Compositions, Densities, Conductivities, and Refractive Indices of Potassium Chloride or/and Sodium Chloride + PEG 4000 + Water at 298.15 and Liquid−Liquid Equilibrium of Potassium Chloride or Sodium Chloride + PEG 4000 + Water at 333.15 K

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Phase diagrams have been measured for the ternary systems KCl + PEG + H_2O and NaCl + PEG + H_2O at 298.15 K and 313.15 K and for the quaternary system NaCl + KCl + PEG + H_2O at 298.15 K. In all the cases PEG of molecular weight 4000 has been used. Density, refractive index and electrical conductivity were also determined for all the saturated solutions at 298.15 K. Equations are proposed in order to correlate the equilibrium and physical properties data of the ternary systems at 298.15 K. At 298.15 K, the PEG addition decreases the solubility of all the experimental systems and only one liquid phase in equilibrium with solid phase is found. In the quaternary system, the presence of two salts decreases the individual salt solubility values, being this effect more important for KCl. At 333.15 K, both ternary systems contain a region with two liquid phases in equilibrium, where a liquid is rich in salt and the other one in PEG. The liquid−liquid-solid equilibrium was determined for both systems. The field of crystallization of the corresponding salt is bigger at 298.15 than to 333.15 K. Similar behavior for both salts, KCl and NaCl was found.

1. Introduction

One of the methods employed in crystallization for producing supersaturation in a solution is termed "drowning out". The method consists of adding a third or new component which is miscible with the original solution in order to decrease the solubility of the salt of interest. This crystallization technique has a series of advantages in comparison with traditional procedures of evaporation or cooling, including increased yields, operation at ambient temperature, high purity of crystals, selectivity and others.[1]

NaCl and KCl are present to a large extent in natural inorganic salt deposits. From longtime ago, the separation of both salts has been a main objective in the inorganic industrial research. In this field, several authors[2−8] have recently studied the effects on the solubilities of these salts by the addition of organic solvents to their aqueous solutions. In this work, we evaluate the potential applicability of the drowning-out procedure using PEG as a technique for selective precipitation of these salts.

Wagner et al.[2] determined solubilities of NaCl in different mixtures of solvents including water + cyclohexane, water + cyclohexanol, water + benzyl alcohol, water + ethanol + cyclohexanol, and water + benzyl alcohol + cyclohexanol at 298.15 K.

Gomis et al.[3,4] studied seven ternary aqueous systems including NaCl and KCl in 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol at 298.15 K. The results shown in these systems present a region with three phases: liquid−liquid-solid. Takiyama et al.[5] studied the morphology of NaCl crystals produced by drowning-out with ethanol at 313.15 K. They found that operational conditions, degree of supersaturation, and mixing greatly influenced crystal form. They concluded that larger, more regular crystals were obtained by using low compositions of anti-solvent and a low initial supersaturation. Hanson and Lynn[6] patented a combined process which included extraction and crystallization for the recuperation of NaCl from mineral deposits, where water was used as a solvent and an amine as a precipitant.

Taboada et al.[7] studied the separation of KCl from pure and industrial grade silvinite by addition of NH_3 to the aqueous solvent.

Ternary and quaternary equilibrium related to the KCl + NaCl + C_2H_5OH + H_2O system also provide information on the possibility of using ethanol to separate KCl from aqueous silvinite solutions. Solubilities, densities, and refractive indices data have been measured by Galleguillos et al.[8] for the ternary systems KCl + C_2H_5OH + H_2O and NaCl + C_2H_5OH + H_2O at (298.15 and 313.15) K. Also, data are also presented on the equilibrium of the quaternary system KCl + NaCl + C_2H_5OH + H_2O at (298.15 and 313.15) K.

The use of soluble polymers as precipitant component is an important alternative in drowning-out processes. The poly (ethylene glycol), PEG, is one of the polymers with major interest in this area because it is a low cost, nontoxic, non-inflammable and easy to handle compound. Frequently the addition of PEG to an inorganic salt aqueous solution generates an aqueous two phase system. This type of

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systems has been widely studied in the literature.[9−13]

Snyder et al.[9] provided partial information for the phase diagrams for aqueous solutions of PEG with $MgSO_4$, Na_2SO_4, $CaCO_3$, $(NH_4)_2SO_4$ and K_2HPO_4. Ho-Gutierrez et al.[10] presented data on the liquid−liquid equilibrium for aqueous mixtures of PEG, having molecular weights of 1000, 3350 and 8000, with Na_2SO_4 at 301 and 308 K and NaCl at 333 K.

Hammer et al.[11] measured the concentrations at liquid−liquid equilibrium in aqueous solutions of PEG and Na_2SO_4 working with polymer molecular weight ranged between 1550 and 6000 and temperatures between 293.15 and 313.15. González-Tello et al.[12] studied the liquid−liquid equilibrium of the PEG (1000, 3350 and 8000) + $MgSO_4$ + H_2O at 298 K. Taboada et al.[13] measured liquid−liquid and liquid−liquid-solid equilibrium of the PEG 4000 + Na_2SO_4 + H_2O at 298.15K. Graber et al.[14,15] presented data on the liquid−liquid equilibrium of the PEG + $NaNO_3$ + H_2O system at 298.15 K using PEG with molecular weights of 2000, 4000, 6000 and 10000.

In this work, we study the equilibrium phase diagrams in order to evaluate the possible use of PEG as precipitant component of NaCl and/or KCl aqueous solutions. We work with two different temperatures which suppose, in the practice, two different alternative processes with one or two liquid phases in the equilibrium.

2. Experimental Section

Materials. Potassium chloride and sodium chloride were supplied by Merck Co. with a purity of 99.8% and 99.5% respectively. All of the chemicals for this study were used without further purification. Salts were dried to constant weight for 48 h at 375.15 K prior to use. Water employed was distilled and deionized (conductivity < 0.5 mS/cm) before the use in all experiments. The synthesis grade polymer PEG (mass-average molar mass 4000 g/mol) was in the form of solid powder; the polydispersity index, as reported by the supplier, was 1.1. In drying for a week at 323.15 K, the polymers showed water content of 0.46 mass %.

Apparatus and Procedures. Liquid−Solid Equilibrium diagrams (298.15 K). The phase equilibrium study was carried out by mixing of known masses of PEG and water with excess salt. For the quaternary system, excess quantities of both salts were also added in known quantities. All the solutions were prepared by mass, using an analytical balance with a precision of ($\pm 1 \times 10^{-4}$ g) (Denver Instrument Co., model AA-200). The resultant supersaturated solutions were contained in suitably sealed glass flasks and mechanically shaken for 48 h. The central portion of the stoppers in the flasks was made of rubber, such that samples could be extracted from the flasks by syringe without losses of solvent by evaporation. All flasks were maintained at working temperatures (± 0.1 K) in a temperature controlled bath. Once equilibria were reached, mixing was interrupted and the solutions were allowed to decant for 60 min at constant temperature.

The clear liquid of each equilibrium solution was collected by syringe and filtered for subsequent determinations of concentration, density, refractive index and electrical conductivity. Syringes and other apparatus used in the procedure were maintained at slightly elevated temperature to avoid any tendency of precipitation of salts from the solutions under study because of drops in temperature. Samples of the solid phase were also filtered and characterized by X-ray diffraction.

The concentration of sodium and potassium in the ternary and quaternary systems was determined by atomic absorption spectrometry (AA) at a wavelength of 589 and 766.5 nm, respectively, using a Varian model SpectrAA 220 instrument. The calibration line was obtained using aqueous solutions of Na or K from 0 to 50 ppm. For the quaternary systems a 1% v/v HCl matrix containing 2000 ppm of KCl or NaCl, respectively was employed. The initial composition of PEG and NaCl or KCl did not show significant influence on the spectrophotometric readings. The measurements, which were carried out in triplicate, gave a reproducibility of ± 0.4%. Based on measurements on standard solutions, an uncertainty of $\pm 3 \times 10^{-2}$ g KCl or NaCl per 100 g of solution was obtained

Liquid−Liquid and Liquid−Liquid−Solid Equilibrium Diagrams (333.15 K). Binodal Curve at 333.15 K. The binodal curve was determined by addition of small amounts of PEG (0.01 g) to an aqueous solution of potassium chloride and sodium chloride, respectively, until turbidity appeared; which indicated the formation of two liquid phases. The composition for each point on the binodal curve was calculated in accordance with the amount of PEG added until turbidity was observed. The binodal curve was completed using the same procedure for aqueous solutions of PEG by adding 0.02 g amounts of potassium chloride and sodium chloride, respectively. All the solutions were maintained at working temperatures (± 0.1 K) in a temperature controlled bath. This procedure was used previously by Taboada et al..[16] and gives accurate results.

Tie lines at 333.15 K. Feed samples of 90 mL yielding roughly equal volumes of the top and the bottom phases were prepared by mixing weight quantities of the three components in 100 mL graduated Pyrex cylinders. Equilibrium measurements were made by preparing mixtures of known mass composition by stirring for 48 h and allowing solutions to settle for a further 24 h at a constant temperature of (333.15 ± 0.1) K to ensure that equilibrium was established. At this time, samples were taken from the two or three equilibrium phases and analyzed. Longer stirring and settling periods than those mentioned above had no measurable effects on the phase compositions.

At the end of each experiment, the phase volumes were determined, and samples were taken from each phase and analyzed. The top phase was sampled first, with care being taken to leave a layer of solution at least 0.5 cm thick above the interface. The bottom phase was withdrawn using a syringe with a long needle. A tiny bubble of air was retained in the needle tip and expelled once the tip is in the bottom phase to prevent contamination with upper-phase material. In cases where precipitated salt was present, care was taken to ensure that the sample was withdrawn without agitation, with the tip of the needle well away from salt crystals.

The sodium or potassium concentrations were measured by atomic absorption using the experimental procedure previously explained. All analyses included three replicate measurements on each sample, and had a mean accuracy of 0.7%.

When appearing, samples of the solid phase were also filtered and characterized by X-ray diffraction.

The composition of PEG was determined, once known the salt concentration, from density and refractive indices measurements at 298.15 K using Mettler-Toledo model DE50 oscillation densimeter and Mettler-Toledo model RE40 refractometer, respectively. Temperature was maintained within ± 0.1 K of their set points using water bath supplied by Haake instruments.

Table 1. Solubility (Mass %), s_{KCl}, Density, ρ, Refractive Index, n_D, and Electrical Conductivity, κ, for the Potassium Chloride + PEG + Water System at 298.15 K at Various Mass Fractions of PEG, w_{PEG}

w_{PEG}	s_{KCl}	ρ/kg·m^{-3}	n_D	κ/mS·cm^{-1}
0.0000	26.67	1177.20	1.3689	377.0
0.0446	24.43	1170.64	1.3745	309.0
0.0955	22.27	1168.16	1.3740	242.7
0.1273	20.67	1166.06	1.3834	203.0
0.1880	18.52	1160.52	1.3896	142.1
0.2120	18.03	1160.46	1.3926	125.0
0.2211	17.74	1157.98	1.3933	115.0
0.3005	15.14	1154.75	1.4016	73.0
0.3129	14.74	1154.22	1.4024	70.0
0.4018	12.26	1152.77	1.4122	35.5
0.4528	10.80	1152.62	1.4190	22.0
0.4932	9.95	1152.80	1.4230	16.0
0.5271	8.85	1152.11	1.4254	12.0

Table 2. Solubility (Mass %), s_{NaCl}, Density, ρ, Refractive Index, n_D, and Electrical Conductivity, κ, for the Sodium Chloride + PEG + Water System at 298.15 K at Various Mass Fractions of PEG, w_{PEG}

w_{PEG}	s_{NaCl}	ρ/kg·m^{-3}	n_D	κ/mS·cm^{-1}
0.0000	26.28	1197.78	1.3795	246.0
0.0446	25.30	1192.76	1.3841	203.0
0.0713	24.02	1190.00	1.3871	179.0
0.1272	22.02	1184.84	1.3924	140.0
0.1856	19.57	1179.90	1.3981	105.8
0.2120	19.19	1178.11	1.4009	92.0
0.2747	16.46	1173.28	1.4075	61.8
0.3597	14.07	1167.35	1.4169	30.9
0.3852	13.37	1167.89	1.4183	34.0
0.4430	11.72	1165.70	1.4240	21.0
0.4735	10.86	1164.48	1.4264	17.0
0.4866	10.47	1163.69	1.4279	15.0

Since the density and refractive index of phase samples depends on the PEG and salt concentration, calibration plots of density and refractive index versus polymer composition were realized for different concentrations of NaCl and KCl, respectively. Triplicate of each mixture were prepared by mass for salt concentrations from (0 to 6) %, and PEG in the range between (0 to 35) % de PEG and analyzed. In this composition intervals both, density and refractive index, show a linear dependence with salt and PEG composition. When necessary, phase samples were diluted in order to analyze salt and PEG composition in the intervals of calibration.

The calibration to density and refractive index was described by the following relationships:

$$\rho/\text{g·cm}^{-3} = 0.9970 + 0.7130w_{NaCl} + 0.1746w_{PEG} \quad (1)$$

$$n_D = 1.3325 + 0.1703w_{NaCl} + 0.1443w_{PEG} \quad (2)$$

$$\rho/\text{g·cm}^{-3} = 0.9970 + 0.6378w_{KCl} + 0.1735w_{PEG} \quad (3)$$

$$n_D = 1.3325 + 0.1336w_{KCl} + 0.1439w_{PEG} \quad (4)$$

Were w_{PEG} is the PEG composition in mass fraction and w_{NaCl} and w_{KCl} are the NaCl and KCl mass fractions, respectively. Good representation of the equations was obtained (relative deviations less than 0.1%, Graber et al.[14]).

Physical Properties. Density measurements were carried out in triplicate using a Mettler-Toledo model DE50 oscillation densimeter, having a precision of 5 × 10^{-2} kg m^{-3}, and a resolution of ±1 × 10^{-2} kg m^{-3}. The temperature was thermostatically controlled to ± 0.1 °C.

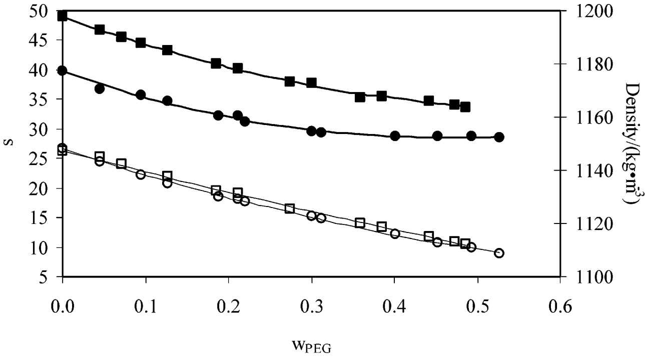

Figure 1. Solubility (mass %), *s*, and density of ternary systems KCl + PEG + H_2O and NaCl + PEG + H_2O at 298.15 K as a function of the PEG mass fraction, w_{PEG}: O, solubility of KCl; □, solubility of NaCl; ●, density of KCl solutions; ■, density of NaCl solutions.

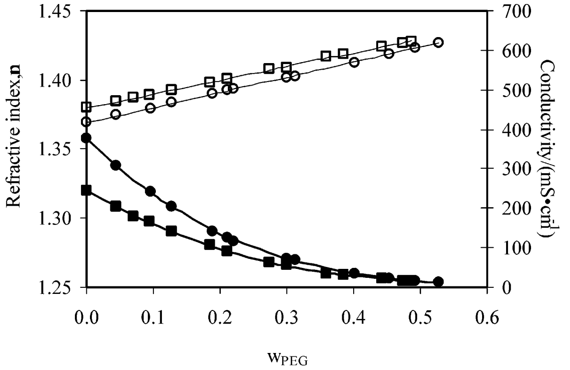

Figure 2. Refractive index, n_D, and electrical conductivity of ternary systems KCl + PEG + H_2O and NaCl + PEG + H_2O at 298.15 K as a function of the PEG mass fraction, w_{PEG}: O, refractive index of KCl solutions; □, refractive index of NaCl solutions; ●, electrical conductivity of KCl solutions; ■, electrical conductivity of NaCl solutions.

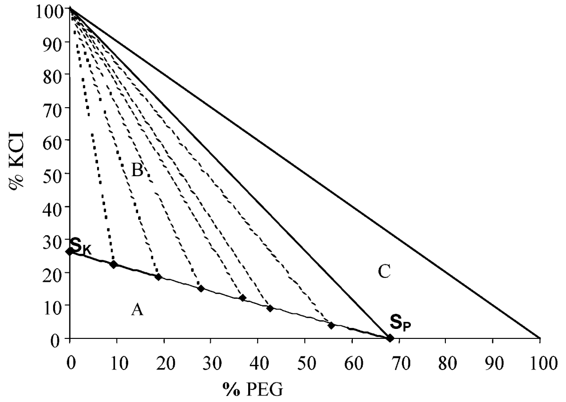

Figure 3. Phase diagram for the KCl + PEG + H_2O system at 298.15 K.

The refractive index of each solution was determined using a Mettler-Toledo model RE40 refractometer with a resolution of 1 × 10^{-4} unit and temperature control to ± 0.1 °C. The measurements were repeated at least three times without appreciable variation.

Electrical conductivity was measured using an Orion model 170 conductivy meter having a precision ≤ 0.5% of the measured value. The solution was held in a jacketed vessel maintained at the working temperature by a thermostatically controlled bath.

3. Results and Discussion

At 298.15 K, for both ternary system and over the entire PEG 4000 composition range studied only one liquid phase

Table 3. Solubility (Mass %) of KCl, s_{KCl}, and NaCl, s_{NaCl}, Density, ρ, Refractive Index, n_D, and Electrical Conductivity, κ, for the Quaternary System KCl + NaCl + PEG + Water at 298.15 K at Various Mass Fractions of PEG, w_{PEG}

w_{PEG}	s_{KCl}	s_{NaCl}	ρ/kg·m^{-3}	n_D	κ/mS·cm^{-1}
0.0000	11.58	20.14	1234.58	1.3851	
0.0856	9.25	17.99	1219.31	1.3932	206.5
0.1438	8.51	15.53	1209.06	1.4006	142.0
0.2272	7.42	13.19	1198.62	1.4087	88.5
0.3053	6.61	10.89	1190.48	1.4173	50.0
0.3684	5.83	9.29	1185.00	1.4245	30.0
0.4444	5.36	7.93	1181.69	1.4292	21.0

was obtained. Data for the solubility, density, electrical conductivity and refractive index for the KCl + PEG + H_2O ternary system at 298.15 K are listed in Table 1, and those for the NaCl + PEG + H_2O system at 298.15 K are listed in Table 2.

Figure 1 presents the solubility diagrams for the two ternary systems at 298.15 K. It can be observed that at 298.15 K the solubility of both salts decreased with the addition of PEG. Both salts show similar behavior, although, with PEG in solutions, slightly superior values of solubility of NaCl are observed for the whole interval of PEG composition studied. The experimental values for the mass fraction solubility (s) of the two ternary systems fit as polynomial functions of the PEG mass fraction, w_{PEG}, with origin in the solubility of the aqueous solution. The mean absolute deviation between all experimental and calculated solubility values is 0.18 g salt/100 g of solution for both ternary systems. Figure 1 shows the fit with the proposed equation as continuous lines.

$$s = 25.47{w_{PEG}}^2 - 46.61w_{PEG} + 26.67 \tag{5}$$

$$s = -33.24w_{PEG} + 26.28 \tag{6}$$

Also, Tables 1 and 2 present the properties of saturated solutions for both ternary systems at 298.15 K. The density and the electrical conductivity of the saturated solutions decrease when increasing the mass fraction of PEG at 298.15 K. The behavior of the density is opposite to that of other systems PEG + H_2O at the same temperature.[17] So, in the density of saturated solutions of KCl + H_2O + PEG and NaCl + H_2O + PEG systems, the effect of the solubility is higher than the effect of increasing PEG composition. However, the index of refraction of the saturated solutions increases with the PEG composition.

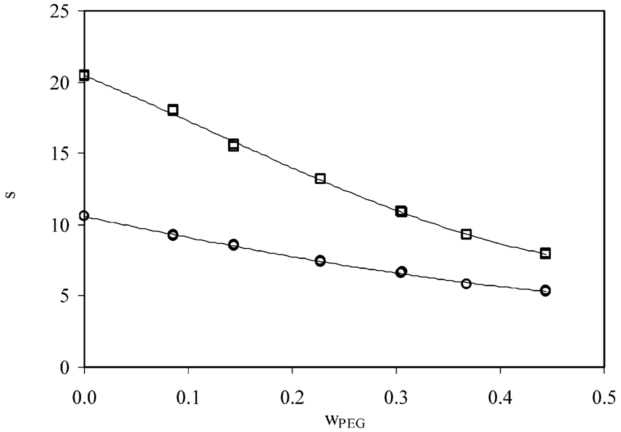

Figure 4. Solubility (mass %), *s*, of the quaternary system KCl + NaCl + PEG 4000 + H_2O at 298.15 K: ○, KCl, □, NaCl + PEG 4000 + H_2O.

Table 4. Binodal Curve Data of the Potassium Chloride + PEG + Water System at 333.15 K at Different Mass Fractions of PEG, w_{PEG}, and KCl, w_{KCl}

w_{PEG}	w_{KCl}	w_{PEG}	w_{KCl}
0.0076[a]	0.2749[a]	0.0888	0.1905
0.0076	0.2949	0.0979	0.1871
0.0132	0.2502	0.0987	0.1917
0.0255	0.2238	0.1074	0.1879
0.0359	0.2169	0.1185	0.1836
0.0400	0.2195	0.1261	0.1813
0.0533	0.2070	0.1338	0.1783
0.0630	0.2018	0.1480	0.1731
0.0705	0.1964	0.2348	0.1488
0.0782	0.1935	0.3280	0.1339
0.0788	0.1967	0.4373	0.1291
0.0805	0.1942	0.4473[a]	0.1191[a]

[a] Indicates saturated solutions in liquid−liquid−solid equilibrium.

Table 5. Binodal Curve Data of the Sodium Chloride + PEG + Water System at (333.15) K at Different Mass Fractions of PEG, w_{PEG}, and NaCl, w_{NaCl}

w_{PEG}	w_{NaCl}	w_{PEG}	w_{NaCl}
0.0073[a]	0.2705[a]	0.0854	0.1844
0.0270	0.2207	0.0914	0.1817
0.0306	0.2128	0.0980	0.1795
0.0341	0.2068	0.1062	0.1725
0.0490	0.2005	0.1215	0.1728
0.0614	0.1940	0.1278	0.1700
0.0590	0.1950	0.1378	0.1664
0.0675	0.1919	0.3106	0.1305
0.0726	0.1877	0.4340	0.1180
0.0795	0.1876	0.4445*	0.1207*

[a] Indicates saturated solutions in liquid−liquid-solid equilibrium.

Solubility, density and refractive index values are lightly higher in NaCl solutions, but KCl solutions show higher electrical conductivity values. When increasing the composition of PEG, the solubility of both salts decreases and the three measured properties values spread to come closer. This effect is very clear with the electrical conductivity.

Figures 1 and 2 illustrate this behavior for density, refractive index and electrical conductivity. For both systems, the three properties were fitted as polynomial functions of the PEG mass fraction, w_{PEG}, with origin in the property value of the aqueous solution. The mean relative standard deviations between all experimental and calculated values is 0.05% for density of KCl + PEG + H_2O system, 0.03% for density of NaCl + PEG + H_2O system, 0.02% for refractive index of both systems and 2% for

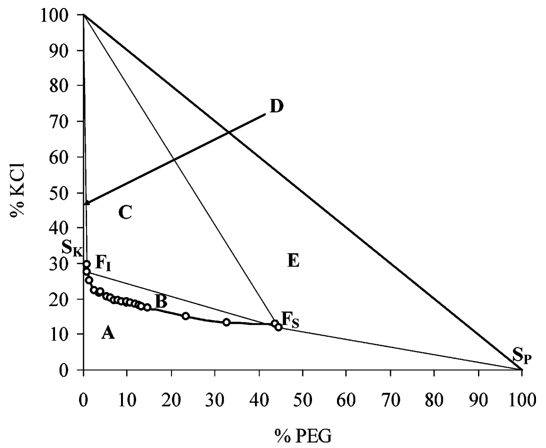

Figure 5. Phase diagram for the KCl + PEG + H_2O system at 333.15 K.

Table 6. Mass Fraction of PEG, w_{PEG}, and KCl, w_{KCl}, and Density, ρ, of Tie Lines of the Potassium Chloride + PEG + Water System at 333.15 K from Various Initial Mass Fractions

initial comp		top phase			bottom phase			partition coefficient
w_{PEG}	w_{KCl}	w_{PEG}	w_{KCl}	ρ/kg·m^{-3}	w_{PEG}	w_{KCl}	ρ/kg·m^{-3}	K
0.0930	0.2015	0.2348	0.1488	1116.4	0.0400	0.2195	1135.0	1.47
0.1008	0.2201	0.3280	0.1339	1124.5	0.0132	0.2502	1153.4	1.87
0.1498[a]	0.2401[a]	0.4473	0.1191	1135.6	0.0076	0.2749	1186.7	2.31

[a] Indicates saturated solutions in liquid−liquid−solid equilibrium.

Table 7. Mass Fraction of PEG, w_{PEG}, and NaCl, w_{NaCl}, and Density, ρ, of Tie Lines of the Sodium Chloride + PEG + Water System at 333.15 K from Various Initial Mass Fractions

initial comp		top phase			bottom phase			partition coefficient
w_{PEG}	w_{NaCl}	w_{PEG}	w_{NaCl}	ρ/kg·m^{-3}	w_{PEG}	w_{NaCl}	ρ/kg·m^{-3}	K
0.0899	0.2005	0.3106	0.1305	1126.4	0.0270	0.2207	1147.2	1.69
0.1000	0.2201	0.3973	0.1228	1134.0	0.0093	0.2529	1169.3	2.06
0.1541[a]	0.2585[a]	0.4445	0.1207	1139.5	0.0073	0.2705	1180.3	2.24

[a] Indicates saturated solutions in liquid−liquid−solid equilibrium.

electrical conductivity of both systems. Figures 1 and 2 shows the fit with the proposed equations as continuous lines.

KCl + PEG + H_2O:

$$\rho/(\mathrm{kg\cdot m^{-3}}) = 120.24w_{PEG}^{2} - 109.72w_{PEG} + 1177.20 \quad (7)$$

$$n_D = 0.1094w_{PEG} + 1.3689 \quad (8)$$

$$\kappa/\mathrm{mS\cdot cm^{-1}} = -1564.6w_{PEG}^{3} + 2715.6w_{PEG} - 1689.9w_{PEG} + 377.0 \quad (9)$$

NaCl + PEG + H_2O:

$$\rho/\mathrm{kg\cdot m^{-3}} = 90.03w_{PEG}^{2} - 113.25w_{PEG} + 1197.78 \quad (10)$$

$$n_D = 0.\ 1001w_{PEG} + 1.3796 \quad (11)$$

$$\kappa/\mathrm{mS\cdot cm^{-1}} = -594.1w_{PEG}^{3} + 1344.3w_{PEG}^{2} - 967.9w_{PEG} + 246.0 \quad (12)$$

Figure 3 shows the complete phase diagram for the KCl−PEG−H_2O system at 298.15 K. We observe the following points, curves, and zones: A, homogeneous zone of unsaturated liquid; B, equilibrium zone between the saturated liquid phase and the solid-phase KCl; C, region with the presence of saturated liquid and two solids (KCl and PEG). S_K, solubility of KCl in water; S_P, solubility of PEG in water; $S_K\,S_P$, saturation curve of KCl in aqueous solutions of PEG.

This phase diagram is very similar to the one obtained using NaCl, given the correspondence in the behavior of both salts in the water−poly(ethylene glycol) mixture.

Table 3 presents the experimental results on solubilities, density, refractive index, and conductivity for the quaternary system that includes KCl + NaCl + PEG + H_2O at 298.15 K. The behavior of the solubilities and the physical properties is very similar to that observed in the ternary systems. The solubility of both salts decreased with increasing PEG/water ratio in the solution. The total solubility is slightly higher than in the individual ternary systems, but the solubility of each one of the salts decreases significantly. In all saturated quaternary solutions obtained, the KCl/NaCl ratio in the solution remained below unity. Work with this system resulted in a greater precipitation of KCl than of NaCl. This selectivity decreases when working with increasing mass fraction ratios of PEG/water. The same trend was observed by Galleguillos et al.[8] for these two salts when using ethanol as a cosolvent.

In Figure 4, the behavior is shown for the solubilities of both salts in the quaternary system.

Finally, working with the two ternary systems KCl + PEG + H_2O and NaCl + PEG + H_2O at 333.15 K, we found aqueous two-phase systems. Usually, the addition of polymers as PEG to aqueous solutions of inorganic salts produces two liquid phases.[9−15] The binodal curve compositions for both ternary systems are given in Tables 4 and 5. To obtain the limit of the two-liquid-phase area, a solution with composition in this area was prepared, being obtained by two liquids in equilibrium with crystals of the corresponding salt. The compositions of these saturated solutions correspond with the extreme values of the curve binodal in Tables 4 and 5.

In the NaCl + PEG + H_2O system, the values obtained for the saturated solutions are very similar to those presented by Ho-Gutiérrez et al.:[10] $w_{PEG} = 0.434$, $w_{NaCl} = 0.118$ and $w_{PEG} = 0.00011$, and $w_{NaCl} = 0.269$. However, they worked with PEG of higher molecular weight (PEG 8000) and obtained lower concentrations of NaCl in the binodal curve than those presented in this work.

Figure 5 shows the complete diagram of the system KCl + PEG + H_2O in which the following areas and points are appreciated: A, liquid unsaturated zone; B, biphasic zone; C, zone of stability of the potassium chloride with two liquids F_I and F_S; D, area of coexistence of solid KCl with a liquid-phase saturated in KCl; E, zones consisting of two solids (KCl and PEG) and a liquid; S_K, solubility of KCl in water at 333.15 K (31.27 (g KCl/100 g solution), Perry[18]); S_P, solubility of PEG in water at 333.15 K (completely soluble, experimental data).

Tables 6 and 7 show tie line compositions obtained from the initial solutions with their compositions situated in the denominated B zone of the diagram. The density of the two liquid phases was also determined.

The two liquid phases occupy a small portion of the total phase diagram. The partition coefficient K, which represents the KCl or NaCl mass percentage ratio between the two liquid phases, ranges from 1.5 to 2.3 for both solids, giving us an indication of the separation obtained by adding a certain amount of PEG to a given brine solution. It may be concluded that the system seems not to be attractive for crystallizing the salt. However, it might be useful as an ATPS for partitioning other compounds. The liquid phase splits in region B into two equilibrium immiscible liquid phases: a PEG-poor, KCl, or NaCl-rich bottom layer and a PEG-rich upper phase that also contains an appreciable concentration of salt. Graber et al.[14] observed the same behavior for the PEG 4000 + $NaNO_3$ + H_2O system. Nevertheless, other salts have stable hydrated forms, such as Na_2SO_4;[12,13,16] they exhibit partition coefficients higher that those in this work, with a salt concentration in the organic phase of close to zero.

Because the sodium chloride solubility shows very little dependence on temperature, at 60°C the solubility of KCl in water is much larger than that of NaCl. For both ternary systems, the presence of PEG in solution decrease the solubility dependence on temperature. Therefore, the solubility values found for NaCl and KCl in PEG−water solution at 333.15 K are very similar.

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