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A Semiempirical Equation for Vapor−Liquid Equilibrium in Water−Acetic Acid−Calcium Chloride Systems

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An equation for the correlation and prediction of the vapor−liquid equilibrium of the water−acetic acid−calcium chloride systems at low pressures has been developed and fitted to experimental data. It is based on the hypothesis that the ternary system can be considered a binary system formed by two pseudocomponents: water + salt and acetic acid + salt. The equation, derived from Galán's equation, can calculate equilibrium data for the ternary system with a knowledge of only the equilibrium data for the water−acetic acid binary system and the vapor pressures of the pure components and the pseudocomponents.

Introduction

The salt effect is simply the modification of the vapor pressure of components in a liquid mixture due to the addition of a soluble salt. As a consequence, when distilling the system the compositions of the vapor in equilibrium are altered. The magnitude of this variation depends on the solubility of the salt and on its concentration in the liquid phase.[1] This phenomenon is very interesting when the relative volatility of the system to separation is almost unity or when the interesting component is less volatile, and a strategy is necessary to obtain it in the distilled fraction.[2] In some systems, with some salts in certain concentrations, the salt effect is so strong that it can produce an inversion in the volatilities, as for example with the water−acetic acid system with the addition of calcium chloride at concentrations ≥10 wt %.[3]

To design a separation process based on the salt effect, referred to as extractive distillation with salts,[4] it is necessary to study the vapor−liquid equilibrium of the system and how it is modified by the presence of salt. Correlating equations which predict the behavior of the system (when the operating conditions are changed) need to be developed.

In the literature, we can find different equations for the correlation and prediction of vapor−liquid equilibrium for salt systems; some of them are empirical,[5−7] and others are semiempirical, based on thermodynamic principles and through certain adjustable parameters interrelate the experimental data. Regarding the semiempirical ones, the most frequently used are the four correlation methods developed by Alvarez and co-workers[8−10] and the modified Barker method.[11]

All these methods were developed for saturated systems, by considering the vapor phase to behave as an ideal gas (except that of Barker) and the ternary system A−B salt to behave as a binary system made of two pseudocomponents: A + salt and B + salt, both saturated.

These methods were developed to interrelate vapor−liquid equilibrium data in systems saturated with salt, but they cannot predict the behavior of the salt systems with salt concentrations less than that of saturation. Therefore, it is necessary to develop methods that permit an interrelation of vapor−liquid equilibrium data in salt systems with intermediate salt concentrations. In this work, an equation is proposed to predict the behavior of binary systems with the addition of a soluble salt, for any salt concentration in the liquid phase and pressures equal to or less than atmospheric.

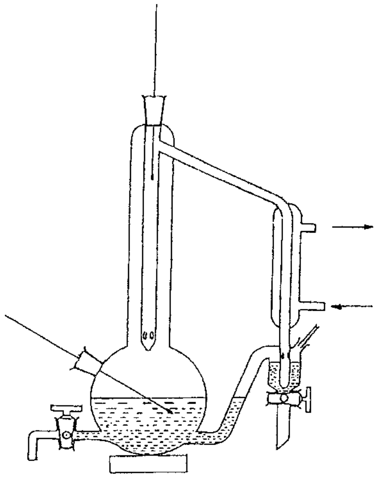

Figure 1. Modified Othmer still.

For fitting this equation, we used the experimental vapor−liquid equilibrium data of the water−acetic acid−calcium chloride system at three different salt concentrations (10, 20, and 30 wt %) of salt in the liquid phase, and three pressures (760, 400, and 125 mmHg).

Experimental Section

Apparatus and Procedures. A modified Othmer still, schematically shown in Figure 1, was used for the measurement of the vapor−liquid equilibrium data. The condensate chamber was connected to the liquid chamber so that recirculation was possible. The still neck was wrapped with a Nichrome wire and electrically heated in order to avoid condensation of the vapor phase. Each vapor−liquid equilibrium determination was carried out after an operation time of at least 5 h. The pressure was measured with a mercury manometer. The temperature was measured to 0.1 °C with a digital thermometer, CRISON 621.

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Table 1. Experimental Vapor−Liquid Equilibrium Data of the Water−Acetic Acid−Calcium Chloride System at 10, 20, and 30 wt % of Salt in the Liquid Phase and 760, 400, and 125 mmHg

	10% $CaCl_2$			20% $CaCl_2$			30% $CaCl_2$		
P/mmHg	T/K	x_i^s	y_i^s	T/K	x_i^s	y_i^s	T/K	x_i^s	y_i^s
760	391.05	0.0353	0.0266	394.75	0.0342	0.0138	397.55	0.2099	0.1051
	387.95	0.1568	0.1548	393.35	0.1223	0.0662	393.85	0.3666	0.2344
	387.55	0.1784	0.1685	390.45	0.2541	0.1970	393.85	0.3752	0.2237
	386.95	0.1968	0.1860	388.05	0.3838	0.3034	392.25	0.4785	0.2882
	386.75	0.2167	0.1956	386.65	0.4605	0.3670	391.85	0.5011	0.3085
	383.25	0.3782	0.3683	386.45	0.4998	0.3665	388.35	0.7059	0.5029
	381.35	0.4885	0.4660	386.15	0.5189	0.3692	386.75	0.8459	0.6227
	379.45	0.6153	0.5825	384.05	0.6171	0.5021	386.05	0.9018	0.7379
	378.15	0.7165	0.6791	381.65	0.7649	0.6191			
	377.25	0.7669	0.7556	380.95	0.814	0.6435			
				379.05	0.895	0.8038			
	R^2		0.9993	R^2		0.9867	R^2		0.9973
	typical uncertainty		0.0092	typical uncertainty		0.0251	typical uncertainty		0.0164
400	371.15	0.0571	0.0325	372.35	0.1923	0.0843	377.95	0.1855	0.0639
	369.35	0.1080	0.1071	371.45	0.2167	0.1232	375.05	0.287	0.1725
	367.65	0.1949	0.1635	370.85	0.2648	0.1443	373.65	0.387	0.2463
	367.65	0.2179	0.1670	370.45	0.2793	0.1800	373.45	0.4332	0.2429
	366.15	0.2831	0.2482	367.85	0.4054	0.2944	372.05	0.4749	0.3254
	365.45	0.3148	0.2877	367.35	0.4373	0.3203	370.95	0.5784	0.3822
	363.75	0.4146	0.3850	367.15	0.4532	0.3385	370.85	0.5966	0.3837
	363.45	0.4393	0.4015	366.85	0.4982	0.3214	370.55	0.6129	0.3837
	363.05	0.4669	0.4274	363.45	0.6645	0.5540	370.35	0.6295	0.3954
	362.55	0.4836	0.4608	363.15	0.7156	0.5564	370.25	0.6394	0.3954
	361.95	0.5347	0.5090	361.95	0.8151	0.6821	369.45	0.7292	0.4777
	360.85	0.6064	0.5808	360.85	0.9094	0.8568	367.85	0.9032	0.7203
	359.45	0.7253	0.6642						
	358.95	0.7708	0.7367						
125	337.05	0.2442	0.2387	340.05	0.3301	0.2012	346.05	0.2907	0.1225
	335.85	0.3746	0.3277	338.95	0.4109	0.2616	345.55	0.3186	0.1537
	334.75	0.4701	0.4187	338.25	0.5042	0.3146	343.45	0.4684	0.2851
	333.65	0.5967	0.4963	338.05	0.5161	0.3291	342.55	0.5515	0.3679
	333.45	0.6269	0.5497	337.35	0.5567	0.4155	342.05	0.6151	0.3992
	333.25	0.6286	0.5786	336.75	0.6363	0.4308	341.85	0.6353	0.4076
	332.55	0.7165	0.6558	335.85	0.7277	0.5289	341.15	0.7332	0.4563
	331.65	0.8458	0.8048	335.65	0.7787	0.5553	340.55	0.7962	0.5192
	330.75	0.9752	0.9777	335.25	0.7904	0.5944	340.25	0.8173	0.5942
				336.55	0.8511	0.7131	339.65	0.9033	0.6654
							339.65	0.908	0.6921

The vapor phase concentration was measured by titration of a known amount of recondensed solution with a standard sodium hydroxide solution and phenolphthalein as indicator. The salt-free basis concentration in the liquid phase was obtained in the same way by first recovering the salt by evaporation and drying. The salt concentration in the liquid phase was measured by accurately weighing the recovered dried salt. More details were given in a previous work.[3]

Materials. All chemicals were of the highest purity available: glacial acetic acid, PROBUS (RA), 99.95%; sodium hydroxide, PANREAC (PRS), 97.0%; potassium biphthalate, PANREAC (PRS), 99.0%; anhydrous calcium chloride, PANREAC (PA), 95.0%. Distilled water was prepared in the laboratory.

The standard potassium biphthalate was prepared by accurately weighing solid potassium biphthalate and dissolving it in a known quantity of distilled water. The sodium hydroxide solution was standardized by a using standard potassium biphthalate solution with phenolphthalein as an indicator. The validity of this procedure was been tested with literature data.[2] The uncertainties of this work and the literature data are shown in Table 1.

Model Development. The thermodynamic criterion of vapor−liquid equilibrium implies that the fugacity of the component *i* in the liquid phase must be equal to the fugacity of the component *i* in the vapor phase. At low pressure, it can be considered that Raoult's law is fulfilled; therefore, the equilibrium criterion is given by

$$y_i P = x_i \gamma_i p_i^{\mathrm{o}} \tag{1}$$

where *x* and *y* are the mole fractions of the liquid and vapor phases in equilibrium, respectively, *P* is the total pressure of the system, γ is the activity coefficient, p^{o} is the vapor pressure and the subscript *i* is the component *i*.

For the acetic acid−water−calcium chloride system, the proposed model considers two hypotheses:

1. The ternary system can be considered as a binary system formed by two pseudocomponents, water + calcium chloride and acetic acid + calcium chloride.
2. The dissolved salt is distributed between the other two components of the system in proportion to their respective molar fractions.

In this way, for the salt system

$$x_1^{\mathrm{s}} + x_2^{\mathrm{s}} = 1; \quad y_1^{\mathrm{s}} + y_2^{\mathrm{s}} = 1 \tag{2}$$

and the criterion of vapor−liquid equilibrium

$$y_i^{\mathrm{s}} \mathrm{P} = x_i^{\mathrm{s}}\, \gamma_i^{\mathrm{s}} (p_i^{\mathrm{o}})^{\mathrm{s}} \tag{3}$$

where the superscript *s* indicates salt system.

If the Galán supposition is admitted as a starting point, then

$$x_i^{s}\,\gamma_i^{s} = K(x_i\gamma_i)^n \tag{4}$$

where *K* and *n* are adjustable parameters that reflect the deviations of the salt system from the system without salt. *K* and *n* have a fixed values for each system and salt, since the Galán equation has been developed for binary systems with salt concentrations up to saturation.

Substituting eq 4 into eq 3, the mole fraction of component *i* in the vapor phase of the salt system can be related to the mole fraction to the liquid phase of the system without salt

$$y_i^{s}P = K(x_i\gamma_i)^n (p_i^{o})^{s} \tag{5}$$

Because it is not necessary to calculate the activity coefficient, the bracketed quantity can be substituted by its value in Raoult's equation for the system without salt, obtaining the Galán equation

$$y_i^{s}P = K\left(\frac{y_iP}{p_i^{o}}\right)^n (p_i^{o})^{s} \tag{6}$$

which relates the mole fractions of the vapor phase of the salt and nonsalt systems through the vapor pressures of the pure components and the pseudocomponents.

For the water−acetic acid−calcium chloride system, the Galán equation referred to water, the most volatile component, is given by

$$y_{H_2O}^{s}P = K\left(\frac{y_{H_2O}P}{p_{H_2O}^{o}}\right)^n (p_{H_2O}^{o})^{s} \tag{7}$$

For different salt concentrations up to saturation, *K* and *n* should reflect the incidence of the salt concentration. In other words, they should be functions of the salt concentration, fulfilling the condition that *K* and *n* may have a value of unity for zero salt concentrations and an identical fixed value to that of Galán for salt concentrations up to saturation.

To determine the expressions for *K* and *n* as functions of the salt concentration, eq 7 was linearized in the form

$$\ln\left[\frac{y_{H_2O}^{s}P}{(p_{H_2O}^{o})^{s}}\right] = \ln K + n\,\ln\left(\frac{y_{H_2O}P}{p_{H_2O}^{o}}\right) \tag{8}$$

Evaluating, for each pressure, an eq 8 for the different salt concentrations, it is possible to plot a straight line to determine the *K* and *n* values from the *y*-intercept and slope, respectively. With those values it will be possible to determine the variation function of *K* and *n* with the salt concentration.

Now it is necessary to know the mole fraction of water in the vapor phase in equilibrium with the different liquid phases in the presence and absence of calcium chloride. The vapor pressures of pure water and solutions with different salt concentrations are also needed.

The first ones were obtained experimentally in the laboratory, using a modified Othmer type apparatus. The results are shown in Table 1.

The second ones were obtained by interpolation of the vapor−liquid equilibrium data of the binary system.[2,12,13]

Vapor pressure data of pure water have been calculated by using the equation of Antoine[15]

$$\ln(p_{H_2O}^{o}) = 18.618 - \frac{3999}{T - 39.547} \tag{9}$$

Table 2. *K* and *n* Values Obtained for 760, 400, and 125 mmHg and 10, 20, and 30 wt % Salt Concentration

P/mmHg	C_{salt}	*K*	*n*
760	10	1.0018	1.2738
	20	1.1521	1.4408
	30	1.6716	1.6500
400	10	1.0025	1.3775
	20	1.2740	1.7017
	30	1.7367	2.0762
125	10	1.0424	1.3544
	20	1.2516	1.7034
	30	1.9011	2.0634

Table 3. n_1, K_1, and K_2 Values for Each Pressure

P/mmHg	n_1	K_1	K_2
760	0.0241	−0.0244	0.0016
400	0.0252	−0.0319	0.0017
125	0.0228	−0.0249	0.0015
intermediate values	0.0240	−0.0271	0.0016

Vapor pressure data of the pseudocomponent water + calcium chloride have been calculated using a modified Antoine equation to reflect the presence of the salt[14]

$$\ln(p_{H_2O}^{o})^{s} = (18.618 + 0.00049C_{salt} - 0.00046C_{salt}^{\;2}) - \frac{3999}{T - 39.547} \tag{10}$$

where C_{salt} is the percentage composition, by weight, of salt in the liquid phase. In both equations, the pressure is expressed in mmHg and the temperature in K. *T* is the boiling temperature of the salt system for the water mole fraction fixed in the liquid phase. Once all the data are known, eq 8 can be applied, to obtain values of *K* and *n* for each pressure and salt concentration. These are shown in Table 2.

From the values obtained, it is observed that for the same pressure, *K* and *n* increase as the salt concentration increases in the liquid phase. However, for a given salt concentration, by changing the pressure, the values of *K* and *n* do not seem to remain constant.

From a study of the variation of *K* and *n* with respect to the salt concentration for each pressure, it is concluded that *n* is a linear function of the salt concentration, while *K* is quadratic, as in the equations

$$n = 1 + n_1C_{salt} \tag{11}$$

$$K = 1 + K_1C_{salt} + K_2C_{salt}^{\;2} \tag{12}$$

The values of n_1, K_1, and K_2 have been calculated by the sum of squared differences method, as

$$\mathrm{SSQ} = \sum\left[\frac{(y_i^{s})_{exp} - (y_i^{s})_{cal}}{(y_i^{s})_{exp}}\right]^2 \tag{13}$$

where $(y_i^{s})_{cal}$ is the mole fraction in vapor phase obtained by eq 7, at the same temperature and salt concentration that $(y_i^{s})_{cal}$ has. The values of n_1, K_1, and K_2 are shown in Table 3. For systems without salt, $n = 1$ and $K = 1$.

Moreover, n_1, K_1, and K_2 have similar values when the pressure is modified, indicating that they can be considered independent of the pressure, as the Galán equation supposes: *K* and *n* are parameters that reflect the deviations of the salt system from the system without salt.

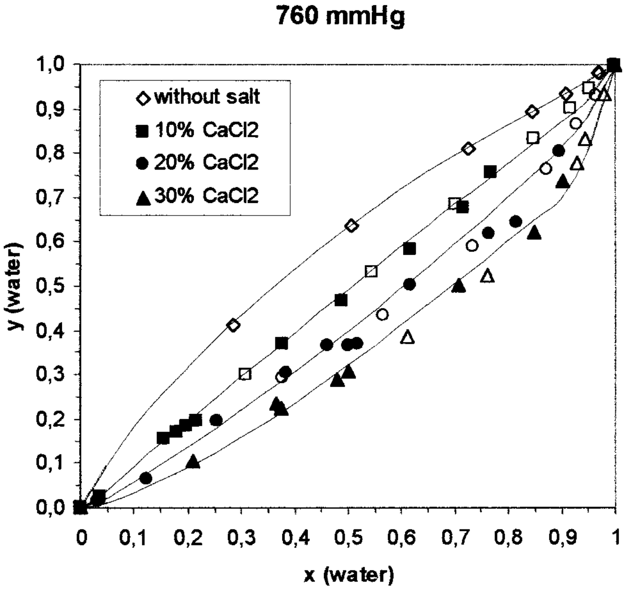

Figure 2. Water–acetic acid–CaCl₂ system at 760 mmHg: full symbols, this work; other symbols, Garwin and Hutchison.[2]

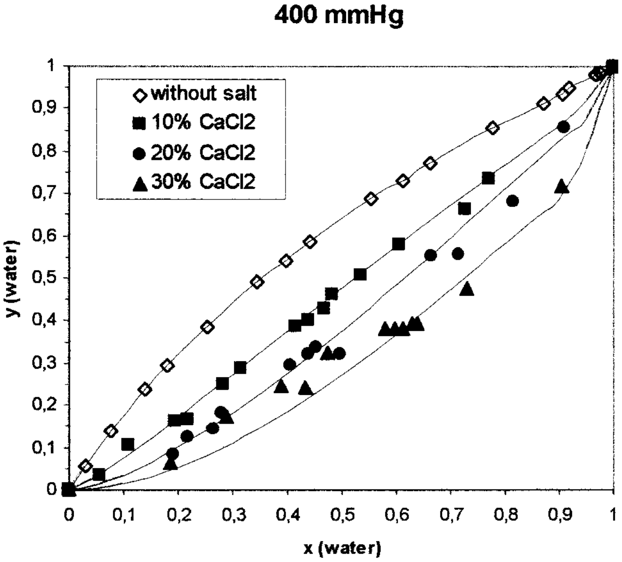

Figure 3. Water–acetic acid–CaCl₂ system at 400 mmHg: full symbols, this work; ◇, Marek.[14]

For the water–acetic acid–calcium chloride system with any salt concentration, the Galán modified equation, with the intermediate values of n_1, K_1, and K_2, is given by

$$\frac{y^{s}_{H_2O}P}{(p^{o}_{H_2O})^{s}} = (1 - 0.0271C_{salt} + 0.0016C_{salt}^{2})\left(\frac{y_{H_2O}P}{p^{o}_{H_2O}}\right)^{(1+0.024C_{salt})} \qquad (14)$$

Figures 2–4 show experimental data (full symbols) and correlations from eq 12 (continuous lines) for the vapor–liquid equilibrium by the water–acetic acid–calcium chloride system at three pressures and three salt concentrations. Literature data[2,12,13] are shown as well (other symbols).

The correlation coefficients for each set of experimental data and calculated data with eq 14 are shown in Table 4. The correlations are in good agreement with the experimental data.

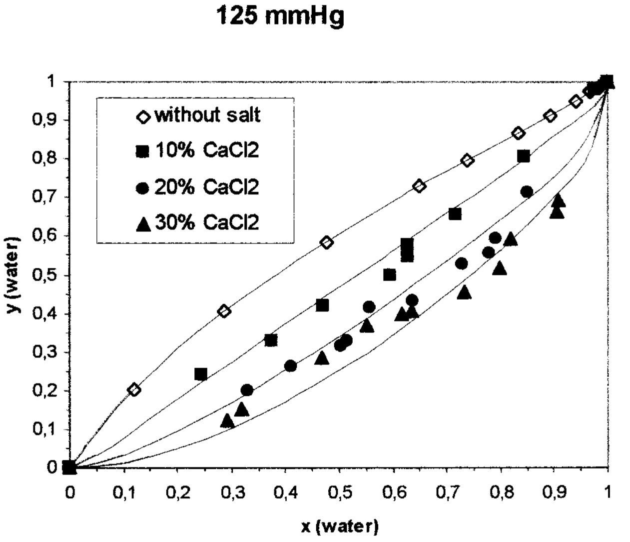

Figure 4. Water–acetic acid–CaCl₂ system at 125 mmHg: full symbols, this work; ◇, Gilmont and Othmer.[13]

Table 4. Correlation Coefficients for Each Set of Data

P/mmHg	10 wt %	20 wt %	30 wt %	overall
760	0.9992	0.9953	0.9969	0.9937
400	0.9983	0.9938	0.9846	0.9909
125	0.9930	0.9873	0.9907	0.9762

Conclusions

The proposed equation can calculate the vapor–liquid equilibrium data of the water–acetic acid–calcium chloride system and predict its behavior at different operating conditions, for all salt concentrations and any pressure at or below 1 atm. Furthermore, the proposed equation is rather simple without using either the electrolyte solution theory or the activity coefficient model.

Nomenclature

x_i: mole fraction in liquid phase
y_i: mole fraction in vapor phase
P: system pressure, mmHg
T: temperature, K
p_i^{o}: vapor pressure, mmHg
γ_i: activity coefficient
K_j, n_j: parameters
C_{salt}: percentage composition, by weight, of salt in the liquid phase
subscript *i*: component *i*
subscript exp: experimental data
subscript cal: calculated data
superscript s: salt system

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