



Vapor-Liquid Equilibrium Studies of the Binary Liquid Mixtures of Ethyl lactate with Amino-, Chloro- and Phenyl-ethanols

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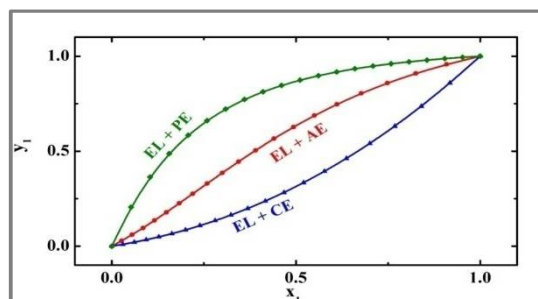
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ABSTRACT

For the binary mixtures of ethyl lactate + aminoethanol, + chloroethanol and + phenylethanol, isobaric vapor-liquid equilibrium (VLE) data is experimentally determined at 95.3 kPa over the entire composition range using a Swietoslowski type ebulliometer. Densities at 303.15 K are reported for the pure liquids. The activity coefficients are correlated with the mole fraction using Wilson, nonrandom two-liquid (NRTL), van Laar and Margules liquid-phase equations and the corresponding binary interaction parameters are reported. The liquid phase activity coefficients are estimated considering the non-ideal behavior of the mixtures. The computed vapor phase mole fractions, activity coefficients, and Gibbs energy values along with optimum Wilson parameters are presented and the results are correlated to the molecular interactions between the dissimilar molecules of the binary mixtures. The studies indicate that all three binary systems are non-ideal liquid mixtures deviating from Raoult's law exhibiting negative values of excess Gibbs energies due to intermolecular hydrogen bonding between unlike molecules and also the non-formation of azeotropic mixtures is observed. The observed trend in the Gibbs energies indicates that the interactions between ethyl lactate and substituted ethanol molecules follow the order: ethyl lactate + aminoethanol > ethyl lactate + chloroethanol > ethyl lactate + phenylethanol.

Graphical Abstract



x_1 - y_1 phase diagram for the binary mixtures of ethyl lactate + aminoethanol, ethyl lactate + chloroethanol and ethyl lactate + phenylethanol systems

Keywords: Vapor liquid equilibrium, Hydrogen bonding, Liquid phase equation, Gibbs energy.

INTRODUCTION

Alternative solvents for green chemistry paid a great deal of attention to replace toxic and volatile organic solvents. Ethyl lactate, one type of alternative solvents that can be easily produced from biomass feedstock, has unique properties like low toxicity, relatively high boiling point, high solvency power, good biodegradability, and recyclability [1-3]. Because of these features, ethyl lactate is used as a green solvent in several applications. Ethyl lactate is an environmentally benign reaction solvent for the synthesis of pharmaceutical compounds [4] and as a food additive with an approval by the US Food and Drug Administration. The customary solvents are replaced by ethyl lactate by considering the recently developed technologies [5-7] because of its production from carbohydrate feed stocks at very low and competitive prices. Chloroethanol (CE) is a polar, bi-functional compound, consisting of both hydroxyl group as a proton donor and halogen atom as a proton acceptor and is widely used in a number of synthetic reactions including the manufacturing of dyes, drugs, pesticides, and plasticizers. It has the characteristics of both alcohol and chlorinated hydrocarbon and a versatile solvent used in many industrial areas [8]. Phenylethanol (PE) is used as a common ingredient [9] in perfumes when rose smell is desired and as a preservative in soaps due to its stability in basic conditions. Ethanolamines [10] are the important class of compounds that are used in a wide variety of household and industrial applications. In the petroleum and natural gas industries, the removal of acid constituents from the process streams is commonly achieved by reacting the impurities with aqueous ethanolamine.

Process modeling has gained a great deal of consideration as a trustworthy tool for attaining effective, clean, and optimal new technologies [11] over the past few decades. Because of the demand from the growth of chemical and allied industries, the increasing progress of process design requires environmental friendly and less energy-consuming conditions. Modeling is mainly dependent on precise knowledge of the phase equilibrium behavior of the chemicals involved. Therefore, the availability of appropriate methods and the reliable physical property data are basic requirements to achieve a proper design [12, 13]. Among various thermo-physical properties needed for the modeling for solvent mixtures, vapor liquid equilibrium (VLE) data are key to the design of industrial plants of the liquids involved. Calculations of VLE in chemical engineering are traditionally performed with an equation of state based on pure liquid/vapor phase properties. In a condition of phase equilibrium, there are some properties that are significantly different between the phases and others that must be identical for all phases to prevent a change in properties within individual phases from occurring. The thermodynamic equilibrium determines how components in a mixture are distributed between phases. These are easy to use and require computational effort and yield qualitative predictions of binary mixture VLE. For the simulation and operation of the extractive distillation process and for determining the optimal values of parameters in the thermodynamic models [14, 15], VLE data play an important role.

The literature survey shows that studies on the phase equilibrium and the corresponding VLE data of the binary liquid mixtures of ethyl lactate with aminoethanol, chloroethanol and phenylethanol are very limited. In this study, the isobaric VLE data on activity coefficients useful for the simulation and design of distillation process for all three binary systems along with the vapor composition of the mixtures at 95.3 kPa are reported and the data are correlated with various phase equilibrium models viz., Wilson, NRTL, Van Laar and Margules.

MATERIALS AND METHODS

Ethyl lactate (Merck, India, > 0.995 mole fraction purity) is distilled at low pressure and stored over freshly activated 0.3 nm molecular sieves. Aminoethanol, chloroethanol and phenylethanol (from SD Fine Chemicals, India, > 0.995 mole fraction purity) are purified by using a fractionating column. The purity of the materials was checked by gas chromatography and was found to be better than 0.993 mass fraction. The details of chemicals used in this work, their purity, structure and purification etc.

are given in table 1. The purity of the chemicals is verified by comparing the densities of the pure compounds with literature values [16-20] and the data is reported in table 2.

Table 1. Details of chemicals used with CAS number, source, purification method and molar mass

Chemical	CAS number	Supplier	Purification technique (Purity% GC)	Molar mass $10^{-3} \text{ kg mol}^{-1}$
Ethyl lactate	97-64-3	Merck	Vacuum distillation(99.7)	118.13
2-aminoethanol	141-43-5	S.D Fine	Fractional distillation(99.6)	61.08
2-chloroethanol	107-07-3	S.D Fine	Fractional distillation(99.3)	80.511
2-phenylethanol	60-12-8	S.D Fine	Fractional distillation(99.5)	122.16

Table 2. Comparison of the experimental density (ρ/kgm^{-3}) of ethyl lactate, aminoethanol, chloroethanol and phenylethanol with the literature data at 303.15 K

Compound	ρ/kgm^{-3}		
	Exp.	Literature	
Ethyl lactate	1022.74	1022.81[16]	1022.89[17]
2-aminoethanol	1008.76	1008.72[18]	1008.74[19]
2-chloroethanol	1192.53	1192.45[18]	1192.48[20]
2-phenylethanol	1012.58	1012.64[18]	1012.65[20]

A single pan electronic balance (Shimadzu AY120) with an uncertainty of ± 0.01 milligram is used for the preparation of various compositions of the liquid mixtures with an uncertainty of 1×10^{-4} in the mole fraction and the prepared mixtures are stored in air-tight glass bottles. The liquids are thoroughly mixed before being transferred into the apparatus used for the determination of density and VLE data. The required properties are measured within one day of the preparation of the mixture. The densities of the mixtures are measured using a vibrating-tube Rudolph Research Analytical density meter, model DDM-2911, automatically thermostated within ± 0.01 K. The uncertainty in density measurements is $\pm 1 \times 10^{-5} \text{ g cm}^{-3}$.

A Swietoslawski type ebulliometer is used to determine the VLE data as a function of the liquid-phase mole fraction at constant pressure. A dry nitrogen gas cylinder and a vacuum pump are connected to the ebulliometer with a closed end manometer in line for the maintenance and measurement of the total pressure of the system at a required level. The required pressure is maintained by adjusting the opening of the needle valve of the gas cylinder or the bypass line of the vacuum pump. By applying the necessary adjustment and regularly reading the mercury columns of the manometer, the total pressure is maintained within ± 0.05 kPa of the required value in this set of experiments. The equilibrium temperature with accuracy of ± 0.05 K is measured with a mercury in glass thermometer. The thermometer is kept in the thermo-well filled with mercury to note the steady-state temperature of the (vapor + liquid) mixture impinging on the Cottrell tube.

It is ensured that the components are adequately mixed before being transferred into the ebulliometer and each binary mixture is used immediately after the preparation. After the binary mixture is transferred into the ebulliometer, the heating rate is slowly increased and adjusted to produce the required boil-up rate so that a drop count of about 30 drops per minute is achieved, in accordance with the proposal of Hala *et al.* [21]. The equilibrium temperature is noted after the steady state is achieved.

RESULTS AND DISCUSSION

Deviations from ideal behavior are likely to occur in the liquid phase than in the vapor phase as the forces of interaction between molecules in the liquid are considerably stronger due to smaller intermolecular distances. In contrast, the vapor phase can be assumed to behave ideally at moderate pressures. The phase behavior of real liquids is frequently described by means of the activity coefficients. The method for determining the phase equilibrium in systems that are non-ideal in liquid

phase is based on the activity coefficient models such as Wilson, NRTL, Van Laar and Margules. For a useful explanation of the behavior of liquid mixtures and process engineering design, consistent and precise vapor–liquid equilibrium data are required. The boiling points of the pure liquids viz., ethyl lactate, aminoethanol, chloroethanol and phenylethanol determined experimentally at various pressures are presented in table 3.

Table 3. Experimental saturated vapor pressure (P/kPa) and boiling point temperature (T/K) data of ethyl lactate, aminoethanol, chloroethanol and phenylethanol

P/kPa	Ethyl lactate	Aminoethanol	Chloroethanol	Phenylethanol
	T/K	T/K	T/K	T/K
95.32	425.65	442.29	399.89	489.80
89.62	423.65	440.43	398.04	487.55
81.48	420.60	437.59	395.21	484.12
75.33	418.11	435.28	392.91	481.34
68.27	415.03	432.43	390.06	477.89
59.98	411.04	428.74	386.38	473.44
54.05	407.88	425.82	383.47	469.92
48.38	404.57	422.77	380.43	466.24
40.87	399.62	418.22	375.89	460.75
33.92	394.27	413.32	371.00	454.85
27.84	388.74	408.27	365.97	448.77

The experimental vapor pressures and boiling point temperatures of the pure liquids are correlated using the three variable Antoine [22] and five variable Riedel [23] equations. Antoine equation is given by:

$$\ln[P/(kPa)] = \left\{ \frac{A-B}{T/(K)+C} \right\} \quad ..(1)$$

where the Antoine constants A, B, and C are determined by fitting the pressure-temperature data using the nonlinear optimization technique. Figure 1 represents experimental saturated vapor pressure (p/kPa) vs temperature (T/K) along with the corresponding Antoine equations for ethyl lactate + aminoethanol, ethyl lactate + chloroethanol and ethyl lactate + phenylethanol.

Riedel equation is expressed as:

$$\ln P = A + \left(\frac{B}{T} \right) + C * \ln(T) + DT^E \quad ..(2)$$

where the Riedel constants A, B, C, D and E are also determined by fitting the pressure-temperature data using the nonlinear optimization technique and are presented in table 4 along with Antoine constants.

Table 4. Antoine and Riedel constants of pure liquids obtained from experimental pressure – boiling point data

Component	A	B	C	D	E
Ethyl lactate					
Antoine constants	14.6444	3411.98	- 87.50	--	--
Riedel constants	17.309	5221.66	-0.160	2.66 x 10 ⁻⁶	2
Aminoethanol					
Antoine constants	17.2478	4882.80	-57.53	--	--
Riedel constants	15.537	3761.90	-0.017	-1.36 x 10 ⁻⁵	2
Chloroethanol					
Antoine constants	17.2369	4861.70	-16.47	--	--
Riedel constants	10.512	3969.17	0.384	1.05 x 10 ⁻⁵	2
Phenylethanol					
Antoine constants	16.9747	5650.32	-34.77	--	--
Riedel constants	17.322	7162.24	0.454	-3.99 x 10 ⁻⁶	2

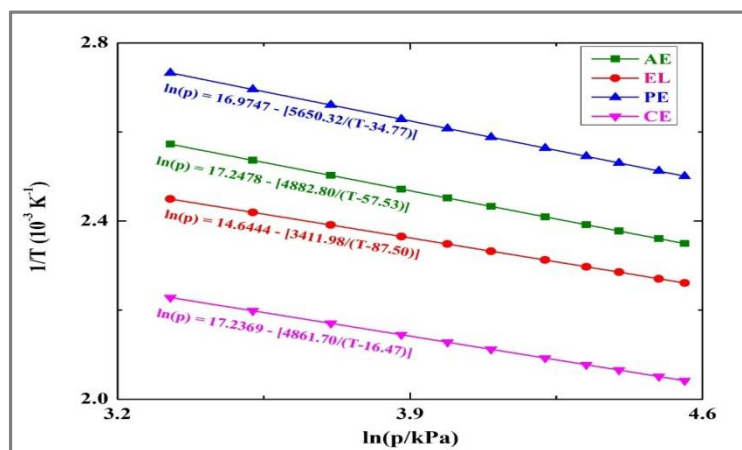


Figure 1. Experimental saturated vapor pressure (p/kPa) vs temperature (T/K) along with the corresponding Antoine's equations for ethyl lactate + aminoethanol, ethyl lactate + chloroethanol and ethyl lactate + phenylethanol

Wilson's Equation: Wilson's equation [24] provides a relation for the excess Gibbs energy for a number of miscible mixtures and is particularly useful for solutions of polar or associating components in non-polar solvents. Based on molecular considerations, the expression proposed by Wilson for the excess Gibbs energy, G^E of a binary solution in terms of the mole fractions of the component liquids x_1 , x_2 , the temperature of the mixture T and the adjustable parameters A_{12} and A_{21} , is:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1) \quad \text{..(3)}$$

Activity coefficients γ_1 and γ_2 derived from this equation are:

$$\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2 \left[\frac{A_{12}}{x_1 + A_{21}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1} \right] \quad \text{..(4)}$$

$$\ln \gamma_2 = -\ln(x_2 + A_{21}x_1) - x_1 \left[\frac{A_{12}}{x_1 + A_{21}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1} \right] \quad \text{..(5)}$$

The adjustable parameters A_{12} and A_{21} are related to the pure component molar volumes and characteristic energy differences by:

$$A_{12} = \frac{v_2}{v_1} \exp \left[-\frac{\lambda_{12} - \lambda_{11}}{RT} \right] \quad \text{..(6)}$$

$$A_{21} = \frac{v_1}{v_2} \exp \left[-\frac{\lambda_{21} - \lambda_{22}}{RT} \right] \quad \text{..(7)}$$

where v_i is the molar liquid volume of pure component i and $\lambda_{12}, \lambda_{11}, \lambda_{21}$ and λ_{22} are energies of interactions between the molecules. For accurate measurements, $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ should be considered temperature dependent but in many cases this dependence can be neglected as it does not account for additional information.

The experimental data are correlated by the Wilson method from which the activity coefficients and excess Gibbs energy are calculated taking into account the non-ideal behavior of the vapor-liquid phases. The adjustable binary parameters assumed in these equations are estimated by nonlinear regression analysis. VLE data, viz., data on liquid phase mole fraction (x_i), experimental boiling point temperature (T_{exp}), vapor phase mole fraction (y_i), activity coefficients (γ_1 and γ_2) and excess Gibbs

energy (G^E) of the binary systems of ethyl lactate (1) + aminoethanol (2), chloroethanol (2) and phenylethanol (2) at 95.3 kPa are reported in table 5.

It is clear that the values of activity coefficients are less than unity for all the three binary liquid systems under investigation, indicating non-ideal nature of these mixtures with a negative deviation from Raoult's law. The observed negative deviations from Raoult's law in all the three systems may be due to the presence of strong intermolecular forces like hydrogen bonding between the binary mixture components. The positive and negative deviations for non-ideal solutions from vapor-liquid studies are well described by Harrison *et al.* [25].

Table 5. Temperature, vapor, phase composition, activity coefficients and excess Gibbs energy for the mixtures of ethyl lactate (EL) + aminoethanol (AE), + chloroethanol (CE) and phenylethanol (PE)

x1	T _{cal} /K	y ₁	γ ₁	γ ₂	log (γ ₁ /γ ₂)	G ^E /J.mol ⁻¹
Ethyl lactate (1) + Aminoethanol (2)						
0.0000	442.29	0.0000	0.6293	--	--	0.000
0.0268	442.26	0.0281	0.6565	0.9994	-0.4203	-43.510
0.0550	442.20	0.0600	0.6836	0.9977	-0.3781	-84.873
0.0847	442.08	0.0958	0.7105	0.9948	-0.3366	-123.849
0.1159	441.90	0.1353	0.7370	0.9908	-0.2960	-160.053
0.1487	441.65	0.1784	0.7629	0.9856	-0.2561	-193.223
0.1835	441.33	0.2255	0.7884	0.9791	-0.2167	-223.305
0.2201	440.92	0.2759	0.8129	0.9715	-0.1782	-249.656
0.2590	440.41	0.3296	0.8368	0.9627	-0.1402	-272.145
0.3002	439.81	0.3859	0.8595	0.9527	-0.1029	-290.215
0.3439	439.10	0.4444	0.8811	0.9415	-0.0662	-303.404
0.3905	438.27	0.5047	0.9014	0.9290	-0.0301	-311.217
0.4402	437.33	0.5658	0.9203	0.9153	0.0055	-313.010
0.4933	436.27	0.6271	0.9376	0.9004	0.0405	-308.091
0.5502	435.09	0.6877	0.9531	0.8843	0.0750	-295.660
0.6113	433.79	0.7470	0.9667	0.8669	0.1089	-274.802
0.6771	432.38	0.8041	0.9782	0.8484	0.1424	-244.453
0.7481	430.86	0.8585	0.9875	0.8286	0.1754	-203.416
0.8251	429.24	0.9095	0.9943	0.8076	0.2080	-150.156
0.9088	427.53	0.9568	0.9986	0.7854	0.2401	-82.995
1.0000	425.75	1.0000	--	0.7620	--	0.000
Ethyl lactate (1) + Chloroethanol (2)						
0.0000	399.89	0.0000	0.6971	-	-	0.000
0.0298	400.54	0.0095	0.7213	0.9995	-0.3261	-34.051
0.0610	401.23	0.0207	0.7453	0.9980	-0.2920	-66.210
0.0935	401.98	0.0335	0.7686	0.9954	-0.2586	-96.134
0.1275	402.79	0.0484	0.7914	0.9919	-0.2258	-123.766
0.1631	403.65	0.0656	0.8135	0.9873	-0.1937	-148.915
0.2003	404.57	0.0852	0.8347	0.9817	-0.1622	-171.306
0.2394	405.56	0.1079	0.8552	0.9752	-0.1313	-190.819
0.2804	406.61	0.1339	0.8746	0.9676	-0.1010	-207.125
0.3235	407.73	0.1637	0.8930	0.9591	-0.0714	-219.965
0.3689	408.91	0.1980	0.9102	0.9495	-0.0423	-229.020
0.4167	410.18	0.2372	0.9262	0.9391	-0.0138	-233.912

0.4672	411.52	0.2822	0.9409	0.9277	0.0142	-234.238
0.5205	412.94	0.3339	0.9541	0.9153	0.0415	-229.535
0.5770	414.45	0.3933	0.9659	0.9021	0.0683	-219.260
0.6369	416.05	0.4616	0.9760	0.8879	0.0945	-202.816
0.7004	417.76	0.5401	0.9844	0.8730	0.1202	-179.562
0.7681	419.57	0.6310	0.9911	0.8571	0.1453	-148.617
0.8403	421.50	0.7361	0.9960	0.8403	0.1700	-109.097
0.9174	423.55	0.8580	0.9990	0.8228	0.1940	-59.984
1.0000	425.75	1.0000	--	0.8045	--	0.000
Ethyl lactate (1) + Phenylethanol (2)						
0.0000	489.80	0.0000	0.8980	--	--	0.000
0.0521	483.44	0.2053	0.9064	0.9997	-0.0980	-21.682
0.1040	477.63	0.3638	0.9147	0.9988	-0.0880	-40.974
0.1556	472.34	0.4869	0.9228	0.9974	-0.0776	-57.862
0.2071	467.50	0.5839	0.9308	0.9952	-0.0670	-72.425
0.2583	463.08	0.6607	0.9384	0.9925	-0.0561	-84.623
0.3092	459.05	0.7222	0.9458	0.9892	-0.0449	-94.485
0.3600	455.34	0.7721	0.9528	0.9852	-0.0335	-102.067
0.4105	451.93	0.8128	0.9594	0.9806	-0.0219	-107.355
0.4608	448.78	0.8463	0.9656	0.9754	-0.0101	-110.384
0.5109	445.87	0.8742	0.9713	0.9696	0.0018	-111.170
0.5607	443.17	0.8975	0.9766	0.9631	0.0139	-109.736
0.6104	440.66	0.9172	0.9814	0.9561	0.0261	-106.095
0.6598	438.33	0.9338	0.9857	0.9485	0.0384	-100.278
0.7091	436.15	0.9480	0.9894	0.9403	0.0509	-92.280
0.7581	434.12	0.9601	0.9926	0.9316	0.0634	-82.150
0.8069	432.22	0.9705	0.9953	0.9223	0.0761	-69.894
0.8555	430.44	0.9795	0.9973	0.9126	0.0888	-55.528
0.9039	428.78	0.9873	0.9988	0.9023	0.1016	-39.071
0.9520	427.22	0.9941	0.9997	0.8916	0.1145	-20.581
1.0000	425.75	1.0000	--	0.8804	--	0.000

Standard uncertainty in temperature $u(T) = 0.05$ K, combined standard uncertainty in composition $u(x) = 0.0001$, and pressure $u(P) = 0.05$ kPa at a confidence level of 95%

NRTL equation: Renon used the concept of local composition in the derivation of the NRTL (nonrandom, two-liquid) equation [26]. This is applicable to partially miscible as well as completely miscible systems. The NRTL equation for the excess Gibbs energy is:

$$g^E = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} \right) \quad \text{..(8)}$$

$$\tau_{12} = (\Delta g_{12} - \Delta g_{22})/RT \quad \text{..(9)}$$

$$\tau_{21} = (\Delta g_{21} - \Delta g_{11})/RT \quad \text{..(10)}$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) G_{21} = \exp(-\alpha_{12} \tau_{21}) \quad \text{..(11)}$$

The significance of g_{ij} is similar to that of λ_{ij} in Wilson's equation; g_{ij} is an energy parameter characteristic of the i - j interaction. Parameter α_{12} is related to the non-randomness in the mixture; when α_{12} is zero, the mixture is completely random and the equation reduces to the two-suffix Margules equation. The NRTL equation contains three parameters. The activity coefficients are:

$$\ln \gamma_1 = -x_2^2 \left[\tau_{21} \left\{ \frac{G_{12}}{x_1 + x_2 G_{21}} \right\}^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad ..(12)$$

$$\ln \gamma_2 = -x_1^2 \left[\tau_{12} \left\{ \frac{G_{12}}{x_2 + x_1 G_{12}} \right\}^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad ..(13)$$

For a solution of m components, the NRTL equation is:

$$\frac{g^E}{RT} = - \sum_{i=1}^m x_i \frac{\sum_{j=1}^m \tau_{ji} G_{ij} x_j}{\sum_{l=1}^m G_{il} x_l} \quad ..(14)$$

where $\tau_{ji} = (g_{ji} - g_{ii})/RT$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (\alpha_{ji} = \alpha_{ij})$$

The activity coefficient for any component i is given by:

$$\gamma_1 = \frac{\sum_{j=1}^m \tau_{ji} G_{ij} x_j}{\sum_{l=1}^m G_{il} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{il} x_l} \left\{ \tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{il} x_l} \right\} \quad ..(15)$$

Van Laar Equation: Van Laar [27] expressed the excess Gibbs free energy of binary liquid mixtures as:

$$\frac{g^E}{RT} = \frac{A_{12} x_1 x_2}{x_1 \left(\frac{A_{12}}{A_{21}} \right) + x_2} \quad ..(16)$$

where the constants A_{12} and A_{21} are obtained by regression of experimental vapor-liquid equilibria data. The activity coefficients of the components are:

$$\ln \gamma_1 = A_{12} \left[\frac{A_{21} x_2}{A_{12} x_2 + A_{21} x_1} \right]^2 \quad ..(17)$$

$$\ln \gamma_2 = A_{21} \left[\frac{A_{12} x_1}{A_{12} x_1 + A_{21} x_2} \right]^2 \quad ..(18)$$

This shows that the constants A_{12} and A_{21} are equal to logarithmic limiting activity coefficients $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$, respectively.

Four suffix Margules equation: A simple thermodynamic model for the excess Gibbs free energy of a liquid mixture proposed by Margules is used to derive an expression for the activity coefficients γ_i of i^{th} component in a liquid and the activity coefficient is a measure for the deviation from ideal solubility. The model has the distinctive feature to describe extreme in the activity coefficient. The Margules Gibbs free energy model for binary liquid mixtures is also known as the Margules activity coefficient model and given by:

$$\frac{G^E}{RT} = x_1 x_2 [A x_2 + B x_1 - C x_1 x_2] \quad ..(19)$$

with the corresponding activity coefficients:

$$\ln \gamma_1 = x_2^2 [A + 2(B - A - C)x_1 + 3Cx_1^2] \quad ..(20)$$

$$\ln \gamma_2 = x_1^2 [B + 2(A - B - C)x_2 + 3Cx_2^2] \quad ..(21)$$

Parameters A, B, and C were estimated using the non-linear regression analysis. The binary interaction parameters obtained from the regression analysis of various models are presented in table 6.

The change in vapor phase mole fraction with the liquid phase mole fraction of ethyl lactate is represented in figure 2 (a). It is observed that the curves are nonlinear in nature. It is noticed from the figure that the mixture forms a non-ideal solution negatively deviating from Raoult's law over the complete composition range. It is also significant to mention here that no azeotropic points are formed in the binary mixtures under investigation at a local atmospheric pressure of 95.3 kPa. Figures 2(b), 2(c) and 2(d) represent T-x-y plot for the three binary liquid mixtures. From these figures, it is apparent that the region with higher temperature is the vapor region, and that of lower temperature is liquid region. The region fringed by the curves is called as the two-phase region.

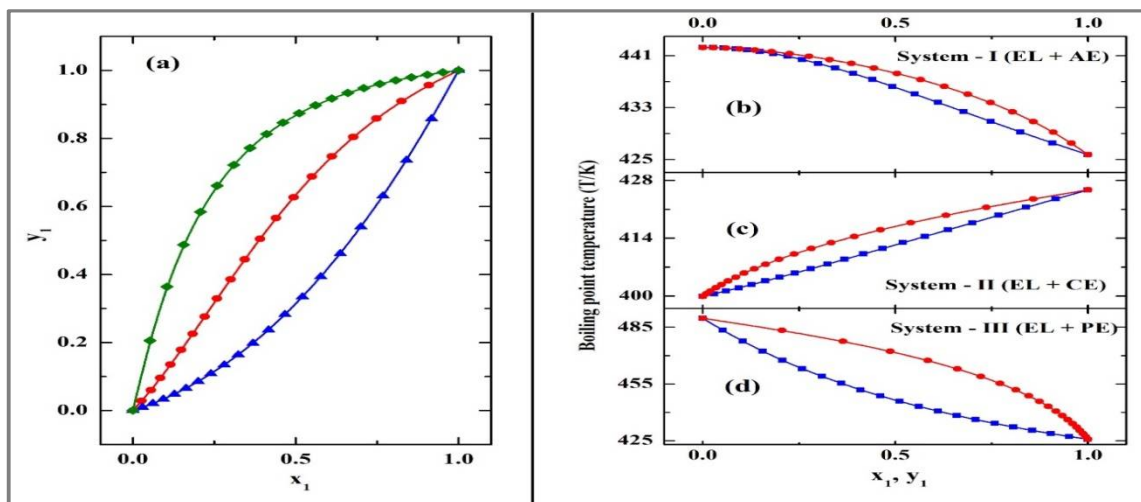


Figure 2. Liquid phase vs vapor phase diagram at a pressure 95.3 kPa (a); experimental boiling points at a pressure 95.3 kPa vs mole fraction of ethyl lactate in liquid phase (x_1) and vapor phase (y_1) for the binary mixtures of ethyl lactate + aminoethanol (b), ethyl lactate + chloroethanol (c) and ethyl lactate + phenylethanol (d) systems

Figure 3 shows a plot representing variation in $\ln(\gamma_1/\gamma_2)$ with the mole fraction of ethyl lactate (x_1) for the three binary systems. From the figure, it is observed that the curve represents both positive and negative values, from which the area above and below the axis is computed to check the thermodynamic constancy test. It is found that all the binary mixtures under investigation passed the Herington's thermodynamic consistency test.

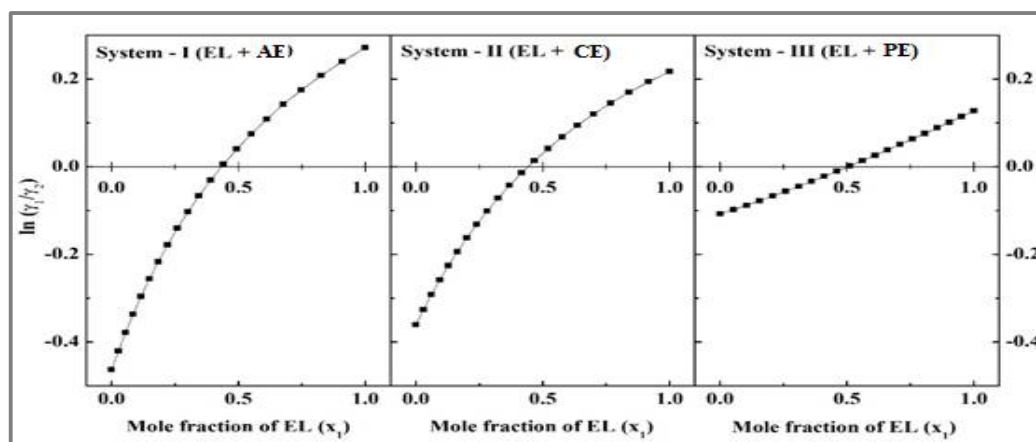


Figure 3. Plot of $\ln(\gamma_1/\gamma_2)$ against mole fraction (x_1) of ethyl lactate for ethyl lactate + aminoethanol, ethyl lactate + chloroethanol and ethyl lactate + phenylethanol

The variation in activity coefficients of the three binary liquid mixtures with the mole fraction of ethyl lactate is depicted in figure 4. From the figure, it is observed that the activity coefficient γ_1 increases with the mole fraction of ethyl lactate and reaches unity while γ_2 decreases from unity with the mole fraction of ethyl lactate in all the three binary mixtures under study. The extent of departure from linearity can be taken as a measure of interaction between unlike molecules.

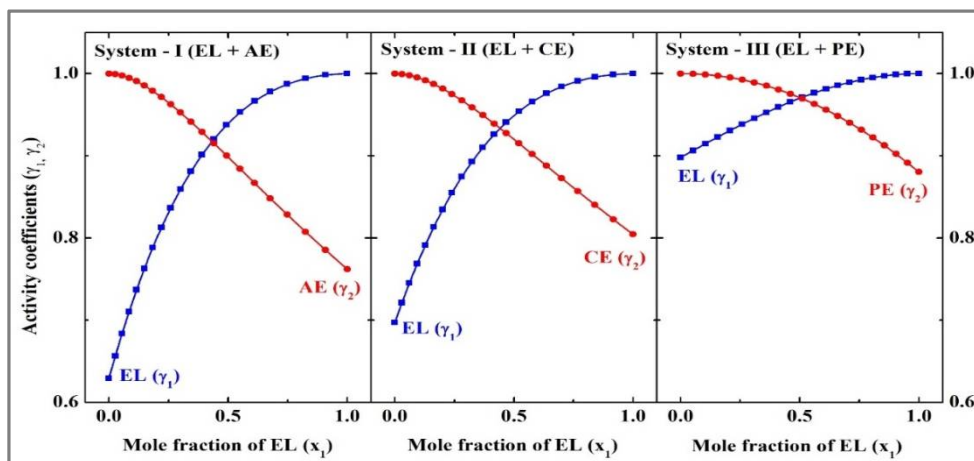


Figure 4. Variation of Activity coefficients (γ_1, γ_2) with the mole fraction (x_1) of ethyl lactate for ethyl lactate + aminoethanol, ethyl lactate + chloroethanol and ethyl lactate + phenylethanol

Figure 5 represents the plot between the excess Gibbs energies of the three binary mixtures with the mole fraction ethyl lactate. The observed negative excess Gibbs energy values can be attributed to strong intermolecular forces operating between unlike molecules [28]. In the case of ethyl lactate and aminoethanol mixture, the intermolecular hydrogen bond between the like molecules of aminoethanol breaks and forms new hydrogen bonds more readily with ethyl lactate molecules. This may be due to more electronegative nitrogen atom which withdraws electrons from the alcohol group, thereby weakening the intermolecular hydrogen bonding between the molecules of aminoethanol and simultaneous formation of new hydrogen bonds between the unlike molecules of aminoethanol and ethyl lactate.

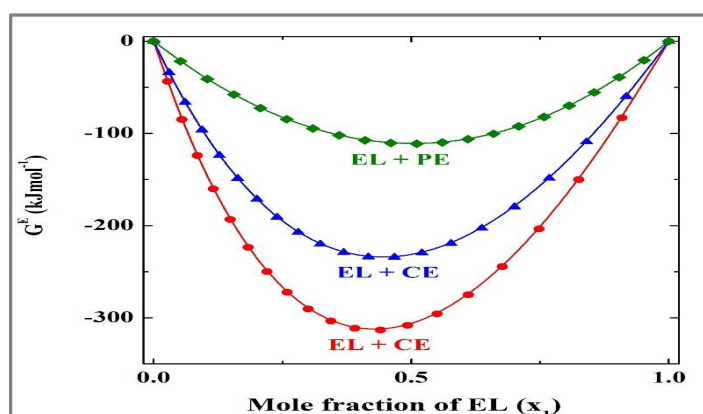


Figure 5. Variation of excess Gibbs energy with mole fraction (x_1) of ethyl lactate for ethyl lactate + aminoethanol, ethyl lactate + chloroethanol and ethyl lactate + phenylethanol binary systems

Whereas, in the binary mixture of ethyl lactate and chloroethanol, chlorine withdraws electrons less when compared to the nitrogen atom of the amino group, thereby possessing less negative values

of Gibbs energy. In ethyl lactate and phenylethanol mixture, the excess Gibbs energy values are much less negative than the other two systems perhaps due to less electron-withdrawing capacity of the phenyl group. In the three binary mixtures investigated the absolute excess Gibbs energy values follows the order:

Ethyl lactate + Aminoethanol > Ethyl lactate + Chloroethanol > Ethyl lactate + Phenylethanol (Table 6).

Table 6. Binary interaction parameters for the binary mixtures of ethyl lactate (EL) + aminoethanol (AE), +chloroethanol (CE) and phenylethanol (PE) using Wilson, NRTL, Van Laar and Margules models at a pressure of 95.3 kPa

Mixture	Wilson		NRTL			Van Laar		Margules		
	A_{12}	A_{21}	Δg_{12}	Δg_{21}	α_{12}	A_{12}	A_{21}	A	B	C
EL + AE	224.4063	-474.0521	-2769.06	2366.92	0.47	-0.460	-0.269	-0.3383	0.0915	-0.0290
EL + CE	86.7109	-390.3399	-2550.89	2474.57	0.47	-0.360	-0.217	-0.2674	0.0691	-0.0179
EL + PE	-156.1147	-280.8856	-2305.61	2606.76	0.47	-0.110	-0.129	-0.1166	-0.0116	0.0030

APPLICATION

To precise the thermodynamic behavior and to study the mechanisms of the processes, physical properties along with phase equilibrium data of binary liquid components are very significant. The process of simulation plays an important role in the design of production plants which largely depends on the thermodynamic models that describe the physical nature of the components of the mixture. To enhance the indicators/parameters of the analytical models used in the simulation packages involved in process design, the VLE data presented in this paper is highly helpful.

CONCLUSION

VLE data for the three binary liquid mixtures of ethyl lactate with aminoethanol, chloroethanol and phenylethanol are measured at 95.3 kPa over the entire composition range with a Swietoslowski-type ebulliometer. The experimental results are found to be well represented by the Wilson model. It is observed from the investigation that all three binary systems are non-ideal liquid mixtures deviating from Raoult's law. Also, it is observed that all three binary systems under investigation exhibit negative values of excess Gibbs energies due to strong intermolecular hydrogen bonding between unlike molecules. Thermodynamic consistencies of the three binary mixtures are checked by using Herington's test. No maximum or minimum boiling point azeotropes formed under the experimental pressure over the entire composition range. The experimental results are also found to be well represented by the other models viz., NRTL, Van Laar and Margules models.

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