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Articles

Salt Effect on the High-Pressure Multiphase Behavior of the Ternary System (Ethene + Water + 2-Propanol)[†]

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At temperatures from (289 to 353) K, the ternary system (ethene + water + 2-propanol) is known to exhibit a region of liquid−liquid−vapor (L_1L_2V) equilibria at elevated pressures that is bordered by the lower (($L_1 = L_2$)V) and upper (L_1(L_2 = V)) critical end point lines. This particular demixing effect is commonly known as "salting out by a supercritical gas". In this work, the effect of adding different electrolytes on the pressure of both critical end points at (293 and 333) K is investigated.

Introduction

The ternary system (ethene + water + 2-propanol) exhibits a phenomenon that is called "salting out with a supercritical gas". That phenomenon was first reported by Elgin and Weinstock.[1] For example, pressurization of a completely miscible binary liquid mixture of water and 2-propanol with a supercritical—or "nearcritical"—gas (e.g., ethene) induces phase separation into a high-density, water-rich phase (L_1) and a propanol-rich phase (L_2) of lower density. That three-phase liquid−liquid−vapor (L_1L_2V) equilibrium exists within a restricted pressure and temperature region. In this context, the term "nearcritical" means that the operational temperature is around the critical temperature of the gas (i.e., $T_c = 282.35$ K for ethene[2]).

Both limiting pressures and temperatures and the composition of the coexisting three phases L_1, L_2, and V were investigated for various ternary systems (gas + water + hydrophilic organic solvent). A 1998 review paper provides an overview of such studies at the University of Kaiserslautern by then.[3] Recently, the ternary system (ethene + water + 2-propanol) was subject to closer investigation, and the corresponding experiments comprised the limiting lower (($L_1 = L_2$)V) and upper (L_1(L_2 = V)) critical end point lines between (288.85 and 353.15) K as well as the composition of the coexisting phases in the three-phase L_1L_2V equilibrium over the entire pressure range at (293.15, 313.15, and 333.15) K.[4] These experiments were further amended by a modeling study using an equation of state approach.[5]

Since the nearcritical gas acts as salting-out agent, the addition of an additional electrolyte compound is expected to enhance the effect and ultimately results in a stronger salting out that manifests in a shift of both the lower (($L_1 = L_2$)V) and the upper (L_1(L_2 = V)) critical end point (abbreviated as LCEP and UCEP, respectively) to lower pressures at a constant temperature with a stronger impact on the lower critical end point due to the preference of the electrolyte for the more hydrophilic phase L_1. That shift is important, for example, when the "salting-out" phenomenon is to be used in downstream processing of biomolecules. In such processes, there are often certain amounts of strong electrolytes (salts), and the pH and/or the ionic strength might be adjusted to avoid a denaturation of the biomolecule and/or to allow its extraction. Here, the influence of adding different electrolytes in different concentrations on the location of both critical end points at (293.15 and 333.15) K was investigated. Moreover, that study was performed as a first step in a series of investigations that deal with the partitioning of biomolecules in coexisting liquid phases in the system (ethene + water + 2-propanol).[6] The electrolytes chosen for this study were pure sodium chloride (NaCl), two binary phosphate buffers (Na_2HPO_4 + KH_2PO_4 and H_3PO_4 + Na_2HPO_4), and the buffer salt hydrous sodium borate ($Na_2B_4O_7 \cdot 10\ H_2O$).

Experimental Section

Materials. Ethene (2.7, volume fraction > 0.997) was supplied by Messer Griesheim, a subsidiary of the Messer Group GmbH, Krefeld, Germany. 2-Propanol (p.a., mass fraction > 0.997), sodium chloride (NaCl, mass fraction > 0.995 (acidimetric analysis)), hydrous sodium borate ($Na_2B_4O_7 \cdot 10\ H_2O$, mass fraction 0.995 to 1.050 (acidimetric analysis)), orthophosphoric acid (H_3PO_4, aqueous solution, mass fraction > 0.85 (acidimetric analysis)), and monopotassium dihydrogen phosphate (KH_2PO_4, mass fraction > 0.995 (acidimetric analysis)) were all from Merck KGaA, Darmstadt, Germany. Disodium monohydrogen phosphate (Na_2HPO_4, assay > 0.995) was purchased from Riedel-de Haën GmbH, Seelze, Germany. Water was deionized and bidistilled before use. All materials were used as supplied.

Apparatus, Procedure, and Experimental Uncertainties. The setup of the experimental arrangement that was used for the investigations reported here was described in detail by Freitag et al.[7] Further details on the equipment are available in Ulanova's doctoral thesis.[6] Therefore, only the main features are repeated here. The apparatus operates in a static-analytical method and can be employed at temperatures between about (263 and 353) K and at pressures up to 30 MPa. Its central part

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is a nonmagnetic, pivot-mounted cylindrical view-cell with sapphire windows at both ends, an internal volume of about 30 cm^3, and two sample loops that are entirely placed inside a thermostat. The pivot allows us to position the lines of the sample loops so that the coexisting phases can be sampled and analyzed individually.

No sampling but visual inspection only is applied for determining the coordinates of the LCEP and UCEP, respectively, since circulation of a critical phase (and the unavoidable changes of pressure) instantaneously results in a phase split.[4] The only possibility to determine critical composition is indirectly by extrapolation from ascertainable compositions of the L_1L_2V equilibrium in the vicinity of the respective critical point. In an experiment, the cell, already at the operational temperature, is charged with an aqueous/organic liquid feed that already contains the electrolyte. Subsequently, the cell is pressurized and equilibrated until a L_1L_2V equilibrium occurs. In the following steps, the critical pressure is gradually approached by adding small portions of solvent or cautiously releasing some of the vapor phase V. Each step is immediately followed by stirring and waiting for a phase split (i.e., the equilibrium state is to be renewed). The imminent vicinity of the critical point is indicated by the appearance of critical opalescence, which is a dispersion effect caused by density fluctuations. When a critical point is approached, the coexisting phases change from colorless over a usually yellowish or orange tint up to finally opaque and black. In the experiments of the present work, critical opalescence manifested itself stronger for the UCEP than for the LCEP. Besides, during the final stages of an experiment for encountering the critical point, it has to be ensured that both phases determined to become critical take approximately equal volumes, and thus the boundary between these phases ultimately disappears maintaining equal-volume constitution. That pressure represents the lower or upper critical end point. When, however, during such an approach the phase boundary is shifted in either direction so that finally one of the liquid phases disappears, the critical end point line is not reached, but the adjacent two-phase region instead.

Higher accuracy was achieved in the determination of the particular critical end point by executing the described procedure several times, each followed by smaller steps during the approach. This stepwise determination provided the critical loci with a smaller uncertainty.

The experimental uncertainties apply on pressure and temperature. Both platinum resistance thermometers and pressure transducers were calibrated (see refs 4 and 6) prior to the experiments. The total uncertainty in the temperature measurement was less than ± 0.05 K, and the corresponding pressure uncertainty amounted to ± 0.005 MPa for pressures lower than 10 MPa and ± 0.01 MPa for higher pressures, respectively. The optimum accuracy is determined by the readings of the pressure transducers.[4,6,7] It should be noted, however, that a lesser compliance with the equal volumes postulate as mentioned above can by far produce a larger error than the intrinsic instrument uncertainties.

Results and Discussion

The determination of critical end points was carried out at (293.15 and 333.15) K, respectively, and covered a pressure range from (5.47 to 16.35) MPa. At those conditions, the ternary phase-forming system (ethene + water + 2-propanol) shows a phase behavior that is illustrated as a so-called "phase prism" in Figure 1. There, the pressure-dependent composition change of the coexisting phases in the three-phase L_1L_2V equilibrium is approximated. A full account for the phase behavior of the system (ethene + water + 2-propanol) providing data on the composition of the coexisting phases L_1, L_2, and V is already given in a previous publication.[4]

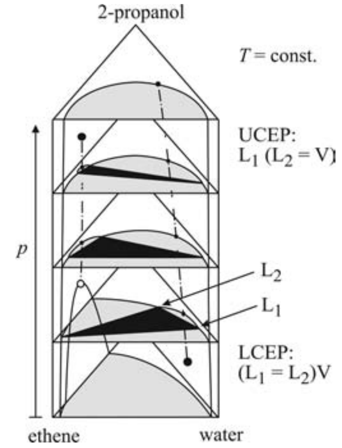

Figure 1. Phase prism that shows the qualitative phase behavior of the ternary system (ethene + water + 2-propanol) at the temperatures investigated in the present study. The shaded area represents two-phase regions (liquid−liquid and vapor−liquid), and the area in black is the three-phase L_1L_2V equilibrium bordered by LCEP and UCEP.

Table 1. Composition of the Electrolyte Systems that Were Added to the Ternary System (Ethene + Water + 2-Propanol)

identifier	compounds	composition
A	NaCl	NaCl: $c = 20\ \text{mmol}\cdot\text{L}^{-1}$
B	$Na_2HPO_4 + KH_2PO_4$	Na_2HPO_4: $c = 5\ \text{mmol}\cdot\text{L}^{-1}$ KH_2PO_4: $c = 5\ \text{mmol}\cdot\text{L}^{-1}$
C	$Na_2HPO_4 + KH_2PO_4$	Na_2HPO_4: $c = 10\ \text{mmol}\cdot\text{L}^{-1}$ KH_2PO_4: $c = 10\ \text{mmol}\cdot\text{L}^{-1}$
D	$H_3PO_4 + Na_2HPO_4$	H_3PO_4: $c = 100\ \text{mmol}\cdot\text{L}^{-1}$ Na_2HPO_4: $c = 20\ \text{mmol}\cdot\text{L}^{-1}$
E	$Na_2B_4O_7\cdot 10\ H_2O$	$Na_2B_4O_7\cdot 10\ H_2O$: $c = 30\ \text{mmol}\cdot\text{L}^{-1}$

At a constant temperature, the three-phase L_1L_2V equilibrium exists within a defined pressure range that is bordered by the lower and upper critical end point. At pressures below the LCEP, water and 2-propanol are completely miscible, and the two other binary subsystems show a vapor−liquid equilibrium. At pressures above the UCEP, a two-phase liquid−liquid equilibrium can be observed, where the second liquid phase exhibits a fluid-like density that is significantly higher than the density of the vapor phase V in the L_1L_2V equilibrium.

Table 1 gives the compositions of the salt-containing aqueous solutions that were employed in the experiments. The results of the experimental investigations are given in Table 2 together with previous results for both LCEP and UCEP for the pristine ternary system (ethene + water + 2-propanol).[4] Additionally, the measurements at (293.15 and 333.15) K were repeated for the electrolyte-free ternary system, and the new results are also given in Table 2.

The electrolyte solutions were prepared as follows: The amount of electrolyte (cf. Table 1) is dissolved in water, and the cell is charged with the resulting homogeneous electrolyte-containing aqueous solution as well as with pure 2-propanol. Then, the phase split is induced by pressurizing with the nearcritical gas, and a L_1L_2V equilibrium is generated. Initially, the two liquid phases have different volumes. There is always electrolyte-containing aqueous solution added during the approximation of the critical end point. At the LCEP, the two (critical) liquid phases L_1 and L_2 are of equal volume. If and only if that criterion of equal volumes is met (i.e., at the LCEP), the ionic strength of the entire liquid phase inside the cell

Table 2. Critical Endpoints that Are Assigned to a Three-Phase L_1L_2V Equilibrium in the Ternary System (Ethene + Water + 2-Propanol)[a]

		p/MPa			relative deviation to the salt-free system/%	
T/K	electrolyte system	LCEP: $(L_1 = L_2)V$	UCEP: $L_1(L_2 = V)$	p(UCEP) − p(LCEP)	LCEP: $(L_1 = L_2)V$	UCEP: $L_1(L_2 = V)$
288.15	salt-free	6.153	12.16	6.01	-	-
293.15	salt-free	7.139	12.95	5.81	-	-
	A	6.469	12.60	6.13	−10.4	−2.8
	B	6.197	12.48	6.28	−15.2	−3.8
	C	5.467	12.21	6.74	−30.6	−6.1
	D	5.505	12.05	6.55	−29.7	−7.5
	E	5.600	12.08	6.48	−27.5	−7.2
303.15	salt-free	8.842	14.22	5.38	-	-
313.15	salt-free	10.17	15.28	5.11	-	-
323.15	salt-free	11.28	16.08	4.80	-	-
333.15	salt-free	12.42	16.94	4.52	-	-
	C	9.930	16.29	6.36	−25.1	−4.0
	D	10.35	16.35	6.00	−20.0	−3.6
	E	10.05	16.15	6.10	−23.6	−4.9
342.15	salt-free	13.23	17.40	4.17	-	-
353.15	salt-free	14.23	17.93	3.70	-	-

[a] Results for the salt-free system and the influence of additional electrolyte compounds.

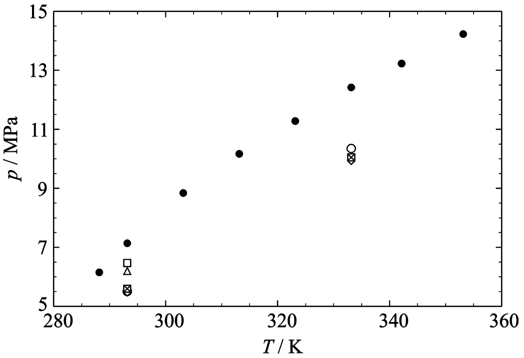

Figure 2. Lower critical end points (LCEPs) in the ternary system (ethene + water + 2-propanol): ●, electrolyte-free system; □, electrolyte A; Δ, electrolyte B; ◇, electrolyte C; ○, electrolyte D; square with an X, electrolyte E.

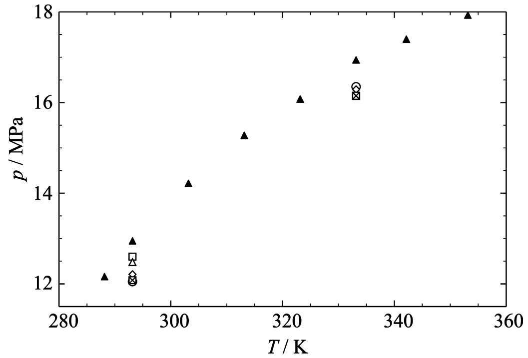

Figure 3. Upper critical end points (UCEPs) in the ternary system (ethene + water + 2-propanol): ▲, electrolyte-free system; □, electrolyte A; Δ, electrolyte B; ◇, electrolyte C; ○, electrolyte D; square with an X, electrolyte E.

amounts to one-half of the aqueous phase L_1. It can rightly be assumed that the vapor phase V that largely consists of ethene contains no electrolyte. As long as the three-phase L_1L_2V equilibrium exists, the electrolyte will be differently distributed between the two liquid phases L_1 (more) and L_2 (less). At the UCEP, where L_2 and V become critical, the electrolyte is supposed to be almost entirely in the aqueous phase L_1 under the experimental conditions. Consequently, the ionic strength solely refers to the aqueous phase L_1.

The experimental results for the critical end points of the electrolyte-containing systems are displayed in Figures 2 (for LCEP) and 3 (for UCEP) together with those for the electrolyte-free system. The results for the electrolyte-free system[4] are shown to demonstrate the influence of the salts on the critical end point lines.

All experiments revealed a salting-out effect; i.e., the pressure region where the three-phase L_1L_2V equilibrium exists is shifted to lower pressures, or in other words, the added electrolyte enhances the impact of the nearcritical gas (the gaseous salting-out agent). As expected, the pressure drop manifested itself stronger for the LCEP ($(L_1 = L_2)V$) because the aqueous L_1 phase is more hydrophilic and thus preferred by ionic compounds, and a higher value for the ionic strength that comes along with higher electrolyte concentrations shifts the critical end points further toward lower pressures. As can be seen from Table 2, a doubling of the ionic strength (i.e., the change from electrolyte B to electrolyte C) at a constant temperature amplifies the pressure drop likewise by about a factor of 2 for the LCEP and to a slightly lesser extent for the UCEP. The pressure difference p(UCEP) − p(LCEP), which monotonously decreases toward increasing temperatures in the electrolyte-free ternary system, becomes larger for the electrolyte-containing systems at both temperatures investigated (from 6.13 MPa for electrolyte A at 293.15 K to 6.74 MPa for electrolyte C at 333.15 K compared to 5.81 (4.52) MPa in the electrolyte-free system at 293.15 (333.15) K). The increase of temperature from (293.15 to 333.15) K reduces the pressure difference p(UCEP) − p(LCEP) in the three systems C, D, and E a little.

For the electrolyte-free ternary system, the course of the critical end point lines allows (by extrapolation to higher temperatures) for a rough estimate of the coordinates of the tricritical point (i.e., $(L_1 = L_2 = V)$). From the data available, the expected coordinates of the tricritical point are to be between (410 and 430) K and (18 to 20) MPa, respectively.[4] However, the observations for the electrolyte-containing systems corroborate a possibly different development for the critical end point lines.

Conclusions and Outlook

New experiments were performed to verify that salting out by a nearcritical gas is amplified by adding a “conventional salt”. The existence of such a pressure-induced three-phase L_1L_2V region is well-known for the ternary system (ethene + water + 2-propanol).[4] Therefore, that system was chosen to study the influence of several electrolytes (with both different composition and different ionic strength) on the pressures that confine the

L_1L_2V equilibrium by featuring LCEP and UCEP at (298.15 and 333.15) K, respectively. A significant shift toward lower pressures that is on equal terms with a stronger salting out was observed in all cases, and the phenomenon always manifested itself stronger on the LCEP than on the UCEP, which is due to the peculiar composition of the aqueous liquid phase (L_1) that becomes critical with the organic liquid phase (L_2) at the LCEP. The maintenance of the UCEP (where the organic liquid phase (L_2) becomes critical with the vapor phase) shows that at the UCEP the solubility of the selected strong electrolytes in the organic liquid is negligible, as the (rather low-density) vapor phase can certainly dissolve only traces of the electrolytes.

In the electrolyte-free system, the difference between the pressure on both critical end point lines decreases with increasing temperature (resulting in a tricritical point at around (415 ± 5) K). In the salt-containing system, that pressure difference decreases with increasing temperature as well, but to a lesser extent. Therefore, no quantitative statement about the shift of the temperature−pressure coordinates of the tricritical point is possible at the moment.

In a conceived application of that particular phenomenon, for example, to employ the coexisting liquid phases L_1 and L_2 in an extraction process,[8] particular consideration has to be given for effects caused by the presence of strong electrolytes (that are either present from the process or added to adjust the pH of the solution).

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