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Solubility of Some Mineral Salts in Polyethylene Glycol and Related Surfactants

The ambient solubility of the mineral salts NaCl, KCl, CsCl, KBr, K_2SO_4 and $CuSO_4$ is reported as a function of composition of mixed binary solvents consisting of water with polyethylene glycol (PEG 200), ethoxylated C_{9-11} alcohols ($C_{10}E_6$) and ethoxylated, or propoxylated C_{10-12} alcohols ($C_{11}E_6P_1$). Solubility gradually decreases with decreasing water content and follows the order PEG 200 > $C_{10}E_6$ > $C_{11}E_6P_1$. Solubility of CsCl and KBr was found to be surprisingly high in neat PEG 200, on the order of 1 mol kg^{-1}, and in neat $C_{10}E_6$, on the order of 0.1 mol · kg^{-1}. The observed solubility trends are explained by the theory of hard and soft acids and bases under the consideration of the polarity of the surfactants.

Key words: Solubility, mineral salts, polyethylene glycol, nonionic surfactants

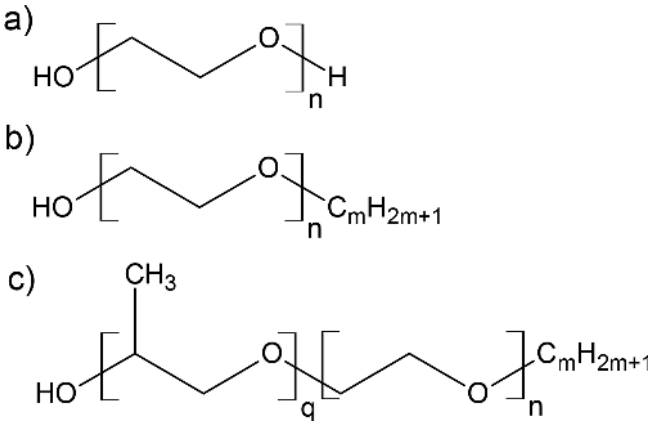
Löslichkeit einiger Mineralsalze in Polyethylenglykol und ähnlichen Tensiden. Die Umgebungslöslichkeit der Mineralsalze NaCl, KCl, CsCl, KBr, K_2SO_4 und $CuSO_4$ wird in Abhängigkeit von der Zusammensetzung der binären Lösungsmittelmischungen angegeben, die aus Wasser mit Polyethylenglykol (PEG 200), ethoxylierten C_{9-11}-Alkohol-Verbindungen ($C_{10}E_6$) bzw. ethoxylierten/propoxylierten C_{10-12}-Alkohol-Verbindungen ($C_{11}E_6P_1$) bestehen. Die Löslichkeit nimmt mit abnehmendem Wassergehalt allmählich ab und folgt der Reihenfolge PEG 200 > $C_{10}E_6$ > $C_{11}E_6P_1$. Es wurde gefunden, dass die Löslichkeit von CsCl und KBr in reinem PEG 200 in der Größenordnung von 1 mol kg^{-1} und in reinem $C_{10}E_6$ in der Größenordnung von 0,1 mol kg^{-1} liegt und überraschend hoch ist. Die beobachteten Löslichkeitstrends werden unter Berücksichtigung der Polarität der Tenside mit der Theorie der harten und weichen Säuren und Basen erklärt.

Stichwörter: Löslichkeit, Mineralsalze, Polyethylenglykol, nichtionische Tenside

1 Introduction

Polyethylene Glycol (PEG) has been shown to be a viable option as an alternative green solvent for chemical synthesis recognizing that PEG is nontoxic, biodegradable, and of low vapor pressure [1–3]. Successful organic synthesis reactions include in particular multi-component one-pot synthesis reactions illustrating that a wide variety of solutes can be solvated in PEG simultaneously [4–6]. Also remarkable is that a number of successful synthesis reactions include salts as reagents. For example, carbonate salts were used as a base for forming functionalized pyridines [7] and N-substituted-2-aminothiazoles [8]. PEG has also recently been used for the synthesis of metal organic frameworks (MOFs) involving mineral salts as reagents [9]. Evidently, these involved mineral salts must be at least somewhat soluble in PEG to be able to serve as a reactant. Although much less recognized, PEG related nonionic surfactants such as shown and defined in Scheme 1, could also serve as an environmentally benign solvent option [10]. We note that PEG is strictly speaking not a surfactant given that it lacks a hydrophobic alkyl structural component. However, as it nevertheless reduces the surface tension of water, it is often included in a broader sense as a nonionic surfactant. For simplicity, we will use the word "surfactants" in this report when referring to all three compounds shown and defined in Scheme 1.

To aid in the green synthesis effort with PEG and related surfactants, we have conducted a solubility study of several common mineral salts and wish to present our findings in this report. Since the surfactants in Scheme 1 are hygroscopic, we conducted the solubility study as a function of mixed water/surfactant solvent composition. From a practical point of view, it is essentially unavoidable that some water impurity be present during industrial chemical synthesis. Therefore, knowledge of how the solubility of mineral salts is affected by present water is desirable. A perusal of the literature reveals that there is a dearth of such solubility data of mineral salts in PEG and related nonionic surfactants or mixed solvents thereof with water. Other than investigations of inorganic salts on the cloud point [11–13], we are only aware of several salt solubility studies in several types of PEG and none in PEG related nonionic surfactants. The solubility of cesium perchlorate was studied over the entire composition range of the binary solvent water-PEG 600 [14]. Other relevant salt solubility studies in PEG-water mixed solvents include sodium carbonate and sodium sulfate with PEG 400 [15], lithium chloride, sodium chloride and potassium chloride with PEG 4000 [16, 17], and ammo-



Scheme 1 a) PEG, b) C_mE_n, and c) $C_mE_nP_q$, where m indicates the number of carbon atoms in the alkyl chain (C), while n and q are the repetition units of ethylene oxide (E) and propylene glycol (P), respectively

nium sulfate in PEG 10000 [18]. The results of these studies are included in our report where appropriate. In addition, there have been a number of studies on mineral salts affecting water-PEG liquid-liquid phase separation within the broader context of aqueous two-phase systems [19–28].

Here, we report the solubility of NaCl, KCl, CsCl, KBr, and K_2SO_4 as a function of water/surfactant composition in PEG 200, $C_{10}E_6$, and $C_{11}E_6P_1$, allowing for the inspection of the effect of surfactant structure and cation and anion choice on the solubility. We hope that this benchmark study will spark a broader interest in the matter of salt solubility in PEG-related surfactants.

2 Experimental

Table 1 lists the vendor and purity specifications of the mineral salts used in this study. Except for $CuSO_4 \cdot 5H_2O$, the salts were generally dried in a muffle oven at a temperature greater than 200 °C prior use. The deionized water used was purified by a Barnstead UV purification system. The polydisperse nonionic surfactants shown in Scheme 1 were generously donated from Rochester Midland Corporation (RMC). RMC purchased the surfactants in large quantities from the following industrial providers: PEG 200 (Dow Chemical Company), $C_{10}E_6$ (Air Products), and $C_{11}E_6P_1$ (Huntsman). Initial batches used for the solubility analysis by atomic absorption spectrometry (AAS) were not characterized in detail. Later batches used for solubility tests by salt addition were analyzed with respect to molecular weight distribution and resulting average molecular weight, and the results are summarized elsewhere [29]. The water content in the surfactants was determined by Karl Fischer titration and was included in the calculation of the composition of the water – surfactant binary solvents. To obtain saturated salt solutions in binary water-surfactant solvents for AAS analysis, the surfactants were mixed with saturated aqueous solutions and additional neat salt was added as needed. The mixture was agitated for at least a week at room temperature, which is climate controlled to be (21 ± 1) °C. For the salt solubility tests by salt addition, salt was added in increments until it did not dissolve even after agitation of at least 24 h. An electronic balance with a precision of 0.1 mg was used for all weight measurements.

For the AAS analysis, portions of the supernatant saturated solutions were taken and centrifuged to ensure complete separation of solutes. Portions of the supernatant were diluted in 25 mL vials with deionized water in 2–3 iterations keeping track of weights until a concentration on the order of 10^{-4} mol · L^{-1} was achieved, which is suitable for AAS analysis. At these low concentrations, molarity is approximately equal to molality. For each concentration analysis using a GBC 932 Atomic Absorption Spectrometer, the instrument response was calibrated against aqueous standards prepared volumetrically using the same salts as listed in Table 1. The typical AAS method included five calibration standards and blank sample that were measured along with the unknown samples in five replicates with 5 s read time.

3 Results and Discussion

The molalities of the saturated salt solutions in the mixed water-surfactant solvents are graphically shown in Figs. 1–3 for PEG 200, $C_{10}E_6$, and $C_{11}E_6P_1$, respectively. For the water-PEG 200 binary solvent the observed phase behavior always consisted of a solid salt phase in equilibrium with a clear, single-phased supernatant solution. The phase behavior of the salts with the binary solvents water-$C_{10}E_6$ and water-$C_{11}E_6P_1$ was more complex. For NaCl in the water-$C_{10}E_6$ binary solvent we observed that the liquid supernatant drawn from $w = 0.41$ and 0.61 samples turned spontaneously into a gel upon centrifugation. We nevertheless analyzed the NaCl content in these gels. The obtained NaCl molalities in these gels are included in Fig. 2a and are consistent in trend with the molalities obtained from the other samples at lower and higher w. In case of water-$C_{11}E_6P_1$ binary solvent with NaCl, the supernatant formed aqueous two-phase systems over a wide range of w and no molality measurements are reported in Fig. 3a for these. Similar phase behavior was observed for CsCl in water-$C_{10}E_6$ and water-$C_{11}E_6P_1$. Liquid-liquid phase separation of the supernatant was also indicated for KCl in water-$C_{10}E_6$ and water-$C_{11}E_6P_1$ near $w = 0.8$. Interestingly, no liquid-liquid phase separation was observed for the supernatant with KBr and K_2SO_4 in the water-$C_{10}E_6$ and water-$C_{11}E_6P_1$ binary solvents.

The observed KBr saturation molalities on the order of 1 mol · kg^{-1} for w approaching 0 in Figs. 1d and 2d, and for CsCl in 1c are surprisingly high compared to the saturation molalities of the other salts in Figs. 1–3 at surfactant rich compositions. Furthermore, for unknown reasons we observed low reproducibility for the NaCl saturation molalities in water-PEG binary solvent mixture (Fig. 1a). This led us to assess measurement accuracy by independently obtaining saturation molalities from a different experimental method, where, as described in the experimental section, we simply added salt in increments to the binary solvent until the salt would not completely dissolve. The results of these measurements are included in Figs. 1a–d, Figs. 2b–d, and Figs. 3a, 3b and 3d and are generally consistent with the solubility measurements employing AAS. However, gels were observed when preparing the binary solvent compositions of water-$C_{10}E_6$ at $w = 0.75$ and water-$C_{11}E_6P_1$ at $w = 0.5$. Based on the generally known phase behavior of PEG re-

Salt	Molecular weight/ g · mol^{-1}	CAS number	Source	Purity
KCl	74.56	7447-40-7	Baker	> 99.9 mass%
KBr	119.90	7758-02-3	Fisher Scientific	> 99.99 mass%
K_2SO_4	174.27	7778-80-5	Fisher Scientific	> 99.95 mass%
NaCl	58.44	7647-14-5	AMResco	"biotechn. grade"
CsCl	168.32	7647-14-8	AMResco	"ultra pure"
$CuSO_4 \cdot 5\ H_2O$	244.68	7758-99-8	Fisher Scientific	> 99.5 mass%

Table 1 Specifications of the mineral salts used in this study

lated nonionic surfactants [30], these gels are likely to be the Lamellar phase. As described in the experimental section, for faster salt dissolution, we used saturated aqueous salt solutions and mixed these with the surfactants to prepare the saturated water-surfactant solutions. We could indeed confirm in the laboratory that the presence of the salt does prevent the gel formation observed in absence of salt.

Since solubility of the salt in the neat surfactant is significantly lower than in water, the graphs in Figs. 1–3 are all increasing functions with water mass fraction, *w*. Especially for KBr and to a lesser extent for NaBr, these increasing functions approach linearity. We also inspected the salt solubilities as a function of mixed solvent mole fraction (not shown). Because of the much larger molar mass of the surfactants compared to water, these functions would deviate largely from linearity. Therefore, solubilities as a function of mixed solvent mass fractions are more suitable to fitting with polynomials, which are shown as solid lines in Figs. 1–

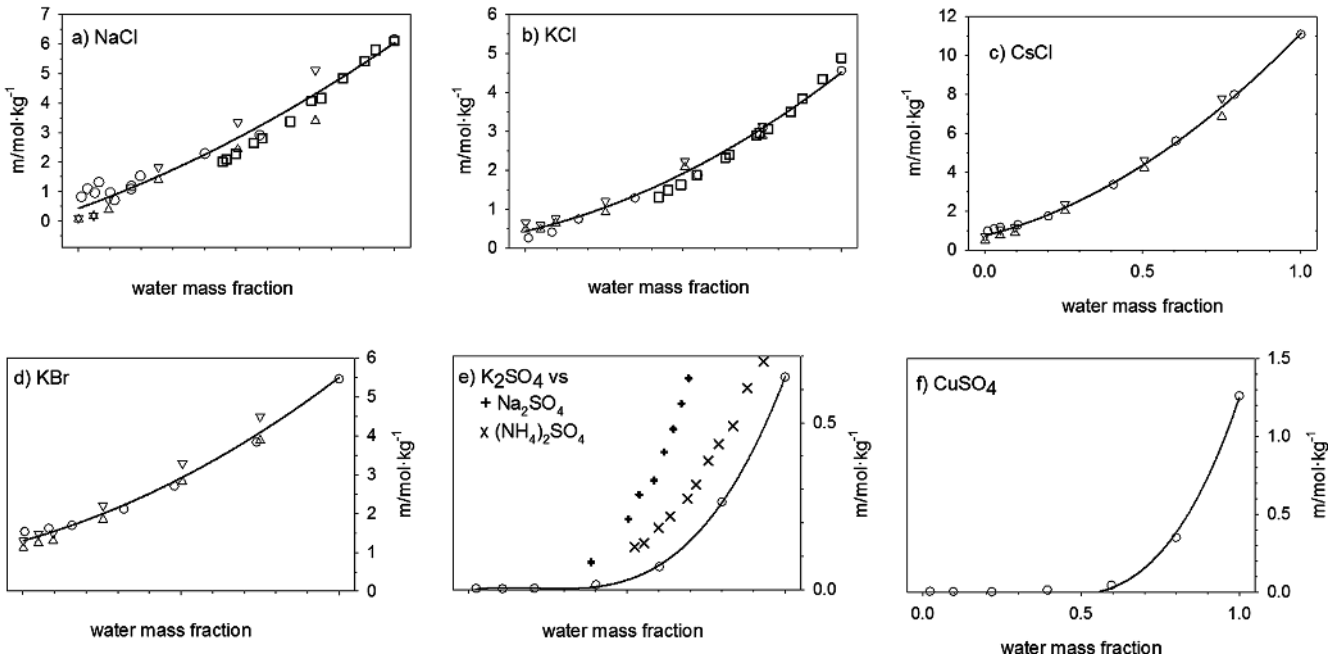


Figure 1 Solubility of various mineral salts in PEG 200 – water mixed solvents: PEG 200, this study using AAS (○) as well as upper (▽) and lower (△) limits from visual observation; PEG 4000, Taboada *et al*. [17] (□); PEG 400, Sadhegi and Jahani [15] (+); PEG 10000, Murari et al. [18] (×). The lines are polynomial fits

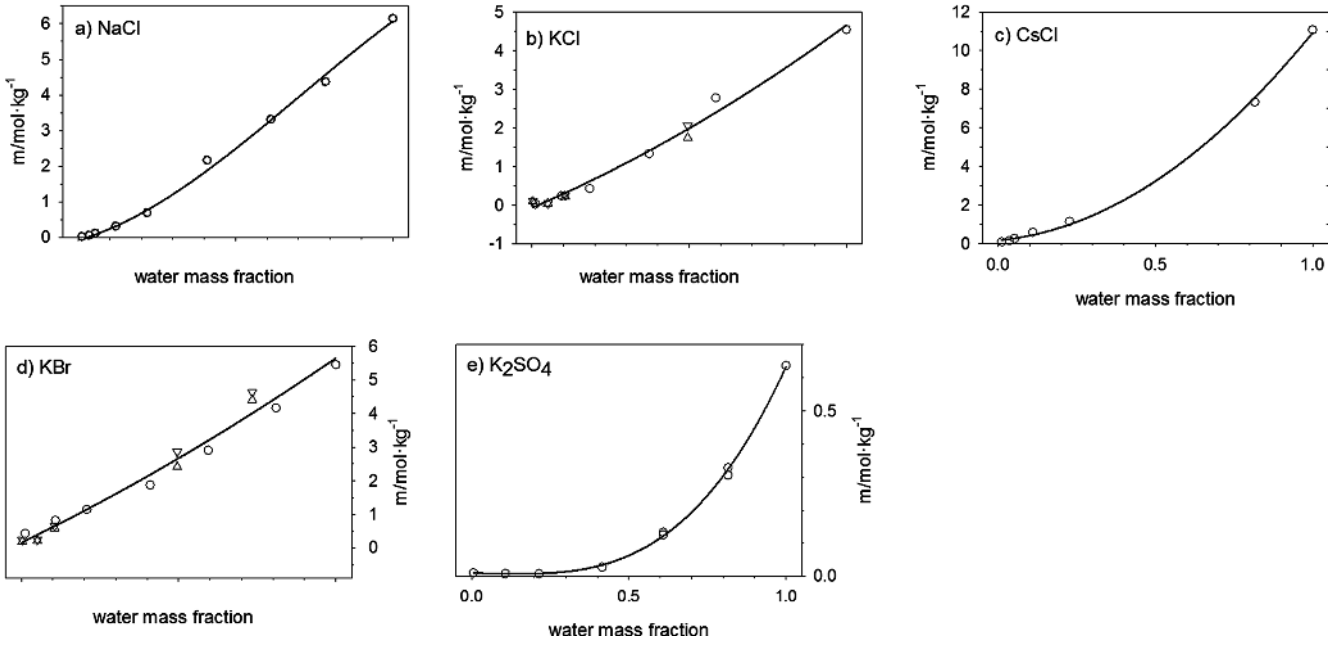


Figure 2 Solubility of various mineral salts in $C_{10}E_6$ – water mixed solvents: this study using AAS (○) as well as upper (▽) and lower (△) limits from visual observation. The lines are polynomial fits

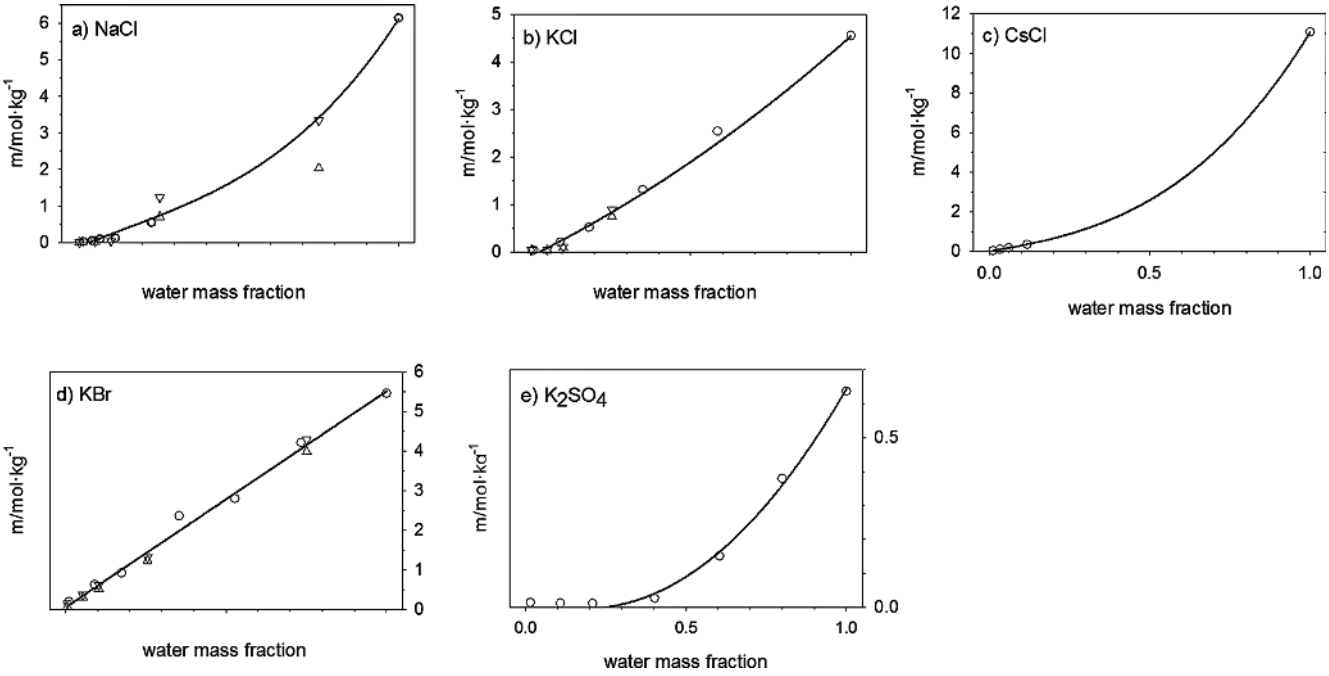


Figure 3 Solubility of various mineral salts in $C_{11}E_6P_1$ – water mixed solvents: this study using AAS (○) as well as upper (▽) and lower (△) limits from visual observation. The lines are polynomial fits

3. The fit coefficients are summarized in Table 1 along with some fit statistics. The standard deviations, σ, listed in Table 2 may be taken as the uncertainty of the solubility measurements. For some fits the calculated saturation molalities would be less than zero at low w. Therefore, the range of w for which the fit equations may be used is indicated as well in Table 2.

The surfactants used in this study are polydisperse. Polydispersity has been shown to affect phase behavior with respect to liquid-liquid equilibria as demonstrated by Yang and Bae [31]. In this respect, it is interesting that solubility of NaCl and KCl in Figs. 1a–b for water-PEG 200 does not differ much compared to solubilities reported for water-PEG 4000 [17], although solubility appears to be increasingly lower compared to water-PEG 200 with decreasing w. A higher solubility of salt in PEG 200 compared to PEG 4000 can be explained by the increased ratio of polar hydroxyl end groups to less polar poly ethylene oxide repeat units for PEG of lower molecular weight [31].

Inspecting the salt solubilities in Figs. 1–3 for w approaching zero as well as the a_0 fit coefficients for the y-intercepts in Table 1, it can be seen that salt solubilities are highest in PEG 200 followed by $C_{10}E_6$ and lowest in $C_{11}E_6P_1$. As one might have expected, the structural replacement of a hydroxyl end group in PEG with a nonpolar alkyl chain significantly reduces salt solubility. Interestingly, the presence of an additional isopropoxy unit in $C_{11}E_6P_1$ further reduces salt solubility by up to one order of magnitude compared to $C_{10}E_6$, except perhaps for K_2SO_4. Nevertheless, salt solubilities especially of CsCl and KBr in $C_{10}E_6$ are still significant, on the order of 0.1 mol · kg^{-1} for these salts. Therefore, $C_{10}E_6$ might prove to be a suitable solvent for chemical synthesis when nonpolar reactants need to be mixed with ionic reactants. Compared to PEG, $C_{10}E_6$ should be more able to dissolve nonpolar reactants because of the nonpolar alkyl chain in its structure while still maintaining the ability to dissolve ionic compounds at the same time.

The surfactants used in this study are certainly less polar than water. We are not aware of available data concerning their dielectric constants as a measure of polarity, but some estimates are possible based on known dielectric constants of related compounds [32]. Tetraethylene glycol with a molecular mass of 194.2 g mol^{-1} can be compared to PEG 200 and has a dielectric constant of 20.4. The effect of replacing one hydroxyl group in PEG with an alkyl chain can be inspected by comparing the dielectric constants of diethylene glycol ($\varepsilon = 31.8$), ethylene glycol mono ethyl either ($\varepsilon = 13.4$), and ethylene glycol dimethyl ether ($\varepsilon = 7.3$). From this series, one may estimate the dielectric constant for $C_{10}E_6$ to be slightly below 10. The dielectric constant of $C_{11}E_6P_1$ should be even lower than for $C_{10}E_6$ because of the extra methyl group from the isopropoxy unit and the slightly longer alkyl chain. The observed salt solubility trend of $C_{11}E_6P_1 < C_{10}E_6 <$ PEG 200 < water ($\varepsilon = 80.1$) can therefore be rationalized by the increasing solvent polarity.

With respect to interpreting solubility trends in terms of the salts, it is instructive to inspect the ionic radii. The ionic radii in 6-fold coordination for the cations Na^+, K^+ and Cs^+ are respectively, 102, 138 and 167 pm and for anions Cl^- and Br^- 181 and 196 pm, respectively [33]. The difference in ionic radii between anion and cation follows then to be in the order CsCl (14 pm) < KCl (43 pm) < KBr (58 pm) < NaCl (79 pm). For the chloride salts, the solubility in the neat surfactant increases with cation size and thus decreases with size difference between cation and Cl^-. The theory of hard and soft acids and bases considers besides ion size additional aspects such as availability of d-orbitals and polarizability of the ion [34]. While Cl^- is characterized as a hard base, Br^- is characterized as borderline between hard and soft bases. Interactions are stronger between hard-hard and soft-soft acids and bases. Therefore, the comparably high solubility of KBr can be explained with the weaker interactions between K^+ and Br^- making it easier to dissolve KBr compared to KCl. In addition to the dissolution of the disso-

ciated ions into the water-surfactant binary solvent, it is important to consider the dissolution of the salts as ion pairs. Hu et al. has shown that ion pairing becomes strongly favored with decreasing solvent polarity for solvents with dielectric constants below $\varepsilon = 10$ [35]. Therefore, it can be expected that the salts are present not only as ions but also as ion pairs as w approaches zero. Ions that are more polarizable, i.e. softer acids and bases, should be able to interact easier with a solvent of low polarity than ions that are less polarizable. This provides additional rationale for explaining the larger solubilities of KBr and CsCl for w approaching zero compared to the other salts. In this regard, for the one other study we are aware of reporting salt solubility for the entire composition range of water-PEG binary solvent, $CsClO_4$ with its much larger anion is actually found to be more soluble in neat PEG 600 (0.200 mol · kg^{-1}) compared to neat water (0.116 mol · kg^{-1}) at 25 °C [14].

While sulfate is also categorized as a hard base and K^+ as a hard acid, Cu^{2+} is borderline between hard and soft acid [34]. The higher solubility of $CuSO_4$ in water compared to K_2SO_4 can therefore be rationalized by weaker interactions between Cu^{2+} and SO_4^{2-} compared to K^+ and SO_4^{2-}. It is interesting that the solubility of $CuSO_4$ decreases more rapidly with decreasing w in Fig. 1f compared to K_2SO_4 in Fig. 1e. One possible reason could be that the interactions between a bivalent cation and anion are too strong in a medium of low polarity to stay solvated. Furthermore, K_2SO_4 has the additional opportunity to form the charged ion pair KSO_4^- to mitigate the decreasing solvent polarity. Because the solubility of $CuSO_4$ can be expected to be even lower in water-$C_{10}E_6$ and water-$C_{10}E_6P_1$, we did not attempt these solubility measurements. We also added in Fig. 1e data for ammonium sulfate and sodium sulfate from reported spinodal phase boundaries [15, 18]. We caution that these equilibrium data may not involve solid salt but precipitated PEG. Nevertheless, we note the similar rapid decline with decreasing w, as observed in Fig. 1e for K_2SO_4.

4 Conclusions

In summary, we have reported new solubility data of several mineral salts in binary systems of water with PEG and related surfactants. To the best of our knowledge, these include the first reported salt solubilities in polyethylene oxide-type nonionic surfactants. The observed trends in solubility were rationalized by the polarity of the surfactant solvent and, with respect to the ions, by the theory of hard and soft acids and basis. The obtained solubility results show that $C_{10}E_6$ could be a viable solvent option for chemical synthesis where nonpolar reactants need to be brought in contact with ionic reactants, especially if these involve soft polarizable ions.

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Salt	a_0	a_1	a_2	a_3	σ/mol · kg^{-1}	R_2	$w >$
PEG 200							
NaCl	0.4286	3.8685	1.7358		0.43	0.929	0.00
KCl	0.4281	1.8727	2.2095		0.16	0.982	0.00
CsCl	0.7231	4.1080	6.2998		0.23	0.995	0.00
KBr	1.3005	2.2446	1.9502		0.21	0.975	0.00
K_2SO_4	–0.0022	0.1486	–0.8411	1.3320	0.0052	0.999	0.30
$CuSO_4$	–0.0394	1.0030	–4.1315	4.4171	0.036	0.997	0.50
$C_{10}E_6$							
NaCl	–0.0686	2.4883	6.8917	–3.2400	0.14	0.996	0.04
KCl	–0.0626	3.5053	1.2212		0.17	0.989	0.03
CsCl	0.1737	1.5095	9.2475		0.18	0.999	0.00
KBr	0.1557	4.5683	0.9284		0.28	0.976	0.00
K_2SO_4	0.0099	0.0039	–0.2090	0.8285	0.010	0.998	0.00
$C_{11}E_6P_1$							
NaCl	–0.1229	3.5634	–1.8655	4.5372	0.19	0.991	0.04
KCl	–0.0974	3.3228	1.3186		0.13	0.992	0.04
CsCl	0.0017	2.6314	1.6804	6.7639	0.0059	0.999	0.00
KBr	0.0503	5.4602			0.15	0.993	0.00
K_2SO_4	0.0292	–0.3446	0.9021	0.0568	0.020	0.997	0.00

Table 2 Polynomial fit parameters for salt molality, m, in mol · kg^{-1} of saturated solution as a function of mixed solvent water mass fraction, w: $m(w) = a_0 + a_1 w + a_2 w^2 + a_3 w^3$

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