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Influence of Solvent Polarity upon Salt Solubilities, III: Solubilities of KCl in Water/Tetrahydrofuran at 25 °C

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The solubilities of KCl in aqueous tetrahydrofuran at a temperature of 25 °C are reported together with a quasi-thermodynamic treatment of the experimental results.

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Einfluß der Lösungsmittelpolarität auf die Löslichkeit von Salzen, 3. Mitt.: Die Löslichkeit von KCl *in wäßrigem Tetrahydrofuran bei 25 °C*

Die Löslichkeit von KCl in wäßrigem Tetrahydrofuran bei einer Temperatur von 25 °C wird zusammen mit einer quasi-thermodynamischen Behandlung der experimentellen Daten diskutiert.

The first contribution[2] of this brief series has presented a quasi-thermodynamic derivation, incorporating the unabridged *Debye-Hückel* theory of electrolytes in solution[6], of the function[9],

$$\ln S = K - q\sqrt{S/D^3}/(1 + m\sqrt{S/D}), \tag{1}$$

whose final term in the second member shows that the influence of solvent polarity, as it is reflected in the saturated solvent's bulk dielectric constant (D), upon salt solubilities (S) is a direct consequence of the key role played by D in fixing the mean activity coefficient of any solute salt in saturated solution. Besides the symbols S and D, already identified, the remaining symbols, K, m and q in eqn. (1) are defined by the following functions:

$$K = Q/RT, \tag{2}$$

$$m = be\sqrt{g\pi N/125\,kT}, \tag{3}$$

and

$$q = \eta \nu e^3 \sqrt{\pi N/500\,(kT)^3}, \tag{4}$$

in which b is the so-called mean ionic diameter of solute salt in the well-known *D.-H.* theory[6] (better called the mean minimum interionic separation), e is the electronic charge, $g = \frac{1}{2}(\eta^2 \nu + \eta \nu^2)$, π and R have their usual significances, Q is a "standard" partial molar free energy of solution, earlier defined as the difference[2] between standard chemical potentials of the solute in the respective solid and saturation states, at atmospheric pressure and the working temperature (T) for the salt in the saturated solvent system, k is the Boltzmann constant, N is the *Avogadro* number, and η and ν are the respective absolute values of the cationic and anionic valences in the solute salt. Although conversion of eqn. (1) to a line-function[2] has helped both to simplify the computer-assisted determination of the parameters, K and m, whose direct estimation from known physical constants [as can readily be done for q through eqn. (4)] is not feasible in most practical cases, and to facilitate its presentation as a quite general descriptive isothermal function, presumably applicable to the solubilities of any salt up to any naturally occurring saturation concentration, it is regrettable that this change in form has inadvertently obscured not only the real nature of the effect of the solvent's D upon salt solubility, whose magnitude is not nearly as large as many "rule-of-thumb" practitioners suppose it to be, but also the fact that, in salt solubilities, the influence of solvent polarity tends to be functionally overshadowed by the "standard" partial molar free energy of solution [to which the parameter, K, in eqn. (1) is directly proportional]. Nevertheless, many careful measurements of salt solubilities have shown that the effects of solvent polarity upon them is definitely not insignificant.

Just as the presence of potassium acetate, as a concentrated solute, causes a strong "salting-out" effect[4] to separate the components of the mixed solvent, water/tetrahydrofuran, so also does the presence of KCl in saturation concentrations act, yet more strongly, to induce such a separation in which not quite all the *THF* is expelled from the eventual principally aqueous phase, leaving in it enough of the organic solvent-component to produce therein a bulk mean polarity rather markedly depressed from the usually relatively high polarity ($D = 78.56$) of water itself, thus giving that aqueous layer a relatively gradually varying range of bulk polarities from one such ternary mixture to another, it has been found[4] that, at equilibrium, the concentrations of KCl in the HCl-saturated organic phase are either zero or negligibly small. This circumstance has already proven itself very useful in preparative organic chemistry[5] where KCl saturation of an aqueous solution containing a comparatively non-polar carbohydrate derivative has made possible the easy recovery of that carbohydrate in a fairly pure from by conventional solvent-extraction into *THF*. Even though this method of extraction works beautifully well on a practical laboratory basis, since the presence of

KCl at saturation does not exclude absolutely all *THF* from the principally aqueous phase, thereby allowing the aforementioned depression of the mean polarity of the mixed-solvent in that phase, it has been of associated interest to learn precisely how the solubility of KCl in that phase is influenced by the presence of *THF* as one of the solvent components therein.

Toward that end, those KCl solubilities at 25 °C have been determined by using almost exactly the same procedures already described in detail[2]

Table 1. *Solubilities of* KCl *in water/tetrahydrofuran at 25 °C in relation to the mean solvent dielectric constants*

Solvent			Solubility [mol l^{-1}]
Composition by Weight		Mean Dielectric Constant	
%H_2O	%*THF*		
30.1	69.9	26.73	0.077
42.9	57.1	37.81	0.176
64.8	35.2	53.55	0.498
78.5	21.5	61.55	1.023
83	17	65.03	1.632
87.3	12.7	69.54	2.302
89	11	70.76	2.941
91.1	8.9	72.28	3.625
98.1	2.9	77.24	3.84

for determining the solubilities of potassium acetate in the same kinds of mixed-solvent media at 25 °C, with only the following changes:

a) The KCl used as solute salt was "Baker-analyzed" reagent-grade material from the J. T. Baker Company;

b) Both the standardization of the starting aqueous salt solution and all analyses of the eventual saturated solutions for their contents of KCl were performed by the well-known *Mohr* volumetric method, using chromate indicator for optimum sensitivity in determining end-points.

Table 1 lists the solubilities so determined, in relation to the estimated[2] (as weighted means of known dielectric constants for the pure solvent components) mean dielectric constants of the respective saturated solvent mixtures, and Table 2 presents the empirical values of K and m obtained as before[2] through fitting the whole body of data from Table 1 to eqn. (1) by aid of the electronic computer after having calculated the value of q

Table 2. *Empirical parameters required to fit the data of Tab. 1 to Equ. (1)*

Parameter	Value
K	—4.2498
m	8.9318

Table 3. *Mean minimum interionic separation (b) at saturation and "standard" partial molar free energy of solution (Q) for* KCl *in water/THF at 25 °C*

Property	Value	Units
b	306 638.17	Ångstroms
Q	—592.5	cal mol^{-1}

through eqn. (4) in which it is seen to be a simple function of well-known universal constants, together with the absolute temperature and the known ionic valences for the solute salt. The associated statistical analyses of this data-fit have shown it to have a chance that the fit is not merely fortuitous (previously called "significance") of 99.99 percent, and that the corresponding multiple correlation coefficient (previously called "reliability") is 0.9996, where a coefficient of unity signifies perfect correlation of the data by the equation. These generally excellent statistical measures tend to reinforce our previously expressed view that eqn. (1) (and also its linear form) is indeed a valid general function to describe the relationship between salt solubility and overall solvent polarity.

As has already been reported[2,3] concerning the similarly uni-univalent potassium carboxylates as solutes, the empirically determined parameters given in Table 2 have been used here to evaluate both the "standard" partial molar free energy (Q) and the mean minimum interionic separation (b) at saturation for KCl in this mixed-solvent at 25° through equations (2) and (3) to give the results presented in Table 3. Comparison of these results with the values for the corresponding physical quantities for the potassium carboxylates already reported[2] shows that the minimum interionic separation for KCl is substantially more than ten thousand times what it is for either carboxylate, and that the "standard" partial molar free energy of solution at 25 °C for KCl is intermediate between the corresponding values found[2] for potassium acetate and benzoate, respectively. At present, we have no facile general explanation of those comparative observations to offer, aside from noting that the empirical value of (b)

listed in Table 3 converts to a distance of a little more than 33 microns, a distance some four orders of magnitude too large to be reasonably attributed the physical significance of a "mean ionic diameter" for KCl, whose individual ionic dimensions, known from independent observations[7] demonstrate the absurdity of attributing to their average a value approximating 33 microns! On the other hand, it is evident that a distance this great is not at all an unreasonable interionic separation, especially for a strongly ionized inorganic salt. Attempts toward full elucidation of the questions raised by these empirical facts seem best deferred to the attention of other, hopefully more insightful, workers who eventually may wish to address the apparently unobvious considerations here involved. In this context, it may be encouraging to recall the precept, established by all scientific experience, that the perception of freshly evocative questions often constitutes no lesser progress than does the discovery of definitive answers. The latter has certainly been true of the well-known maze of puzzles which has stimulated development of the fruitful *Debye-Hückel* theory of electrolytes in solution[6].

Keeping in mind the apparent Law of Nature that the frequency and intensities of opinions usually are inversely proportional to the degree of actual understanding of those who promote them, we tend to believe that this communication, together with its precursors in this brief series, serves at last, some three-score years (a virtual "instant" in the long history of chemistry) after the promulgation of the *D.-H.* theory, to reinforce reasons to accept that theory's general validity—an acceptance which, since its first two decades (an even more "instantaneous" interval in the historical perspective just suggested), has principally rested upon copious confirmations of the *D.-H.* "limiting law", which is regrettably applicable only at extreme dilutions—"slightly contaminated solvents" as inveterate scoffers have pleased themselves to term them—largely based upon abundant meticulous electrical conductivity measurements upon numerous felicitously selected salts, whose reports have emanated from the laboratories of the Ohio State University. Readers of these last reflections may find it informative to know that they have doubtless been prompted by a thoroughly memorable piece of counsel[8] often given to perplexed research students by the late Professor Dr. *James W. McBain* of Stanford University. It may be fairly paraphrased as "An apparently 'intractable' problem is one for which any eventually found solution, that conforms to Nature, will most probably be correct".

References and Notes

[1] This is our third and final posthumous report upon the results of solubility determinations made by the late Dr. *John A. McNaney* during his active work in this laboratory; the previous contributions are references[1] and[2].

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[9] This function is seen to be identical to equation (15f) of reference[2] when one recalls that the symbols (*S*) and (*C*) have the same meaning in saturated solutions.