess molar volumes, V_m^E, partial molar volumes, $\overline{V_i}$, thermal expansivities, α, and excess thermal expansivities, α^E, are also estimated. For all systems, measured ρ, $\overline{V_i}$ and α values are fitted to polynomial equations of appropriate forms, whereas, V_m^E and α^E are fitted to the Redlich–Kister equations. In the whole range of composition, V_m^E are positive for n-heptane + toluene but negative for the other two systems. In n-heptane + toluene, dispersive forces are suggested to dominate, whereas, in the other two 'favorable geometric fitting' seem to overpower due to increasing number of –CH_3 as substituent in the relevant aromatic hydrocarbons.

1. Introduction

Density and its related properties are increasingly used as tools for investigating the physico-chemical behavior of liquid systems and also to focus on the intermolecular interactions in liquids and their mixtures. In an extending approach towards the study on liquid–liquid binary systems, our present interest is on some aromatic hydrocarbons as well as their binary mixtures with aliphatic hydrocarbons. For aliphatic hydrocarbons that are basically known to be non-polar the acting forces within molecules are mostly of van der Waals type. In homo and hetero molecular systems of aliphatic hydrocarbons, factors that mainly influence the strength of interaction are found to be: i) chain length, ii) branching of the carbon chain, iii) size and shape of the component molecules, and iv) size and shape of the hetero species as a whole etc. On the other hand, factors that can further influence the strength of interaction in binary systems involving an aromatic hydrocarbon as the second component are supposed to be: i) nature of the aromatic ring, ii) types of groups/substituents present in the aromatic hydrocarbon, iii) position and number of groups attached to the aromatic ring, and iv) overall size and shape of the aromatic hydrocarbon etc.

A good number of literature survey shows that though attempts have already been made to study binary mixtures of aliphatic hydrocarbons and aromatic hydrocarbons, some systematic studies with composition and temperature dependences are still scarce. Iloukhani et al.[1] studied the volumetric and viscometric properties of toluene + n-alkanes (C_5–C_{10}) at 298.15 K; Lal et al.[2] on densities, viscosities and refractive indices for benzene + hexane, + decane, + hexadecane and + squalane at 298.15 K and Diaz et al.[3] reported on densities and refractive indices of cyclohexane, or *n*-heptane + *o*-xylene, or *m*-xylene, or *p*-xylene, or ethylbenzene also only at 298.15 K. However, Aminabhavi and Patil [4] measured densities, refractive indices and viscosities for ethylbenzene + n-alkanes (C_6–C_{11}) between 298.15 and 308.15 K, Linek and Moravkova [5] reported on densities of octane + benzene or toluene or 1,3-xylene or 1,3,5-trimethylbenzene between 298.15 and 328.15 K. These investigations have prompted us to study on physical properties of some systems of aliphatic hydrocarbon + aromatic hydrocarbons further. Like Diaz [3] and Linek and Moravkova [5], keeping the aliphatic hydrocarbon fixed the number of substituents is varied in the aromatic hydrocarbons. The present investigation thus reports on the density and some of its related properties for n-heptane + toluene, + o-xylene and + mesitylene in the whole range of composition between 303.15 and 323.15 K at an interval of 5 K. This would enable us further to see the effects due to increasing the number of a substituent as well as varying its position in the selected aliphatic hydrocarbon + aromatic hydrocarbon systems. So far we know data on n-heptane + mesitylene is yet to be reported.

2. Experimental section

Liquids used to prepare binary mixtures with quoted purities n-heptane (NHP): 99.6%, o-xylene (OXN): 99.0% and mesitylene (MSN): 99% was procured from Aldrich Chemical Co. Ltd. and toluene (TN): >99%

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doi:10.1016/j.molliq.2011.05.012

was from Merck. All the chemicals were used without further treatment. The experimental densities (ρ/g.cm^{-3}) along with reported data are tabulated in Table 1 and are found to be in good agreement with literature values. Binary mixtures of various compositions were prepared by mixing pure components at different proportions (by mass). Densities were measured by using a 10 cm^3 bi-capillary pycnometer previously calibrated with twice distilled water. Weighings were done with the help of an electronic balance (College B 204-S, METTLER TOLEDO) accurate up to ±0.0001 g. A thermostatic water bath controlled up to ±0.01 K was used for all measurements. The mole fraction was accurate up to 10^{-4}, while the uncertainty in the measured density was estimated as $\pm 1\times 10^{-4}$ g.cm^{-3}.

3. Results and discussion

3.1. Density

Densities, ρ, of NHP + TN, NHP + OXN and NHP + MSN in the whole range of composition measured at an interval of 5 K between 303.15 and 323.15 K are summarized in Table 2. At a particular temperature the ρ values were fitted by a five-degree polynomial equation of the form:

$$\rho\,/\,g.cm^{-3} = \sum_{i=0}^{n} a_i x_2^i \tag{1}$$

All the coefficient a_i and relevant R^2 are tabulated in Table 3. As the Table 2 shows, at a particular temperature ρ of pure liquids varies in the order: OXN > MSN ≥ TN > NHP. For the binary systems, ρ increases systematically as the concentration of the aromatic hydrocarbon increases and the order of increment also follows: NHP + OXN > + MSN > + TN.

Table 1
Comparison of experimental density, ρ(g.cm^{-3}) of pure liquids with literature values at different temperatures.

Sample	T/K	Density (ρ/g.cm^{-3})		
		This work	Literature	
n-heptane	303.15	0.6750	0.6750[a]	0.6751[b]
	308.15	0.6706	0.6707[c]	0.6709[d]
	313.15	0.6663	0.6663[a]	0.6664[e]
	318.15	0.6619	0.6623[f]	0.66259[g]
	323.15	0.6574	0.6574[h]	0.65837[i]
toluene	303.15	0.8575	0.8575[j]	0.8576[k]
	308.15	0.8528	0.85293[l]	0.85286[m]
	313.15	0.8481	0.8482[k]	0.8482[n]
	318.15	0.8433	0.8435[j]	0.84349[l]
	323.15	0.8385	0.8385[o]	0.8387[p]
o-xylene	303.15	0.8715	0.8716[q]	0.87136[r]
	308.15	0.8673	0.8677[j]	0.86706[l]
	313.15	0.8630	0.8629[s]	0.86279[l]
	318.15	0.8587	0.8597[j]	0.85853[l]
	323.15	0.8544	0.8555[j]	
mesitylene	303.15	0.8574	0.8571[t]	0.85754[l]
	308.15	0.8533	0.85289[m]	
	313.15	0.8491	0.84971[l]	
	318.15	0.8451	0.84478[m]	
	323.15	0.8408	0.84073[u]	

[a] Ref. [6].
[b] Ref. [7].
[c] Ref. [8].
[d] Ref. [9].
[e] Ref. [10].
[f] Ref-[11].
[g] Ref. [12].
[h] Ref. [13].
[i] Ref. [14].
[j] Ref. [15].
[k] Ref. [16].
[l] Ref. [17].
[m] Ref. [5].
[n] Ref. [18].
[o] Ref. [19].
[p] Ref. [20].
[q] Ref. [21].
[r] Ref. [22].
[s] Ref-[23].
[t] Ref-[24].
[u] Extrapolated value of Ref-[5].

Table 2
Densities, ρ (g.cm^{-3}) and excess molar volumes, V_m^E (cm^3.mol^{-1}) of the systems of NHP (x_1) + TN (x_2), + OXN (x_2) and + MSN (x_2) for different molar ratios at different temperatures.

x_2	ρ	V_m^E	x_2	ρ	V_m^E	x_2	ρ	V_m^E
NHP (x_1) + TN (x_2)			NHP (x_1) + OXN (x_2)			NHP (x_1) + MSN (x_2)		
T = 303.15 K								
0.0000	0.6750	0.0000						
0.1001	0.6883	0.0626	0.1001	0.6915	−0.0135	0.1000	0.6924	−0.0170
0.1991	0.7022	0.1258	0.2000	0.7087	−0.0506	0.1993	0.7101	−0.0800
0.3002	0.7175	0.1402	0.3005	0.7267	−0.0936	0.3000	0.7282	−0.1302
0.3996	0.7335	0.1498	0.3999	0.7452	−0.1357	0.4000	0.7463	−0.1621
0.5000	0.7506	0.1752	0.5000	0.7645	−0.1647	0.5000	0.7645	−0.1723
0.6000	0.7690	0.1608	0.6002	0.7845	−0.1758	0.5998	0.7828	−0.1685
0.6999	0.7887	0.1376	0.7001	0.8050	−0.1444	0.6992	0.8010	−0.1227
0.8001	0.8100	0.0954	0.8001	0.8264	−0.1175	0.7990	0.8196	−0.0986
0.9001	0.8327	0.0718	0.9000	0.8487	−0.0929	0.9000	0.8386	−0.0677
1.0000	0.8575	0.0000	1.0000	0.8715	0.0000	1.0000	0.8574	0.0000
T = 308.15 K								
0.0000	0.6706	0.0000						
0.1001	0.6839	0.0558	0.1001	0.6872	−0.0369	0.1000	0.6881	−0.0385
0.1991	0.6978	0.1132	0.2000	0.7044	−0.0745	0.1993	0.7059	−0.1211
0.3002	0.7131	0.1217	0.3005	0.7224	−0.1167	0.3000	0.7239	−0.1478
0.3996	0.7290	0.1445	0.3999	0.7409	−0.1572	0.4000	0.7421	−0.1955
0.5000	0.7462	0.1477	0.5000	0.7602	−0.1833	0.5000	0.7603	−0.1997
0.6000	0.7645	0.1458	0.6002	0.7802	−0.1902	0.5998	0.7786	−0.1892
0.6999	0.7841	0.1342	0.7001	0.8007	−0.1532	0.6992	0.7968	−0.1353
0.8001	0.8054	0.0880	0.8001	0.8221	−0.1198	0.7990	0.8154	−0.1024
0.9001	0.8281	0.0614	0.9000	0.8445	−0.1027	0.9000	0.8345	−0.0788
1.0000	0.8528	0.0000	1.0000	0.8673	0.0000	1.0000	0.8533	0.0000
T = 313.15 K								
0.0000	0.6663	0.0000						
0.1001	0.6796	0.0476	0.1001	0.6829	−0.0421	0.1000	0.6838	−0.0420
0.1991	0.6935	0.0978	0.2000	0.7001	−0.0837	0.1993	0.7016	−0.1276
0.3002	0.7087	0.1185	0.3005	0.7181	−0.1291	0.3000	0.7196	−0.1552
0.3996	0.7246	0.1341	0.3999	0.7366	−0.1714	0.4000	0.7378	−0.2030
0.5000	0.7417	0.1480	0.5000	0.7559	−0.1982	0.5000	0.7561	−0.2252
0.6000	0.7600	0.1394	0.6002	0.7759	−0.2046	0.5998	0.7743	−0.1927
0.6999	0.7796	0.1218	0.7001	0.7964	−0.1655	0.6992	0.7926	−0.1531
0.8001	0.8009	0.0702	0.8001	0.8178	−0.1292	0.7990	0.8112	−0.1153
0.9001	0.8235	0.0531	0.9000	0.8402	−0.1083	0.9000	0.8303	−0.0859
1.0000	0.8481	0.0000	1.0000	0.8630	0.0000	1.0000	0.8491	0.0000
T = 318.15 K								
0.0000	0.6619	0.0000						
0.1001	0.6752	0.0392	0.1001	0.6786	−0.0682	0.1000	0.6795	−0.0629
0.1991	0.6891	0.0817	0.2000	0.6957	−0.0907	0.1993	0.6973	−0.1458
0.3002	0.7042	0.1149	0.3005	0.7137	−0.1379	0.3000	0.7153	−0.1688
0.3996	0.7201	0.1232	0.3999	0.7322	−0.1808	0.4000	0.7335	−0.2111
0.5000	0.7372	0.1304	0.5000	0.7515	−0.2069	0.5000	0.7518	−0.2264
0.6000	0.7555	0.1159	0.6002	0.7716	−0.2286	0.5998	0.7702	−0.2233
0.6999	0.7750	0.1089	0.7001	0.7921	−0.1851	0.6992	0.7885	−0.1733
0.8001	0.7962	0.0665	0.8001	0.8135	−0.1434	0.7990	0.8071	−0.1240
0.9001	0.8188	0.0445	0.9000	0.8359	−0.1163	0.9000	0.8263	−0.0998
1.0000	0.8433	0.0000	1.0000	0.8587	0.0000	1.0000	0.8451	0.0000
T = 323.15 K								
0.0000	0.6574	0.0000						
0.1001	0.6707	0.0317	0.1001	0.6741	−0.0714	0.1000	0.6751	−0.0881
0.1991	0.6846	0.0678	0.2000	0.6913	−0.1165	0.1993	0.6929	−0.1717
0.3002	0.6997	0.0950	0.3005	0.7093	−0.1633	0.3000	0.7110	−0.2145
0.3996	0.7155	0.1169	0.3999	0.7278	−0.2045	0.4000	0.7291	−0.2335
0.5000	0.7326	0.1187	0.5000	0.7471	−0.2275	0.5000	0.7475	−0.2651
0.6000	0.7509	0.0993	0.6002	0.7672	−0.2450	0.5998	0.7659	−0.2566
0.6999	0.7704	0.0887	0.7001	0.7878	−0.2123	0.6992	0.7842	−0.1996
0.8001	0.7914	0.0581	0.8001	0.8092	−0.1628	0.7990	0.8029	−0.1605
0.9001	0.8141	0.0333	0.9000	0.8316	−0.1269	0.9000	0.8220	−0.1098
1.0000	0.8385	0.0000	1.0000	0.8544	0.0000	1.0000	0.8408	0.0000