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Salt Effect in Liquid–Vapor Equilibrium: Ethanol–Water System Saturated with Strontium Bromide, Barium Nitrate, and Strontium Nitrate

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Isobaric liquid–vapor equilibrium and solubility data for the ethanol–water system saturated with strontium bromide, barium nitrate, and strontium nitrate have been measured and reported at 700 mmHg. Only strontium bromide breaks the azeotrope. Thermodynamic consistency was checked by the Herington method as modified by Jaques and Furter. The data were correlated by the method of Alvarez and Vega.

Introduction

Over a number of years this department has been studying the effect of various salts at saturation on the liquid–vapor equilibrium (LVE) of binary solvent mixtures which exhibit azeotropic behavior. In the present investigation isobaric LVE data for ethanol–water saturated with strontium bromide, barium nitrate, and strontium nitrate were obtained at 700 ± 1 mmHg pressure by using an Othmer equilibrium still. Strontium bromide, which is appreciably soluble in both alcohol and water, breaks the azeotrope, whereas the other two salts, which are soluble in water and virtually insoluble in ethanol, fail to break the azeotrope. This is in agreement with previous findings in this field (*3*).

Experimental Section

Purity of Materials. Absolute alcohol was produced by using benzene. The GLC trace showed only one peak. The refractive index and density values at 25 °C are as follows (the corresponding literature values (*8*) are in parentheses for comparison): refractive index 1.3593 (1.3594); density 0.7853 (0.7851).

Analytical grade salts were dried prior to use and doubly distilled water was used without further treatment.

Apparatus and Procedure. The LVE data were determined with slightly modified Othmer equilibrium still which is described elsewhere (*7*). Equilibrium temperatures were read with mercury-in-glass thermometers with an accuracy of ±0.1 °C. These boiling points were referred to 700 mmHg by using Craft's rule.

$$\Delta t = 0.0001(273 + t_{\mathrm{obsd}})(700 - \pi) \qquad (1)$$

Daily pressures varied between 690 and 705 mmHg and were obtained from a nearby meterological station whose height above sea level differed by less than 10 m from that of this laboratory.

The determination of the composition of liquid-phase samples and the solubility of the salt in the solvent mixtures at the boiling point required separation of solid and liquid by distillation (for the detailed procedure see Alvarez (*1*)). This distillate and the vapor-phase samples from the Othmer still were analyzed by picnometry (duplicate samples which differed by more than 0.0004 were rejected).

Results and Correlation

The experimental results are given in Tables I–III. Comparison of the LVE data at 700 mmHg pressure for the solvent mixture with and without salt is shown on Figures 1 and 2.

Table I. Liquid-Vapor Equilibrium and Solubility Data for the Ethanol-Water System Saturated with Strontium Bromide

x, mol %	y, mol %	solubility, g/100 g of solvent	obsd bp, °C	pressure, mmHg	calcd bp,[a] °C
0.4	29.2	254.2	133	695	133
5.8	75.9	208.9	96.7	694	96.9
6.7	78.5	203.8	94.8	692	95.1
8.2	78.6	195.8	94.5	692	94.8
8.9	79.5	193.3	93.4	690	93.8
22.2	81.8	146.5	90.7	697	90.3
27.8	82.1	134.5	90.1	693	90.3
29.3	82.6	129.8	89.7	694	89.9
38.4	83.4	104.1	88.9	694	89.1
40.2	83.9	103.4	88.2	698	88.3
52.0	85.7	86.3	86.8	697	86.9
55.8	87.1	78.6	86.3	698	86.4
62.4	88.3	75.4	85.6	696	85.7
66.1	89.3		85.1	694	85.3
70.2	90.4	69.8	84.7	695	84.9
77.5	91.4	66.2	84.3	693	84.6
78.3	92.2	64.5	84.0	697	84.1
79.5	93.2	63.6	83.8	696	83.9
81.2	93.3	61.0	83.6	699	83.6
87.6	94.4	61.5	83.4	697	83.5
88.4	95.7		83.0	696	83.1
97.0	97.4	55.8	82.4	693	82.7

[a] At 700 mmHg.

Table II. Liquid-Vapor Equilibrium and Solubility Data for the Ethanol-Water System Saturated with Barium Nitrate

x, mol %	y, mol %	solubility, g/100 g of solvent	obsd bp, °C	pressure, mmHg	calcd bp,[a] °C
2.2	29.3		88.7	697	88.8
5.0	37.2		87.0	697	87.1
9.1	43.6	14.1	84.2	690	84.5
11.5	47.7	11.0	83.3	689	83.7
12.4	48.8	11.1	83.0	692	83.3
12.5	49.5		82.6	694	82.8
14.4	50.2	9.2	82.0	694	82.2
14.5	50.5	9.4	82.3	696	82.4
16.2	51.8	9.2	81.9	699	81.9
17.5	52.0	7.2	81.5	696	81.7
21.6	54.7	6.0	80.7	696	80.9
22.3	55.4	6.1	80.7	696	80.9
27.5	56.2	3.7	80.0	697	80.1
28.9	56.9	3.4	79.7	695	79.9
31.9	59.2	3.2	79.4	695	79.6
34.3	58.6	2.9	79.2	695	79.4
35.9	60.0	2.5	79.2	698	79.3
43.6	62.3	2.3	78.3	693	78.5
49.2	64.4	1.6	77.9	690	78.3
51.3	65.3	1.7	77.8	691	78.1
60.9	69.8		77.3	695	77.5
65.8	73.1	1.1	77.0	693	77.2
72.2	76.7		76.9	697	77.0
77.0	80.0	1.0	76.5	691	76.8
82.5	83.9		76.4	693	76.6
87.1	87.5		76.2	693	76.4
88.3	89.0	1.0	76.3	695	76.5

[a] At 700 mmHg.

Strontium bromide breaks the ethanol–water azeotrope as has been found previously (*3*) for salts which are appreciably soluble

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Table III. Liquid-Vapor Equilibrium and Solubility Data for the Ethanol-Water System Saturated with Strontium Nitrate

x, mol %	y, mol %	solubility, g/100 g of solvent	obsd bp, °C	pressure, mmHg	calcd bp,[a] °C
1.2	19.6	113.2	97.3	690	97.7
2.5	38.2	93.1	92.2	694	92.4
4.5	41.6	77.6	88.8	696	88.9
4.6	41.8	80.9	87.0	700	87.0
6.9	52.2	71.8	84.7	695	84.9
7.4	53.4	67.8	83.8	695	84.0
9.8	55.1	63.4	82.5	701	82.5
12.1	58.8	56.0	81.9	702	81.8
18.1	62.3	42.6	80.6	700	80.6
26.5	64.9	29.1	79.8	699	79.8
32.8	65.3	22.0	79.4	698	79.4
36.0	65.3	19.6	79.0	693	79.3
42.3	66.3	14.2	78.7	693	78.9
47.3	68.5	10.4	78.4	695	78.6
55.9	70.3	6.3	78.0	697	78.1
67.2	74.9	2.6	77.6	700	77.6
71.5	77.1	2.0	77.3	697	77.4
76.7	79.2	1.3	76.9	693	77.2
78.5	81.1	0.9	76.9	696	77.0
81.9	83.1	1.1	76.8	692	77.1
84.2	86.1	1.4	76.7	690	77.1
87.0	87.5	1.1	76.9	703	76.8
87.2	88.0	0.8	76.3	681	77.0
88.0	88.3	1.2	76.9	699	76.9
88.7	88.8	0.8	76.8	699	76.8

[a] At 700 mmHg.

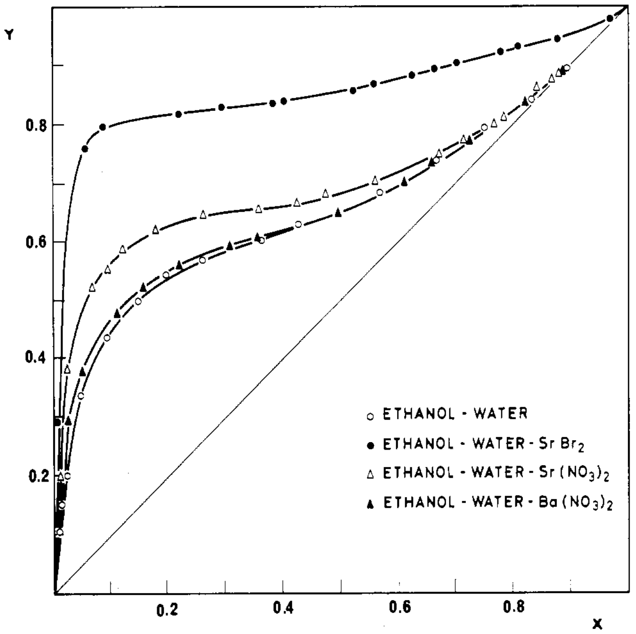

Figure 1. y-x diagram for ethanol-water-saturated salt systems.

in both pure solvents. The other two salts, which are relatively insoluble in ethanol compared to water, have little or no effect on the azeotrope.

The thermodynamic consistency test of Herington as modified by Jaques and Furter for use with salt-saturated binary solvent systems (*5*) was satisfied by the data for all three systems. It is perhaps worth pointing out that Jaques (*4*) has shown that this consistency test is a necessary but not a unique condition for good quality data in the salt effect field.

The LVE data were correlated by the modified mole fraction procedure of Alvarez and Vega (*2*) using eq 2. The values of

$$\log x'_i = A_i \log x_i + \log B_i \qquad (2)$$

the arbitrary constants A and B are given in Table IV. Figures 3 and 4 for ethanol and water, respectively, show that eq 2 can

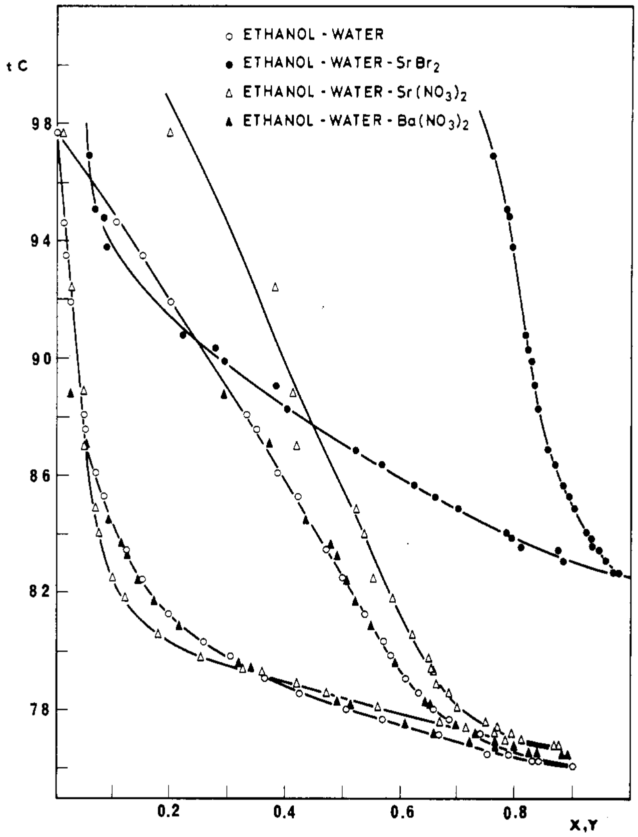

Figure 2. Boiling point-composition diagram for ethanol-water-saturated salt systems.

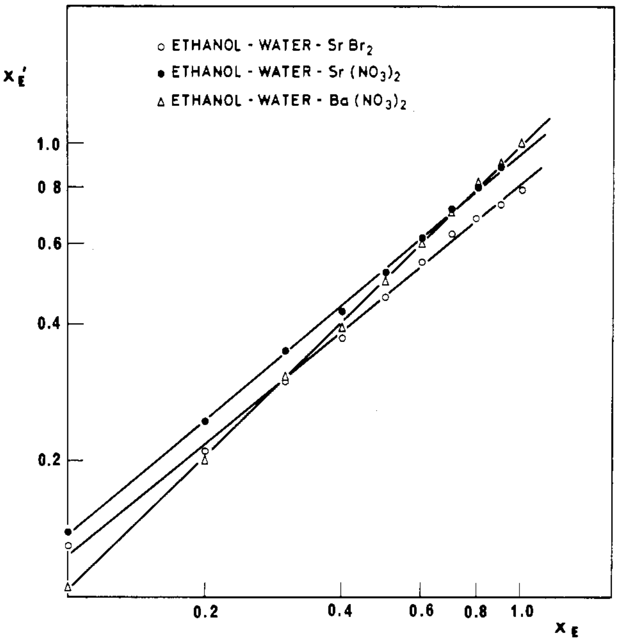

Figure 3. Modified mole fraction plot for ethanol.

Table IV. Calculated Values of Constants A and B in Equation 2

salt	liquid component	A	B
$SrBr_2$	ethanol	0.81	0.81
$SrBr_2$	water	0.85	0.26
$Ba(NO_3)_2$	ethanol	0.99	0.99
$Ba(NO_3)_2$	water	0.99	0.98
$Sr(NO_3)_2$	ethanol	0.84	0.95
$Sr(NO_3)_2$	water	0.91	0.82

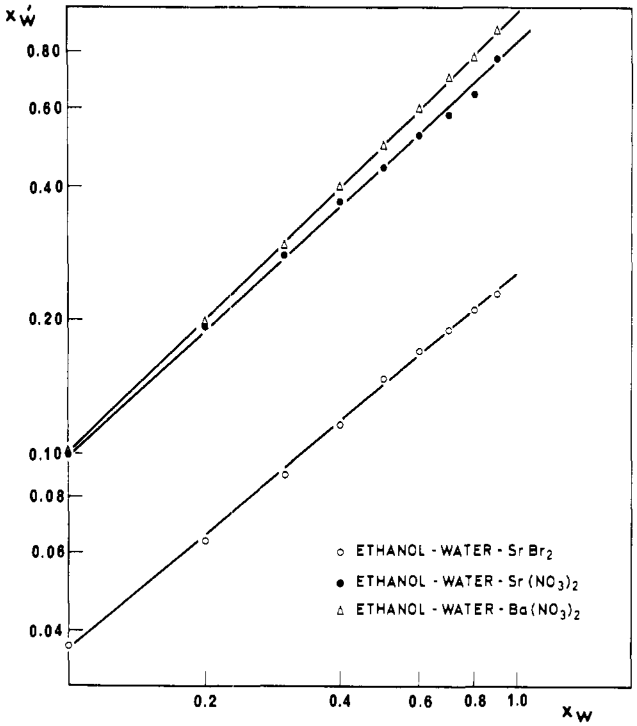

Figure 4. Modified mole fraction plot for water.

be used to correlate the three sets of data in the 0.1–1.0 mole fraction range.

Acknowledgment

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Glossary

A_i, B_i	arbitary constants in eq 2 for liquid component i
$p°$	saturation vapor pressure of pure liquid component, mmHg
p	partial vapor pressure of liquid component in mixture
t	temperature, °C
x	mole fraction of ethanol in the liquid phase, calculated on a salt-free basis
x'	modified mole fraction (*6*) defined for ethanol: $= x/[x(p_E°/p_E) + (1 - x)(p_W°/p_W)$
y	mole fraction of ethanol in the vapor phase
Δt	temperature correction, °C
π	atmospheric pressure, mmHg

Subscripts

E	ethanol
i	either liquid component
W	water

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Partial Molar Volumes and Expansibility in the Binary System Dodecanoic Acid–Hexanedioic Acid

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The experimental values of density and the calculated values of molar volumes and expansibility are given for the binary system dodecanoic (lauric) acid–hexanedioic (adipic) acid.

Introduction

As a part of a wider research on the physicochemical properties of pure and mixed organic melts (*2–4*, *6*), the results of measurements of density in the binary system dodecanoic (lauric) acid–hexanedioic (adipic) acid are reported in this paper for temperature ranging from 326.8 to 479.2 K. As used herein, components 1 and 2 are hexanedioic acid and dodecanoic acid, respectively.

Experimental Section

The density measurements were performed by means of the Archimedian method described in the literature (*5*). A Mettler balance H20T, placed upon the thermoregulated furnace, was used. The height of the furnace was changed by means of an elevator. From the pan of the balance a gold chain joined to a steel double cone bob by means of a steel wire (0.05 mm diameter and 1 cm length) allows the measurements to be performed. The melt was placed in a Pyrex container dipped in the central zone of the furnace, that was raised as long as the bob and the half of the steel wire was dipped. This condition was observed by means of a set of mirrors. The furnace was thermoregulated by means of a chromel–alumel thermocouple connected to a Leeds & Northrup CAT system and the temperature of the melt was read by means of a second thermocouple, dipped in the melt, checked against a Pt-resistance thermometer certified by NBS and connected to a Leeds & Northrup K-3 potentiometer. The system was calibrated by means of H_2O, KCNS, $LiNO_3$, and $NaNO_3$ (*5*, *7*) and the following equation was obtained for the volume (cm^3) of the bob until 350 °C: $V = 1.172_0 + (8.71 \times 10^{-5})t$. In order to minimize the