

Compositions, Densities, and Refractive Indices of Potassium Chloride + Ethanol + Water and Sodium Chloride + Ethanol + Water Solutions at (298.15 and 313.15) K

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Solubilities, densities, and refractive indices data have been measured for the ternary systems $\text{KCl} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ and $\text{NaCl} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ at (298.15 and 313.15) K, with mass fractions of ethanol ranging from 0 to 0.9. Polynomial equations of fit are proposed for solubility of the saturated solutions as a function of the mass fraction of ethanol. Density and refractive index were also determined for the same ternary systems with varied undersaturated salt concentrations. Values for both properties were correlated with the salt concentrations and proportions of alcohol in the solutions. The equations proposed also account for the saturated solutions. Finally, data are also presented on the equilibrium of the quaternary system $\text{KCl} + \text{NaCl} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ at (298.15 and 313.15) K. The solubility equilibrium was obtained beginning from supersaturated solutions of both salts using a known ethanol-to-water ratio. The concentrations, densities, and refractive indices were determined for the saturated solutions.

Introduction

One of the methods employed in crystallization for producing supersaturation in a solution is termed "drowning out". The method consists of adding a solvent 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, and others.¹

Studies are available in the literature on solubilities of various salts in water + organic solvents, the objectives of which have been to evaluate the potential applicability of the drowning-out procedure as a technique for separation of these salts.^{2–8} NaCl and KCl are present to a large extent in natural inorganic salt deposits; several authors^{9–13} have recently studied the effects on the solubilities of these salts by the addition of organic solvents to their aqueous solutions.

Wagner et al.⁹ 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.^{10,11} 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 of this study were unusual in that in addition to the solid–liquid equilibrium, and these systems produced biphasic regions which showed the presence of a liquid–liquid equilibrium zone.

Hanson and Lynn¹² 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.

Takiyama et al.¹³ 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 concentrations of anti-solvent and a low initial supersaturation.

A monograph by Linke and Seidell¹⁴ reported experimental data on the solubility for the two ternary systems presently studied, which included a broad range of concentrations at (298.15 and 313.15) K. These experimental data form a review of several studies, some quite antiquated (e.g., from 1865 and 1897), for which it was considered important to re-determine solubilities in these systems, as well as to measure the densities and refractive indexes of all the saturated solutions. This information does not appear in the above cited monograph. No information has been found in the literature concerning experimental data from the presently studied quaternary system.

Ternary and quaternary equilibria related to the $\text{KCl} + \text{NaCl} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ system also provide information on the possibility of using ethanol to separate KCl from aqueous silvinitic solutions.

Prior study has involved the addition of an inorganic solvent for the separation of mixtures of sodium and potassium chlorides which are generally found associated in abundance in the salt deposits of northern Chile. Taboada et al.¹⁵ studied the separation of KCl from pure and industrial grade silvinitic by addition of NH_3 to the aqueous solvent.

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Experimental Section

Ethanol, potassium chloride, and sodium chloride were supplied by Merck Co. with a purity of 99.8%, 99.5%, and 99.5% respectively. All of the chemicals used in 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.

The phase equilibrium study was carried out by mixing of known masses of ethanol and water with excess salt. For the quaternary system, excess quantities of both salts were also added in known quantities. All of 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). Ethanol was the last reagent to be added to the solution to avoid its evaporation. The solutions were prepared within an accuracy of $\pm 2 \times 10^{-4}$ g. 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 and refractive index. 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.

Total concentrations of the saturated solutions were determined in triplicate by evaporation of known masses of solution (15 to 30 g) to dryness in a muffle furnace at 393.15 K, to give anhydrous salts. Mass of the anhydrous salt was considered constant only when successive measurements of the same sample differed by less than 1×10^{-3} g. On this basis, the reproducibility of the concentration of the solutions was $\pm 2 \times 10^{-2}$ g of salt per 100 g of solution.

The concentration of potassium in the quaternary system was determined by atomic absorption spectrometry (AA) at a wavelength of 766.5 nm, using a Varian model SpectrAA 22 instrument. The calibration line was obtained using aqueous solutions of KCl from 0 to 50 ppm in an 1 volume % HCl matrix containing NaCl. The initial concentration of ethanol and NaCl did not show significant influence on the spectrophotometric readings. The measurements, which were carried out in triplicate, gave a reproducibility of $\pm 0.4\%$. An accuracy of $\pm 3 \times 10^{-2}$ g KCl per 100 g of solution was obtained based on measurements on standard solutions. The concentration of NaCl was determined by difference based on the total dry weight of salt. The procedure for the determination of the concentration of the quaternary solution was checked by analyzing sodium by AA at 589 nm.

The densities of the saturated solutions were measured using a Mettler Toledo Co. model DE-50 vibrating tube densimeter. A minimum of three independent measurements was made for each sample, producing a precision of ± 0.00005 g·cm⁻³. Experimental values for refractive index were obtained using a Mettler Toledo Co. model RE-40 refractometer. A minimum of three readings were obtained for each sample, obtaining a precision of ± 0.0002 . Both instruments were calibrated prior to initiation of each series of measurements, using air and deionized distilled

Table 1. Solubility, s , Density, ρ , and Refractive Index, n_D , for the Potassium Chloride (1) + Ethanol (2) + Water (3) System at (298.15 and 313.15) K

| w_2 | w_2/w_3 | $s/(g/100 \text{ g solution})$ | $\rho/(g \cdot \text{cm}^{-3})$ | n_D |
|----------|-----------|--------------------------------|---------------------------------|--------|
| 298.15 K | | | | |
| 0.0000 | 0.0000 | 26.67 | 1.17720 | 1.3689 |
| 0.0842 | 0.1214 | 22.21 | 1.12959 | 1.3673 |
| 0.2491 | 0.4004 | 12.87 | 1.03042 | 1.3658 |
| 0.3328 | 0.5966 | 10.94 | 0.99467 | 1.3658 |
| 0.4095 | 0.8001 | 7.87 | 0.96882 | 1.3653 |
| 0.4797 | 1.0200 | 5.00 | 0.94296 | 1.3653 |
| 0.5997 | 1.6270 | 3.17 | 0.89853 | 1.3647 |
| 0.6997 | 2.4397 | 1.35 | 0.86770 | 1.3641 |
| 0.8003 | 4.1020 | 0.46 | 0.83417 | 1.3632 |
| 0.8999 | 9.0807 | 0.10 | 0.80731 | 1.3617 |
| 313.15 K | | | | |
| 0.0000 | 0.0000 | 28.41 | 1.18180 | 1.3695 |
| 0.1353 | 0.2004 | 18.97 | 1.09531 | 1.3664 |
| 0.2446 | 0.4001 | 14.40 | 1.03511 | 1.3651 |
| 0.3066 | 0.5341 | 11.94 | 0.99922 | 1.3639 |
| 0.4012 | 0.8002 | 9.74 | 0.96789 | 1.3625 |
| 0.4582 | 1.0073 | 8.69 | 0.94179 | 1.3618 |
| 0.5954 | 1.6179 | 3.66 | 0.88365 | 1.3602 |
| 0.6995 | 2.4656 | 1.68 | 0.84957 | 1.3586 |
| 0.7997 | 4.1052 | 0.55 | 0.81903 | 1.3573 |
| 0.8991 | 9.1745 | 0.29 | 0.80736 | 1.3566 |

Table 2. Solubility, s , Density, ρ , and Refractive Index, n_D , for the Sodium Chloride (1) + Ethanol (2) + Water (3) System at (298.15 and 313.15) K

| w_2 | w_2/w_3 | $s/(g/100 \text{ g solution})$ | $\rho/(g \cdot \text{cm}^{-3})$ | n_D |
|----------|-----------|--------------------------------|---------------------------------|--------|
| 298.15 K | | | | |
| 0.0000 | 0.0000 | 26.28 | 1.19778 | 1.3795 |
| 0.0955 | 0.1387 | 21.58 | 1.13624 | 1.3770 |
| 0.1334 | 0.2005 | 20.11 | 1.11506 | 1.3765 |
| 0.2391 | 0.4098 | 17.74 | 1.06803 | 1.3743 |
| 0.3202 | 0.6001 | 14.62 | 1.02953 | 1.3728 |
| 0.3900 | 0.7959 | 12.00 | 0.99304 | 1.3718 |
| 0.4478 | 0.9991 | 10.40 | 0.96425 | 1.3706 |
| 0.5999 | 1.6846 | 4.40 | 0.89960 | 1.3673 |
| 0.6999 | 2.5086 | 2.11 | 0.86859 | 1.3655 |
| 0.7972 | 4.0945 | 0.81 | 0.83279 | 1.3638 |
| 0.8837 | 7.9613 | 0.53 | 0.82247 | 1.3631 |
| 313.15 K | | | | |
| 0.0000 | 0.0000 | 26.93 | 1.18817 | 1.3772 |
| 0.1350 | 0.2007 | 19.24 | 1.10855 | 1.3738 |
| 0.2387 | 0.4073 | 17.52 | 1.05162 | 1.3718 |
| 0.3210 | 0.6019 | 14.57 | 1.01202 | 1.3703 |
| 0.3937 | 0.7922 | 10.93 | 0.98153 | 1.3683 |
| 0.4508 | 0.9927 | 9.51 | 0.95811 | 1.3667 |
| 0.6001 | 1.6814 | 4.30 | 0.88987 | 1.3619 |
| 0.6999 | 2.5572 | 2.64 | 0.85328 | 1.3602 |
| 0.7995 | 4.1339 | 0.71 | 0.81335 | 1.3574 |
| 0.8999 | 9.1733 | 0.20 | 0.78688 | 1.3551 |

water as reference substances. The undersaturated solutions were also prepared by mass using an analytical balance. Measurements of density and refractive index were carried out using the same methodology as described above for the saturated solutions and as described in previous studies.¹⁶

Results and Discussion

Data for the solubility, density, and refractive index for the KCl + C₂H₅OH + H₂O ternary system are listed in Table 1, and those for the NaCl + C₂H₅OH + H₂O system are listed in Table 2. It can be observed that at a fixed temperature the solubility of both salts decreased with the addition of C₂H₅OH. Figure 1 presents the solubility diagrams for the two systems at 298.15 K.

Figure 1 demonstrates similar behavior for both salts, although with more pronounced curvature of the KCl saturation curve. The difference in solubility between the

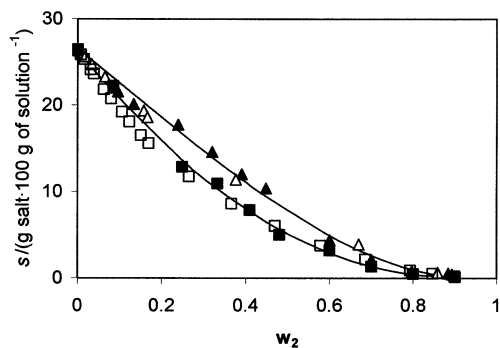


Figure 1. Solubility, s , of the ternary systems KCl + ethanol + water and NaCl + ethanol + water at 298.15 K as a function of the ethanol mass fraction, w_2 : ■, solubility of KCl in this study; □, solubility of KCl in ref 14; ▲, solubility of NaCl in this study; △, solubility of NaCl in ref 14. Lines were calculated using eq 1.

Table 3. Parameters of eq 1 for Solubility Fits

| A_0 | A_1 | A_2 | A_3 | AAD ^a |
|--|----------|----------|----------|------------------|
| g/100 g solution | | | | |
| KCl + C ₂ H ₅ OH + H ₂ O | | | | |
| 298.15 K | | | | |
| 26.6700 | -60.1129 | 35.2645 | -1.41650 | 0.28 |
| 313.15 K | | | | |
| 28.4100 | -69.0487 | 54.1358 | -13.4844 | 0.49 |
| NaCl + C ₂ H ₅ OH + H ₂ O | | | | |
| 298.15 and 313.15 K | | | | |
| 26.3100 | -33.5231 | -24.2583 | 32.1126 | 0.49 |

^a AAD = $|\sum(s^{\text{exp}} - s^{\text{cal}})/n|$, where n is the number of experimental points.

salts is appreciable only at intermediate values of ethanol concentrations (20–60%) in the saturated solutions. Experimental values reported by Linke and Seidell¹⁴ have been included in Figure 1 for reference and are in agreement with values obtained in the present study. The same occurred with solubility values obtained at 313.15 K. The values for solubility at both temperatures in the absence of ethanol when compared with those reported in the literature¹⁷ showed an average mean absolute deviation of 0.285 g/100 g solution for the KCl + H₂O system and 0.215 g/100 g solution for the NaCl + H₂O system.

The presence of ethanol decreased the effect of temperature on the solubility of KCl. For intermediate values of ethanol concentration, the solubility of KCl increased slightly with temperature; however, at low ($w_2 \approx 0.1$) or high ($w_2 > 0.6$) levels of ethanol, the concentrations of KCl in the saturated solutions practically coincided at the two study temperatures. Increases in temperature hardly affected the NaCl + C₂H₅OH + H₂O ternary equilibrium. The solubility curves at (298.15 and 313.15) K overlapped and crossed each other over the entire interval of concentrations of ethanol with this salt.

The experimental values for solubility (s , as g salt per 100 g of solution) of the two ternary systems fit the following expression for each temperature:

$$s = A_0 + A_1 w_2 + A_2 w_2^2 + A_3 w_2^3 \quad (1)$$

where w_2 is the mass fraction of the ethanol and A_i are empirical constants whose values are listed in Table 3, together with the absolute average deviation (AAD) of the fit. Given that the deviation obtained in the equations of fit assayed for the NaCl + C₂H₅OH + H₂O system was greater than the thermal variation in solubility of NaCl, a

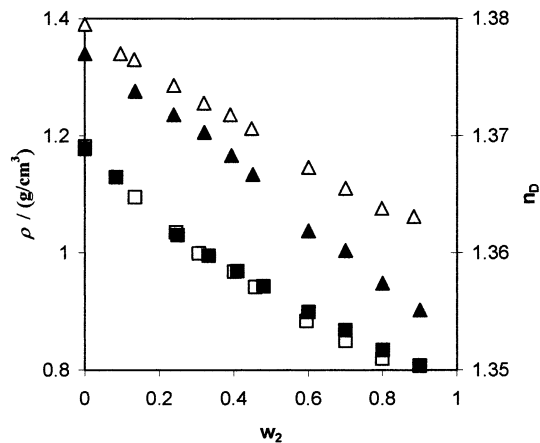


Figure 2. Density, ρ , of the saturated ternary solutions KCl + ethanol + water and refractive indices, n_D , of the saturated ternary solutions NaCl + ethanol + water at (298.15 and 313.15) K as a function of the ethanol mass fraction, w_2 : ■, density of KCl solutions at 298.15 K; □, density of KCl solutions at 313.15 K; ▲, refractive index of NaCl solutions at 298.15 K; △, refractive index of NaCl solutions at 313.15 K.

single correlation equation is proposed for the temperature interval of this study. Figure 1 shows the results of the fit with the proposed equations for 298.15 K as continuous lines.

Tables 1 and 2 show decreases in the values for density and refractive index for both saturated ternary systems with increase in the mass fraction of ethanol, a behavior observed at both temperatures. In the KCl + C₂H₅OH + H₂O system, increase in the solubility of the salt counteracted, in part, the decrease expected in the density and refractive index with temperature. Thus, at low concentrations of ethanol, values were observed which were very similar to the density and refractive index of saturated solutions at the two study temperatures. With increase in the concentration of ethanol, the temperature effect increased, and thus, lower values for both properties were obtained at 313.15 K compared to 298.15 K. Figure 2 illustrates this behavior for density. In the NaCl + C₂H₅OH + H₂O system, no appreciable effect was observed of temperature on solubility. The decrease in the density and refractive index with temperature was similar to the effect exercised by temperature on these properties in the solvents. Figure 2 shows the variation in refractive index for this system.

Densities and refractive indexes in both ternary systems were measured in undersaturated solutions in completion of this study. Work was carried out varying the concentrations of salt in the solutions using the same mass ratios employed with the solubility equilibria. These values, besides providing basic information on the behavior of these systems, may be useful for the operation of a crystallization process. Tables 4 and 5 present the experimental values from the potassium chloride + ethanol + water system at temperatures of (298.15 and 313.15) K, respectively. Tables 6 and 7 present the same data for the sodium chloride + ethanol + water system. The values of the measured properties increased with concentrations of salt and decreased with increase in temperature. With increase in the ethanol/water ratio while maintaining the remaining variables constant, the density of the solutions decreased and the refractive index increased. No appreciable variation was observed in the development of any of the properties upon reaching the solubility equilibrium concentrations.

Figure 3 shows the density values for the sodium chloride + ethanol + water system as a function of the salt

Table 4. Density, ρ , and Refractive Index, n_D , for the Potassium Chloride (1) + Ethanol (2) + Water (3) Undersaturated System at 298.15 K

| 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D | 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D |
|--------------------|-------------------|------------------------------------|--------|-------------------|-------------------|------------------------------------|--------|
| $w_2/w_3 = 0.1214$ | | | | | | | |
| 15.998 | 9.102 | 1.08366 | 1.3604 | 3.999 | 10.396 | 1.00454 | 1.3447 |
| 12.000 | 9.527 | 1.05670 | 1.3551 | 0.000 | 10.835 | 0.97929 | 1.3396 |
| 8.000 | 9.963 | 1.03026 | 1.3499 | | | | |
| $w_2/w_3 = 0.4004$ | | | | | | | |
| 9.999 | 25.730 | 1.01311 | 1.3628 | 3.999 | 27.442 | 0.97728 | 1.3557 |
| 7.999 | 26.306 | 1.00148 | 1.3603 | 2.000 | 28.014 | 0.96528 | 1.3535 |
| 5.999 | 26.882 | 0.98925 | 1.3581 | 0.000 | 28.589 | 0.95333 | 1.3512 |
| $w_2/w_3 = 0.5966$ | | | | | | | |
| 8.998 | 34.005 | 0.98923 | 1.3649 | 2.999 | 36.246 | 0.95446 | 1.3585 |
| 6.999 | 34.749 | 0.97812 | 1.3625 | 1.000 | 36.991 | 0.94297 | 1.3564 |
| 4.999 | 35.496 | 0.96594 | 1.3607 | 0.000 | 37.367 | 0.93725 | 1.3554 |
| $w_2/w_3 = 0.8001$ | | | | | | | |
| 6.999 | 41.339 | 0.96231 | 1.3648 | 2.999 | 43.116 | 0.93945 | 1.3608 |
| 6.498 | 41.555 | 0.95932 | 1.3643 | 1.000 | 44.002 | 0.92811 | 1.3590 |
| 4.998 | 42.221 | 0.95061 | 1.3629 | 0.000 | 44.452 | 0.92255 | 1.3577 |
| $w_2/w_3 = 1.0199$ | | | | | | | |
| 4.000 | 48.474 | 0.93123 | 1.3635 | 1.000 | 49.988 | 0.91463 | 1.3606 |
| 3.000 | 48.979 | 0.92577 | 1.3624 | 0.000 | 50.494 | 0.90896 | 1.3596 |
| 2.000 | 49.484 | 0.92014 | 1.3616 | | | | |
| $w_2/w_3 = 1.6270$ | | | | | | | |
| 2.800 | 60.200 | 0.89790 | 1.3645 | 1.000 | 61.315 | 0.88830 | 1.3628 |
| 2.000 | 60.693 | 0.89393 | 1.3637 | 0.000 | 61.933 | 0.88285 | 1.3618 |

Table 5. Density, ρ , and Refractive Index, n_D , for the Potassium Chloride (1) + Ethanol (2) + Water (3) Undersaturated System at 313.15 K

| 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D | 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D |
|--------------------|-------------------|------------------------------------|--------|-------------------|-------------------|------------------------------------|--------|
| $w_2/w_3 = 0.4001$ | | | | | | | |
| 8.000 | 26.290 | 0.99162 | 1.3564 | 0.000 | 28.575 | 0.94360 | 1.3470 |
| 4.021 | 27.424 | 0.96737 | 1.3507 | | | | |
| $w_2/w_3 = 0.5445$ | | | | | | | |
| 7.000 | 32.787 | 0.97122 | 1.3577 | 0.000 | 35.254 | 0.93027 | 1.3493 |
| 4.000 | 33.843 | 0.95326 | 1.3542 | | | | |
| $w_2/w_3 = 0.8002$ | | | | | | | |
| 6.000 | 41.783 | 0.94505 | 1.3590 | 0.000 | 44.449 | 0.91092 | 1.3529 |
| 3.000 | 43.120 | 0.92762 | 1.3556 | | | | |
| $w_2/w_3 = 1.007$ | | | | | | | |
| 4.000 | 48.171 | 0.91958 | 1.3582 | 0.000 | 50.181 | 0.89776 | 1.3542 |
| 2.000 | 49.178 | 0.91026 | 1.3558 | | | | |
| $w_2/w_3 = 1.6179$ | | | | | | | |
| 3.000 | 59.948 | 0.88723 | 1.3591 | 0.000 | 61.803 | 0.87051 | 1.3562 |
| 1.000 | 61.184 | 0.87620 | 1.3572 | | | | |
| $w_2/w_3 = 2.4656$ | | | | | | | |
| 0.919 | 70.491 | 0.85316 | 1.3578 | 0.000 | 71.144 | 0.84829 | 1.3569 |
| 0.459 | 70.818 | 0.85059 | 1.3574 | | | | |

concentration in undersaturated and saturated solutions at 298.15 K. The densities of the saturated solutions generally followed the same tendency as the undersaturated solutions although small deviations were observed in the solutions having higher ethanol/water ratios.

Experimental values for density and refractive index for each ternary system and temperature, both in saturated and undersaturated solutions fit the following expression:

$$Y = (A_0 + A_1 w_1 + A_2 w_2 + A_3 w_1 w_2 + A_4 w_1 w_2^2) \times \exp\left[A_5 \left(\frac{w_2}{w_3}\right) + A_6 \left(\frac{w_2}{w_3}\right)^2\right] \quad (2)$$

where Y represents density (g/cm^3), or the refractive index of the ternary system, and the A_i values are empirical constants whose values are listed in Tables 8 and 9,

Table 6. Density, ρ , and Refractive Index, n_D , for the Sodium Chloride (1) + Ethanol (2) + Water (3) Undersaturated System at 298.15 K

| 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D | 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D |
|--------------------|-------------------|------------------------------------|--------|-------------------|-------------------|------------------------------------|--------|
| $w_2/w_3 = 0.1387$ | | | | | | | |
| 19.997 | 9.744 | 1.12382 | 1.3744 | 7.999 | 11.204 | 1.03391 | 1.3538 |
| 15.997 | 10.230 | 1.09238 | 1.3675 | 3.999 | 11.706 | 1.00544 | 1.3472 |
| 11.999 | 10.716 | 1.06306 | 1.3606 | 0.000 | 12.194 | 0.97747 | 1.3405 |
| $w_2/w_3 = 0.4098$ | | | | | | | |
| 14.999 | 24.705 | 1.05282 | 1.3737 | 4.500 | 27.612 | 0.98517 | 1.3589 |
| 12.499 | 25.435 | 1.03547 | 1.3700 | 2.499 | 28.351 | 0.96881 | 1.3552 |
| 9.998 | 26.169 | 1.01873 | 1.3664 | 0.000 | 29.072 | 0.95258 | 1.3516 |
| 7.500 | 26.888 | 1.00178 | 1.3626 | | | | |
| $w_2/w_3 = 0.6001$ | | | | | | | |
| 12.499 | 32.818 | 1.01656 | 1.3727 | 4.999 | 35.630 | 0.96809 | 1.3624 |
| 9.999 | 33.756 | 1.00005 | 1.3693 | 2.500 | 36.566 | 0.95231 | 1.3590 |
| 7.500 | 34.691 | 0.98401 | 1.3658 | 0.000 | 37.505 | 0.93669 | 1.3555 |
| $w_2/w_3 = 0.7959$ | | | | | | | |
| 9.999 | 39.882 | 0.98474 | 1.3707 | 3.999 | 42.537 | 0.94698 | 1.3630 |
| 7.998 | 40.777 | 0.97158 | 1.3682 | 2.000 | 43.430 | 0.93477 | 1.3604 |
| 5.999 | 41.661 | 0.95922 | 1.3655 | 0.000 | 44.319 | 0.92260 | 1.3579 |
| $w_2/w_3 = 0.9991$ | | | | | | | |
| 8.000 | 45.978 | 0.95921 | 1.3692 | 2.000 | 48.976 | 0.92203 | 1.3620 |
| 6.000 | 46.977 | 0.94625 | 1.3668 | 1.000 | 49.478 | 0.91604 | 1.3607 |
| 4.000 | 47.979 | 0.93414 | 1.3644 | 0.000 | 49.979 | 0.91043 | 1.3579 |
| $w_2/w_3 = 1.6846$ | | | | | | | |
| 3.001 | 60.868 | 0.89818 | 1.3654 | 1.000 | 62.123 | 0.88662 | 1.3631 |
| 2.000 | 61.495 | 0.89246 | 1.3643 | 0.000 | 62.751 | 0.88081 | 1.3618 |

Table 7. Density, ρ , and Refractive Index, n_D , for the Sodium Chloride (1) + Ethanol (2) + Water (3) Undersaturated System at 313.15 K

| 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D | 100w ₁ | 100w ₂ | $\rho/\text{g}\cdot\text{cm}^{-3}$ | n_D |
|--------------------|-------------------|------------------------------------|--------|-------------------|-------------------|------------------------------------|--------|
| $w_2/w_3 = 0.2007$ | | | | | | | |
| 11.998 | 14.709 | 1.04694 | 1.3596 | 0.000 | 16.716 | 0.96404 | 1.3406 |
| 5.999 | 15.719 | 1.00474 | 1.3503 | | | | |
| $w_2/w_3 = 0.4073$ | | | | | | | |
| 10.000 | 26.045 | 1.00842 | 1.3622 | 0.000 | 28.940 | 0.94282 | 1.3463 |
| 5.000 | 27.493 | 0.97526 | 1.3548 | | | | |
| $w_2/w_3 = 0.6019$ | | | | | | | |
| 8.000 | 34.570 | 0.97521 | 1.3621 | 0.000 | 37.575 | 0.92530 | 1.3508 |
| 4.000 | 36.073 | 0.95055 | 1.3558 | | | | |
| $w_2/w_3 = 0.7922$ | | | | | | | |
| 6.000 | 41.547 | 0.94793 | 1.3609 | 0.000 | 44.202 | 0.91119 | 1.3529 |
| 3.000 | 42.876 | 0.92947 | 1.3570 | | | | |
| $w_2/w_3 = 0.9927$ | | | | | | | |
| 5.500 | 47.077 | 0.93145 | 1.3614 | 0.000 | 49.817 | 0.89847 | 1.3543 |
| 2.500 | 48.572 | 0.91417 | 1.3575 | | | | |
| $w_2/w_3 = 1.6814$ | | | | | | | |
| 2.500 | 61.138 | 0.88307 | 1.3595 | 0.000 | 62.707 | 0.86841 | 1.3562 |
| 1.500 | 61.766 | 0.87735 | 1.3583 | | | | |

together with the absolute average deviation (AAD) of the fit. The solid line in Figure 3 represents the density values for the sodium chloride + ethanol + water system obtained using the equation of fit.

Finally, Table 10 presents the experimental results on solubilities, density, and refractive index for the quaternary system which included $\text{KCl} + \text{NaCl} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ at (298.15 and 313.15) K. These values were obtained by starting with ethanol/water solutions saturated with excess KCl and NaCl. The solubility of both salts decreased with increase in the ethanol/water ratio in the solution. In all saturated quaternary solutions obtained, the KCl/NaCl ratio in the solution remained below unity. Work with this system resulted in greater precipitation of KCl than of NaCl. This selectivity increased slightly at 298.15 K when working with mass fraction ratios of ethanol/water of over 0.4. On the other hand, with increase in temperature, the solubility of the KCl increased more than that of NaCl

Table 8. Parameters of Eq 2 for the KCl + C₂H₅OH + H₂O System

| A_0^a | A_1 | A_2 | A_3 | A_4 | A_5 | A_6 |
|--------------------------------------|----------|-----------|-----------|-----------|-----------|-----------|
| Density | | | | | | |
| 298.15 K | | | | | | |
| 0.997050 AAD = 0.09% ^b | 0.667676 | -0.050117 | -0.320605 | 0.242394 | -0.082031 | 0.016411 |
| 313.15 K | | | | | | |
| 0.992766 AAD = 0.16% | 0.605426 | -0.135584 | 0.236785 | -1.248329 | -0.030630 | 0.003364 |
| Refractive Index | | | | | | |
| 298.15 K | | | | | | |
| 1.332870 AAD = 0.02% | 0.126377 | 0.106533 | 0.091253 | -0.081822 | -0.024248 | -0.004827 |
| 313.15 K | | | | | | |
| 1.330510 AAD = 0.03% | 0.138334 | 0.076362 | 0.140079 | -0.347529 | -0.011802 | 0.001440 |

^a A_0 for density has units g·cm⁻³. ^b AAD = $1/n|\sum (Y_{\text{exp}} - Y_{\text{cal}})/Y_{\text{exp}}| \times 100$.

Table 9. Parameters of eq 2 for the NaCl + C₂H₅OH + H₂O System

| A_0^a | A_1 | A_2 | A_3 | A_4 | A_5 | A_6 |
|--------------------------------------|----------|-----------|-----------|-----------|-----------|----------|
| Density | | | | | | |
| 298.15 K | | | | | | |
| 0.990010 AAD = 0.09% ^b | 0.779568 | 0.013170 | -0.342263 | 0.148762 | -0.115167 | 0.024409 |
| 313.15 K | | | | | | |
| 0.992000 AAD = 0.15% | 0.749889 | -0.090867 | -0.541736 | 0.425951 | -0.064973 | 0.012498 |
| Refractive Index | | | | | | |
| 298.15 K | | | | | | |
| 1.332870 AAD = 0.03% | 0.174514 | 0.104724 | 0.046066 | -0.101046 | -0.023012 | 0.004357 |
| 313.15 K | | | | | | |
| 1.330510 AAD = 0.02% | 0.195670 | 0.070301 | -0.181272 | 0.254215 | -0.008012 | 0.039366 |

^a A_0 for density has units g·cm⁻³. ^b AAD = $1/n|\sum (Y_{\text{exp}} - Y_{\text{cal}})/Y_{\text{exp}}| \times 100$.

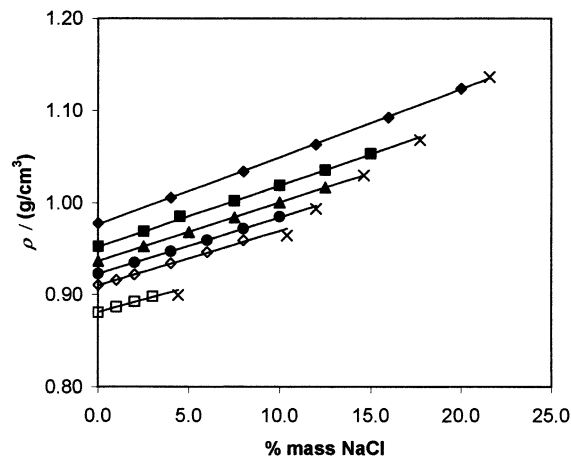


Figure 3. Densities of the NaCl (1) + ethanol (2) + water (3) system at 298.15 K, as a function of % mass of NaCl, and different w_2/w_3 ratio. ♦, 0.1387; ■, 0.4098; ▲, 0.6001; ●, 0.7959; ◇, 0.9991; □, 1.6846; ×, saturation. Lines were calculated using eq 2.

producing approximation of the two values to each other. The selectivity of KCl precipitation is greater when operating at 298.15 K than at 313.15 K. Our solubility values without ethanol (KCl + NaCl + H₂O) at 298.15 K showed an absolute deviation of 0.44 g/100 g of solution for KCl and 0.28 g/100 g solution for NaCl when compared with literature values.¹⁴ At 313.15 K, this deviation was 0.13 g/100 g solution for KCl and 0.18 g/100 g solution for NaCl.

Table 10. Solubility, s , Density, ρ , and Refractive Index, n_D , for the Potassium Chloride (1) + Sodium Chloride (2) + Ethanol (3) + Water (4) System at 298.15 K and 313.15 K

| w_3 | w_2/w_3 | s | | ρ /(g·cm ⁻³) | n_D |
|----------|-----------|------------------|------------------|-------------------------------|--------|
| | | g/100 g solution | g/100 g solution | | |
| 298.15 K | | | | | |
| 0.0000 | 0.0000 | 11.58 | 20.14 | 1.23458 | 1.3851 |
| 0.1268 | 0.2013 | 8.77 | 15.54 | 1.14218 | 1.3802 |
| 0.2352 | 0.4009 | 6.48 | 11.34 | 1.08104 | 1.3771 |
| 0.3193 | 0.6019 | 5.27 | 9.76 | 1.03235 | 1.3746 |
| 0.3867 | 0.8002 | 4.01 | 8.99 | 1.00419 | 1.3739 |
| 0.4451 | 1.0000 | 3.33 | 7.63 | 0.97710 | 1.3725 |
| 313.15 K | | | | | |
| 0.0000 | 0.0000 | 13.29 | 20.25 | 1.23627 | 1.3841 |
| 0.1249 | 0.2015 | 9.47 | 16.05 | 1.14347 | 1.3793 |
| 0.2285 | 0.4000 | 7.71 | 12.31 | 1.08142 | 1.3762 |
| 0.3131 | 0.6003 | 6.09 | 10.45 | 1.03548 | 1.3732 |
| 0.3825 | 0.8003 | 4.98 | 8.98 | 1.00085 | 1.3710 |
| 0.4424 | 0.9999 | 4.25 | 7.26 | 0.97252 | 1.3691 |

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