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Modeling and simulation of Azeotropic distillation

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ABSTRACT

Azeotropic distillation is a special case of multicomponent distillation used for separation of binary mixtures which are either difficult or impossible to separate by ordinary fractionation. The work is mainly focus on the separation of azeotropic mixtures. Selection of solvent plays an important role in industry to break the azeotropes in easy way. The solvent is selected in such a way that it should break the azeotropic mixture and also should form azeotropic mixture with one of the original component. Determining the existence of homogeneous azeotropes together with their composition, temperature and pressure is important from both theoretical and practical standpoints in the analysis of phase behavior and in the synthesis and design of separation system employing distillation. Different moles of solvent are added to the existence composition of azeotropic mixtures at constant temperature and pressure. Raoult's law is taken in the modeling to get vapor mixture from given liquid mixture calculated after addition of the solvent to the original azeotropic mixture.

Introduction

An azeotropic mixture distills without change in composition and in general it has a boiling point higher or lower than that of any of its pure constituents. A constant boiling mixture is an azeotropic mixture. Azeotropes are a special form of non-ideal solution. Azeotopes exist in solution because of molecular dissimilarity of the components of the mixture. Ewell et al.,1944 [1] have published an interesting approach to predicting azeotropes formation based on the concept of hydrogen bonds. The deviation from ideality which results in azeotropes is attributed to hydrogen bonds or internal pressure, the former being more important. The hydrogen bond concept is stated as follows. Hydrogen can co-ordinate between two molecules of oxygen, nitrogen of fluorine. It can also co-ordinate between one of these donor atoms (oxygen, nitrogen, fluorine) and a carbon atom, provided a sufficient number of negative atoms or groups are attached to the carbon atom. Hydrogen can not co-ordinate between two carbon atoms, depending upon the atoms between which hydrogen is co-ordinating.

Toshihiko et al., 1994 [2] have conducted experiments for isobaric vapor-liquid equilibria for acetone+chloroform+methanol and for the constituent binary systems chloroform+methanol and chloroform+acetone which were measured at 101.3 Kpa using a liquid-vapor ebullition-type equilibrium still. The experimental data were correlated with extended Redlich-Kister and Wilson equations. The data were best correlated and completely calculated for the ternary and three binary azeotropic data using extended Redlich-Kister equation.

Orge B et al., 1995 [3] have conducted experiments for vapor liquid equilibrium results for the Acetone+Methanol+Chlorobenzene at a constant pressure of 101.3 Kpa. The equilibrium data have been compared with those predicted by ASOG, UNIFAC, UNIFAC-Dortmund and UNIFAC-Lyngby group contribution methods, with lower standard deviations of the vapor molar fraction and temperature being calculated by the latter.

Stadtherr MA et al., 1999 [4] have determined the existence and composition of homogeneous azeotropes together with their composition and temperature which is important from both theoretical and practical standpoints in the analysis of phase behavior and in the synthesis and design of separation systems employing distillation. They have described a new method that reliably locates any and all homogeneous azeotropes for multicomponent mixtures and also verifies the nonexistence of homogeneous azeotropes if none are present. The method is based on interval analysis, and provides a mathematical and computational guarantee that all azeotropes are located. The technique is general purpose and can be applied in connection with any thermodynamic model describing vapor-liquid equilibrium. An example using a five-component mixture modeled with the NRTL equation is presented.

Vicente Martinez-Soria et al., 1999 [5] have conducted experiments for vapor-liquid equilibria, which were conducted for binary systems of *tert*-butyl alcohol with toluene, isooctane and methylcyclohexane at 101.3 Kpa using recirculating still. Experimental values of the vapor pressure of non-oxygenated pure components have been obtained. The accuracy of experimental measurements was ±0.01 K in temperature, ±0.001 Kpa in pressure, and ±0.001 in mole fractions. The results are thermodynamically consistent according to point-to-point consistency test. The data were correlated with five liquid phase activity coefficients models (Margules, Van Laar, Wilson, NRTL, UNIQUAC).

Vicente Martinez-Soria et al., 1999 [6] have conducted experiments for vapor-liquid equilibria, which were conducted for binary systems of *iso*-butyl alcohol with toluene, isooctane and methylcyclohexane at 101.3 Kpa using recirculating still. Experimental values of the vapor pressure of non-oxygenated pure components have been obtained. The accuracy of experimental measurements was ±0.01 K in temperature,

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±0.001 Kpa in pressure, and ±0.001 in mole fractions. The results are thermodynamically consistent according to point-to-point consistency test. The data were correlated with five liquid phase activity coefficients models (Margules, Van Laar, Wilson, NRTL, UNIQUAC).

Miguel Iglesias et al., 1999 [7] have conducted experiments for vapor-liquid equilibria at 101.325Kpa which were conducted for the ternary system, acetone+methanol+water in an equilibrium still with circulation phases. Satisfactory results were obtained for the prediction of activity coefficients and the equilibrium compositions with group contribution models(ASOG, UNIFAC, UNIFAC-Dortmund and UNIFAC-Lyngby). Small standard deviations of vapor molar fraction and temperature were calculated. Azeotropic behavior was observed only in the acetone+methanol mixture. The correlation parameters for the Tamir-Wisniak and UNIQUAC equations were presented.

Bossen B.S. et al., 1993 [8] have described the computational tools needed for simulation, design, and analysis of azeotropic distillation operations. These tools include simple methods to identify the existence of binary and ternary azeotropes and to classify ternary mixtures as homogeneous or heterogeneous. The tools also include more complex methods to compute the phase diagram (or a heterogeneous liquid boiling surface), predict liquid-vapor phase equilibrium, and/or predict liquid-liquid-vapor phase equilibrium for simulations of batch and continuous distillation column operations. Important new features of these tools are the incorporation of a fast and efficient method for test of phase stability in simulation of distillation operations, the ability to handle a large range of mixtures (including mixtures with supercritical compounds), and the ability for computations covering wide ranges of temperature and pressure. On the basis of these tools, simple and consistent design algorithms are developed. The applicability of the design algorithms is verified through process simulation and analysis of the predicted behavior and data from the open literature. Conditions are given for examples illustrating (when and how possible distillation boundaries can be crossed) how multiple steady states can be obtained. Finally, the effect of changes in operating conditions on the dynamic behavior of the azeotropic distillation columns and the sensitivity of design to the prediction of phase equilibria are presented.

The computation of homogeneous azeotropes is problem that has been explored by several researchers and that has been reviewed by Widagdo et al., 1996 [9]. Most of these solution techniques are based on iterative processes that require some initial guess to begin the search. Although these techniques are very efficient for locating some solutions, they do not provide a guarantee that all solutions will be found. Moreover if no solution are found using these techniques, this does not provide a guarantee that no solutions exist. Fidkowski et al., 1993 [10] have worked on azeotropic mixtures and applied on continuation techniques. While these techniques are reported to be very reliable, they still provide no theoretical guarantee that all existing azeotropes have been found. Harding et al., 1997 [11] have applied a global optimization procedure, based on branch and bound techniques to solve the problem. While this techniques does provide a mathematical guarantee that all solutions will be found, in practice it is possible that computational problems due to rounding error may result in the loss of one or more solutions.

The determination of azeotropes strictly from the experiment can be expensive. Predicting azeotropes computationally is one method of reducing the cost, as the computational results can be used to narrow the experimental search space. It is obviously important that the computational used be capable of finding all azeotropes or determing with certainty that there are none, and doing this at a reasonable cost in terms computer time.

In the present work, a simple method for finding, breaking of azeotropic mixture by addition of solvent is proposed. Raoult's law is applied to various case studies. Simulation results for various case studies are given to show the efficiency of the proposed method.

Mathematical modelling:

For an ideal solution Raoult's law is given by

$$p^*{}_a = P_a x_a \tag{1}$$

$$p^*{}_b = P_b(1-x_a) \tag{2}$$

If the vapor is also ideal, Dalton's law is applicable

$$p_t = p^*{}_a + p^*{}_b = P_a x_a + P_b(1-x_a) \tag{3}$$

$$y_a = \frac{p_a{}^*}{p_t} \tag{4}$$

$$1-y_a = \frac{p^*{}_b}{p_t} = \frac{P_b(1-x_a)}{p_t} \tag{5}$$

Where P_a and P_b are the vapor pressures, which are calculated by Antoine equation. It is given by

$$\ln P = A - \frac{B}{(T+C)} \tag{6}$$

Where A, B and C are the Antoine constants. T is in degree Kelvin.

To allow for deviation from Raoult's law the activity coefficient 'γ' must be taken into consideration. With this factor equations for non ideal solutions may be written as follows

$$p_a = \gamma_a P_a x_a \tag{7}$$

$$p_b = \gamma_b P_b x_b \tag{8}$$

The coefficient γ is not a constant. It's numerical value is a function of all components in the solution and of their concentrations. The activity coefficient of each component increases as the solvent concentration increases from 0 to 100%. The activity coefficients are calculated from Van Laar equation or Margules equations.

Among the most useful relationships are the Van Laar equations

$$\ln\gamma_1 = \frac{A}{(1+\frac{Ax_1}{Bx_2})^2} \tag{9}$$

$$\ln\gamma_2 = \frac{B}{(1+\frac{Bx_2}{Ax_1})^2} \tag{10}$$

Where A and B are empirical constants. Another set of equations developed by Margules can be written as

$$\ln\gamma_1 = x_2{}^2(A+2x_1(B-A)) \tag{11}$$

$$\ln\gamma_2 = x_1{}^2(B+2x_2(A-B)) \tag{12}$$

Simulation results

In this section, Raoult's law is applied to various case studies of azeotropic mixtures by writing programming in Matlab. Separation of azeotropic mixture by adding third component is analyzed in the following case studies.

Case studies

Consider the following binary systems

1. IBA(1)+Toluene(2) at 101.3 Kpa
2. IBA(1)+Isooctane(2) at 101.3 Kpa
3. IBA(1)+Methylcyclohexane at 101.3 Kpa

Normal boiling points T_b and densities ρ are reported in table 1. Antoine constants of the above binary systems are reported in table 2. Azeotropic data for the two binary systems at 101.3 Kpa are reported in table 3. Experimental isobaric vapor liquid equilibrium data are reported in table 4. Computed results for Chlooform(1)+Methanol(2) at 101.3 Kpa by addition of solvent i.e Acetone are reported in table 5.

Results and discussions

It is used for finding the azeotropic mixture composition from vapor-liquid equilibrium which is obtained from literature. There is a looped area exist in fig 1, fig 2 and fig 4 i.e equlibrium curve is somewhat far away from 45 degree line. Hence there is separation of various azeotropic mixture by addition of various third component, solvent. From fig 3, there is again azeotropic composition (x1=y1=0.08 from Table 4) . hence there is no separation at x1=y1=0.08 . In this article, selection of third component is a key role to separate azeotropic mixture. The determination of azeotropes strictly from the experiment can be expensive. Predicting azeotropes computationally is one method of reducing the cost, as the computational results can be used to narrow the experimental search space. It is obviously important that the computational used be capable of finding all azeotropes or determing with certainty that there are none, and doing this at a reasonable cost in terms computer time.

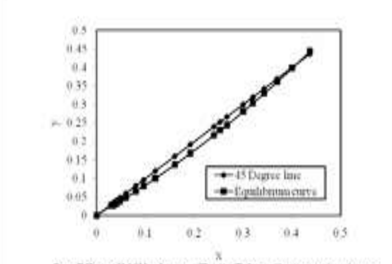

fig 1: Effect of MCH solvent on IBA(1)+Toluene(2) azeotropic mixture

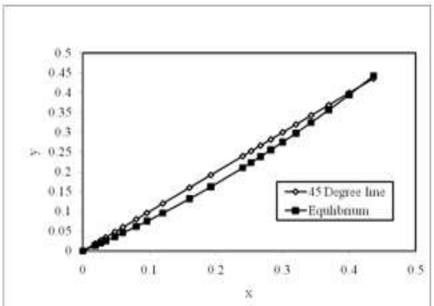

fig 2: Effect of Isooctane solvent on IBA(1)+Toluene(2) azeotropic mixture

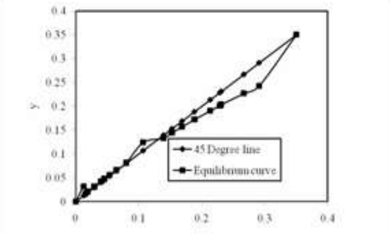

fig 1: Effect of toluene solvent on IBA(1)+Isooctane azeotropic mixture

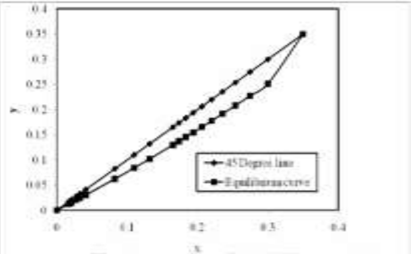

fig 4: Effect of Isooctane solvent on IBA(1)+MCH(2) Azeotropic mixture

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Table 1: Antoine constants for chemicals used

Name of chemical	A	B	C
IBA	15.07065	3001.427	-93.9496
Isooctane	13.8022	2999.098	-45.9600
MCH	13.7438	2891.014	-53.8124
Toluene	13.8453	2998.040	-58.7957

Table 2. Computed results for IBA(1)+Toluent(2), binary systems at 101.3 Kpa by addition of solvent i.e. MCH

x_1	x_2	x_3	y_1	y_2	y_3	T(K)
0.4364	0.4727	0.0909	0.4437	0.4440	0.1115	381.555
0.4000	0.4333	0.1667	0.3981	0.4005	0.4005	380.968
0.3692	0.4000		0.3611	0.3646	0.2751	380.492
0.3428	0.3714	0.2857	0.3296	0.3340	0.3364	380.022
0.3200	0.3467	0.3333	0.3038	0.3087	0.3888	379.680
0.3000	0.3250	0.3750	0.2809	0.2860	0.4329	379.304
0.2667	0.2889	0.4445	0.2440	0.2500	0.5050	378.730
0.2526	0.2737	0.4737	0.2296	0.2354	0.5349	378.497
0.2400	0.2600	0.5000	0.2164	0.2220	0.5614	377.460
0.1920	0.2080	0.6000	0.1679	0.1735	0.6585	377.460
0.1600	0.1733	0.6667	0.1370	0.1422	0.7206	376.908
0.1200	0.1300	0.7500	0.1003	0.1046	0.7962	376.254
0.0960	0.1040	0.8000	0.0788	0.0826	0.8385	375.798
0.0800	0.0866	0.8337	0.0650	0.0682	0.8668	375.508
0.0600	0.0650	0.8750	0.0482	0.0506	0.9012	375.171
0.0480	0.0520	0.9000	0.0380	0.0403	0.9215	374.961
0.0400	0.0433	0.9167	0.0317	0.0333	0.9349	374.821
0.0343	0.0371	0.9286	0.0270	0.0285	0.9444	374.720
0.0300	0.0325	0.9375	0.027	0.0285	0.9514	374.64

Table 3: computed results for IBA(1)+Toluene(2) binary mixture at 101.3 Kpa by addition of solvent i.e. Isooctane

x_1	x_2	x_3	y_1	y_2	y_3	T(K)
0.4364	0.4727	0.0909	0.4421	0.4418	0.1161	381.455
0.4000	0.4333	0.1667	0.3946	0.3966	0.2088	380.730
0.3692	0.4000	0.2307	0.3561	0.3596	0.2842	380.110
0.3428	0.3714	0.2857	0.3245	0.3290	0.3472	379.605
0.3200	0.3467	0.3333	0.2975	0.3027	0.3998	379.109
0.3000	0.3250	0.3750	0.2750	0.2806	0.4452	378.730
0.2823	0.3059	0.4117	0.2552	0.2611	0.4837	378.344
0.2667	0.2889	0.4445	0.2383	0.2445	0.5179	378.040
0.2526	0.2737	0.4737	0.2231	0.2295	0.5473	377.730
0.2400	0.2600	0.5000	0.2099	0.2164	0.5736	377.470
0.1920	0.2080	0.6000	0.1619	0.1681	0.6700	376.485
0.1600	0.1733	0.6667	0.1315	0.1373	0.7311	375.820
0.1200	0.1300	0.7500	0.0956	0.1005	0.8038	374.990
0.0960	0.1040	0.8000	0.0750	0.0790	0.8467	374.540
0.0800	0.0866	0.8333	0.0617	0.0650	0.8729	374.170
0.0600	0.0650	0.8750	0.0457	0.0484	0.9068	373.793
0.0480	0.0520	0.9000	0.0361	0.0384	0.9254	373.506
0.0343	0.0371	0.9286	0.0255	0.0272	0.9473	373.222
0.0267	0.0289	0.9445	0.0197	0.0211	0.9591	373.060
0.0185	0.0200	0.9615	0.0136	0.0145	0.9718	372.895

Table 4: computed results for IBA(1)+Isooctane(2) binary mixture at 101.3 Kpa by addition of solvent i.e. Toluene

x_1	x_2	x_3	y_1	y_2	y_3	T(K)
0.2909	0.6182	0.0910	0.2425	0.6846	0.0729	376.183
0.2667	0.5667	0.1667	0.2270	0.6373	0.1357	376.740
0.2307	0.5230	0.2307	0.2034	0.6034	0.1931	377.680
0.2286	0.4857	0.2857	0.2012	0.5598	0.2389	377.680
0.2133	0.4533	0.3333	0.1904	0.5275	0.2818	378.010
0.1882	0.4000	0.4118	0.1719	0.4737	0.3547	378.643
0.1684	0.3579	0.4736	0.1566	0.4295	0.4138	379.131
0.1523	0.3238	0.5238	0.1440	0.3933	0.4637	379.580
0.1391	0.2956	0.5652	0.1331	0.3621	0.5049	379.890
0.1067	0.2267	0.6667	0.1239	0.3361	0.5409	380.205
0.0800	0.1700	0.7500	0.0811	0.2173	0.7016	381.480
0.0640	0.1360	0.8000	0.0659	0.1759	0.7581	381.933
0.0533	0.1133	0.8333	0.0556	0.1479	0.7973	382.268
0.0450	0.0971	0.8571	0.0474	0.1275	0.8259	382.517
0.0400	0.0755	0.8890	0.0422	0.0994	0.8583	382.580
0.0290	0.0618	0.9091	0.0311	0.0821	0.8868	382.944
0.0188	0.0400	0.9411	0.0203	0.0533	0.9265	383.268
0.0150	0.0324	0.9524	0.0163	0.0436	0.9409	383.393
0.0123	0.0261	0.9615	0.0314	0.0351	0.9516	383.455

Table 5: computed results for IBA(1)+MCH(2) binary mixture at 101.3 Kpa by addition of solvent i.e. Isooctane

x_1	x_2	x_3	y_1	y_2	y_3	T(K)
0.3000	0.6090	0.0910	0.2512	0.6473	0.1011	376.303
0.2750	0.5583	0.1667	0.2277	0.5880	0.1837	376.005
0.2540	0.5154	0.2310	0.2081	0.5392	0.2526	375.730
0.2357	0.4780	0.2860	0.1918	0.4976	0.3113	375.554
0.2200	0.4467	0.3333	0.1776	0.4622	0.3602	375.333
0.2062	0.4187	0.3750	0.1654	0.4313	0.4039	375.178
0.1940	0.3941	0.4117	0.1546	0.4038	0.4412	374.990
0.1833	0.3722	0.4444	0.1454	0.3800	0.4746	374.866
0.1736	0.3526	0.4740	0.1369	0.3587	0.5043	374.730
0.1650	0.3350	0.5000	0.1297	0.3398	0.5305	374.630
0.1320	0.2680	0.6000	0.1022	0.2689	0.6297	374.241
0.1100	0.2233	0.6670	0.0842	0.2218	0.6940	373.930
0.0825	0.1675	0.7500	0.0622	0.1649	0.7727	373.580
0.0410	0.0840	0.8750	0.0303	0.0814	0.8882	373.046
0.0330	0.0670	0.9000	0.0243	0.0648	0.9106	372.930
0.0275	0.0560	0.9170	0.0202	0.0540	0.9262	372.867
0.0206	0.0418	0.9375	0.0150	0.0402	0.9446	372.784
0.0183	0.0372	0.9444	0.0134	0.0358	0.9508	372.750
0.0165	0.0335	0.9500	0.0120	0.0322	0.9561	372.740