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The Effect of Sodium Sulfate, Ammonium Chloride, Ammonium Nitrate and Salt Mixtures on Aqueous Phase Partitioning of Organic Compounds

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TOC Art

Abstract

Dissolved inorganic salt(s) influence the partitioning of organic compounds into the aqueous phase. This influence is especially significant in atmospheric aerosol, which usually contains large amount of ions, including sodium, ammonium, chloride, sulfate and nitrate. However, empirical data on this salt effect are very sparse. Here, the partitioning of numerous organic compounds into solutions of Na_2SO_4 , NH_4Cl and NH_4NO_3 was measured and compared with existing data for NaCl and $(\text{NH}_4)_2\text{SO}_4$. Salt mixtures were also tested in order to establish whether the salt effect is additive. In general the salt effect showed a decreasing trend of $\text{Na}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{NaCl} > \text{NH}_4\text{Cl} > \text{NH}_4\text{NO}_3$ for the studied organic compounds, implying the following relative strength of the salt effect of individual anions: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ and cations: $\text{Na}^+ > \text{NH}_4^+$. The salt effect of different salts is moderately correlated. Predictive models for the salt effect have been developed based on the experimental data. The experimental data indicate that the salt effect of mixtures may not be entirely additive. However, the deviation from additivity, if it exists, is small. Data of very high quality are required to establish whether the effect of constituent ions or salts is additive or not.

Introduction

In the environment, for example in atmospheric or sea water, a mixture of different inorganic salts is usually present. Important ions in atmospheric waters include Na^+ , NH_4^+ , SO_4^{2-} , NO_3^- , and Cl^- , originating from both natural (e.g. sodium chloride from sea spray) and anthropogenic sources (e.g. nitrate and sulfate from NO_x and SO_2). The ionic strength in atmospheric aqueous phases varies with liquid water content, and ranges from 10^{-4} M for dilute cloud, fog, and rain droplets to >10 M for deliquescent aerosol particles.¹ Salts are also present in other aqueous systems, e.g. in brine pockets occurring in growing sea ice, in wastewater from the oil and gas extraction industry or in fresh water systems impacted by road salt applications. The presence of dissolved inorganic salt(s) has an effect on an organic compound's partitioning into the aqueous phase, i.e., its solubility or activity coefficient in water. This is known as the salt effect and can be described by the Setschenow equation:^{2, 3}

$$\log (K_{1/\text{saltwater}}/K_{1/\text{water}}) = K_S C_{\text{salt}} \quad (1)$$

where $K_{1/\text{saltwater}}$ and $K_{1/\text{water}}$ are partitioning coefficients of an organic compound between a non-aqueous phase 1 and a salt solution or water, K_S is the Setschenow or salting constant (L mol^{-1}),

and C_{salt} is the concentration of the salt solution (mol L^{-1}). There is a salting out effect when K_S is positive and a salting in effect when it is negative. The term $\log (K_{I/saltwater}/K_{I/water})$ describes the degree of salting out or salting in at the concentration C_{salt} .

While it is important to understand the influence of individual ions and salt mixtures on phase partitioning and solubility of organic compounds in the aqueous phase, the natural association of anions with cations makes it difficult to measure the salt effect of individual ions. Instead, we can measure and compare the effect of different salts on an organic compound's solubility and partitioning, and eventually compare the effect of individual ions indirectly. Endo et al.⁴ and Wang et al.⁵ measured the salting out of a large variety of organic compounds from NaCl and $(\text{NH}_4)_2\text{SO}_4$ solutions, respectively, and developed poly-parameter linear free energy relationships (pp-LFERs) for the prediction of Setschenow constants of these two salts. While these data sets allow for a systematic comparison of the effect of these two salts, data for other salts are sparse.⁶⁻¹⁰ In particular, the empirical database is too small to derive information on the relative salt effect of individual ions for a larger set of compounds. Furthermore, except for the group contribution methods based on UNIFAC^{11,12} and AIOMFAC¹³ which predict activity coefficients of chemical species in inorganic-organic mixtures, no models have been developed specifically for the prediction of the effect for salts other than NaCl and $(\text{NH}_4)_2\text{SO}_4$.

Little is known about the salt effect in salt mixtures, even though salts are usually present as mixtures. To the best of our knowledge, the salt effect for salt mixtures has only been reported for naphthalene at moderate ionic strengths in binary mixtures of NaCl with MgCl_2 , Na_2SO_4 , CaCl_2 , KBr and CsBr,¹⁴ for fluorene and thiophene in Na-Ca brines¹⁵ and for glyoxal in $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 mixtures.¹⁰ With respect to whether the effect of multiple salts in a mixed solution is additive, contradictory results have been found. The effect for naphthalene was additive in inorganic salt mixtures, but non-additive if the mixtures contained organic salts.¹⁴ Comparing two salts with one common ion, the effects of salts was found to be non-additive (based on individual ions) for toluene¹⁶ but additive for benzene.¹⁷ Poulson et al.¹⁶ hypothesized that toluene's dipole moment might allow for additional interactions in mixed electrolyte systems that could cause the non-additive effect. However, the presence of a dipole moment in thiophene had no effect on the additivity of NaCl and CaCl_2 Setschenow constants.¹⁵ Clearly, the literature on this issue is inconsistent and no general conclusion can be drawn from the small number of studies that vary in terms of scope, quality and the treatment of uncertainty. Findings are

generally qualified or their validity is limited to the specific salts and organic compounds being studied.

A systematic and in-depth investigation of the salt effect of a large variety of organic compounds in different salt solutions and salt mixtures is essential for understanding organic compound behavior in complex aqueous solutions such as aerosol water, biological systems, brine water, and industrial waste water. This topic has not been well studied despite both practical and fundamental importance. One reason is the difficulty of these measurements. While it is often challenging to accurately and precisely measure the water solubility of organic chemicals,¹⁸ it is particularly difficult to precisely determine the relatively small difference in water solubility caused by the salt effect. It is even more difficult to acquire such data with a quality and precision that allows for an unequivocal assessment of the additivity of the salt effect. The present study thus had the following objectives: (1) to determine and compare the salt effect for different salts; (2) to test the additivity of the salt effect for salt solution mixtures as well as for ions; (3) to develop and compare models for predicting Setschenow constants for different salts.

Methods

Experimental Methods

We measured K_S in solutions of Na_2SO_4 , NH_4Cl , and NH_4NO_3 for the same group of 38 compounds with diverse functional groups as studied for NaCl by Endo et al.⁴ and for $(\text{NH}_4)_2\text{SO}_4$ by Wang et al.⁵ (Table 1). Salt effects in binary salt mixtures of 1:1 mole of NaCl and $(\text{NH}_4)_2\text{SO}_4$ were measured for selected compounds.

The shared headspace passive dosing (SHPD) method and the negligible depletion solid phase micro extraction (SPME) method described in Endo et al.⁴ and Wang et al.⁵ were used to measure the salt effect for different compounds (see detailed description of the experimental methods in the supporting information). Table S1 in the supporting information indicates which method was used for which compounds. Concentrations of the salt solutions, and the mixture compositions are provided in Table S2. The salt solutions used in this study were not buffered and their pH at different concentrations is given in Table S2. While pH might influence the salt effect, it should be minor for the studied salts and organic compounds, because the latter are primarily (>99%) in their neutral form under the pH conditions of these salt solutions. The exceptions are atrazine and 4-aminobiphenyl, which have a pK_a of 1.7 and 4.35, respectively.¹⁹

103 Method for Testing Additivity

104 To test the additivity of the salt effects in a salt mixture we hypothesized that the following
 105 equation should be valid if the effect is additive.

$$106 \quad K_{s,\text{mix}} = \sum_{i=1}^n (f_i K_{s,i}) \quad (2)$$

107 where f_i is the molar fraction of the i^{th} salt in the mixture, $K_{s,i}$ and $K_{s,\text{mix}}$ are the Setschenow
 108 constants of the i^{th} salt and the salt mixture, respectively. In the specific case of a mixture of
 109 $(\text{NH}_4)_2\text{SO}_4$ and NaCl tested here, equation 2 reads:

$$110 \quad K_{s,\text{mix}} = f_{\text{NaCl}} K_{s(\text{NaCl})} + f_{(\text{NH}_4)_2\text{SO}_4} K_{s((\text{NH}_4)_2\text{SO}_4)} \quad (3)$$

111 We also hypothesized that if the salt effect is additive for the ions in a solution, the following
 112 equation should hold:

$$113 \quad K_{s,\text{salt},i} = n_{\text{cation}} K_{s(\text{cation})} + n_{\text{anion}} K_{s(\text{anion})} \quad (4)$$

114 where $K_{s,\text{salt},i}$ is the Setschenow constant for salt i , n_{cation} and n_{anion} are the numbers of cations and
 115 anions in salt i and $K_{s(\text{cation})}$ and $K_{s(\text{anion})}$ are the Setschenow constants for the cation and anion,
 116 respectively.

117 The additivity of the effect of ions can be tested by comparing salts with one common cation or
 118 anion. For instance, by comparing the difference of K_s between NaCl and Na_2SO_4 , and between
 119 NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$, we can test whether the effect of a given salt is the sum of individual
 120 contributions of the component ions for organic compound j . If individual ion effects are
 121 additive, the difference in K_s values between two salts with one common ion should be
 122 independent of the identity of the common ion. For example, for the same organic compound we
 123 would expect the difference in K_s between NaCl and NH_4Cl to be $\frac{1}{2}$ of the difference in K_s
 124 between Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.

$$125 \quad K_{s(\text{Na}_2\text{SO}_4,j)} - K_{s((\text{NH}_4)_2\text{SO}_4,j)} = 2(K_{s(\text{NaCl},j)} - K_{s(\text{NH}_4\text{Cl},j)}) \quad (5)$$

126 Similarly, the difference between $K_{s(\text{Na}_2\text{SO}_4,j)}$ and $2K_{s(\text{NaCl},j)}$ should equal the difference between
 127 $K_{s((\text{NH}_4)_2\text{SO}_4,j)}$ and $2K_{s(\text{NH}_4\text{Cl},j)}$.

$$128 \quad K_{s(\text{Na}_2\text{SO}_4,j)} - 2K_{s(\text{NaCl},j)} = K_{s((\text{NH}_4)_2\text{SO}_4,j)} - 2K_{s(\text{NH}_4\text{Cl},j)} \quad (6)$$

An alternative approach is to compare whether the salt effect in mixtures of the same amount and species of ions is equal by testing the validity of the following equation.

$$K_{S(\text{Na}_2\text{SO}_4, \text{j})} + 2K_{S(\text{NH}_4\text{Cl}, \text{j})} = K_{S((\text{NH}_4)_2\text{SO}_4, \text{j})} + 2K_{S(\text{NaCl}, \text{j})} \quad (7)$$

Modeling Method

The measured data are used to calibrate pp-LFERs for the prediction of K_S in Na_2SO_4 , NH_4NO_3 , and NH_4Cl solutions. Specifically, multiple linear regressions yielded equations of the following type:

$$K_S = c + eE + sS + aA + bB + vV \quad (8)$$

where E , S , A , B and V are solute descriptors representing a solute's excess molar refraction, dipolarity/polarizability, hydrogen-bond acidity, hydrogen-bond basicity and McGowan volume ($\text{cm}^3 \text{mol}^{-1}$) divided by 100, respectively. Descriptors for the organic solutes studied here were taken from the UFZ-LSER database²⁰ and are listed in the supporting information (Table S3). The regression coefficients are denoted by a , b , s , e and v ; c is the regression constant.

Results and Discussion

Setschenow Coefficients in Different Salt Solutions

The K_S measured in different salt solutions are shown in Table 1. The K_S values for a few compounds in NH_4NO_3 solutions are not reported, because a low salt effect made it difficult to achieve high quality data. For comparison, the 2-ketones were measured with both methods; data obtained with the SHPD method are in the supporting information (Table S4). Absolute differences between the two methods are in the range of 0~0.024 L mol^{-1} for NH_4NO_3 , 0.012~0.053 L mol^{-1} for NH_4Cl and 0.001~0.143 L mol^{-1} for Na_2SO_4 , indicating generally good agreement. We note however that the discrepancy between the two methods (ΔK_S in Table S4) is sometimes larger than the reported precision of the K_S values (standard error, SE, in Tables 1 and S4), which was derived as described in the Supporting Information. It is thus possible that the random errors as expressed in the SE values in Tables 1 and S4 underestimate the true uncertainty of the reported K_S values, i.e. there is the possibility of some bias.

In general, linear relationships (with high R^2 and low SE of the linear regression in Table 1) between the extent of the salt effect and the salt concentration were observed for all the measured

organic compounds in the range of salt concentrations used in the study. This indicates that the Setschenow equation (eq. 1) is valid for a wide variety and concentrations of salt solutions and Setschenow coefficients (salting out/in coefficients) are constants up to the highest studied salt concentrations (Table S2).

The measured K_S values range from 0.296 ± 0.057 to 1.379 ± 0.123 for Na_2SO_4 , from -0.027 ± 0.007 to 0.215 ± 0.012 for NH_4Cl and from -0.094 ± 0.006 to 0.130 ± 0.026 for NH_4NO_3 (in unit of L mol^{-1}). Pentylbenzene (0.176), heptanal (0.146) and 2-decanone (0.123) have the highest SE for Na_2SO_4 , indicating less precise results. 6:2 FTOH and 2-decanone have the highest SE for NH_4Cl (0.012 and 0.015) and NH_4NO_3 (0.026 and 0.010). A relatively large SE can occur when quantification is challenged by a compound's low concentration/solubility in salt solutions (e.g. 2-decanone, pentylbenzene, and 6:2 FTOH). The relatively large SEs for 6:2 FTOH may be due to its relatively high volatility, which may cause loss during sampling of the aqueous solutions using a syringe.

Among all the measured compounds, 4-nitroaniline had the lowest K_S in different salt solutions, including in NaCl and $(\text{NH}_4)_2\text{SO}_4$. In NH_4NO_3 and NH_4Cl solutions 4-nitroaniline was found to salt in ($K_S < 0$); 4-nitroanisole did the same in NH_4NO_3 solutions. These two compounds are relatively polar, a structural attribute that has previously been identified as causing a low salting out effect.^{4, 5} In another study, nitrobenzaldehyde was found to salt into solutions of nitrate salts, which suggests a possible effect of the nitro-group in the non-electrolyte.²¹ The NH_4NO_3 and NH_4Cl solutions are both acidic, which might alter the electron distribution of the nitro-group and render the organic compounds containing nitro-groups more polar, causing it to salt in under acidic conditions. Others also observed a salting in effect for polar compounds such as glyoxal and amino acids.^{10, 22, 23} Other than 4-nitroaniline and 4-nitroanisole, the studied compounds all had positive K_S values in different salt solutions.

Comparison with earlier studies is difficult due to the dearth of literature data, with only toluene having been previously measured in Na_2SO_4 and NH_4Cl ,^{6, 9, 24} ethylbenzene and propylbenzene in Na_2SO_4 ⁹ and 1-naphthol in NH_4Cl .²⁵ Table S5 compares K_S reported in the literature with the values measured here. The generally small differences (absolute difference between 0.033 and 0.1 for Na_2SO_4 and between 0.024 and 0.071 for NH_4Cl) are acceptable in light of uncertainties in the experimental and analytical methods from different studies.

187 Table 1 Setschenow constants (K_S [L mol⁻¹]) for organic compounds in different salt
 188 solutions

	NH ₄ NO ₃			NH ₄ Cl			Na ₂ SO ₄			(NH ₄) ₂ SO ₄ ^a	NaCl ^b
	K _S	SE ^c	R ^{2 c}	K _S	SE	R ²	K _S	SE	R ²	K _S	K _S
toluene	0.071	0.006	0.95	0.112	0.005	0.98	0.590	0.040	0.96	0.465	0.221
ethylbenzene	0.088	0.006	0.96	0.126	0.009	0.95	0.660	0.062	0.93	0.525	0.238
n-propylbenzene	0.097	0.006	0.97	0.135	0.010	0.95	0.848	0.060	0.96	0.594	0.262
n-butylbenzene	0.103	0.005	0.98	0.140	0.010	0.96	0.940	0.109	0.89	0.614	0.285
pentylbenzene	0.072	0.005	0.96	0.153	0.006	0.99	1.067	0.176	0.80	0.572	0.300
heptanal	0.051	0.009	0.83	0.107	0.012	0.92	0.732	0.146	0.71	0.447	0.237
octanal	0.071	0.009	0.87	0.143	0.007	0.97	0.829	0.081	0.91	0.545	0.265
4:2 FTOH	0.080	0.005	0.96	0.181	0.010	0.98	0.778	0.096	0.87	0.611	0.273
6:2 FTOH	0.130	0.026	0.83	0.215	0.012	0.98	1.166	0.109	0.92	0.729	0.378
2-hexanone	0.056	0.003	0.98	0.131	0.008	0.97	0.710	0.038	0.98	0.481	0.198
2-heptanone	0.060	0.004	0.97	0.157	0.008	0.98	0.812	0.027	0.99	0.506	0.228
2-octanone	0.063	0.005	0.95	0.193	0.004	1.00	0.983	0.032	0.99	0.556	0.267
2-nonanone	0.083	0.005	0.97	0.167	0.006	0.98	1.075	0.075	0.96	0.598	0.306
2-decanone	0.117	0.010	0.93	0.188	0.015	0.94	1.379	0.123	0.94	0.612	0.321
benzophenone	0.037	0.006	0.85	0.114	0.004	0.99	0.715	0.065	0.94	0.602	0.262
valerophenone	0.041	0.005	0.90	0.125	0.005	0.98	0.854	0.061	0.96	0.604	0.271
bisphenol a	0.028	0.003	0.84	0.094	0.008	0.91	0.504	0.055	0.87	0.359	0.174
1-naphthol	0.018	0.004	0.69	0.030	0.007	0.65	0.576	0.038	0.95	0.297	0.182
1-hexanol	0.075	0.002	0.99	0.115	0.002	0.99	0.610	0.035	0.97	0.466	0.221
4-ethyl-3-hexanol	0.087	0.004	0.97	0.135	0.005	0.98	0.695	0.039	0.96	0.533	0.291
2-butoxyethanol	0.069	0.005	0.92	0.102	0.005	0.96	0.709	0.054	0.93	0.400	0.211
2-phenylphenol	0.047	0.004	0.94	0.102	0.007	0.95	0.879	0.068	0.95	0.496	0.274
4-nitroaniline	-0.094	0.006	0.95	-0.027	0.007	0.53	0.296	0.057	0.68	0.216	0.099
4-nitroanisole	-0.028	0.005	0.73	0.039	0.003	0.95	0.469	0.081	0.79	0.423	0.126
2,5-dimethylpyrazine	0.040	0.003	0.94	0.102	0.004	0.98	0.600	0.031	0.97	0.467	0.209
acetanilide	0.042	0.007	0.74	0.090	0.006	0.95	0.674	0.049	0.93	0.393	0.197
metallochlor	0.060	0.007	0.84	0.166	0.007	0.98	0.992	0.097	0.92	0.699	0.296
4-aminobiphenyl	0.056	0.006	0.87	0.152	0.008	0.97	1.049	0.077	0.95	0.585	0.208
atrazine	0.065	0.005	0.94	0.164	0.006	0.98	1.184	0.068	0.97	0.581	0.274
methyl phenyl sulfoxide	0.053	0.005	0.89	0.128	0.011	0.92	0.681	0.061	0.91	0.393	0.166
tri-n-butylphosphate	0.112	0.007	0.96	0.188	0.005	0.99	1.069	0.051	0.98	0.571	0.428
d-n-propylphthalate	0.087	0.004	0.97	0.176	0.005	0.99	1.108	0.044	0.99	0.680	0.374
1-nitrohexane	0.026	0.007	0.69	0.120	0.006	0.97	0.775	0.066	0.93	0.561	0.236
1-nitropentane	NA	NA	NA	0.084	0.004	0.98	0.459	0.033	0.95	0.347	0.203
4-fluorophenol	NA	NA	NA	0.051	0.004	0.91	0.369	0.031	0.92	0.246	0.168
4-iodophenol	NA	NA	NA	0.059	0.004	0.95	0.566	0.039	0.94	0.276	0.162
caffeine	NA	NA	NA	0.040	0.004	0.86	0.476	0.055	0.84	0.383	0.114
carbazole	NA	NA	NA	0.032	0.003	0.91	0.499	0.080	0.81	0.452	0.232

189 ^a measurements by Wang et al.,⁵ ^b measurements by Endo et al.,⁴ ^c Standard Error (SE) and coefficient of
 190 determination (R²) of a linear regression between the extent of the salt effect (represented by $\log(K_{I/salt\ water}/K_{I/water})$,
 191 and the salt concentration.

192 Comparison and Correlation of K_S for Different Salts

193 For all organic compounds measured in this study, we find a general trend in the magnitude of
194 the salt effect, namely a sequence of decreasing K_S according to: $\text{Na}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{NaCl} >$
195 $\text{NH}_4\text{Cl} > \text{NH}_4\text{NO}_3$. This order also applies for the two compounds with a salting in effect. This
196 indicates very distinct salt effects of different salts on a given organic compound and the same
197 order of salt effect for various organic compounds despite their different size, functional groups
198 and polarity. The salts with a doubly charged anion (SO_4^{2-}) have a larger salting out effect, which
199 agrees with findings in other studies.^{7, 8, 26} For the same cation (Na^+ or NH_4^+), SO_4^{2-} salts have a
200 higher salting out effect than Cl^- salts, while for the same anion (Cl^- or SO_4^{2-}), Na^+ salts always
201 have a higher salting out effect than NH_4^+ salts, in agreement with previous studies for other
202 compounds.^{7, 8, 26} NO_3^- tends to have the lowest salting out effect among all studied anions. Both
203 Görgényi et al.⁷ and Waxman et al.¹⁰ reported nitrate salts having the lowest salting out effect
204 among anions. In this study, the trend of salt effect by different salts was observed for a large
205 variety of organic compounds. The order of the salt effect by different anions agrees with the
206 Hofmeister series, which ranks the relative influence of ions on the physical behavior of a wide
207 variety of aqueous processes for protein.^{27, 28} The average coefficient of variation for K_S among
208 different organic compounds for one salt (ranging from 0.29 to 0.70 with an average of 0.41) is
209 smaller than that among all the salts for an individual compound (ranging from 0.60 to 1.66 with
210 an average of 0.88). Overall, this indicates that the extent of the salt effect is largely determined
211 by the salt species but also varies for different organic compounds.

212 The K_S for each pair of salts are significantly correlated, as shown in Figure S3, with correlation
213 coefficients (r) between 0.703 and 0.861 ($p < 0.01$). Such correlations had previously been
214 observed between NaCl and $(\text{NH}_4)_2\text{SO}_4$,⁵ between NaCl and KCl , and between NaCl and
215 CaCl_2 .¹⁵ The observation that the salt effect follows a specific order and K_S for different salts are
216 significantly correlated suggests that the identity of the salts determines the order of the salt
217 effect (ion-water interaction), while the identity of the organic solutes determines its specific
218 value (organic-water or organic-ion interaction). The K_S for a specific compound is largely
219 determined by the salt species' properties. The variability in the effect of different salts has been
220 proposed to be related to the varying structure, size, charge density, hydration and dielectric
221 constant of their constituent ions.²⁹ To a lesser extent, it also depends on the organic compound's
222 properties. Previous work identified size/volume and polarity of an organic solute as influencing

its K_S .^{4-6, 30, 31} The consistent salting order among different salts confirms that the organic molecular size and polarity only change the overall magnitude of the salt effect without greatly affecting the variations among different salt species.

The multitude of intermolecular interactions involving various combinations of ions, organic solutes and solvents (usually water) renders the salt effect very complex. As discussed above, the magnitude and direction of the effect of a salt on an organic solute in solution depends on the properties of both salt and solute. Several qualitative and quantitative theories and mechanisms of the salt effect have been presented. While they can explain some aspects of the salt effect, none of these theories appears capable of explaining all of the observations. Long and McDevit³⁰ and Grover and Ryall²⁹ reviewed those theories thoroughly. In the following, we attempt to explain the relative order of the salt effect for different salts based on some of those theories.

According to the hydration theory, the formation of hydration shells around ionic species effectively reduces the availability of free water molecules for solvating organic compounds, thus leading to a salting out effect. The magnitude of the salt effect has been related to the charge density (valency per ionic volume) of the corresponding ions: ions with a bigger charge density have larger hydration shells, and thus exhibit a stronger salting-out effect.⁸ A similar theory based on the Born equation³² relates K_S with the square of the charge of the ion (z^2) and the reciprocal of the radius of the ion (r).³³ The Born equation calculates the Gibbs free energy of solvation (ΔG_{solv}), i.e. the energy of hydration (ΔG_{hyd}) in the case of water as solvent, which is negatively proportional to z^2/r . The lower ΔG_{hyd} indicates a stronger interaction of ion with water, thus a higher salting out effect.³⁴ The sequence in z^2/r is $\text{SO}_4^{2-} > \text{Cl}^- \approx \text{NO}_3^-$ for the anions, and $\text{Na}^+ > \text{NH}_4^+$ for the cations (Table S6) and thus follows the same trend as the measured salt effect, except for NO_3^- , which exhibits a lower K_S than would be expected based on this theory. The sequence in ΔG_{hyd} from the literature (Table S6) is $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ for the anions, and $\text{Na}^+ > \text{NH}_4^+$ for the cations, in agreement with the trend of the salt effect.

pp-LFERs Development

The theoretical understanding of the salt effect is currently insufficient to make quantitative predictions. Therefore, prediction methods based on the regression of empirical data have an important role to play. The experimental data from this study were used to calibrate the following pp-LFERs for K_S in solutions of Na_2SO_4 , NH_4Cl and NH_4NO_3 :

$$K_S(\text{Na}_2\text{SO}_4) = 0.339 (\pm 0.125) - 0.022 (\pm 0.073) E - 0.120 (\pm 0.110) S - 0.289 (\pm 0.106) A - 0.152 (\pm 0.122) B + 0.536 (\pm 0.099) V \quad (n=38, R^2=0.623, \text{SD}=0.166) \quad (9)$$

$$K_S(\text{NH}_4\text{Cl}) = 0.054 (\pm 0.022) - 0.018 (\pm 0.013) E - 0.039 (\pm 0.020) S - 0.043 (\pm 0.019) A - 0.009 (\pm 0.022) B + 0.095 (\pm 0.018) V \quad (n=38, R^2=0.726, \text{SD}=0.030) \quad (10)$$

$$K_S(\text{NH}_4\text{NO}_3) = 0.048 (\pm 0.022) - 0.013 (\pm 0.013) E - 0.060 (\pm 0.020) S - 0.001 (\pm 0.020) A - 0.007 (\pm 0.023) B + 0.060 (\pm 0.018) V \quad (n=33, R^2=0.679, \text{SD}=0.029) \quad (11)$$

There are fewer measured data available for NH_4NO_3 due to experimental challenges. Thus, the pp-LFER developed for NH_4NO_3 in this study has a smaller application domain. The relative large and positive values of v , and relative small and negative values of e , s , a , and b agree with previous pp-LFERs for the K_S in NaCl and $(\text{NH}_4)_2\text{SO}_4$ solutions,^{4, 5} suggesting a large and positive influence of molecular volume and a small and negative influence of polar interactions on K_S . The absolute values of the regression coefficients of the pp-LFER for Na_2SO_4 are the highest among all the five pp-LFERs, followed by those for $(\text{NH}_4)_2\text{SO}_4$ and NaCl . The pp-LFERs for NH_4NO_3 and NH_4Cl have the smallest absolute regression coefficients. The R^2 and standard deviation (SD) of the pp-LFERs calibrated for Na_2SO_4 , NH_4Cl and NH_4NO_3 are not as good as in the pp-LFERs for NaCl and $(\text{NH}_4)_2\text{SO}_4$. For all pp-LFERs, there is a significant positive correlation of V with K_S ($p < 0.05$). However, the other regression coefficients (a , b , s and e) are not always significant. Parameter a was only significant for $K_S(\text{Na}_2\text{SO}_4)$ and $K_S(\text{NH}_4\text{Cl})$ and s for $K_S(\text{NH}_4\text{NO}_3)$. It is likely that the salt effect arises primarily from differences in the behavior of the particular salt solutions toward the “cavity” created by the organic molecule (which is determined by the size of the molecule), and that polar interactions, if present, have a modifying influence.

If we retain only the solute descriptors whose contribution to the variability in K_S was significant, we obtain the following pp-LFERs:

$$K_S(\text{Na}_2\text{SO}_4) = 0.400 (\pm 0.113) - 0.185 (\pm 0.060) S - 0.263 (\pm 0.101) A + 0.461 (\pm 0.077) V \quad (n=38, R^2=0.605, \text{SD}=0.165) \quad (12)$$

$$K_S(\text{NH}_4\text{Cl}) = 0.062 (\pm 0.020) - 0.061 (\pm 0.011) S - 0.045 (\pm 0.018) A + 0.093 (\pm 0.014) V \quad (n=38, R^2=0.709, \text{SD}=0.030) \quad (13)$$

$$K_S(\text{NH}_4\text{NO}_3) = 0.053 (\pm 0.020) - 0.076 (\pm 0.011) S + 0.059 (\pm 0.014) V$$

$$(n=33, R^2=0.668, \text{SD}=0.028) \quad (14)$$

K_S for compounds measured in this study and in the literature (Table S5 and S7) are compared with values predicted from the calibrated pp-LFERs (equations 12 to 14) (Figure 1). The predictions generally agree well with the measurement, with a root-mean-square error (RMSE) of 0.028, 0.028 and 0.133 L mol⁻¹ for NH₄NO₃, NH₄Cl and Na₂SO₄ for all the measured data, and a RMSE of 0.027, 0.028 and 0.078 L mol⁻¹ for literature data only.

Figure 1 Comparison of experimentally determined K_S with PP-LFER fitted K_S ; dashed line denotes the 1:1 line, dotted lines indicate a deviation of 0.05 for NH₄NO₃ and NH₄Cl and 0.25 for Na₂SO₄, respectively.

It is important to recognize that a K_S predicted by ppLFER quantifies only the effect of a salt on the aqueous solvation of an organic compound, and can thus not be expected to predict the “effective” salting behavior of compounds that undergo additional reactions within an aqueous salt solution. For example, there has been evidence that sulfate could modify the hydration equilibrium of glyoxal and both ammonium and sulfate may react with glyoxal.³⁵ A ppLFER can thus not describe the combined effect of hydration, reaction and salt effect that is observed experimentally.¹⁰

Among the measured compounds, there are two groups of compounds that differ only by the number of methylene (-CH₂-) group, namely the 2-ketones and alkylbenzenes. The similarity of their structures provides an opportunity to analyze the influence of molecular size on K_S . Generally, with increasing number of methylene group in the molecule (also an increase of volume), K_S increases linearly for both groups of compounds (Figure S4). The increments of K_S

with an increasing number of methylene and with increasing McGowan volume are illustrated by the slopes of the linear regressions in Figure S4. The increments of K_S for the 2-ketones are significantly larger than for the alkylbenzenes ($p < 0.05$, analysis of covariance), but in both cases they are in the same order as the general trend of the salting out effect: $\text{Na}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{NaCl} > \text{NH}_4\text{Cl} \approx \text{NH}_4\text{NO}_3$. It is difficult to differentiate the increments for $K_S(\text{NH}_4\text{Cl})$ and $K_S(\text{NH}_4\text{NO}_3)$ because the K_S values are relatively small. The different increments for the two groups of compounds suggest an influence of the structure of the compounds. The R^2 of the linear regression in Figure S4 also indicates that the McGowan volume alone can explain 83%-98% of the variation between the K_S values for 2-ketones and 64%-98% of the variation for the alkylbenzenes in different salt solutions.

Additivity of Ions in Salt Solutions

The additivity of the effects of ions in solution was tested through equations (5) to (7), which compare K_S for two salts with a common ion. In addition to the 38 compounds measured in this study, literature data were also included for comparison (listed in Table S7). Figure 2 plots the terms on either side of equations (5) to (7) against each other (the data are provided in Table S8). A data point falls on the 1:1 line, if the effect of ions is perfectly additive for an organic solute. A paired t-test was used to test whether the average of the difference between the terms on both sides of equations (5) to (7) is significantly different from zero. The paired t-test indicated no significant difference between the values on either side of the equations ($p > 0.05$) for the data generated in this study and for all data including literature values, suggesting that there is not sufficient evidence to indicate that the salt effect is not additive with respect to the individual ions. Literature data sufficiently accurate to test additivity with statistical rigor had not been available in the past. Earlier results reported for benzene and toluene had been contradictory (i.e. additive for benzene but non-additive for toluene).^{16, 17} Note that the values for any one compound in Table S8 may not indicate additivity, i.e., not all points fall on the 1:1 line in Figure 2. This means the additivity of the effect of ions may not apply for all compounds. However, these points do not change the result of the statistical analysis since the t-test is comparing the overall agreement.

Figure 2 Additivity for ions. The error bars were calculated from standard errors of K_S for each individual salt.

Additivity in Salt Mixtures

The salting out of the five 2-ketones from solutions containing different concentrations of a mixture of NaCl and $(\text{NH}_4)_2\text{SO}_4$ (1:1 on a molar basis) was measured with both SPME and SHPD methods. As in single salt solutions, linear relationships between $\log(K_{1/\text{salt water}}/K_{1/\text{water}})$ and salt concentrations were observed (Figure 3), allowing Setschenow coefficients in salt mixtures ($K_{S,\text{mix}}$) to be derived from their slopes. Error bars in Figure 3 illustrate the deviation among four experimental replicates. To test the additivity of the salting out effect, Figure 3 compares this observed effect (blue squares) with a calculated additive effect (red squares), obtained using equation 2, and the K_S for NaCl and $(\text{NH}_4)_2\text{SO}_4$ from Endo et al.⁴ and Wang et al.,⁵ respectively.

Both the observed and the calculated $K_{S,\text{mix}}$ fall between the K_S for NaCl (orange circles) and $(\text{NH}_4)_2\text{SO}_4$ (purple circles). Even though they are generally quite close to each other, the calculated $K_{S,\text{mix}}$ values are consistently higher than the observed ones for all five compounds (Figure 3), suggesting lower than additive salting out from salt mixtures. In order to test whether the difference between observed and calculated $K_{S,\text{mix}}$ is significant or not, we applied analysis of covariance to compare the slopes of the two linear regressions. The results suggest that within the uncertainty of the measurements, the salting out effect is additive for 2-hexanone and 2-heptanone ($p > 0.05$, i.e. the two slopes not significant different) but not additive for the other three compounds ($p < 0.05$). Some of the observed values have relatively large uncertainty, because it is difficult to precisely quantify small amounts of sparingly soluble substances sorbed

to the SPME fibers. For instance, the data for 2-decanone at 3 M was excluded in the regression analysis due to large uncertainty.

Figure 3 Salting out effect in salt mixtures (1: 1 mole ratio NaCl and $(NH_4)_2SO_4$) measured using the SPME method. The degree of salting out, i.e., $\log(K_{1/salt\ water}/K_{1/water})$, was calculated from the logarithm of the ratio between GC peak areas of the extracted fibers in salt solution and pure water as shown by the Y axis ($\log(A/A_0)$). Blue and red squares (with equation and R^2) show the observed salting out effect in the salt mixtures and the salting out effect calculated assuming additivity. Error bars for the observed values were calculated from 4 replicates at each concentration. Error bars for the calculated $K_{S,mix}$ values were calculated from standard errors of K_S for individual salt according to equation (2). For comparison, the salting out effect in NaCl and $(NH_4)_2SO_4$ solutions is shown with orange and purple circles, respectively. p-values from analysis of covariance are shown for each compound.

Figure S5 shows results for the 2-ketones using the SHPD method. Unlike the results from the SPME method, there is no consistent trend in the discrepancy of the calculated and measured $K_{S,mix}$. Except for 2-hexanone, the observed and calculated slopes are not significantly different ($p>0.05$), indicating additivity. The observed slope for 2-hexanone is much lower than expected from additivity, which might be partially due to experimental uncertainties. In order to explain the different observations of additivity for 2-ketones using the two experimental methods, we compared the measurements of K_S for individual salts in Table S9. For all the salts except for NH_4NO_3 , the SHPD measurements always have a higher relative standard error (SE/K_S in Table S9). This indicates the SPME measurements for the 2-ketones are generally more precise than the SHPD measurements. The fact that the SHPD measurements indicate additivity more frequently than the SPME method is possibly due to the lower precision of the SHPD measurements. This is because more uncertain measurements are more likely to overlap with values calculated by assuming additivity, leading to no significant difference in the statistical analysis.

Discussion of the Additivity of the Salt Effect

From a statistical point of view, we found no significant difference between the values on either side of equations (5) to (7). As a result, for the compounds and salts measured in the present study we cannot reject the hypothesis of an additive salt effect of ions, given the experimental accuracy. However, Figure 2 also indicates considerable differences between different organic solutes in terms of how close to additive the effect of different ions appears to be; some were close to the 1:1 line, other were quite far from that line. For the 2-ketones in salt mixtures, the results were somewhat inconclusive as well: even though the statistical analyses showed non-additivity for some compounds, the observed salting out effects in a salt mixture were generally quite close to the calculated values using both experimental methods (Figure 3 and Figure S5).

It is conceivable that this inconsistency is indicative of real differences between compounds and between salts, as the specific interactions of an ion with an organic compound may vary between ions and compounds. If that is the case, the specific interactions may prevent the extrapolation of the relations found in this study to other compounds and salt solutions. On the other hand, we cannot discount experimental uncertainty as the source of that inconsistency, especially as experimental errors can be compound specific and the investigation of the additivity of the salt effects is particularly sensitive to data uncertainty. The analysis depicted in Figure 3 is based on

data from three K_S measurements, i.e. the K_S for NaCl, $(\text{NH}_4)_2\text{SO}_4$, and the mixture, which all have an error. The analyses depicted in Figure 2 even required measured K_S for four different salts. It is noteworthy that panel c in Figure 2 (based on eq. 7) appears to give a clearer indication of additivity than panels a and b (based on eqs. 5 and 6). We believe that this is due to the comparison of larger and therefore relatively less uncertain terms (note that the scales in Figure 2a and 2b are smaller than in Figure 2c). Clearly, the relative error of the difference between the K_S of two salts (Figure 2a and 2b) is larger than the error of the sum of the K_S for two salts (Figure 2c). Equation of type (7) may thus be better suited to test additivity of the salt effect of ions than equations of type (5) and (6).

The salt effect is a very complex phenomenon and it is even more complex in salt mixtures. Theoretically, we would expect an additive salt effect in mixtures if the effect of ions is additive for individual salts according to equations (2) and (4). While our experimental data indicate that the salt effect of mixtures may not be entirely additive, the deviation from additivity seems quite small for the compounds and aqueous solutions studied. For most practical applications, it may be justified to assume additivity of the salt effect, as the error introduced by this assumption is likely small relative to the overall uncertainty in the magnitude of the salt effect.

More measurements with high quality and precision in salt mixtures for compounds with various structures (or properties such as polarities) are needed in order to unravel the salt effect in mixtures of salts and potential difference between various compounds. We note that for data analysis, especially for testing additivity, K_S measurements need to not only be of high quality, but also of known quality. It is thus very important to report K_S measurement uncertainties, such as standard deviations/errors.

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Supporting Information

Additional information on the experimental method used for each compound, information for the salt solutions, data from the literature, solute descriptors, and additional tables and figures

referenced in the text is provided in Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Supporting Information for

The Effect of Sodium Sulfate, Ammonium Chloride, Ammonium Nitrate and Salt Mixtures on Aqueous Phase Partitioning of Organic Compounds

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Text 1 Shared Headspace Passive Dosing (SHPD) Method

As illustrated in Figure S1, in a closed glass container, a spiked non-volatile organic solvent was used as a donor phase (i.e. 100 mL olive oil) providing the test compounds to water and salt solutions in small petri dishes (25 mL solution each). The transfer of chemicals from the organic solvent to the aqueous phases takes place via the headspace, which is shared by all individual aqueous phases in the petri dishes in the closed container. At equilibrium, samples of aqueous phase solution were taken through a septum on top of the big glass container. The aqueous solutions were then extracted with solvents and analyzed using GC-MS. The relative difference in the concentrations of the test solutes in the aqueous solutions reflects the degree of salting-out.

Figure S 1 Experiment setup of the shared headspace passive dosing method. K_{aw} is the partitioning coefficient of the organic solute between the headspace and the water phase. The blue and orange color arrows illustrate the transfer of organic compounds between the headspace and the aqueous solutions and between the headspace and the olive oil, respectively.

The values of K_S can be calculated using the following equation based on GC peak areas.

$$\log A_{[\text{salt}]} = -K_S [\text{salt}] + c \quad (\text{S1})$$

where $A_{[\text{salt}]}$ is the measured peak area of an organic compound for a given salt concentration $[\text{salt}]$, and K_S and c are the slope and intercept, respectively, of the linear regression. The regression analysis was typically performed using at least 12 measured peak areas (four replicates $\times$ at least three salt concentrations as shown in Table S2). The standard error (SE as shown in Table 1 for each compound) of the slope was calculated to indicate the error in the determined K_S .

Text 2 Negligible Depletion Solid Phase Micro-extraction (SPME) Method

In this method (Figure S2), pure water and salt solutions of the same volume receive a constant amount of test compound and a piece of SPME fiber. Organic compounds partition between the aqueous solution and the SPME fiber. At equilibrium, the SPME fibers were then extracted with solvents and analyzed using GC-MS. If the fibers absorb only a negligible amount of compounds and if the headspace volume is small enough, aqueous concentrations remain constant across the solutions with different salt concentrations (i.e. negligible depletion). The relative fiber phase concentrations directly reflect the salting out effects.

Figure S 2 Experiment setup of the solid phase micro-extraction method. K_{fw} is the partitioning coefficient of the organic solute between the SPME fiber and the water phase. The blue color arrows illustrate the transfer of organic compounds between the aqueous solutions and the SPME fiber.

The values of K_S can be calculated using the following equation based on GC peak areas.

$$\log A_{[\text{salt}]} = K_S [\text{salt}] + c \quad (\text{S2})$$

where $A_{[\text{salt}]}$ is the measured peak area of an organic compound in an SPME fiber that was extracted from a given salt concentration $[\text{salt}]$, and K_S and c are the slope and intercept, respectively, of the linear regression. The regression analysis was typically performed using at least 20 measured peak areas (four replicates $\times$ at least five salt concentrations as shown in Table S2). The standard error (SE as shown in Table 1 for each compound) of the slope was calculated to indicate the error in the determined K_S .

Table S 1 Information on the experimental methods

Name	Method ^a	Name	Method ^a
Toluene	SHPD	1-naphthol	SPME with PA
Ethylbenzene	SHPD	1-hexanol	SPME with PA
n-propylbenzene	SHPD	4-ethyl-3-hexanol	SPME with PA
n-butylbenzene	SHPD	2-butoxyethanol	SPME with PA
Pentylbenzene	SHPD	2-phenylphenol	SPME with PDMS
Heptanal	SHPD	4-nitroaniline	SPME with PA
Octanal	SHPD	4-nitroanisole	SPME with PDMS
1-nitrohexane	SHPD	2,5-dimethylpyrazine	SPME with PA
1-nitropentane	SHPD	acetanilide	SPME with PA
4:2 FTOH	SHPD	metallochlor	SPME with PDMS
6:2 FTOH	SHPD	4-aminobiphenyl	SPME with PDMS
2-hexanone	SHPD & SPME with PA	atrazine	SPME with PDMS
2-heptanone	SHPD & SPME with PA	methyl phenyl sulfoxide	SPME with PA
2-octanone	SHPD & SPME with PA	tri-n-butylphosphate	SPME with PDMS
2-nonanone	SHPD & SPME with PA	d-n-propylphthalate	SPME with PDMS
2-decanone	SHPD & SPME with PA	4-fluorophenol	SPME with PA
benzophenone	SPME with PDMS	4-iodophenol	SPME with PA
valerophenone	SPME with PDMS	caffeine	SPME with PA
bisphenol a	SPME with PA	carbazole	SPME with PDMS

^a SHPD is the shared headspace passive dosing method, SPME is the solid phase microextraction method using fibres made from either PA (Polyacrylate fibers, 36 µm coating thickness, 16.5 µL/m coating volume) or PDMS (Polydimethylsiloxane fibers, 30 µm coating thickness, 13.2 µL/m coating volume).

Table S 2 Concentration and pH of the salt solutions used during the experiment.

	Concentration (mol/L)	pH ^a	pH ^b		Concentration (mol/L)	pH ^a	pH ^b
NH ₄ NO ₃	2.5	4.73	4.461	(NH ₄)SO ₄ ^c	0.38	5.34	5.160
	3.75	4.52	4.351		0.76	5.30	5.158
	5	4.44	4.240	NaCl ^d	0.86	6.34	6.067
NH ₄ Cl	0.93	4.90	4.698		1.72	6.72	6.537
	1.87	4.74	4.640	NaCl/(NH ₄) ₂ SO ₄ mixture (1:1 molar ratio)	0.5	5.29	5.277
	3.74	4.52	4.381		1	5.32	5.188
Na ₂ SO ₄	0.18	5.89	5.752		2	5.25	5.157
	0.28	6.04	5.909		3	5.19	5.081
	0.35	6.14	5.906				

^{a,b} pH measured with different pH meters, ^c ref.¹, ^d ref.²

Table S 3 Solute descriptors for studied compounds from UFZ-LSER database³

Compound	E	S	A	B	V
toluene	0.601	0.52	0	0.14	0.8573
ethylbenzene	0.613	0.51	0	0.15	0.9982
propylbenzene	0.604	0.5	0	0.15	1.1391
butylbenzene	0.6	0.51	0	0.15	1.28
pentylbenzene	0.594	0.51	0	0.15	1.4209
heptanal	0.14	0.65	0	0.45	1.1106
octanal	0.16	0.65	0	0.45	1.2515
1-nitrohexane	0.203	0.95	0	0.29	1.1282
1-nitropentane	0.212	0.95	0	0.29	0.9873
4:2 FTOH	-0.67	0.2	0.55	0.25	1.352
6:2 FTOH	-1.04	0.2	0.55	0.25	1.7846
2-hexanone	0.136	0.68	0	0.51	0.9697
2-heptanone	0.123	0.68	0	0.51	1.1106
2-octanone	0.108	0.68	0	0.51	1.2515
2-nonanone	0.119	0.68	0	0.51	1.3924
2-decanone	0.108	0.68	0	0.51	1.5333
benzophenone	1.447	1.5	0	0.5	1.4808
valerophenone	0.795	0.95	0	0.5	1.4366
bisphenol a	1.607	1.56	0.99	0.91	1.8643
1-naphthol	1.52	1.1	0.66	0.34	1.1441
1-hexanol	0.21	0.42	0.37	0.48	1.0127
4-ethyl-3-hexanol	0.17	0.36	0.33	0.57	1.2945
2-butoxyethanol	0.201	0.53	0.26	0.83	1.0714
2-phenylphenol	1.55	1.4	0.56	0.49	1.3829
4-nitroaniline	1.22	1.92	0.46	0.35	0.9904
4-nitroanisole	0.97	1.29	0	0.4	1.0902
2,5-dimethylpyrazine	0.626	0.9	0	0.69	0.916
acetanilide	0.9	1.37	0.48	0.67	1.1137
metolachlor	1.15	1.01	0.07	1.38	2.2811
4-aminobiphenyl	1.565	1.48	0.26	0.48	1.424
atrazine	1.22	1.29	0.17	1.01	1.6196
methylphenylsulfoxide	1.104	1.8	0	0.91	1.08
tri-n-butylphosphate	-0.1	0.9	0	1.21	2.239
di-n-propylphthalate	0.713337	1.4	0	0.88	1.9924
4-fluorophenol	0.67	0.97	0.63	0.23	0.8128
4-iodophenol	1.38	1.22	0.68	0.2	1.0333
caffeine	1.5	1.82	0.08	1.25	1.3632
carbazole	1.787	1.42	0.47	0.26	1.3154
o-xylene	0.663	0.56	0	0.16	0.9982

Table S 3 (continued)

Compound	E	S	A	B	V
m-xylene	0.623	0.52	0	0.16	0.9982
p-xylene	0.61	0.52	0	0.16	0.9982
naphthalene	1.34	0.92	0	0.2	1.0854
chloroform	0.425	0.49	0.15	0.02	0.6167
benzene	0.61	0.52	0	0.14	0.7164
chlorobenzene	0.718	0.65	0	0.07	0.8388
anisole	0.708	0.75	0	0.29	0.916
n-hexane	0	0	0	0	0.954
phenanthrene	2.06	1.29	0	0.29	1.454
chlorobenzene	0.72	0.65	0	0.07	0.839
1,4-dichlorobenzene	0.83	0.75	0	0.02	0.961

Table S 4 K_S (L/mol) for 2-ketones using SHPD method

	NH ₄ NO ₃				NH ₄ Cl				Na ₂ SO ₄			
	K_S	SE	R ²	ΔK_S^a	K_S	SE	R ²	ΔK_S^a	K_S	SE	R ²	ΔK_S^a
2-hexanone	0.045	0.003	0.97	0.011	0.078	0.008	0.93	0.053	0.567	0.040	0.95	0.143
2-heptanone	0.065	0.003	0.99	0.005	0.125	0.007	0.97	0.032	0.887	0.050	0.97	0.075
2-octanone	0.066	0.004	0.98	0.004	0.148	0.005	0.99	0.045	0.987	0.066	0.96	0.003
2-nonanone	0.083	0.006	0.97	0.000	0.180	0.008	0.98	0.013	1.197	0.084	0.95	0.122
2-decanone	0.093	0.011	0.91	0.024	0.200	0.023	0.89	0.012	1.378	0.157	0.92	0.001

^a ΔK_S is the absolute difference of K_S between SPME and SHPD methods.

Table S 5 Comparison with literature data for K_S (L/mol)

	NH ₄ Cl		Na ₂ SO ₄		(NH ₄) ₂ SO ₄		NaCl	
	literature	this study	literature	this study	literature	Wang et al. ¹	Literature	Endo et al. ²
1-naphthol	0.101±0.005 ^a	0.03±0.007	NA	-	NA	-	0.209±0.008 ^a	0.182±0.009
toluene	0.055 ^b	0.112±0.05	0.65 ^b	0.59±0.04	0.415 ^b	0.465±0.016	0.267 ^b	0.221±0.024
toluene	0.136 ^c	0.112±0.05	0.651 ^c	0.59±0.04	0.428 ^c	0.465±0.016	0.225 ^c	0.221±0.024
toluene	NA	-	0.684 ^d	0.59±0.04	NA	-	0.242 ^d	0.221±0.024
ethylbenzene	NA	-	0.693 ^d	0.66±0.062	NA	-	0.28 ^d	0.238±0.025
propylbenzene	NA	-	0.748 ^d	0.848±0.06	NA	-	0.281 ^d	0.262±0.025

^a Almeida et al.⁴ ^b Sada et al.⁵ ^c Xie et al.⁶ ^d Sanemasa et al.⁷

Table S 6 Parameters of the ions

ion	radius ^a (r, Å)	charge (z)	z^2/r	ΔG_{hyd} (kJ/mol) ^b	ΔG_{hyd} (kJ/mol) ^c
SO ₄ ²⁻	2.58	2	1.55	NA.	-1080
Cl ⁻	1.84	1	0.54	-378	-340
NO ₃ ⁻	1.79	1	0.56	-314	-300
NH ₄ ⁺	1.37	1	0.73	-307	NA.
Na ⁺	1.02	1	0.98	-406	-365

^a data from <http://www.wiredchemist.com/chemistry/data/atomic-and-ionic-radii>

^b absolute enthalpies of hydration of gaseous ions from <http://www.wiredchemist.com/chemistry/data/enthalpies-hydration>

^c predicted hydration energies from ref.⁸

Table S 7 Literature data (K_S in L/mol) for pp-LFER comparison in Figure 2 and additivity testing in Figure 3

	NH ₄ NO ₃	NH ₄ Cl	Na ₂ SO ₄	(NH ₄) ₂ SO ₄	NaCl	References
chloroform	0.0239±0.034	0.0717±0.022	0.502±0.014	0.309±0.031	0.208±0.037	ref. ⁹
benzene	0.0746±0.03	0.124±0.021	0.519±0.016	0.366±0.035	0.248±0.060	ref. ⁹
chlorobenzene	0.0342±0.031	0.126±0.026	0.565±0.02	0.374±0.042	0.257±0.052	ref. ⁹
anisole	0.0123±0.031	0.118±0.023	0.635±0.016	0.415±0.021	0.225±0.033	ref. ⁹
benzene	NA.	0.103	0.548	0.405	0.195	ref. ⁶
toluene	NA.	0.136	0.651	0.428	0.225	ref. ⁶
o-xylene	NA.	0.102	0.641	0.496	0.227	ref. ⁶
m-xylene	NA.	0.153	0.691	0.551	0.248	ref. ⁶
p-xylene	NA.	0.099	0.656	0.499	0.251	ref. ⁶
naphthalene	NA.	0.071	0.695	0.476	0.260	ref. ⁶
n-hexane	NA.	0.181	0.788	NA.	NA.	ref. ⁶
biphenyl	NA.	NA.	0.846	NA.	NA.	ref. ⁶
phenanthrene	NA.	NA.	0.784	NA.	NA.	ref. ⁶
chlorobenzene	NA.	NA.	0.580	NA.	NA.	ref. ⁶
p-dichlorobenzene	NA.	NA.	0.586	NA.	NA.	ref. ⁶

Figure S 3 Correlation of K_S for different salts (N=33 for NH_4NO_3 and N=38 for other salts). The error bars show the standard error in each measurement. The correlation between the K_S for NaCl and $(\text{NH}_4)_2\text{SO}_4$ has been previously described⁵ and is not shown here.

		2-ketones	Alkylbenzenes
number of methylene group	Na ₂ SO ₄	$Y=(0.160\pm0.020)X+(0.192\pm0.105) R^2=0.954$	$Y=(0.123\pm0.009)X+(0.574\pm0.022) R^2=0.985$
	(NH ₄) ₂ SO ₄	$Y=(0.035\pm0.003)X+(0.374\pm0.018) R^2=0.972$	$Y=(0.030\pm0.013)X+(0.493\pm0.032) R^2=0.644$
	NaCl	$Y=(0.030\pm0.003)X+(0.114\pm0.015) R^2=0.971$	$Y=(0.021\pm0.001)X+(0.220\pm0.002) R^2=0.994$
	NH ₄ Cl	$Y=(0.012\pm0.006)X+(0.105\pm0.029) R^2=0.615$	$Y=(0.010\pm0.001)X+(0.114\pm0.002) R^2=0.978$
	NH ₄ NO ₃ ^a	$Y=(0.015\pm0.004)X+(0.003\pm0.020) R^2=0.830$	$Y=(0.010\pm0.002)X+(0.074\pm0.003) R^2=0.943$
McGowan molar volume/100	Na ₂ SO ₄	$Y=(1.136\pm0.144)X+(-0.430\pm0.182) R^2=0.954$	$Y=(0.875\pm0.063)X+(-0.176\pm0.073) R^2=0.985$
	(NH ₄) ₂ SO ₄	$Y=(0.251\pm0.024)X+(0.236\pm0.030) R^2=0.973$	$Y=(0.214\pm0.092)X+(0.310\pm0.106) R^2=0.644$
	NaCl	$Y=(0.213\pm0.021)X+(-0.003\pm0.027) R^2=0.979$	$Y=(0.145\pm0.006)X+(0.095\pm0.007) R^2=0.994$
	NH ₄ Cl	$Y=(0.212\pm0.018)X+(-0.119\pm0.023) R^2=0.954$	$Y=(0.068\pm0.006)X+(0.056\pm0.007) R^2=0.978$
	NH ₄ NO ₃ ^a	$Y=(0.104\pm0.027)X+(-0.054\pm0.034) R^2=0.830$	$Y=(0.0732\pm0.013)X+(0.012\pm0.014) R^2=0.943$

^a Data for pentylbenzene in NH₄NO₃ were excluded due to quality.

Figure S 4 Dependence of K_s on number of methylene group and McGowan molar volume (cm³/mol) for 2-ketones and alkylbenzenes for different salts

Table S 8 Data used in Figure 3

	NaCl-NH ₄ Cl		1/2(Na ₂ SO ₄ -(NH ₄) ₂ SO ₄)		Na ₂ SO ₄ -2NaCl		(NH ₄) ₂ SO ₄ -2NH ₄ Cl		Na ₂ SO ₄ +2*NH ₄ Cl		2*NaCl+(NH ₄) ₂ SO ₄	
	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE
Toluene	0.109	0.025	0.062	0.022	0.148	0.063	0.240	0.020	0.810	0.040	0.910	0.050
Ethylbenzene	0.112	0.026	0.068	0.033	0.184	0.080	0.274	0.030	0.910	0.060	1.000	0.060
propylbenzene	0.127	0.027	0.127	0.031	0.324	0.078	0.323	0.026	1.120	0.060	1.120	0.050
Butylbenzene	0.145	0.026	0.163	0.055	0.370	0.119	0.334	0.028	1.220	0.110	1.180	0.050
pentylbenzene	0.147	0.025	0.247	0.093	0.467	0.182	0.265	0.061	1.370	0.180	1.170	0.080
heptanal	0.130	0.018	0.142	0.075	0.258	0.149	0.234	0.037	0.950	0.150	0.920	0.040
octanal	0.122	0.022	0.142	0.044	0.299	0.092	0.259	0.038	1.110	0.080	1.080	0.050
1-nitrohexane	0.116	0.012	0.107	0.033	0.303	0.069	0.321	0.017	1.010	0.070	1.030	0.020
1-nitropentane	0.119	0.010	0.056	0.018	0.053	0.037	0.180	0.016	0.630	0.030	0.750	0.020
4:2 FTOH	0.092	0.012	0.084	0.049	0.232	0.097	0.249	0.025	1.140	0.100	1.160	0.020
6:2 FTOH	0.163	0.013	0.218	0.057	0.410	0.109	0.299	0.041	1.600	0.110	1.490	0.030
2-hexanone	0.067	0.009	0.114	0.020	0.314	0.039	0.219	0.020	0.970	0.040	0.880	0.010
2-heptanone	0.076	0.009	0.153	0.016	0.346	0.028	0.193	0.023	1.130	0.030	0.970	0.020
2-octanone	0.080	0.005	0.214	0.018	0.437	0.032	0.171	0.018	1.370	0.030	1.100	0.020
2-nonanone	0.134	0.007	0.238	0.039	0.473	0.075	0.265	0.024	1.410	0.080	1.200	0.020
2-decanone	0.126	0.018	0.384	0.062	0.751	0.124	0.235	0.038	1.760	0.130	1.240	0.030
benzophenone	0.148	0.006	0.056	0.034	0.191	0.066	0.375	0.019	0.940	0.070	1.130	0.020
valerophenone	0.146	0.013	0.125	0.032	0.312	0.065	0.354	0.023	1.100	0.060	1.150	0.030
bisphenol a	0.080	0.013	0.073	0.029	0.156	0.058	0.172	0.025	0.690	0.060	0.710	0.030
1-naphthol	0.152	0.011	0.139	0.019	0.212	0.042	0.236	0.015	0.640	0.040	0.660	0.020
1-hexanol	0.106	0.005	0.072	0.018	0.168	0.036	0.235	0.008	0.840	0.040	0.910	0.010
4-ethyl-3-hexanol	0.156	0.007	0.081	0.021	0.113	0.040	0.262	0.016	0.970	0.040	1.110	0.010
2-butoxyethanol	0.109	0.011	0.154	0.029	0.287	0.057	0.196	0.025	0.910	0.050	0.820	0.030
2-phenylphenol	0.172	0.013	0.191	0.036	0.331	0.071	0.292	0.027	1.080	0.070	1.040	0.030

Table S 8 (continued)

	NaCl-NH ₄ Cl		1/2(Na ₂ SO ₄ -(NH ₄) ₂ SO ₄)		Na ₂ SO ₄ -2NaCl		(NH ₄) ₂ SO ₄ -2NH ₄ Cl		Na ₂ SO ₄ +2*NH ₄ Cl		2*NaCl+(NH ₄) ₂ SO ₄	
	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE	<i>K_S</i>	SE
4-nitroaniline	0.126	0.010	0.040	0.029	0.098	0.058	0.270	0.018	0.240	0.060	0.410	0.020
4-nitroanisole	0.087	0.012	0.023	0.040	0.217	0.084	0.345	0.010	0.550	0.080	0.680	0.030
2,5-dimethylpyrazine	0.107	0.008	0.066	0.016	0.182	0.034	0.264	0.014	0.800	0.030	0.890	0.020
acetanilide	0.107	0.007	0.141	0.025	0.280	0.050	0.213	0.016	0.850	0.050	0.790	0.020
metalochlor	0.130	0.009	0.146	0.050	0.400	0.098	0.366	0.026	1.320	0.100	1.290	0.020
4-aminobiphenyl	0.056	0.012	0.232	0.043	0.633	0.079	0.281	0.041	1.350	0.080	1.000	0.040
atrazine	0.110	0.008	0.302	0.034	0.636	0.068	0.252	0.015	1.510	0.070	1.130	0.010
methyl phenyl sulfoxide	0.038	0.012	0.144	0.031	0.349	0.062	0.136	0.026	0.940	0.060	0.730	0.020
tri-n-butylphosphate	0.240	0.008	0.249	0.035	0.213	0.052	0.194	0.049	1.450	0.050	1.430	0.050
d-n-propylphthalate	0.198	0.007	0.214	0.024	0.360	0.045	0.328	0.023	1.460	0.040	1.430	0.020
4-fluorophenol	0.117	0.006	0.062	0.016	0.033	0.032	0.143	0.012	0.470	0.030	0.580	0.010
4-iodophenol	0.103	0.005	0.145	0.020	0.242	0.039	0.159	0.009	0.680	0.040	0.600	0.010
caffeine	0.074	0.008	0.047	0.030	0.248	0.057	0.302	0.025	0.560	0.060	0.610	0.030
carbazole	0.200	0.007	0.023	0.043	0.035	0.081	0.388	0.032	0.560	0.080	0.920	0.030
chloroform ^a	0.136	0.043	0.097	0.017	0.086	0.075	0.166	0.054	0.645	0.046	0.725	0.080
benzene ^a	0.124	0.064	0.077	0.019	0.023	0.121	0.118	0.055	0.770	0.040	0.860	0.130
chlorobenzene ^a	0.131	0.058	0.096	0.023	0.051	0.106	0.122	0.067	0.820	0.060	0.890	0.110
anisole ^a	0.107	0.040	0.110	0.013	0.185	0.068	0.179	0.051	0.870	0.050	0.870	0.070
benzene ^b	0.092	NA	0.072	NA	0.158	NA	0.199	NA	0.754	NA	0.795	NA
toluene ^b	0.089	NA	0.112	NA	0.201	NA	0.156	NA	0.923	NA	0.878	NA
o-xylene ^b	0.125	NA	0.073	NA	0.187	NA	0.292	NA	0.845	NA	0.950	NA
m-xylene ^b	0.095	NA	0.070	NA	0.195	NA	0.245	NA	0.997	NA	1.047	NA
p-xylene ^b	0.152	NA	0.079	NA	0.154	NA	0.301	NA	0.854	NA	1.001	NA
naphthalene ^b	0.189	NA	0.110	NA	0.175	NA	0.334	NA	0.837	NA	0.996	NA

^a Data from ref.⁹ ^b Data from ref.⁶

Table S 9 Comparison between SHPD and SPME Measurements

		SHPD					SPME				
		2-hexanone	2-heptanone	2-octanone	2-nonanone	2-decanone	2-hexanone	2-heptanone	2-octanone	2-nonanone	2-decanone
NH₄NO₃	<i>K_S</i>	0.045	0.065	0.066	0.083	0.093	0.056	0.060	0.063	0.083	0.117
	SE	0.003	0.003	0.004	0.006	0.011	0.003	0.004	0.005	0.005	0.010
	R ²	0.975	0.988	0.981	0.965	0.907	0.977	0.970	0.950	0.968	0.927
	SE/ <i>K_S</i>	6%	4%	5%	7%	12%	6%	7%	9%	6%	8%
NH₄Cl	<i>K_S</i>	0.078	0.125	0.148	0.180	0.200	0.131	0.157	0.193	0.167	0.188
	SE	0.008	0.007	0.005	0.008	0.023	0.008	0.008	0.004	0.006	0.015
	R ²	0.929	0.965	0.988	0.982	0.890	0.975	0.981	0.997	0.985	0.938
	SE/ <i>K_S</i>	10%	6%	3%	4%	12%	6%	5%	2%	4%	8%
Na₂SO₄	<i>K_S</i>	0.567	0.887	0.987	1.197	1.378	0.710	0.812	0.983	1.075	1.379
	SE	0.040	0.050	0.066	0.084	0.157	0.038	0.027	0.032	0.075	0.123
	R ²	0.953	0.969	0.957	0.953	0.917	0.981	0.992	0.993	0.958	0.940
	SE/ <i>K_S</i>	7%	6%	7%	7%	11%	5%	3%	3%	7%	9%
(NH₄)₂SO₄^a	<i>K_S</i>	0.464	0.492	0.540	0.642	N.A.	0.481	0.506	0.556	0.598	0.612
	SE	0.015	0.020	0.032	0.046	N.A.	0.012	0.016	0.016	0.021	0.022
	R ²	0.994	0.990	0.979	0.970	N.A.	0.994	0.990	0.992	0.988	0.987
	SE/ <i>K_S</i>	3%	4%	6%	7%	N.A.	2%	3%	3%	4%	4%
NaCl^b	<i>K_S</i>	N.A.	0.235	0.281	0.296	0.299	0.198	0.228	0.267	0.306	0.321
	SE	N.A.	0.018	0.015	0.017	0.013	0.004	0.003	0.003	0.003	0.009
	R ²	N.A.	0.949	0.976	0.970	0.984	0.997	0.999	0.999	0.999	0.994
	SE/ <i>K_S</i>	N.A.	8%	5%	6%	4%	2%	1%	1%	1%	3%

^a ref.¹ ^b ref.²

Figure S 5 Salting out effect in salt mixture (1: 1 mole ratio NaCl and $(\text{NH}_4)_2\text{SO}_4$) measured using the SHPD method. The Y axis $\log(K_{I/\text{salt water}}/K_{I/\text{water}})$ in the SHPD method corresponds to the logarithm of the ratio between GC peak areas in pure water and salt solutions ($\log(A_0/A)$). Because in the SHPD method, the aqueous phase concentration were measured. Blue and red squares (with equation and R^2) show observed salting out effect in the salt mixtures and calculated salting out effect by assuming additivity. Error bars for the observed values were calculated from 4 replicates at each concentration. Error bars for the calculated $K_{S,\text{mix}}$ values were calculated from standard errors of K_S for individual salt according to equation (2). In order to compare salting out effect of the mixtures to NaCl and $(\text{NH}_4)_2\text{SO}_4$, the salting out effect in NaCl and $(\text{NH}_4)_2\text{SO}_4$ solutions was shown by the orange and purple circles, respectively. p-values from analysis of covariance were shown for each compound.

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