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Excess refractive indices and validation of mixing rules using binary mixture of methyl laurate + Pentan-2-ol at various temperatures (298.15, 303.15, 308.15, 313.15, and 318.15K)

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Refractive index is a characteristic parameter of fluids with numerous industrial uses. The values of refractive indices of many pure liquids are known or can be found in the literature. However, when experimental values of the liquid mixtures are not available then refractive indices of binary mixtures and multi-component liquids are frequently assessed from the pure constituents using mixing rules. The refractive indices (n_D) of binary mixture and pure liquids methyl laurate (M.L) and pentan -2-ol (P) over the entire mole fraction range at five temperatures (298.15, 303.15, 308.15, 313.15, and 318.15K) were measured using an Anton-Paar Abbemat 3200 refractometer and were tested with the traditional equations, viz Gladstone-Dale (G.D), Lorentz-Lorentz (L.L), Weiner-relation (W.R) and Heller-relation (H.R). The excess refractive indices (n_D^E) were calculated using measured experimental refractive indices (n_D) and (n_D^{id}) ideal refractive indices. The values of excess refractive indices were found to be negative at low mole fractions and positive over the high mole fractions. The experimental data for binary mixture involving methyl laurate + Pentan-2-ol authenticate the mixing rules.

Key words: Excess refractive index, binary mixture, mixing rules, methyl laurate.

INTRODUCTION

In conventional compression ignition engines, the performance and rejection of exhaust gases like CO, SO_2, etc. and particulate matter are of great concern. It leads to pollution and even degrades the performance of engine. So to counter the pollution problems and to improve the performance of conventional ignition engines the researcher is looking for an alternate fuel. Biofuels can be the best alternative of conventional fuels because it can be used directly in the compression of conventional ignition engines. But, the thermo-physical properties of biofuels and conventional fuels are different due to differences in their molecular structures. It may affect the combustion, exhaust emission and injection timing (Tat and Van Gerpen, 2003; Caresana, 2011; Boehman et al.,

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Table 1. The refractive indices of pure components methyl laurate (M.L) and pentan-2-ol (P).

Liquid	(298.15K)	(303.15K)	(308.15K)	(313.15K)	(318.15K)
Methyl laurate (M.L)	1.4299	1.4278	1.4257	1.4236	1.4215
Pentan-2-ol (P)	1.4044	1.4015	1.3982	1.3960	1.3938

Source: Authors

2004). The injection process is vital for attaining optimum combustion and reducing the emissions and this injection process is greatly affected by the properties like surface tension, viscosity, refractive index, etc. (Gouw and Vlugter, 1964; Ndiaye et al., 2012). So, experimental and theoretical refractive index values are very important since they provide information about the nature of molecular interactions. Besides molecular interactions, refractive index also provides the quantitative data of liquid mixtures required for designing technical processes and answering problems related to engineering (Hossain et al., 2016; Rahman et al., 2014). Even the properties related to refractive index are widely used in designing the process such as mass transfer, heat flow, etc., as inter molecular interactions are widely used in elucidation of fluids structures (Fucaloro, 2002). Refractive index and theoretical models based on refractive index help in determination of intermolecular interactions hence in this research work we have measured refractive indices of binary mixture.

MATERIALS AND METHODS

Methyl laurate was supplied by TCI (with purity ≥ 99.5%). Pentan-2-ol was purchased from Sigma- Aldrich (with purity ≥ 99%). All the mixtures were prepared gravimetrically during the performance of experiment, to avoid variation in chemical composition which may be caused due to absorption of some impurities and moisture from air. Abbemat refractometer 3200 was used to measure refractive indices of liquid mixture. This refractometer is equipped with an automatic peltier temperature control providing a fast and precise automatic temperature control of the sample with uncertainty ± 0.01K (Pandey et al., 2020; Srivastava et al., 2018; Almasi and Iloukhani, 2010; Li et al., 2022; Mohammadi and Hamzehloo, 2019). Calibration of refractometer was done by using doubly distilled water (Bhatia et al., 2002). Micro syringe was used to inject the liquid mixtures and the whole prism was covered with magnetic sample cover to prevent evaporation. The excess refractive indices (n_D^E) were calculated using measured refractive index values over the whole mole fraction range at different temperatures (298.15, 303.15, 313.15, and 318.15K). Four mixing rules (Gladstone – Dale (G.D), Lorentz-Lorentz (L.L), Weiner-relation (W.R) and Heller-relation (H.R)) were used to calculate refractive indices of binary mixture involving methyl laurate and pentan-2-ol (P2).

RESULTS AND DISCUSSION

The refractive indices (n_D) of pure and binary liquid mixtures were measured using the refractometer at five various temperatures (298.15, 303.15, 313.15, and 318.15K). Refractive indices of pure components at various temperatures are represented in Table 1 and that of binary mixtures involving methyl laurate (x_i) and pentan-2-ol (1-x_i) are represented over whole mole fraction in Table 2.

In earlier days, refractive indices of mixtures were assessed by using mixing rules (Mandava et al., 2015). In this research work attempt was made to validate the mixing rules, viz Gladstone-Dale (G.D), Lorentz-Lorentz (L.L), Weiner-relation (W.R), and Heller-relation (H.R) by comparing experimental values of refractive indices of binary mixtures with the calculated (n_D) values using Equations 1 to 4. The refractive indices and experimental values are shown in Table 2. Lorentz-Lorentz (L-L):

$$\frac{n_{L.L}^2-1}{n_{L.L}^2+2}=\left(\frac{n_1^2-1}{n_1^2+2}\right)\Phi_1+\left(\frac{n_2^2-1}{n_2^2+2}\right)\Phi_2 \quad (1)$$

Gladstone-Dale (G.D)

$$n_{G.D}-1=(n_1-1)\,\Phi_1+(n_2-1)\,\Phi_2 \quad (2)$$

Weiner-relation (W.R)

$$\frac{n_{W.R}^2-n_1^2}{n_{W.R}^2+2n_2^2}=\left(\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right)\Phi_2 \quad (3)$$

Heller-relation (H.R)

$$\frac{n_{H.R}-n_1}{n_1}=\frac{3}{2}\left[\frac{\left(\frac{n_2}{n_1}\right)^2-1}{\left(\frac{n_2}{n_1}\right)^2+2}\right]\Phi_2 \quad (4)$$

where x_i is mole fraction and Φ_1 and Φ_2 are volume fractions and n is the refractive index of liquid mixture x_1 and x_2 and pure components have refractive index n_1 and n_2, the volume fractions are obtained by using volumes and mole fractions of liquids involved in binary mixture methyl laurate (M.L) and pentan-2-ol (P) using equation:

$$\Phi_1=\frac{x_1v_1}{x_1v_1+x_2v_2} \quad (5)$$

where v_1 and v_2 are the molar volume of constituents 1 and 2.

Table 2. The experimental and theoretical values over the complete mole fraction range (x_i) at five different temperatures (293.15, 303.15, 308.15, 313.15, and 318.15K).

x_i	$n_{(EXP)}$	$n_{G.D}$	$n_{L.L}$	$n_{H.R}$	$n_{W.R}$
At 298.15k					
0.01436	1.4051	1.404456	1.404456	1.404383	1.405061
0.04993	1.4063	1.404656	1.404653	1.404582	1.405255
0.10684	1.4076	1.405227	1.40522	1.405155	1.405811
0.21491	1.4096	1.408084	1.408056	1.408021	1.408594
0.25923	1.4106	1.409946	1.409907	1.409888	1.410407
0.31614	1.4121	1.412725	1.412675	1.412676	1.413117
0.42066	1.4152	1.418258	1.418201	1.418224	1.418516
0.52189	1.4183	1.423003	1.422958	1.422983	1.423152
0.61245	1.4209	1.426043	1.426013	1.426031	1.426124
0.72435	1.4237	1.428225	1.42821	1.42822	1.42826
0.76703	1.4245	1.428424	1.428411	1.42842	1.428455
0.80041	1.4259	1.429223	1.429217	1.429221	1.429237
0.81464	1.4268	1.429878	1.429878	1.429878	1.429879
0.90356	1.4284	1.429775	1.429773	1.429774	1.429777
At 303.15k					
0.01436	1.4023	1.401558	1.401558	1.40148	1.402202
0.04993	1.4038	1.404046	1.404025	1.403975	1.404622
0.10684	1.4056	1.402353	1.402345	1.402277	1.402975
0.21491	1.4076	1.405327	1.405296	1.405259	1.405868
0.25923	1.4086	1.407247	1.407205	1.407185	1.407738
0.31614	1.4101	1.410113	1.41006	1.41006	1.41053
0.42066	1.4132	1.415829	1.415768	1.415793	1.416103
0.52189	1.4162	1.420705	1.420656	1.420684	1.420863
0.61245	1.4187	1.423839	1.423808	1.423828	1.423926
0.72435	1.4216	1.426081	1.426066	1.426076	1.426118
0.76703	1.4224	1.426277	1.426264	1.426273	1.42631
0.80041	1.4238	1.427099	1.427092	1.427097	1.427114
0.81464	1.4248	1.427778	1.427777	1.427778	1.427778
0.90356	1.4264	1.427671	1.427669	1.42767	1.427673
At 308.15k					
0.01436	1.3992	1.398261	1.39826	1.398175	1.398966
0.04993	1.4012	1.398466	1.398464	1.398381	1.399166
0.10684	1.4032	1.399092	1.399084	1.399009	1.399773
0.21491	1.4058	1.402183	1.40215	1.402109	1.402776
0.25923	1.4069	1.404181	1.404136	1.404114	1.404719
0.31614	1.4083	1.407169	1.407111	1.407111	1.407626
0.42066	1.4113	1.413136	1.41307	1.413096	1.413437
0.52189	1.4142	1.418253	1.4182	1.41823	1.418427
0.61245	1.4167	1.42154	1.421506	1.421527	1.421635
0.72435	1.4195	1.423884	1.423867	1.423878	1.423925
0.76703	1.4203	1.424099	1.424084	1.424094	1.424135
0.80041	1.4218	1.424967	1.42496	1.424965	1.424983
0.81464	1.4228	1.425677	1.425676	1.425677	1.425677
0.90356	1.4244	1.425565	1.425563	1.425564	1.425568
At 313.15k					
0.01436	1.3971	1.396061	1.39606	1.395974	1.396773

Table 2. Contd.

0.04993	1.3991	1.396267	1.396265	1.396181	1.396973
0.10684	1.4012	1.396895	1.396887	1.396811	1.397582
0.21491	1.4038	1.399997	1.399964	1.399923	1.400596
0.25923	1.4049	1.402003	1.401957	1.401935	1.402546
0.31614	1.4064	1.405002	1.404943	1.404943	1.405463
0.42066	1.4094	1.41099	1.410923	1.41095	1.411294
0.52189	1.4123	1.416126	1.416073	1.416102	1.416301
0.61245	1.4147	1.419416	1.419381	1.419402	1.419512
0.72435	1.4175	1.421777	1.421761	1.421772	1.421819
0.76703	1.4183	1.421993	1.421978	1.421988	1.422029
0.80041	1.4198	1.422864	1.422857	1.422862	1.422881
0.81464	1.4208	1.423577	1.423576	1.423576	1.423577
0.90356	1.4224	1.423464	1.423463	1.423464	1.423467
At 318.15k					
0.01436	1.3945	1.393861	1.393861	1.393774	1.394579
0.04993	1.3971	1.394068	1.394066	1.393981	1.39478
0.10684	1.3995	1.394689	1.394681	1.394604	1.395383
0.21491	1.4023	1.397802	1.397769	1.397727	1.398407
0.25923	1.4035	1.399815	1.399769	1.399746	1.400363
0.31614	1.4049	1.402825	1.402766	1.402766	1.40329
0.42066	1.4078	1.408835	1.408768	1.408795	1.409141
0.52189	1.4105	1.413989	1.413936	1.413966	1.414166
0.61245	1.4129	1.4173	1.417265	1.417287	1.417398
0.72435	1.4157	1.419671	1.419654	1.419665	1.419713
0.76703	1.4165	1.419887	1.419872	1.419882	1.419924
0.80041	1.4179	1.420762	1.420754	1.420759	1.420778
0.81464	1.4189	1.421476	1.421476	1.421476	1.421477
0.90356	1.4204	1.421364	1.421362	1.421363	1.421367

Source: Authors

Excess refractive indices

The deviation in refractive indices of binary mixture containing methyl laurate (M.L) + pentan-2-ol (P) from the ideal refractive indices were measured in terms of excess refractive indices (n_D^E) and it is measured by using equations (Garcia-Mardones et al., 2013):

$$n_D^E = n_D - n_D^{id} \quad (6)$$

$$n_D^{id} = [\Phi_1.n_{D.1}^2 + \Phi_2.n_{D.2}^2]^{1/2} \quad (7)$$

where n_D is refractive index of liquid mixture, Φ_1 and Φ_2 are the volume fraction of constituents 1 and 2 and n_D^{id} is ideal refractive index of mixture and $n_{D.1}^2$ and $n_{D.2}^2$ are refractive indices of pure constituents 1 and 2, respectively. n_D^E values over the complete mole fraction range at five various temperatures are shown in Table 3 and variations of n_D^E as a function of mole fraction of methyl laurate (M.L) + pentan-2-ol(P) are as shown in Figure 1.

Excess refractive indices (n_D^E) at low mole fractions (≤ 0.38) are positive and at high mole fractions n_D^E are negative. The maxima of binary mixture at all temperature are observed at $(x_i$ = 0.15) and minima are observed at $(x_i$ = -0.061). The significant strong interactions between components of binary mixture lead to positive values of n_D^E while the weak interactions lead to negative n_D^E values (Ali et al., 2013). When methyl laurate is added to pentan-2-olthen the strong intermolecular interactions (H bond) between hydroxyl (-OH) of pentan-2-ol and oxygen of carbonyl part of ester methyl laurate get generated. After a certain mole fraction (0.28 to 0.38) as the concentration of methyl laurate in liquid mixture increases, the interactions between the components may weaken due to dominance of bulky

Table 3. Excess refractive indices (n_D^E) of binary mixture involving methyl laurate (M.L) (x_i) + pentan-2-ol(P) (1- x_i) as a function of mole fraction (x_i) at various temperatures (298.15, 303.15, 308.15, 313.15, and 323.15K).

x_i	ϕ_1	n_D^E(298.15)	n_D^E**(303.15)**	n_D^E**(308.15)**	n_D^E**(313.15K)**	n_D^E**(318.15K)**
0.01436	0.00221	0.0006	0.0007	0.0009	0.001	0.001
0.04993	0.01002	0.0016	0.002	0.0027	0.0028	0.003
0.10684	0.03243	0.0024	0.003	0.0041	0.0043	0.0048
0.21491	0.14482	0.0015	0.0022	0.0036	0.0038	0.0045
0.25923	0.21749	0.0006	0.0013	0.0027	0.0029	0.0036
0.31614	0.32649	-0.0007	-0.0001	0.0011	0.0013	0.002
0.42066	0.54380	-0.0031	-0.0027	-0.0019	-0.0017	-0.0011
0.52189	0.72920	-0.0047	-0.0046	-0.0041	-0.0039	-0.0035
0.61245	0.84873	-0.0052	-0.0052	-0.0049	-0.0048	-0.0044
0.72435	0.93430	-0.0045	-0.0045	-0.0044	-0.0043	-0.004
0.76703	0.94211	-0.0039	-0.0039	-0.0038	-0.0037	-0.0034
0.80041	0.97334	-0.0033	-0.0033	-0.0032	-0.0031	-0.0029
0.81464	0.99915	-0.0031	-0.003	-0.0029	-0.0028	-0.0026
0.90356	0.99508	-0.0014	-0.0013	-0.0012	-0.0011	-0.001

Source: Authors

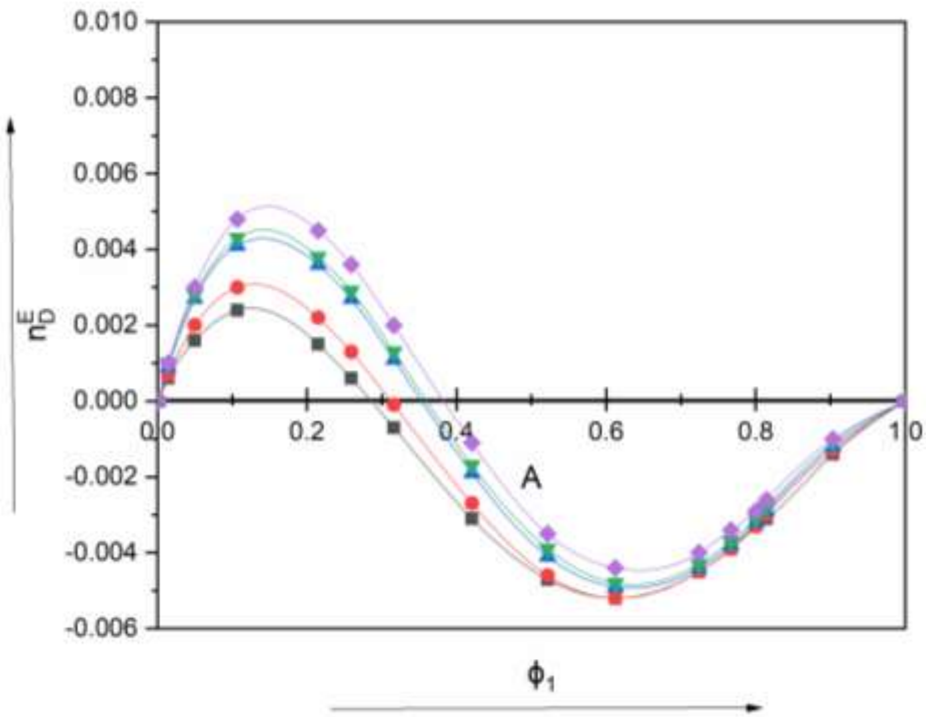

Figure 1. Excess refractive indices (n_D^E) of binary mixture involving methyl lauarte (x_i) + pentan-2-ol (1- x_i) as a function of mole fraction (x_i)at various temperatures (■)298.15, (●)303.15, (▲)308.15, (▼)313.15, and (♦)318.15K.
Source: Authors

alkyl group in ester, methyl laurateso at high mole fraction range negative values of n_D^E are observed. As the temperature increases the thermal energy helped in breaking the intermolecular interactions existing between the molecules of methyl laurate and alcohol in their pure form and subsequently lead to formation of new hydrogen bonds between methyl laurate and pentan-2-ol so n_D^E increases with increasing temperature for the binary mixture (Ali et al., 2013).

Conclusion

The refractive indices (n_D) and the excess refractive indices (n_D^E) of binary mixture methyl laurate + pentan-2-ol were measured at five various temperatures (293.15, 303.15, 303.15, 313.15, and 318.15k) over the complete mole fraction range. The mixing rules were found to be in finest settlement with experimental results. n_D^E values are positive and negative over the complete mole fraction range.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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