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Density, Viscosity and Refractive Index of the Ternary System (Ethanol + N-Hexane +3-Methyl Pentane) at 20, 30, 40 °C and 101.325 Kpa

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Abstract

Experimental densities, viscosities η, and refractive indices n_D data of the ternary ethanol+ n-hexane + 3-methyl pentane system have been determined at temperatures 293.15,303.15 and 313.15 K and at atmospheric pressure then these properties were calculated theoretically by using mixing rules for densities, viscosities and refractive indices .After that the theoretical data and the experimental data were compared due to the high relative errors in viscosities an equation of viscosity was proposed to decrease the relative errors.

Key Words: Thermodynamic properties, Measuring, Viscometer, Pycnometer , Refractive indices.

Introduction

Prediction of the thermodynamic properties of materials associated with the process can greatly affect the design, cost, and in some cases even determine the feasibility of a given unit operation. The need for accurate values of thermodynamic properties of an increasing variety of materials to support the design of processes places a strong emphasis on the development of techniques with predictive capabilities that can be used for a wide range of process conditions and mixtures with limited reliance on experimental data beyond that used at the early stages of the process development [1].

In such regard, thermodynamic and transport properties of fluid mixtures are required that might sometime obtained from tables but it is usually found that even the most extensive physic-chemical tables do not contain all the data necessary for designing a technological process. In such cases, properties have only been studied for pure components from which the mixture is constituted where method is required for estimating the properties of the mixtures. Such predictions usually entail large difficulties [2].

Finally, Properties alone remain elusive; failure to reach this goal as follows from an inadequate fundamental understanding of liquid structure and intermolecular forces. All macroscopic properties are related to molecular structure, which determines the magnitude and predominant type of the intermolecular forces [3].

Experimental Section

1- Materials

Ethanol, *n*-hexane and 3-methyl pentane were used in preparing the binary and ternary systems studied and acetone was used for cleaning the glassware were all purchased from Sigma and Thomas Baker with purity over 99%. Table 1 lists values of the properties of chemicals used in this study given by literature [4].

Table 1, Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Pure Compounds Used in This Work Compared with Literature Data at t = 20°C, t = 30°C and 40°C at atmospheric pressure

t = 20°C						
Compound	ρ / g.Cm^{-3}		η /mpa.s		n_D	
	Exp.	Lit.	Exp.	Lit	Exp.	Lit.
Ethanol	0.7895	0.790(75)	1.247	1.184(79)	1.3618	1.3618(79)
n-hexane	0.6480	0.655(34)	0.364	0.301(27)	1.3718 (98)	1.376
3-methyl pentane	0.659	0.6537(15)	0.301	0.292(41)	1.376	1.376(98)
t = 30°C						
Ethanol	0.7702	0.7709(76)	1.1514	0.997(79)	1.3600	---
n-hexane	0.64078	0.651(15)	0.3280	0.2956(79)	1.3730	---
3-methyl pentane	0.659	0.65369(15)	0.2674	0.263796(41)	1.3714	---
t = 40°C						
Ethanol	0.7614	0.7728(76)	0.8742	0.793(76)	1.3574	---
n-hexane	0.63118	0.6411(77)	0.29681	0.2537(79)	1.3695	---
3-methyl pentane	0.6435	0.6440(15)	0.2357	0.2398(41)	1.3689	---

2- Measurements

Densitie ρ measurements were measured, by pycnometer, while viscosity and refractive index measurements were made by using the Cannon-Fenske routine viscometer and refractometer respectively.

Results and Discussion

1- Density

The densities of the pure components ethanol and n-hexane were calculated using equations (1) and (4) respectively, while the density of pure water was determined by using equation (5). As for the density of pure component 3-methyl pentane equation (9) was used.

$$\frac{\rho_\circ - \rho}{\rho} = 0.200 \log_{10} \left[\frac{(B+P)}{(B+P_\circ)} \right] \quad \text{... (1)}$$

Po = 0.1013 MPa

Where :

$$\rho_o = \rho^c \{1 + \sum_{i=1}^{5} ai \ (1\text{-}T_r)^{(i/3)}\} \quad \text{... (2)}$$

And

$$\frac{B}{\text{MPa}} = 331.2083 - 713.86\ T_r + 401.61\ T_r^2 - F \quad \text{... (3)}$$

For ethanol:

$$\frac{B}{Mpa} = 520.23 - 1240\ T_r + 827\ T_r^2 - F \quad \text{... (4)}$$

For water:

$\rho = 999.84 + 0.053\ (T- 273.15) – 7.315*10^{-3}\ (T-273.15)^2 + 3.03*10^{-5}\ (T-273.15)^3$ ... (5)

For 3-methyl pentane using equation (6):

$\frac{Vs}{V*} = V_R^{(0)}\ [\ 1 - W_{SRK}\ V_R^{(\delta)}\ ]$ ... (6)

Where:

$V_R^{(0)} = 1+ a\ [1- T_r]^{(1/3)} + b\ (1-T_r)^{(2/3)} + c\ (1-T_r) + d\ (1-T_r)^{(4/3)}$ ... (7)

$0.25 < Tr < 0.95$

And

$V_R^{(\delta)} = \frac{[\ e + F\ Tr + g\ Tr^2 + h\ Tr^3]}{(\ Tr - 1.00001\ )}$ ... (8)

$0.25 < Tr < 1.00$

For, T_c obtained from table 2.

Table 2, pure component parameters for The Hankinson-Brobst- Thomson and The Rackett Liquid volume correlations

3-methyl pentane			
T_c (K)	P_c (bar)	W_{SRK}	V* (L /mol)
504.34	31.2	0.2741	0.3633

The values of the constants in equations above are:

a = -1.52816 , b =1. 43907,
c = - 0.81446 , d = 0.190454
e = -0.296123 , F = 0.386914,
g = - 0.0427258, h = - 0.0480645.

As listed in table 2 V* is a pure component characteristic volume generally within 1 to 4 percent of the critical volume, W_{SRK} is the acentric factor which forces the Soave equation to give a best fit, of existing vapor pressure data. Values of V* and W_{SRK} are given in table 2 [5, 6 , 7].Thomson et all have extended the HBT method to allow prediction by generalizing the constants in the Tait equation [7], Thus :

$V = Vs\ (1- c\ Ln\ \frac{\beta + P}{\beta + Pvp}\ )$ ... (9)

Where Vs is defined as the saturated liquid volume at the vapor pressure P_{vp} , which obtained from equation (6). The rest of the parameters β, Pvp and c are obtained from as illustrated below in equations 10, 11, 12 and 13:

$\beta/\ PC = -1 + a\ (1- Tr)^{(1/3)} + b\ (1- Tr)^{(2/3)} + d\ (1- Tr) + e\ (1- Tr)^{(4/3)}$ ... (10)

Where [3]

$Ln\ (Pvp\ /P_c) = (1-x)^{-1}\ [(VP_A)\ x + (VP_B)\ x^{1.5} + (VP_C)\ x^3 + (VP_D)\ x^6]$ ... (11)

$X = 1- \frac{T}{Tc}$ ... (12)

Values of VP_A, VP_B, VP_C and VP_D are given in table 3.

Table 3, Vapor Pressure, in bars

3-methyl pentane			
V_{PA}	V_{PB}	V_{PC}	V_{PD}
-7.27084	1.26113	-2.81741	-2.17642

$e = \exp (f + g\ w_{sRK} + h\ w^2_{sRK})$ … (13)

And

$c = j + k\ w_{SRK}$ ... (14)

a = - 9.070217 , b = 62.45326,
d = -135.1102 , f = 4.79594,
g = 0.250047 , h = 1.14188,
j = 0.0861488 , k = 0.034483

Equation (15) applied to ternary system to calculate the density for the ternary system (ethanol +n-hexane +3-methyl pentane):

$$\rho_{mix} = w_1 * \rho_1 + w_2 * \rho_2 + w_3 * \rho_3 \ldots (15)$$

Where ρ_1, ρ_2, ρ_3 were the densities of pure component 1, 2, 3 and w_1, w_2 , w_3 were the weight fractions of component 1,2,3.

$$\%Er = ABS\left(\frac{(Experimental\ value - Calculated\ value)}{Eeperimental\ value}\right) \ldots (16)$$

The density of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) was calculated using the pure density of each component and the weight fraction and equation 15. The results were compared with experimental values by calculating the % relative error (%Er) given by equation 16. Table 4 lists the results of the comparison at 20 °C while table 5 and 6 lists values at 30 °C and 40 °C respectively.

Table 4, Density (ρ) of ternary system, ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) at temperatures 20℃

$Wt._1$	$Wt._2$	ρ exp.	ρ equ. (15)	%Er
0.00000.145	0.950	0.6480	0.6552	1.10
0.166	0.813	0.6643	0.6743	1.50
0.195	0.793	0.6663	0.6771	1.62
0.374	0.765	0.6702	0.6810	1.61
0.472	0.595	0.6902	0.7045	2.07
0.545	0.502	0.7031	0.7175	2.04
0.705	0.433	0.7116	0.7271	2.19
1.000	0.281	0.7331	0.7483	2.06
	0.000	0.7895	0.7873	0.28
			Average	1.61

Table 5, Density (ρ) of ternary system, ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) at temperatures 30℃

$Wt._1$	$Wt._2$	ρ exp.	ρ equ.(15)	%Er
0.000	0.950	0.6408	0.6461	0.84
0.145	0.813	0.6539	0.6653	1.74
0.195	0.765	0.6610	0.7200	1.67
0.374	0.595	0.6812	0.6956	2.12
0.472	0.502	0.6890	0.7086	2.85
0.545	0.433	0.7037	0.7183	2.08
0.705	0.281	0.7257	0.7395	1.91
0.837	0.155	0.7543	0.7571	1.37
1.000	0.000	0.7702	0.7787	1.10
			Average	1.63

Table 6, Density (ρ) of ternary system, ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) at temperatures 40℃

$Wt._1$	$Wt._2$	ρ exp.	ρ equ. (15)	%Er
0.000	0.950	0.6312	0.6370	0.92
0.144	0.813	0.6431	0.6561	2.01
0.212	0.749	0.6514	0.6651	2.11
0.393	0.577	0.6722	0.6892	2.53
0.486	0.488	0.6846	0.7016	2.50
0.547	0.431	0.6937	0.7097	2.30
0.711	0.275	0.7163	0.735	2.12
1.000	0.000	0.7614	0.7700	1.13
			Average	1.95

2- Viscosity

The viscosity values for the pure components and the ternary system was measured. The viscosity of pure components ethanol and n-hexane was calculated from equation (17) while viscosity of water was calculated by using equation (18), and finally the viscosity for 3-methyl pentane was determined by using equation (19).

$$\eta^* = \left(\frac{16}{5}\right)(2\ N_A)^{(1/3)}\ \pi^{(1/2)}\left(\frac{1}{MRT}\right)^{(1/2)}\left(\frac{\eta V_m(2/3)}{R_\eta}\right) \ldots (17)$$

$$Ln\ \eta = A + B/T + C * T + D * T^2 \ldots (18)$$

$$Ln\ \frac{\eta_L}{\rho_{L\ .\ M}} = A + \frac{B}{T} \ldots (19)$$

Where η_L=Liquid Viscosity, in Cpand ρ_L is the liquid density at 20 C˚ in g/cm^3. M is the molecular weight in g/mole and T is the temperature in K and the constants A and B are given in table 7 [8].

Table 7, the parameters of Orrick and Erbar method

3-methyl pentane	
A	B
-(6.95 + 0.21n)	275+ 99n
-0.15	35

When n = the carbon number.

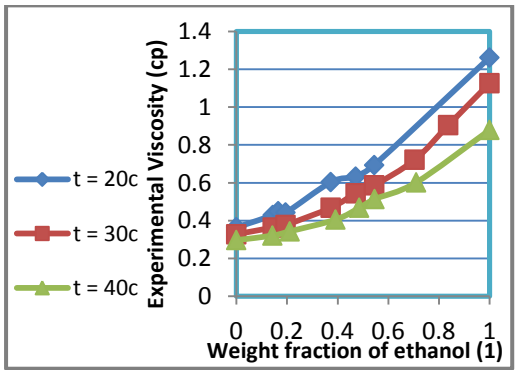

Fig. 1, The data given in tables 6, 7 and 8 are plotted as viscosity verses weight fraction at temperatures t = 20 ^{o}C , 30 ^{o}C and 40 ^{o}C

Figure (1) shows the experimental values of viscosity as plotted versus weight fraction of ethanol for ternary system it was noted the increase in the value of viscosity as weight fraction of ethanol increases in such respond, we proposed an equation that involves the use of activity coefficients as shown in equation (20) for determination of viscosity values in ternary system.

$$\eta = A^* \eta_{mix} * \left(\frac{\Upsilon 2}{\Upsilon 1}\right)^B \quad \text{... (20)}$$

η_{mix} is defined by equation (21),and Υ_1 and Υ_2 known as activity coefficients of component 1 and 2 determined from Wilson model. While A, η_{mix} and B are determined from following equations.

$$\eta_{mix} = w_1 * \eta_1 + w_2 * \eta_2 + w_3 * \eta_3 \text{... (21)}$$

$$A = \frac{(\rho 1 - \rho c1)}{(\rho 2 - \rho c2)} \quad \text{... (22)}$$

$$B = \frac{(1-A)}{Z} \quad \text{... (23)}$$

Where ρ_c is the critical density of a component. When equation (20) was applied on the above ternary system the relative errors have been reduced as noticed in tables 8, 9 and 10.

Table 8, Viscosities (η) of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) at temperature of 20^{o}C determined using equation (20).

$Wt._1$	$Wt._2$	Υ_1	Υ_2	η equ 20	η exp.	Er%
0.000	0.950	19.428	1.000	0.2716	0.3645	25.48
0.144	0.813	2.648	1.231	0.3903	0.4285	8.92
0.166	0.793	2.387	1.278	0.4070	0.4497	9.49
0.195	0.765	2.114	1.346	0.4304	0.4423	2.69
0.373	0.595	1.379	1.851	0.5717	0.6039	5.34
0.471	0.502	1.221	2.203	0.6496	0.6328	2.65
0.545	0.433	1.146	2.506	0.7079	0.6938	2.04
1.000	0.000	1.000	5.584	1.0747	1.2473	14.86
					Average	5.19

Table 9, Viscosities (η) of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) at temperature of 30°C determined using equation (20).

$Wt._1$	$Wt._2$	Υ_1	Υ_2	η equ 20)(	η exp.	Er%
0.000	0.950	40.38	1.000	0.239	0.328	26.90
0.145	0.813	3.078	1.270	0.347	0.363	4.41
0.195	0.765	2.411	1.400	0.383	0.377	1.62
0.374	0.595	1.502	1.996	0.509	0.468	8.66
0,472	0.502	1.302	2.447	0.578	0.544	6.28
0.545	0.433	1.205	2.866	0.630	0.586	7.48
0.705	0.281	1.075	4.143	0.746	0.722	3.33
0.837	0.155	1.022	5.808	0.842	0.904	6.87
1.000	0.000	1.000	9.322	0.963	1.151	14.48
					Average	5.57

Table 10, Viscosities (η) of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) at temperature of 40°C determined using equation (20).

$Wt._1$	$Wt._2$	Υ_1	Υ_2	η equ 20	η exp.	Er%
0.000	0.950	35.553	1.000	0.2261	0.2968	23.82
0.144	0.813	3.078	1.261	0.3058	0.3208	4.68
0.212	0.749	2.254	1.437	0.3405	0.3434	0.84
0.393	0.577	1.451	2.061	0.4328	0.4055	6.72
0.486	0.488	1.277	2.506	0.4808	0.4682	2.69
0.547	0.431	1.201	2.854	0.5119	0.5140	0.42
0.711	0.275	1.071	4.158	0.5972	0.6022	0.84
1.000	0.000	1.000	9.149	0.7515	0.8742	14.48
					Average	2.70

3- Refractive index

The refractive index of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) was calculated from pure component data by using equation (23) and using the volume fraction via equation (24).

$$n_D = [\, 1 + \varphi_1 (n_{D1}^2 - 1) + \varphi_2 (n_{D2}^2 - 1) + \varphi_3 (n_{D3}^2 - 1)]^{(1/2)} \quad \ldots (23)$$

$$\varphi_i = \frac{x_i M_i}{x_1 M_1 + x_2 M_2 + x_3 M_{23}} \cdot \frac{\rho}{\rho i} \quad \ldots (24)$$

It seemed as pointed out in table 1 the experimental data of pure compounds obtained in the present study are in good agreement with their corresponding literature values.

Tables 11, 12 and 13 lists the refractive index of the ternary system determined from above equation and compared with experimental values at 20 °C, 30 °C, 40 °C.

Table 11, Refractive indices (n_D) of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) and at 20℃ by using equation (23)

$Wt._1$	$Wt._2$	φ_1	φ_2	n_D mix.	n_D exp.	Er %
0.000	0.950	0.000	0.950	1.3729	1.3725	0.031
0.145	0.813	0.125	0.834	1.3724	1.3720	0032
0.195	0.765	0.171	0.792	1.3721	1.3718	0.026
0.374	0.595	0.337	0.636	1.3707	1.3702	0.037
0.545	0.433	0.506	0.476	1.3686	1.3682	0.034
0.705	0.281	0.672	0.317	1.3661	1.3658	0.026
1.000	0.000	1.000	0.000	1.3600	1.3600	0.000
					Average	0.027

Table 12, Refractive indices (n_D) of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) and at 30℃ by using equation (23)

$Wt._1$	$Wt._2$	φ_1	φ_2	φ_3	n_D Mix.	n_D exp.	Er %
0.000	0.950	0.000	0.950	0.000	1.3720	1.3718	0.015
0.144	0.813	0.123	0.838	0.044	1.3722	1.3715	0.048
0.212	0.749	0.183	0.782	0.041	1.3720	1.3710	0.076
0.393	0.577	0.352	0.624	0.033	1.3711	1.3708	0.025
0.486	0.488	0.444	0.537	0.028	1.3703	1.3690	0.097
0.711	0.275	0.675	0.315	0.017	1.3675	1.3670	0.034
0.832	0.159	0.808	0.187	0.010	1.3654	1.3650	0.027
1.000	0.000	1.000	0.000	0.000	1.3618	1.3618	0.000
						Average	0.04

Table 13, Refractive indexes (n_D) of the ternary system ethanol (1) + n-hexane (2) + 3-methyl pentane (3) at different weight fractions of ethanol ($Wt._1$) and at 40℃ by using equation (23)

$Wt._1$	$Wt._2$	φ_1	φ_2	n_D mix.	n_D exp.	Er %
0.000	0.950	0.000	0.950	1.3695	1.3690	0.034
0.144	0.814	0.123	0.838	1.3694	1.3687	0.049
0.212	0.749	0.183	0.782	1.3691	1.3683	0.061
0.393	0.577	0.352	0.624	1.3679	1.3674	0.037
0.486	0.488	0.444	0.537	1.3669	1.3662	0.053
0.547	0.431	0.504	0.479	1.3662	1.3658	0.027
0.711	0.275	0.675	0.315	1.3636	1.3630	0.047
1.000	0.000	1.000	0.000	1.3574	1.3574	0.000
					Average	0.038

Conclusion

The collected experimental data for the densities and the refractive indices of the ternary system are in good agreement with the theoretical data.

Because of close matching between experimental and theoretical data we found there is no need to propose new correlation for the determination of density and refractive index for predicting ternary system from pure component data. While for the viscosities of the binary and ternary systems, the relative errors were high so a new correlation was.

The new proposal gave good results and could be suitable for liquid solutions.

Nomenclature

%Er: Relative error
ρ: Density at T and P
$\rho_{\circ}$: Density at To and Po
ρc: Density at Tc and Pc
ABS: Absolute value
Ai: Constant in equation 2[9]
B: Pressure correction in equation 3:
F: Constant in equation 3
NA: Avogadros constant
nD: Refractive index of mixture
nDi: Refractive index of component i
PC: Critical pressure
Po: Reference pressure
Pve: Vapor pressure
R: Universal gas constant
T: Temprature
TC: Critical temperature
Tr: Reduced temprature
V: volume
Vm: Molar volume
VR(0): Reduced volume defined by equation 7
VR(δ): Reduced volume defined by equation 8
VS: Volume at saturation
wi: Weight fraction of component i
WSRK: Acentric factor
Z: Coordination number[9]
β: Pressure term in equation 10
η: viscosity
ηmix: Viscosity of mixture
π: pi
ρmix: Density of mixture
ϒi: Activity coefficient of component i

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