Isobaric Vapor–Liquid Equilibrium Data for the Ethanol–Water–Strontium Bromide System

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Isobaric experimental data of vapor–liquid equilibrium for the ethanol–water–strontium bromide system at different mole fractions of strontium bromide have been measured at 100.6 kPa. Data were correlated by Jaques and Furter's method. Thermodynamic consistency was checked by Herington's method with satisfactory results.

Introduction

Well-established equations are available for the correlation and prediction of VLE data of systems composed of volatile substances. However, salt-containing systems present greater treatment difficulties than nonelectrolyte systems. The salt effect on vapor–liquid equilibria of volatile substances was noted some centuries ago, and has aroused great interest among many researchers. Several correlations for solvent mixtures containing salt have been proposed over the last few decades, but neither of them has succeeded in explaining the salt effect phenomenon. Reliable data shortage may be the cause, and also the fact that most available data are at saturation. The scarce available data were reviewed by Ciparis (*1, 2*), and no other databook exists on the salt effect in vapor–liquid equilibria. It is significant that the most complete *Vapor-Liquid Equilibrium Data Collection*, in the DECHEMA Chemistry Data Series, does not include any data of salt-containing systems.

The first approximations to modeling VLE in salt-containing systems were empirical ones. These have been comprehensively and critically reviewed by Furter (*3, 4*).

Some proposed methods for experimental data correlation [Natarajan (*5*), Schmitt and Vogelpohl (*6*), and Vercher et al. (*7*)] consider that solvent mixtures containing salt can be treated as pseudobinary systems.

Recently, Chen et al. (*8, 9*) developed an excess free energy equation for electrolyte systems combining a long-range interaction contribution described by the Pitzer's (*10–12*) extended form of the Debye–Hückel equation and a short-range interaction contribution described by the Renon and Prausnitz (*13*) NRTL model. Sander et al. (*14*) in turn proposed a modified UNIQUAC equation to describe the short-range interaction contribution. Also, Tan (*15*) has proposed a model based on Wilson's local volume fraction concept. However, no method to predict the salt effect on VLE is in use.

The present study reports vapor–liquid equilibrium data of the ethanol–water–strontium bromide system at different salt concentrations. The vapor–liquid equilibrium of the ethanol–water system saturated with strontium bromide has been studied by Galán et al. (*16*), but we have not found in the literature any reported vapor–liquid equilibrium data for ethanol and water with varying concentrations of strontium bromide below saturation.

Experimental Section

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.5 wt %), distilled water, and strontium bromide (Probus, >99.5 wt %).

The equilibrium apparatus was a recirculating still of the Labodest model, manufactured by Fischer. The vapor–liquid equilibrium data were obtained at 100.60 ± 0.04 kPa. The vapor pressure of water with a varying concentration of salt was also measured with the same apparatus.

Every experimental point was obtained from an initial sample prepared gravimetrically by using a Sartorius analytical balance with a precision of ±0.0001 g, and afterward by adding different quantities of ethanol, water, ethanol–salt solution, or water–salt solution.

Compositions of the condensed vapor phase were analyzed by using a Hewlett-Packard 5700 A gas chromatograph with a thermal conductivity detector, connected to a Hewlett-Packard 3394 A integrator. The chromatographic column (2 m × 1/8 in.) was packed with Porapak P. The gas carrier was helium flowing at 50 cm^3/min, and the column temperature was 383 K. The calibration was carried out by preparing various mixtures of ethanol and water of known compositions to cover the entire composition range from pure ethanol to pure water. The accuracy of the measured vapor-phase mole fraction is ±0.0015.

The liquid phase was composed of ethanol, water, and strontium bromide. Salt composition in the liquid phase was gravimetrically determined after separating the volatile components by evaporation to dryness. Water and ethanol compositions in the liquid phase containing dissolved salt were obtained by density measurements with an Anton Paar DMA 55 densimeter matched to a Julabo circulator with a proportional temperature control and an automatic drift correction system that kept the samples at 298.15 ± 0.01 K. The densimeter was calibrated by measuring a set of standard solutions with known mole fractions of ethanol, water, and salt in the ternary mixtures, and the correlation obtained was used to calculate the ethanol mole fraction with the known salt mole fraction. The average error in the measurement of the ethanol and water mole fractions in the liquid phase was ±0.003. This method of analyzing the composition of salt-containing mixtures was found to be reproducible, more convenient, and of better consistent accuracy than the method where the solvent–salt mixture was distilled to dryness followed by the analysis of the distillate obtained. Analysis by gas chromatography, using a filter placed before the analyzing column to avoid the nonvolatile salt being accumulated in the column, was also found not to be reliable.

Results and Discussion

In Table 1 the experimental vapor–liquid equilibrium data for the ethanol (1)–water (2)–strontium bromide (3) system

0021-9568/94/1739-0316$04.50/0

Table 1. Vapor–Liquid Equilibrium Data for the Ethanol–Water–Strontium Bromide System at 100.6 kPa

T/K	x_1	x_2	x_3	y_1	γ_I	γ_{II}	T/K	x_1	x_2	x_3	y_1	γ_I	γ_{II}
378.6	0.009	0.927	0.064	0.224	9.164	0.996	353.9	0.302	0.677	0.021	0.664	1.985	1.129
372.3	0.012	0.937	0.051	0.283	10.863	1.003	354.6	0.303	0.655	0.042	0.728	2.111	1.158
368.8	0.015	0.952	0.033	0.283	9.809	0.987	354.2	0.309	0.657	0.034	0.704	2.035	1.158
370.6	0.015	0.934	0.050	0.336	10.715	0.987	354.2	0.317	0.647	0.036	0.712	2.004	1.177
370.2	0.023	0.914	0.063	0.431	9.162	0.988	354.1	0.319	0.647	0.034	0.707	1.984	1.170
366.0	0.023	0.954	0.023	0.318	7.859	0.986	354.1	0.326	0.638	0.037	0.718	1.977	1.187
363.5	0.037	0.930	0.032	0.433	7.270	0.972	353.8	0.328	0.651	0.021	0.673	1.865	1.160
364.8	0.040	0.897	0.062	0.540	8.017	1.003	354.0	0.333	0.634	0.033	0.710	1.916	1.189
360.0	0.045	0.911	0.044	0.575	9.135	0.927	353.9	0.342	0.626	0.032	0.713	1.884	1.188
362.2	0.046	0.907	0.047	0.536	7.630	0.956	353.7	0.342	0.637	0.021	0.680	1.810	1.170
361.4	0.053	0.927	0.020	0.443	5.673	0.978	353.6	0.348	0.639	0.014	0.662	1.742	1.170
360.9	0.055	0.899	0.046	0.560	7.032	0.960	354.2	0.350	0.611	0.039	0.739	1.885	1.210
360.8	0.057	0.884	0.059	0.613	7.532	0.979	353.6	0.351	0.627	0.023	0.686	1.790	1.187
360.0	0.060	0.909	0.031	0.516	6.173	0.972	353.8	0.359	0.609	0.032	0.717	1.812	1.216
359.2	0.068	0.887	0.045	0.587	6.366	0.976	353.7	0.373	0.596	0.031	0.720	1.759	1.236
359.3	0.074	0.906	0.020	0.499	4.981	0.977	353.5	0.377	0.599	0.024	0.700	1.703	1.218
360.2	0.074	0.917	0.009	0.457	4.374	0.972	353.6	0.386	0.583	0.031	0.721	1.707	1.261
358.4	0.079	0.876	0.045	0.605	5.783	0.972	353.3	0.388	0.592	0.020	0.693	1.652	1.225
358.0	0.090	0.865	0.044	0.613	5.233	0.981	353.8	0.396	0.568	0.037	0.750	1.718	1.269
358.5	0.091	0.896	0.013	0.519	4.298	0.952	353.5	0.396	0.574	0.030	0.725	1.681	1.265
358.4	0.093	0.851	0.056	0.663	5.444	0.961	353.3	0.402	0.586	0.013	0.675	1.555	1.241
357.5	0.097	0.859	0.044	0.623	5.051	0.978	353.4	0.403	0.572	0.025	0.712	1.626	1.260
357.6	0.102	0.879	0.019	0.544	4.188	0.979	353.3	0.421	0.552	0.027	0.728	1.597	1.282
357.1	0.106	0.850	0.043	0.632	4.744	0.980	353.8	0.427	0.535	0.038	0.762	1.617	1.357
356.9	0.111	0.860	0.029	0.585	4.245	0.990	353.1	0.434	0.548	0.018	0.706	1.518	1.276
356.7	0.120	0.838	0.043	0.641	4.340	0.990	353.2	0.445	0.526	0.028	0.741	1.546	1.331
357.0	0.122	0.862	0.016	0.554	3.634	0.989	353.7	0.447	0.515	0.038	0.770	1.568	1.392
357.0	0.129	0.817	0.054	0.686	4.249	0.986	353.5	0.449	0.517	0.034	0.761	1.554	1.363
356.8	0.132	0.858	0.010	0.540	3.306	1.010	353.7	0.456	0.506	0.038	0.773	1.543	1.412
356.4	0.133	0.849	0.018	0.575	3.556	0.991	353.7	0.457	0.506	0.037	0.775	1.545	1.395
356.4	0.133	0.824	0.042	0.646	3.972	1.006	353.7	0.458	0.504	0.038	0.775	1.542	1.429
356.6	0.140	0.849	0.011	0.547	3.183	1.015	352.9	0.461	0.528	0.011	0.693	1.413	1.322
356.1	0.145	0.813	0.042	0.654	3.733	1.011	353.2	0.475	0.495	0.030	0.756	1.480	1.402
356.1	0.147	0.834	0.019	0.585	3.303	1.004	352.8	0.484	0.500	0.017	0.721	1.405	1.347
356.4	0.147	0.841	0.011	0.558	3.112	1.010	353.1	0.501	0.468	0.031	0.773	1.439	1.454
355.9	0.150	0.822	0.028	0.612	3.413	1.007	352.6	0.515	0.475	0.010	0.714	1.319	1.387
356.1	0.153	0.835	0.012	0.569	3.083	1.007	353.6	0.521	0.440	0.039	0.806	1.414	1.606
355.9	0.157	0.802	0.041	0.658	3.509	1.022	353.8	0.525	0.434	0.042	0.816	1.410	1.656
356.2	0.161	0.787	0.053	0.699	3.593	1.022	352.5	0.531	0.454	0.015	0.738	1.326	1.411
355.9	0.167	0.821	0.013	0.579	2.904	1.012	353.7	0.537	0.423	0.040	0.818	1.388	1.675
355.6	0.170	0.812	0.018	0.596	2.961	1.017	353.6	0.548	0.412	0.040	0.819	1.365	1.728
355.5	0.174	0.785	0.041	0.666	3.254	1.036	352.8	0.551	0.421	0.028	0.786	1.346	1.539
355.7	0.178	0.809	0.013	0.585	2.771	1.025	353.7	0.560	0.398	0.042	0.831	1.351	1.837
355.4	0.186	0.774	0.040	0.669	3.065	1.048	353.5	0.562	0.400	0.038	0.823	1.344	1.739
355.3	0.188	0.797	0.015	0.594	2.701	1.043	353.4	0.574	0.389	0.038	0.825	1.325	1.795
355.3	0.190	0.769	0.041	0.673	3.025	1.050	352.3	0.582	0.405	0.013	0.755	1.247	1.492
355.1	0.192	0.782	0.026	0.629	2.826	1.046	353.3	0.586	0.377	0.036	0.831	1.311	1.798
355.1	0.193	0.782	0.025	0.628	2.801	1.036	353.2	0.598	0.367	0.036	0.834	1.297	1.829
355.2	0.199	0.761	0.040	0.677	2.918	1.056	352.5	0.601	0.374	0.025	0.802	1.273	1.626
355.2	0.203	0.757	0.040	0.674	2.856	1.064	353.8	0.604	0.352	0.045	0.857	1.288	2.232
355.0	0.203	0.781	0.016	0.607	2.585	1.049	353.1	0.608	0.357	0.035	0.838	1.284	1.858
355.1	0.208	0.752	0.040	0.680	2.816	1.066	353.0	0.622	0.344	0.034	0.842	1.266	1.911
355.0	0.211	0.749	0.040	0.680	2.790	1.076	352.1	0.632	0.356	0.012	0.774	1.188	1.569
355.0	0.215	0.746	0.039	0.679	2.727	1.075	352.9	0.634	0.333	0.033	0.846	1.254	1.915
354.8	0.221	0.762	0.017	0.618	2.439	1.062	354.0	0.646	0.307	0.047	0.881	1.229	2.633
354.7	0.221	0.751	0.028	0.651	2.577	1.057	352.8	0.647	0.322	0.031	0.851	1.240	1.913
354.7	0.229	0.755	0.016	0.620	2.371	1.068	352.3	0.653	0.326	0.021	0.819	1.207	1.720
354.9	0.232	0.730	0.038	0.684	2.562	1.084	352.7	0.668	0.302	0.030	0.857	1.215	2.008
354.6	0.236	0.739	0.025	0.647	2.415	1.073	351.9	0.680	0.310	0.010	0.794	1.141	1.664
355.2	0.240	0.713	0.047	0.716	2.561	1.097	352.6	0.684	0.287	0.029	0.862	1.198	2.104
354.5	0.245	0.737	0.018	0.628	2.261	1.088	352.0	0.700	0.281	0.019	0.835	1.161	1.837
354.7	0.247	0.716	0.037	0.686	2.431	1.106	352.5	0.701	0.272	0.028	0.867	1.181	2.164
354.5	0.251	0.717	0.032	0.676	2.374	1.086	352.4	0.718	0.256	0.026	0.874	1.168	2.172
354.6	0.263	0.701	0.037	0.690	2.310	1.123	352.3	0.738	0.237	0.025	0.881	1.149	2.294
354.3	0.264	0.717	0.019	0.639	2.153	1.105	351.9	0.747	0.237	0.016	0.853	1.115	1.951
354.4	0.280	0.684	0.036	0.696	2.201	1.132	352.2	0.757	0.219	0.024	0.887	1.131	2.509
354.4	0.282	0.683	0.036	0.697	2.193	1.130	352.1	0.773	0.205	0.022	0.895	1.123	2.479
354.1	0.284	0.696	0.020	0.647	2.042	1.131	351.7	0.790	0.197	0.013	0.871	1.086	2.123
354.3	0.289	0.675	0.035	0.699	2.148	1.145	352.0	0.800	0.179	0.021	0.905	1.101	2.772
354.1	0.290	0.695	0.015	0.639	1.974	1.127	351.9	0.825	0.156	0.020	0.914	1.082	3.257
354.3	0.293	0.672	0.035	0.700	2.124	1.143	350.7	0.830	0.159	0.011	0.888	1.096	2.399
354.0	0.297	0.680	0.023	0.667	2.020	1.126	351.5	0.866	0.125	0.009	0.906	1.038	2.531
354.3	0.299	0.665	0.036	0.703	2.092	1.159	351.5	0.900	0.093	0.007	0.922	1.017	3.008

at a pressure of 100.6 kPa are reported. There we show, in the first column, the equilibrium temperature for every experimental point. In columns 2–4, we report the mole fractions of ethanol (x_1), water (x_2), and salt (x_3) in the ternary liquid phase. In column 5, we show the ethanol mole fraction in the vapor phase (y_1).

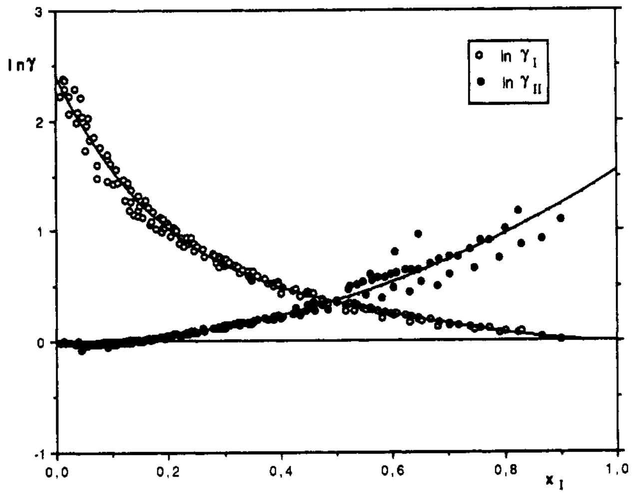

Figure 1. Experimental solvent activity coefficients for the system ethanol–water–strontium bromide at 100.6 kPa.

To make possible the thermodynamic treatment of vapor–liquid equilibrium data, it is necessary to calculate the activity coefficients in both phases. In the vapor phase, an ideal behavior of the mixture is assumed. To date, no satisfactory theory has been developed for predicting the activity coefficients in the liquid phase of mixed-solvent electrolytes.

We postulate that, in the range of liquid phase salt compositions studied, the salt is in ionic form and it is associated only with the water. Therefore, the ternary system can be treated as a pseudobinary one composed of pure ethanol (I) and water–salt (II) components. When equilibrium is established between vapor and liquid phases, the activity coefficients of both pseudocomponents will be given by these expressions:

$$\gamma_I = \frac{y_I P}{x_I P_I^\circ} \qquad \gamma_{II} = \frac{y_{II} P}{x_{II} P_{II}^\circ} \tag{1}$$

where x_I is the mole fraction of pseudocomponent I, x_{II} is the mole fraction of pseudocomponent II, P_I° is the vapor pressure of pure ethanol (P_1°), and P_{II}° is the vapor pressure of pseudocomponent II, both calculated at the equilibrium temperature. The value of P_{II}° depends on the temperature and on the salt concentration. Jaques and Furter (*17*) propose that this dependency can be expressed as

$$P_{II}^\circ = P_2^\circ(T)\ \epsilon(x_3^*) \tag{2}$$

where P_2° is the vapor pressure of pure water and ϵ is the vapor pressure correction factor, which only depends on x_3^*, the salt mole fraction in pseudocomponent II.

The vapor pressure correction factor was computed by the method followed by Jaques and Furter (*17*) from experimental data of the vapor pressure of water with different amounts of salt, and the vapor pressure of pure water obtained from the Antoine equation with the parameters given in the literature (*18*), both at the same temperature.

The correlation equation obtained from experimental data for the vapor pressure correction factor (ϵ) with the salt mole fraction in pseudocomponent II (x_3^*), for the entire range of salt concentrations studied, is

$$\epsilon = 1 - 2.3257x_3^* - 67.3602(x_3^*)^2 + 330.1488(x_3^*)^3 \tag{3}$$

For each experimental data, the activity coefficients of the ethanol and water in the liquid phase have been calculated following the described procedure. The values of γ_I and γ_{II} obtained are shown in columns 6 and 7 of Table 1.

In Figure 1, the logarithms of γ_I and γ_{II} are plotted against x_I. In this figure, it can be observed that the logarithms of activity coefficients for both pseudocomponents can be adjusted to one curve whatever the salt concentration may be. This fact implies that the pseudobinary model proposed explains the behavior of the system.

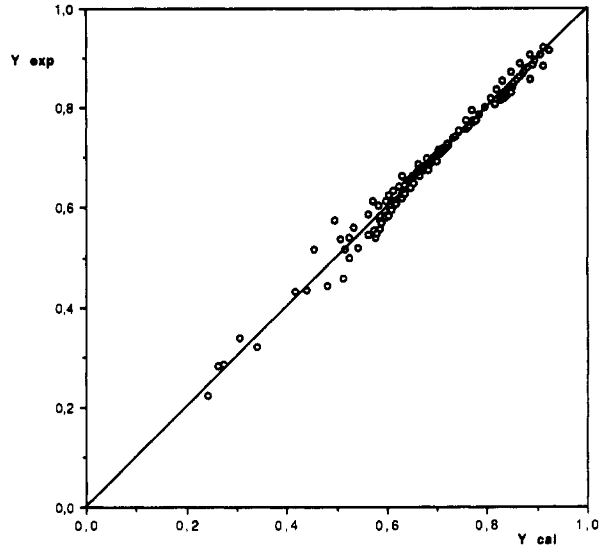

Figure 2. Comparison of calculated vapor composition with experimental values.

The thermodynamic consistency of the experimental data was tested by the integral method described by Herington (*19, 20*) and Redlich and Kister (*21*). The area test parameters, D and J, obtained were

$$D = 9.87\%,\quad J = 11.93\%,\quad \text{and}\quad D - J = -2.06\%$$

According to Herington's interpretation of the area test results, the experimental data were probably consistent.

For the purpose of reproducing experimental data, the activity coefficients obtained for every pseudocomponent were adjusted against their composition in the liquid phase, and the equations found were

$$\ln \gamma_I^* = (2.4080 - 5.7787x_I + 9.2154x_I^2 - 3.1057x_I^3)(1 - x_I)^2 \tag{4}$$

$$\ln \gamma_{II}^* = (1.54 - 0.12722x_{II})(1 - x_{II})^2 \tag{5}$$

These equations were used to recalculate vapor composition and temperature values in equilibrium from the liquid-phase composition. From comparison of experimental and calculated values, we found

$Y_{\text{exptl}} - Y_{\text{calcd}}$: mean, 0.011
standard deviation, 0.016

$T_{\text{exptl}} - T_{\text{calcd}}$: mean, 0.81 K
standard deviation, 1.04 K

The experimental values are plotted against the corresponding calculated ones in Figure 2 for the vapor composition and in Figure 3 for the temperature. In these figures, it can be noted the agreement between both experimental and calculated data.

Nomenclature

P = system pressure (kPa)
P_1° = vapor pressure of pure ethanol (kPa)
P_2° = vapor pressure of pure water (kPa)
P_I° = vapor pressure of pseudocomponent I (kPa)
P_{II}° = vapor pressure of pseudocomponent II (kPa)
T = equilibrium temperature (K)

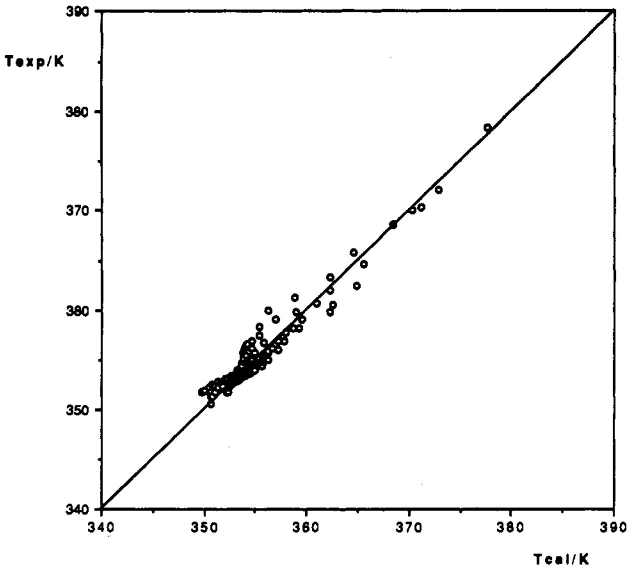

Figure 3. Comparison of calculated bubble points with experimental values.

x_1 = mole fraction of ethanol in the liquid ternary mixture
x_2 = mole fraction of water in the liquid ternary mixture
x_3 = mole fraction of strontium bromide in the liquid ternary mixture
$x_3{}^*$ = mole fraction of the component salt in the pseudocomponent II [$=x_3/(x_2 + x_3)$]
$x_{\rm I}$ = mole fraction of pseudocomponent I in the liquid phase ($=x_1$)
$x_{\rm II}$ = mole fraction of pseudocomponent II in the liquid phase ($=x_2 + x_3$)
y_1, $y_{\rm I}$ = mole fraction of ethanol in the vapor phase
y_2, $y_{\rm II}$ = mole fraction of water in the vapor phase
$\gamma_{\rm I}$ = activity coefficient in the liquid phase of pseudocomponent I
$\gamma_{\rm II}$ = activity coefficient in the liquid phase of pseudocomponent II
ϵ = vapor pressure correction factor for the calculation of the activity coefficient

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Received for review July 9, 1993. Accepted November 15, 1993.[•]

[•] Abstract published in *Advance ACS Abstracts*, January 1, 1994.