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Isobaric Vapor–Liquid Equilibrium Data for the Ethanol–Water–Potassium Acetate and Ethanol–Water–(Potassium Acetate/Sodium Acetate) Systems

E. Vercher, R. Muñoz, and A. Martínez-Andreu*

Departamento de Ingeniería Química, Facultad de Química, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

Isobaric experimental data of vapor–liquid equilibrium for the ethanol–water–potassium acetate system at different mole fractions of potassium acetate (0.060, 0.080, and 0.100) are presented. Also, the vapor–liquid equilibrium for the ethanol–water–(potassium acetate/sodium acetate) (2:1) system at different mole fractions of salt (0.040 and 0.060) is studied. For each system, both the activity coefficient and relative volatility were calculated. The effect of the salt mixture on the vapor–liquid equilibrium is the same as the effect of potassium acetate being alone.

Introduction

A salt dissolved in a mixture of volatile components may affect the activities of the components through the formation of complexes. If this interaction is selective, the relative volatility of the volatile components may change drastically, depending on the salt concentration, and thus facilitate the separation of close-boiling components or even of azeotropic mixtures. This effect has been used successfully for obtaining absolute ethanol from aqueous solutions.

The industrial success of salt-effect extractive distillation is conditioned to the solid agent recovery. One of the techniques described (*1*) to maintain an anhydrous hygroscopic salt during feeding to the reflux stream is as a molten salt. Then the economy of the process depends strongly on the salt melting point.

Therefore, a good solid agent to rectify the ethanol–water mixtures must be sufficiently soluble in both components, produce an important salting-out effect, and have a relatively low melting point. Potassium acetate seems to be the most effective salt (*2*).

Several authors (*3*–*9*) have studied the vapor–liquid equilibrium of the ethanol–water system saturated with potassium acetate. Only Schmitt (*10*) has reported vapor–liquid equilibrium data for ethanol and water with varying concentrations of potassium acetate below saturation.

Gorhan (*1*) suggested the use of potassium and sodium acetate mixtures as extractive agents to obtain anhydrous ethanol, but he has not reported vapor–liquid equilibrium data for this system. The synergistic effects attributable to salt mixtures can decrease the melting point of the mixture. We have verified that a potassium and sodium acetate mixture in a molar ratio of 2:1 has a minimum melting point of about 245 °C (the potassium acetate melting point is 292 °C). This fact should make this mixture especially suitable as an extractive agent for rectifying ethanol–water mixtures.

The present study determines the vapor–liquid equilibrium of ethanol–water–potassium acetate and ethanol–water–(potassium acetate/sodium acetate) (2:1) systems to check the efficiency of the latter in relation to the former.

Experimental Section

The chemicals were absolute ethanol (Baker Analyzed Reagent, >99.5 wt %), distilled water, potassium acetate (Probus, 98 wt %), and sodium acetate (Panreac, 98 wt %).

The equilibrium apparatus was a recirculating still of the type described by Walas (*11*) (Labodest model), manufactured by Fischer Labor-und Verfahrenstechnik. The vapor–liquid equilibrium data were obtained at atmospheric pressure, which remained practically constant in the range 764 ± 2 mmHg. The vapor pressure of water with a varying concentration of salt was also measured with the same apparatus.

For each experimental point, the feed to the recirculating still was prepared gravimetrically by using a Sartorius analytical balance with a precision of ±0.0001 g. The fit of the salt molar fraction in the feed with the desired quantity (0.04, 0.06, 0.08, or 0.10) was obtained with a precision of ±0.0005. The same procedure was used for preparing the densimeter calibration (used for the measurement of the liquid-phase composition) and gas chromatograph calibration (used for the measurement of the vapor-phase composition).

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 110 °C. The accuracy of the measured vapor-phase mole fraction is ±0.0015.

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 proportional temperature control and an automatic drift correction system that kept the samples at 25.00 ± 0.01 °C. The accuracy of the liquid-phase mole fractions depends on the accuracy of the salt mole fractions in the mixture. It was assumed that the salt mole fraction in the liquid phase in equilibrium was the same as that initially fed to the recirculating

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Table I. Vapor–Liquid Equilibrium Data for Ethanol–Water–Potassium Acetate

P, mmHg	N_3	T, °C	x	y	γ_1	γ_2	α_s
766	0.060	89.4	0.037	0.512	9.176	0.918	27.31
	0.060	85.7	0.070	0.571	6.209	0.964	17.68
	0.060	84.0	0.102	0.605	4.815	0.983	13.48
	0.060	82.8	0.145	0.620	3.634	1.041	9.62
	0.060	81.7	0.220	0.640	2.580	1.130	6.30
	0.060	81.0	0.301	0.671	2.031	1.185	4.74
	0.060	80.4	0.395	0.694	1.639	1.305	3.47
	0.060	79.9	0.510	0.733	1.367	1.435	2.64
	0.060	79.6	0.659	0.806	1.177	1.516	2.15
	0.060	79.6	0.742	0.842	1.092	1.632	1.85
	0.060	79.6	0.799	0.875	1.054	1.658	1.76
	0.060	79.7	0.829	0.903	1.044	1.506	1.92
	0.060	79.8	0.867	0.932	1.026	1.352	2.10
	0.060	79.8	0.909	0.939	0.986	1.772	1.54
	0.060	79.6	0.919	0.969	1.015	1.020	2.76
762	0.080	89.5	0.038	0.542	9.374	0.934	29.96
	0.080	86.0	0.067	0.580	6.481	1.011	19.23
	0.080	84.2	0.099	0.610	4.938	1.044	14.23
	0.080	82.8	0.148	0.642	3.668	1.071	10.32
	0.080	81.6	0.217	0.663	2.706	1.151	7.10
	0.080	81.0	0.304	0.698	2.081	1.189	5.29
	0.080	80.4	0.391	0.718	1.704	1.300	3.97
	0.080	80.1	0.508	0.751	1.388	1.438	2.92
	0.080	80.1	0.646	0.815	1.184	1.485	2.41
	0.080	79.9	0.736	0.859	1.104	1.530	2.19
	0.080	80.0	0.773	0.881	1.074	1.495	2.17
	0.080	80.1	0.810	0.902	1.045	1.465	2.16
	0.080	80.4	0.843	0.935	1.029	1.162	2.68
	0.080	80.2	0.883	0.958	1.015	1.016	3.02
764	0.100	90.4	0.031	0.542	11.147	0.975	36.99
	0.100	87.5	0.047	0.579	8.742	1.018	27.89
	0.100	84.6	0.096	0.629	5.185	1.059	15.97
	0.100	83.4	0.134	0.652	4.031	1.088	12.11
	0.100	82.0	0.219	0.680	2.715	1.173	7.58
	0.100	81.4	0.292	0.714	2.188	1.184	6.05
	0.100	80.9	0.391	0.731	1.706	1.321	4.23
	0.100	80.6	0.504	0.784	1.436	1.319	3.57
	0.100	80.5	0.643	0.832	1.199	1.431	2.75
	0.100	80.5	0.726	0.872	1.113	1.420	2.57
	0.100	80.5	0.781	0.886	1.051	1.583	2.18
	0.100	80.5	0.821	0.913	1.031	1.478	2.29
	0.100	80.7	0.845	0.933	1.015	1.304	2.55
	0.099	80.5	0.943	0.967	0.950	1.760	1.77

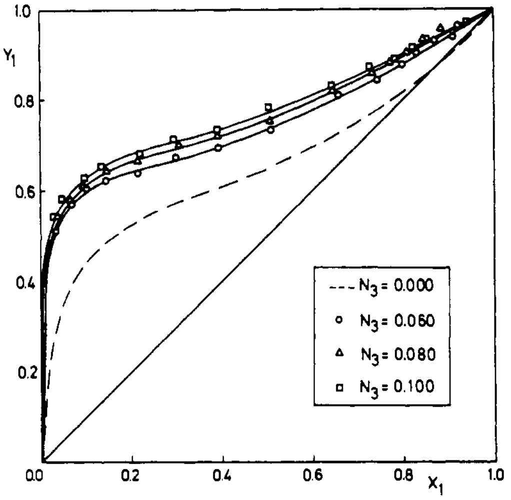

Figure 1. Vapor–liquid equilibrium for the system ethanol–water–potassium acetate at different N_3 values.

Table II. Vapor–Liquid Equilibrium Data for Ethanol–Water–(Potassium Acetate/Sodium Acetate) (2:1)

P, mmHg	N_3'	T, °C	x	y	γ_1	γ_2	α_s
762	0.040	89.8	0.031	0.448	9.394	0.933	25.37
	0.040	85.8	0.067	0.533	6.001	0.956	15.89
	0.040	84.0	0.099	0.582	4.748	0.952	12.67
	0.040	82.8	0.141	0.589	3.532	1.029	8.73
	0.040	81.6	0.212	0.613	2.561	1.108	5.89
	0.040	80.8	0.291	0.631	1.981	1.213	4.17
	0.040	80.1	0.384	0.655	1.601	1.343	3.05
	0.040	79.5	0.496	0.706	1.368	1.433	2.44
	0.040	79.0	0.636	0.762	1.174	1.639	1.83
	0.040	78.8	0.717	0.803	1.106	1.760	1.61
	0.040	78.7	0.776	0.837	1.070	1.847	1.48
	0.041	78.7	0.807	0.851	1.046	1.960	1.37
	0.040	78.7	0.851	0.886	1.033	1.942	1.36
	0.040	78.7	0.890	0.912	1.016	2.031	1.28
	0.040	78.8	0.957	0.969	1.000	1.822	1.40
766	0.060	90.2	0.030	0.491	10.539	0.903	31.19
	0.060	86.1	0.059	0.560	7.116	0.942	20.30
	0.060	84.7	0.084	0.585	5.505	0.964	15.37
	0.060	83.0	0.134	0.615	3.871	1.012	10.32
	0.060	81.9	0.204	0.637	2.748	1.085	6.85
	0.060	81.1	0.278	0.662	2.161	1.150	5.09
	0.060	80.6	0.371	0.694	1.731	1.219	3.85
	0.060	80.1	0.481	0.714	1.401	1.410	2.69
	0.060	79.8	0.616	0.782	1.212	1.470	2.24
	0.060	79.6	0.698	0.816	1.125	1.590	1.92
	0.060	79.5	0.751	0.834	1.073	1.747	1.67
	0.060	79.5	0.789	0.858	1.051	1.764	1.62
	0.060	79.5	0.826	0.886	1.036	1.717	1.64
	0.060	79.5	0.858	0.921	1.037	1.458	1.93
	0.060	79.3	0.941	0.954	0.987	2.060	1.30
	0.060	79.3	0.952	0.961	0.983	2.147	1.24
	0.060	79.4	0.971	0.984	0.983	1.452	1.84

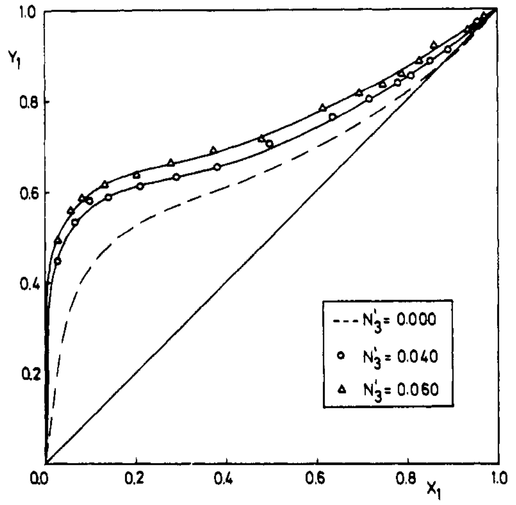

Figure 2. Vapor–liquid equilibrium for the system ethanol–water–(potassium acetate/sodium acetate) (2:1) at different N_3' values.

still. It was checked that the error introduced with this assumption was smaller than the experimental error in the preparation of the sample. The error in the measurement of the salt mole fraction in the liquid phase was always less than 0.001. The average error in the measurement of the ethanol and water mole fractions in the liquid phase was ±0.002, becoming ±0.005 near pure ethanol.

Results and Discussion

In Table I the experimental vapor–liquid equilibrium data for the ethanol–water–potassium acetate system are reported. In Figure 1 these experimental data and those obtained from the literature (*12*) for the ethanol–water system are plotted in an *x*–*y* diagram. These experimental data have been compared to Schmitt data (*10*). The similarity is very close in the range of high ethanol concentrations ($x_1 > 0.45$), whereas in the range of low ethanol concentrations ($x_1 < 0.45$) our vapor-phase ethanol compositions are slightly higher than Schmitt's.

Table III. Vapor Pressure Correction Factors ϵ_2

Ethanol-Water-Potassium Acetate System

N_3	ϵ_2
0.060	0.8239
0.080	0.7535
0.100	0.6946

Ethanol-Water-(Potassium Acetate/Sodium Acetate) (2:1) System

N_3'	ϵ_2
0.040	0.8928
0.060	0.8413

Likewise, in Table II the experimental vapor-liquid equilibrium data for ethanol-water-(potassium acetate/sodium acetate) (2:1) are presented. In Figure 2 these results and those corresponding to the ethanol-water system are plotted. We could not find any published data on the ethanol-water-(potassium acetate/sodium acetate) system.

In Figures 1 and 2 the extractive agent effect on vapor-liquid equilibrium of the ethanol-water system can be observed qualitatively. In these figures it is observed that the presence of potassium acetate (Figure 1) or potassium and sodium acetate mixtures (Figure 2) increases the ethanol molar fraction in the vapor phase and this effect increases with the salt concentration in the liquid phase.

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. Some proposed methods (*13*, *14*) consider that, for ethanol-water solutions saturated with salts, the ternary system can be treated as a pseudobinary composed of ethanol saturated with salt as one component and water saturated with salt as the other component. In this case, the expression used for calculating the activity coefficients in the liquid phase was

$$\gamma_i = \frac{y_i P}{x_i P^*_i} \qquad i = 1, 2 \qquad (1)$$

where P^*_i is the vapor pressure of component i saturated with salt, at the equilibrium temperature.

When the liquid phase is not saturated with salt, Schmitt (*10*) proposes the hypothesis that a salt added to a mixture of solvents complexes with the solvent components in proportion to its maximum solubilities in these components, at the respective temperature. He uses eq 1, defining P^*_i as the vapor pressure of component i, at the salt concentration and temperature in question.

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. The expressions used for calculating the activity coefficients were

$$\gamma_1 = \frac{y_1P}{x_1P^\circ_1} \qquad \gamma_2 = \frac{y_2P}{x_2P^*_2} \qquad (2)$$

where P°_1 is the vapor pressure of pure ethanol and P^*_2 is the vapor pressure of water with a given salt concentration, both at equilibrium temperature. The value of P^*_2 depends on the temperature and on the salt concentration. Jaques and Furter (*13*) propose that this dependency can be expressed as

$$P^*_2(T,N_3) = P^\circ_2(T)\epsilon_2(N_3) \qquad (3)$$

where P°_2 is the vapor pressure of pure water and ϵ_2 is the vapor pressure correction factor.

The vapor pressure correction factor was computed by the method followed by Jaques and Furter (*13*) 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 (*12*), both at the same temperature.

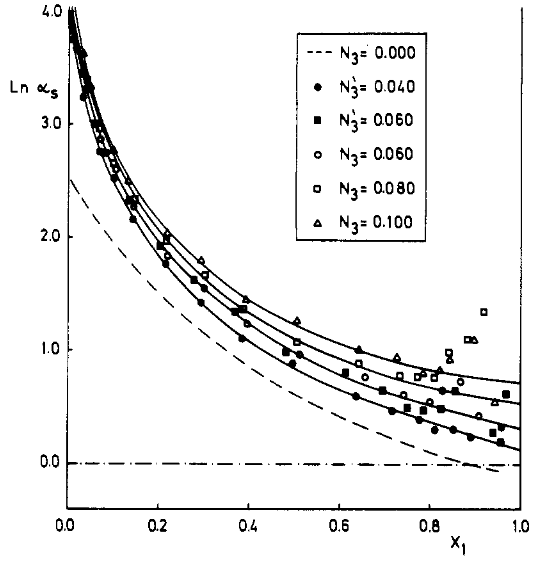

Figure 3. Relative volatility of ethanol/water at different concentrations of salt.

In Table III the vapor pressure correction factors for the range of salt or mixed salt concentrations studied are listed.

For each experimental data, the activity coefficients of the ethanol and water in the liquid phase have been calculated following the described procedure. The relative volatilities of the ethanol in relation to the water were also calculated through the expression

$$\alpha_s = \frac{y_1/x_1}{y_2/x_2} \qquad (4)$$

In Tables I and II the values of γ_1, γ_2, and α_s obtained, along with the experimental data, are shown.

In Figure 3, the variation of relative volatility, α_s, is plotted against the x_1 data for the different conditions tested. In this figure it can be observed that the effect of potassium acetate/sodium acetate mixtures (in a molar ratio 2:1) on the vapor-liquid equilibrium is the same as the effect of potassium acetate being alone for a salt molar fraction in the liquid phase of 0.060. So, then, the use of the salt mixture proposed does not decrease the salting-out effect, whereas it presents some advantages on the salt recovering since its melting point is smaller than the potassium acetate melting point. The only disadvantage that the use of salt mixtures presents is their low solubility in the ethanol-water mixtures, which prevents the use of concentrations as high as in the case of pure potassium acetate.

In Figure 3 it can be also observed that for a mole fraction of salt mixtures of N_3' = 0.040, the azeotrope was already removed since the relative volatility was higher than the unity in the entire liquid composition range.

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Nomenclature

component 1 ≡ ethanol
component 2 ≡ water

N_3 = salt mole fraction in the ethanol-water-potassium acetate liquid phase = (mol of potassium acetate)/(mol of potassium acetate + mol of ethanol + mol of water)

N_3' = salt mole fraction in the ethanol-water-salt mixtures liquid phase = (mol of potassium acetate + mol of sodium acetate)/(mol of potassium acetate + mol of sodium acetate + mol of ethanol + mol of water)

P = system pressure (mmHg)

P°_i = vapor pressure of pure component i (mmHg)

P^*_i = corrected vapor pressure of component i (mmHg)

T = temperature liquid phase (°C)

x_i = mole fraction of component i in the liquid phase, calculated on a salt free basis = (mol of ethanol or water)/(mol of ethanol + mol of water)

y_i = mole fraction of component i in the vapor phase = (mol of ethanol or water)/(mol of ethanol + mol of water)

α_s = relative volatility of ethanol in the presence of the salt

γ_i = activity coefficient in the liquid phase of component i

ϵ_2 = vapor pressure correction factor for the calculation of the activity coefficient

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Densities and Viscosities of NH_4Br–NH_3 and NH_4I–NH_3 Systems

Hideki Yamamoto* and Junji Tokunaga*

Department of Chemical Engineering, Faculty of Engineering, Kansai University, Yamate-cho, Suita, Osaka, 564 Japan

Densities of the NH_4Br-NH_3 and NH_4I-NH_3 systems in liquid phase have been measured over a wide range of temperatures and concentrations. Densities of saturated solutions of the NH_4Br-NH_3 and NH_4I-NH_3 systems have also been measured over the temperature range from 0 to 76.5 °C and from 0 to 69.5 °C, respectively. The accuracy of this measurement was ±0.1%. Observed densities were expressed as a function of temperature and concentration by means of polynomial equations. These equations could calculate values to an accuracy within ±0.5% of the observed data. For the sake of the viscometry of these systems, a falling-body viscometer with use of a He-Ne laser was assembled. The viscosities of NH_4Br-NH_3 and NH_4I-NH_3 systems were measured in the ranges of mass percent of ammonium halide from 10.0% to 59.8% and from 9.81% to 70.1% under the wide temperature range respectively. The accuracy of these viscometry was within ±1.2% deviation against standard liquid to calibrate this viscometer.

Introduction

Very little information for the physical properties of ammoniated salts in the liquid phase is available for the concentrated solution. Most of the investigations of ammonium salts in the literature involve mainly aqueous solutions. Although dilute aqueous solutions have greatly contributed to the development of physical chemistry, the behavior of concentrated nonaqueous electrolytic solutions has not yet been completely investigated. Progress in theoretical descriptions of these ammoniated salts requires the availability of experimentally determined data.

In recent years, some ammoniated salts were used as working system for chemical heat pumps and energy storage (*1*, *2*). However, most of the studies in the literature involving ammoniated salts have been carried out at or near normal boiling point to avoid experimentation at high pressures. Some physical and thermodynamic properties of NH_4Br-NH_3 and NH_4I-NH_3 (i.e. vapor pressures, solubilities, specific heats, and heats of mixing) were already measured in this laboratory (*3*, *4*).

In this paper, the densities in the wide temperature and concentration ranges were measured by using the special equipment that was made to facilitate measurements at high pressure. Observed densities were expressed as the function of temperature and concentration, using the method of least-squares. Furthermore, the viscosities of these systems were measured by using the falling-body viscometer, which was specially assembled for the measurement of the solution under high pressure. This paper is concerned with the densities and viscosities of the NH_4Br-NH_3 and NH_4I-NH_3 systems.

Materials. Ammonium iodide (NH_4I) and ammonium bromide (NH_4Br) from Wako Pure Chemical Industries, Ltd., were of guaranteed reagent grade and were specified as the pure grade, having minimum purities of 99.5%, and used without further purification. The powdered crystal was thoroughly dried at 100 °C and stored over silica gel in a desiccator. Ammonia gas of 99.99% purity was provided by Seitetu Kagaku Co., Ltd.

The standard liquid for calibration viscometers was used in order to examine the accuracy of the falling-body viscometer from Showa Shell Sekiyu Co., Ltd. The range of viscosities for the standard liquid was 0.1–5.0 Pa s.

Apparatus and Procedures

Density Measurement. A schematic diagram of the experimental apparatus for density measurements is shown in Figure 1. The two vessels (I and J) are made of pressure-resistant glass (up to 2 MPa); one is a 20-mL vessel for measuring the volume of liquid ammonia (ammonia vessel), and the other is a 100-mL vessel for determining the densities (reaction vessel) that can be agitated by a magnetic stirrer (B).

Two vessels were immersed in a constant-temperature water bath separately, and its accuracy was within ±0.05 °C. The pressure in the reaction vessel was measured by a strain gauge transducer (A) with a accuracy of 0.1% of full scale (2 MPa).

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