Refractometric studies of liquid mixtures

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Abstract
Refractometric investigations have been conducted on selected quaternary liquid mixtures to analyse their optical properties and intermolecular interactions at a controlled temperature of 298.15K. The studied systems include:

a) n-Pentane + Toluene + n-Heptane + Cyclohexane
b) n-Pentane + n-Hexane + Benzene + Toluene
c) n-Heptane + n-Hexane + Cyclohexane + Benzene

The refractive indices of these mixtures were measured to examine the deviations from ideal behaviour, providing insights into molecular interactions, structural arrangements and composition-dependent optical properties. The results indicate a satisfactory correlation between experimental values and theoretical predictions, confirming the reliability of the refractometric approach in characterizing multicomponent liquid systems. These findings contribute to a better understanding of the optical and thermodynamic behaviour of hydrocarbon-based quaternary mixtures, which are of significant relevance in industrial and scientific applications.

Keywords: Refractive index, sound speed, molar polarization, total polarization, induced polarization, dipole movement, polar molecules and permittivity.

Introduction

A knowledge of refractive index of liquid mixtures is often desirable in many multiphase systems. Several workers[1,2,5,6,9,10,12] have experimentally measured this property. Various refractometers are available for the accurate measurements of this property. Several workers[11] have measured refractive index of various types of systems and discussed their merits and demerits. Refractive index has been correlated with a number of other properties. Some of the correlations are as follows:

- density(ρ)
- Sound speed(u)

Determination of "n" from sound speed is given by:

$$\left(\frac{u}{u_o}\right)^{1/4} = n$$

$$\frac{u}{u_o} = n^4$$

where u_o =345 ms^{-1}

The speed in air is given by:

$$\left(\frac{u}{u_o}\right) = n^4 \quad (1)$$

From this relation the values of n can be determined through u and u_o.

Material and Methods

The molar refractions, R_m, is given by:

$$R_m = \frac{n^2-1}{n^2+2}.\frac{M}{\rho} = \frac{n^2-1}{n^2+2}.V_m \quad (2)$$

R_m is related to molar polarizability (α_p)

$$R_m = \frac{N\alpha_p}{3\epsilon_o} \quad (3)$$

where ε_o is the permittivity free space and N is the Avogadro number. ε_o is given by:

$$\epsilon o = 8.854X10^{-12}(C^2N^{-1}m^{-2}) \quad (4)$$
$$\epsilon o = 8.854X10^{-12}(kg^{-1}m^{-3}s^2) \quad (5)$$

Calculation of molar polarization (P_m) and dipole moment (μ)

The molar polarization P_m is given by:

$$P_i = \frac{D-1}{D+2}.\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_p \quad (6)$$

If the system obeys the Clausius-Mosotti equation, the induced molar polarization (P_i) is given by:

$$Pi = \frac{D-1}{D+2}.\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_P \quad (7)$$

where D is dielectric constant for polar molecules, the quantity measures orientation polarization (P_o), hence the total molar polarization (P_t) is given by:

$$P_t = \frac{D-1}{D+2}.\frac{M}{\rho} = P_i + P_o \quad (8)$$

Po is given by:

$$P_o = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \quad (9)$$

where μis the dipole movement, k is Boltzmann constant and π = 22/7

The molar polarization P_m is given by:

$$P_m = \frac{(D-N^2)(2D-N^2)}{9D} \quad (10)$$

Experimental values of sound speed (u) of three quaternary mixtures namely; n-pentane (x_1) + toluene (x_2) + n-heptane (x_3) + cyclohexane (x_4), pentane (x_1) + n-hexane (x_2) + benzene (x_3) + toluene (x_4), n-heptane (x_1) + n-hexane (x_2) + cyclohexane (x_3) + benzene (x_4) was determined along with their percentage derivations from Junjie, Auerbach and Altenberg relation. table 1 to 4 are reported in the values of α, ß, ρ and Flory's parameters Ṽ, V*, P* and T* are shown in the table.

The refractive indices of the liquid mixtures were measured at different compositions and temperatures. The results show a systematic variation in refractive index with composition, suggesting molecular interactions between the components.

Results and Discussion

In general, the refractive index increased with an increase in the mole fraction of the more optically dense component. To analyse the deviation from ideal mixing, the refractive index data were compared with values predicted using mixing rules. The deviations observed indicate non-ideal behaviour, which can be attributed to specific molecular interactions such as hydrogen bonding, dipole-dipole interactions and dispersion forces. Excess refractive index is the ideal value based on volume fraction mixing rules. Positive deviations suggest stronger interactions between unlike molecules, while negative deviations indicate weaker interactions or molecular size disparities. The effect of temperature on refractive index was also examined.

As expected, the refractive index decreased with an increase in temperature due to reduction in molecular density and weaker intermolecular forces. The rate of decrease varied depending on the nature of the components and their interactions.

The results obtained were compared with existing literature values for similar systems. The consistency of data validates the experimental approach, though slight deviations were observed, likely due to differences in purity, measurement techniques and temperature control.

Table 1
Parameters for the pure components at 298.15K

Components	α	β_T	P	P_m	C_m	Ṽ	V*	P*	T*	u
n-pentane	1.6226	212.3	0.6216	0.0182	0.235662	1.3628	85.1754	4.2319	4144.84	990
Toluene	1.074	92.15	0.8627	0.0591	0.413218	1.2627	84.5867	5.5403	5032.94	1304
n-heptane	1.2589	142.4	0.6791	0.0147	0.288002	1.2985	113.638	4.4441	4642.94	1131
Cyclohexane	1.215	114	0.7734	0.0136	0.362041	1.2902	84.292	5.2895	4724.33	1252
n-hexane	1.3897	170.9	0.6552	0.0143	0.27056	1.3225	99.456	4.2403	4432.14	1076.6
Benzene	1.2265	96.7	0.8732	0.0446	0.418248	1.2924	69.2198	6.3162	4702.41	1296

Table 2
Calculated values of mole fraction (x), molar volume (V_m), molar refraction (R_m), molar polarizability (α_p), induced molar (P_i), total molar polarization (P_t) of n-pentane (X_1) + toluene (X_2) + n-heptane (X_3) + cyclohexane (X_4)

X_1	X_2	X_3	V_m	$R_m(1)$	$R_m(2)$	$R_m(3)$	$R_m(4)$	$\alpha_p(1)$	$\alpha_p(2)$	$\alpha_p(3)$	$\alpha_p(4)$	$P_i(1)$	$P_i(2)$	$P_i(3)$	$P_i(4)$	$P_t(2)$
0.0404	0.6358	0.1544	124.23	24.98	31.67	28.00	30.95	1.10	1.40	1.24	1.37	2.78	3.53	3.12	3.44	5.17
0.056	0.5737	0.1284	117.25	21.92	27.79	24.58	27.16	0.97	1.23	1.08	1.20	2.44	3.09	2.74	3.02	5.73
0.0735	0.5474	0.112	116.10	21.71	27.52	24.33	26.89	0.96	1.21	1.07	1.19	2.42	3.06	2.71	2.99	5.70
0.0935	0.5282	0.0959	116.67	21.82	27.66	24.46	27.02	0.96	1.22	1.08	1.19	2.43	3.08	2.72	3.01	5.72
0.1141	0.5054	0.0793	115.72	21.64	27.43	24.25	26.80	0.95	1.21	1.07	1.18	2.41	3.05	2.70	2.98	5.69

0.0948	0.1351	0.1794	0.1991	0.1783	0.1126	0.1071	0.1709	0.1511	0.1134
0.3338	0.11	0.602	0.22	0.2147	0.4267	0.4099	0.4395	0.4602	0.4948
0.2524	0.1484	0.1481	0.1674	0.1637	0.1137	0.0783	0.0338	0.0487	0.066
83.23	49.23	141.43	137.05	75.31	120.20	115.80	109.33	117.70	114.26
15.66	9.21	26.45	25.63	14.08	22.48	21.65	20.44	22.01	21.37
19.85	11.67	33.53	32.49	17.85	28.49	27.45	25.92	27.90	27.09
17.55	10.32	29.65	28.73	15.79	25.20	24.27	22.92	24.67	23.95
19.40	11.40	32.76	31.74	17.44	27.84	26.82	25.32	27.26	26.47
0.69	0.41	1.17	1.13	0.62	0.99	0.96	0.90	0.97	0.94
0.88	0.51	1.48	1.43	0.79	1.26	1.21	1.14	1.23	1.19
0.77	0.46	1.31	1.27	0.70	1.11	1.07	1.01	1.09	1.06
0.86	0.50	1.44	1.40	0.77	1.23	1.18	1.12	1.20	1.17
1.74	1.02	2.94	2.85	1.57	2.50	2.41	2.28	2.45	2.38
2.21	1.30	3.73	3.62	1.99	3.17	3.06	2.88	3.11	3.01
1.95	1.15	3.30	3.20	1.76	2.80	2.70	2.55	2.75	2.67
2.16	1.27	3.65	3.53	1.94	3.10	2.99	2.82	3.03	2.95
4.85	3.94	6.37	6.26	4.63	5.81	5.70	5.52	5.75	5.65

Table 3
Calculated values of mole fractions (x), molar volume (V_m), molar refraction (R_m), molar polarizability (α_p), induced molar (P_i), total molar polarization (P_t) of n-pentane (X_1) + n-hexane (X_2) + benzene (X_3) + toluene (X_4)

X_1	X_2	X_3	V_m	R_m (1)	R_m (2)	R_m (3)	R_m (4)	αp (1)	αp (2)	αp (3)	αp (4)	Pi (1)	Pi (2)	Pi (3)	Pi (4)	Pt (2)
0.0943	0.0918	0.4587	101.83	19.04	20.77	24.14	24.14	0.84	0.92	1.06	1.06	2.12	2.31	2.69	2.69	4.95
0.13	0.1373	0.2974	106.07	19.83	21.64	25.14	25.14	0.87	0.95	1.11	1.11	2.21	2.41	2.80	2.80	5.05

0.1568	0.0524	0.066	0.1372	0.1866	0.1691	0.125	0.1819	0.1823	0.1843	0.1492	0.145	0.1278
0.0468	0.1434	0.1053	0.158	0.0826	0.2041	0.1665	0.1606	0.164	0.1484	0.1384	0.1291	0.1288
0.4582	0.4201	0.7033	0.5548	0.125	0.2218	0.2455	0.3842	0.3613	0.2711	0.3421	0.3376	0.3589
101.30	103.38	97.66	102.19	108.23	109.38	107.64	105.61	106.10	107.29	105.50	105.31	104.77
18.94	19.33	18.26	19.11	20.24	20.45	20.13	19.75	19.84	20.06	19.73	19.69	19.59
20.67	21.09	19.92	20.85	22.08	22.31	21.96	21.55	21.65	21.89	21.52	21.48	21.37
24.01	24.51	23.15	24.22	25.65	25.93	25.52	25.04	25.15	25.43	25.01	24.96	24.84
24.01	24.51	23.15	24.22	25.65	25.93	25.52	25.04	25.15	25.43	25.01	24.96	24.84
0.84	0.85	0.81	0.84	0.89	0.90	0.89	0.87	0.88	0.88	0.87	0.87	0.86
0.91	0.93	0.88	0.92	0.97	0.98	0.97	0.95	0.95	0.97	0.95	0.95	0.94
1.06	1.08	1.02	1.07	1.13	1.14	1.13	1.10	1.11	1.12	1.10	1.10	1.10
1.06	1.08	1.02	1.07	1.13	1.14	1.13	1.10	1.11	1.12	1.10	1.10	1.10
2.11	2.15	2.03	2.13	2.25	2.28	2.24	2.20	2.21	2.23	2.20	2.19	2.18
2.30	2.35	2.22	2.32	2.46	2.48	2.44	2.40	2.41	2.44	2.40	2.39	2.38
2.67	2.73	2.58	2.70	2.86	2.89	2.84	2.79	2.80	2.83	2.78	2.78	2.76
2.67	2.73	2.58	2.70	2.86	2.89	2.84	2.79	2.80	2.83	2.78	2.78	2.76
4.94	4.99	4.86	4.96	5.1	5.15	5.08	5.04	5.05	5.08	5.04	5.03	5.02

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Table 4
Calculated values of mole fractions(x), molar volume (V_m), molar refraction (R_m), molar polarizability (α_p), induced molar (P_i), total molar polarization (P_t) of pentane (X_1), n-hexane (X_2), cyclohexane (X_3) and benzene (X_4)

X_1	X_2	X_3	V_m	$R_m(1)$	$R_m(2)$	$R_m(3)$	$R_m(4)$	$\alpha_p(1)$	$\alpha_p(2)$	$\alpha_p(3)$	$\alpha_p(4)$	$P_i(1)$	$P_i(2)$	$P_i(3)$	$P_i(4)$	$P_t(2)$
0.0488	0.1238	0.1831	99.34	18.58	20.27	23.01	23.55	0.82	0.89	1.01	1.04	2.07	2.26	2.56	2.62	4.9
0.0658	0.1078	0.2036	99.52	18.61	20.30	23.05	23.59	0.82	0.90	1.02	1.04	2.07	2.26	2.57	2.63	4.9
0.0813	0.0934	0.2238	99.71	18.65	20.34	23.10	23.64	0.82	0.90	1.02	1.04	2.08	2.26	2.57	2.63	4.9
0.1006	0.0798	0.243	100.03	18.70	20.41	23.17	23.71	0.82	0.90	1.02	1.05	2.08	2.27	2.58	2.64	4.91
0.118	0.0629	0.2615	100.13	18.72	20.43	23.19	23.74	0.83	0.90	1.02	1.05	2.08	2.27	2.58	2.64	4.91
0.1243	0.0466	0.2842	100.06	18.71	20.41	23.18	23.72	0.83	0.90	1.02	1.05	2.08	2.27	2.58	2.64	4.91
0.141	0.1304	0.3129	104.57	19.55	21.33	24.22	24.79	0.86	0.94	1.07	1.09	2.18	2.37	2.70	2.76	5.01
0.156	0.1262	0.1513	101.67	19.01	20.74	23.55	24.10	0.84	0.91	1.04	1.06	2.12	2.31	2.62	2.68	4.95
0.1285	0.1192	0.5888	109.09	20.40	22.25	25.27	25.86	0.90	0.98	1.11	1.14	2.27	2.48	2.81	2.88	5.12
0.1537	0.0925	0.1685	100.53	18.80	20.51	23.29	23.83	0.83	0.90	1.03	1.05	2.09	2.28	2.59	2.65	4.92
0.1649	0.1013	0.5177	107.93	20.18	22.02	25.00	25.58	0.89	0.97	1.10	1.13	2.25	2.45	2.78	2.85	5.09
0.1368	0.1258	0.1507	101.13	18.91	20.63	23.43	23.97	0.83	0.91	1.03	1.06	2.10	2.30	2.61	2.67	4.94

0.091	0.1721	0.6137	110.79	20.72	22.60	25.66	26.26	0.91	1.00	1.13	1.16	2.31	2.52	2.86	2.92	5.16
0.0645	0.1378	0.1103	98.94	18.50	20.19	22.92	23.45	0.82	0.89	1.01	1.03	2.06	2.25	2.55	2.61	4.89
0.181	0.1656	0.2971	106.80	19.970	21.79	24.74	25.32	0.88	0.96	1.09	1.12	2.22	2.43	2.75	2.82	5.078

Conclusion

It can be concluded from the present study that Altenberg's relation should be used in preference to the Auerbach relation, while Junjie's relation can also be solely used in some multicomponent liquid mixtures[4].

The refractometric study of liquid mixtures provides valuable insight into molecular interactions and deviations from ideal behaviour. The observed trends in refractive index and excess properties highlight the significance of intermolecular forces in determining optical properties of liquid mixtures. These findings can be useful in applications such as solution chemistry, optical sensor development and industrial formulation of binary and multicomponent liquid systems.

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