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The Solubilities of Two Representative Potassium Carboxylate Salts at 25 °C in the Aqueous Cyclic Ethers, 1,4-Dioxane and Tetrahydrofuran, and Their Relationship to Mean Solvent Polarity

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New measurements upon the respective solubilities of potassium acetate and benzoate at 25 °C in aqueous 1,4-dioxane and in aqueous tetrahydrofuran are reported, together with a quasi-thermodynamic development, from the union of chemical thermodynamics with the unrestricted result of the *Debye-Hückel* theory of electrolytes in solution, of a general theoretical function which in principle provides a summary descriptive expression of the relationship between the solibilities of any salt at any natural limiting concentrations and the polarities of its solvents.

(Keywords: Cyclic ethers, aqueous, as solvents for salts; Free energy of solution, "standard" partial molar, isothermal estimation; Interionic distances for potassium carboxylates at saturation in aqueous cyclic ethers at 25 °C; Potassium carboxylates, solubilities at 25 °C in aqueous cyclic ethers; Salt solubilities and solvent polarities; Solubilities of potassium carboxylates in aqueous cyclic ethers at 25 °C)

Die Löslichkeit von Kalium-Carboxylat-Salzen bei 25 °C in wäßrigen Lösungen von 1,4-Dioxan und Tetrahydrofuran und ihre Beziehung zur mittleren Lösungsmittelpolarität

Neue Messungen der Löslichkeiten von K-Acetat und K-Benzoat in wäßrigen Lösungen von 1,4-Dioxan bzw. THF wurden durchgeführt. Es wird eine quasi-thermodynamische Behandlung der Daten mit einer Kombination

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[†] This is an initial posthumous publication of solubility determinations performed by Dr. *John A. McNaney* before his untimely death during the afternoon of June 24, 1980 after he had cooperated in plans for their eventual disclosure in this manner.

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von chemischer Thermodynamik und einer uneingeschränkten *Debye-Hückel*-Theorie der Elektrolyte in Lösung angewandt; diese theoretische Beschreibung liefert eine Beziehung zwischen der Löslichkeit eines Salzes und der Lösungsmittelpolarität.

Introduction

The binary liquid mixture[1] resulting from the addition of 1,4-dioxane (Dioxan) to aqueous KOH have been found[2] to afford excellent media in which to accomplish the mild alkaline cleavage of several carbohydrate esters at room temperature. When we began to use this cleavage medium for preparative work[2], it was supposed upon intuitive grounds that the actual ester cleavages occurred principally at the biphasic interfaces of the mixture and that the byproduct potassium salt became dissolved in the principally aqueous phase, while the carbohydrate remained at all times in the principally organic layer from which the primary carbohydrate product was finally recovered. At length, after having admitted the fundamental fallibility of so facile an assumption in the absence of empirical facts to substantiate it, we began the first of a projected series of systematic investigations to determine the solubility behaviours in aqueous 1,4-dioxane of all the solute components present in the aforementioned reaction mixture. The first publication to result from those investigations[3] has shown that the byproduct salt, potassium acetate (KO*Ac*), resulting from the cleavage of a carbohydrate acetate, not only contributes its share to the "salting-out" effect which procedures the aforementioned biphasic character peculiar to electrolyte-containing aqueous 1,4-dioxane despite the usual miscibility of those solvent-components in all proportions in the absence of any electrolytic solute, but also becomes distributed in a partition equilibrium between the two liquid phases into which it helps to cause the solvent mixture to become divided. Further, it was subsequently observed that potassium benzoate (KO*Bz*), which is an analogous byproduct in the aforementioned alkaline cleavage of a carbohydrate benzoate, not only wholly fails to induce any salting-out between the components of aqueous 1,4-dioxane so that it cannot possibly become distributed between the layers of a resultant biphasic system as does KO*Ac*, but rather is precipitated as the pure salt when 1,4-dioxane is added to fairly concentrated aqueous KO*Bz*. Precisely the same phenomenon also ensues when tetrahydrofuran is added to the aqueous KO*Bz*, instead of 1,4-dioxane. These latter observations point directly toward the remarkable, too-obvious hypothesis that KO*Bz* is not at all ionically dissociated in these mixed-solvent media, because if it were a wholly ionized typical "strong" electrolyte, one would naturally expect its presence to produce a detectable salting-out effect between the respective components of the mixed solvent instead of the salt precipitation actually found. Although direct electrical conductivity measurements upon the saturated residual K*OBz* solutions resulting from the aforementioned mixtures would obviously appear to offer the best test of any such hypothesis concerning the ionization of K*OBz* as a strong electrolyte in these mixed-solvent media, we have chosen here to examine the question through solubility measurements chiefly because this approach both is much less costly and also offers opportunity to develop a theoretical rationale to describe mathematically the general relationship between salt solibilities and solvent polarity. To the extent the new function so derived may correctly describe this relationship, it has further appeared that the present comparative study of the respective solubilities of both K*OBz* and K*OAc* in similar mixed-solvent media affords a way to gain interesting physico-chemical insights into the relative conditions of the two salts in their saturated solutions.

Theory

In the attempt to devise a quantitative theoretical rationale to describe the relationship between salt solubilities and the polarities of their solvents, as reflected in the latter's dielectric constants, it has appeared that the soundest approach is to develop a straightforward union between the wholly general principles of chemical thermodynamics and the general result of the well-established *Debye-Hückel* theory of electrolytes in solution[4], carefully avoiding any recourse to the customary limiting approximations of that result which restrict its validity to extremely dilute solutions. In this way, the reasoning can be expected to lead directly to a solubility function able correctly to describe the foregoing relationship for the solubilities of any salt whatsoever at any usual saturation concentration likely to occur in nature. Having thus stated the methodology to be pursued, we first describe and define the several quantities that enter into the deduction, and then proceed to the method of reasoning itself, which is basically a very simple exercise in elementary algebra, employing the theoretical components already indicated.

Notation, Special Premises, and Conventions

Notation

Let the following symbols represent the quantities appearing in the subsequent reasoning.

A	a parameter of convenience, defined below, which is characteristic of the temperature and the solvent polarity.

a	chemical activity (energetically effective concentration) of the solute salt in saturated solution.
a_0	chemical activity of the solute salt in the solid state.
B	a second parameter of convenience, defined below, which also is characteristic of the temperature and the solvent polarity.
b	the so-called mean ionic diameter (better styled the mean distance of closest interionic approach) characteristic of the solute salt in saturated solution.
C	total concentration (moles per liter) of the solute salt in saturated solution.
D	mean dielectric constant, defined below, of a binary mixed solvent.
$D_{i,j}$	dielectric constant of a pure component, i or j, which becomes part of a binary mixed solvent.
e	the electronic charge.
$F_{i,j}$	weight-fraction of a given component, i or j, in a binary mixed solvent.
f	mean activity coefficient of a solute salt in saturated solution.
g	a proportionality coefficient, defined below, between ionic strength and total concentration of a solitary solute salt in saturated solution.
η	absolute value of cationic valence in the solute salt.
i	the so-called ionic strength of a saturated salt solution containing only one principal solute salt.
K	a third parameter of convenience, defined below, which is characteristic of the temperature and the chemical nature of the system.
k	the *Boltzmann* constant.
m	a fourth parameter of convenience, defined below, which is characteristic of both the temperature and the condition of the solute salt in saturated solution.
μ	chemical potential (partial molar free energy) of the solute salt in saturated solution.
μ^0	"standard" chemical potential of the solute salt in saturated solution.
μ_0	chemical potential of pure solute salt in the solid state.
μ_0^0	"standard" chemical potential of pure solute salt in the solid state.
N	the *Avogadro* number.
n	a fifth parameter of convenience, defined below, which is characteristic of both the temperature and the chemical nature of the saturated solution.
ν	absolute value of anionic valence in the solute salt.
Q	"standard" partial molar free energy of solution, defined below, for the solute salt in the mixed solvent.
q	a sixth parameter of convenience, defined below, which is characteristic of the temperature, the solvent polarity, and the valence-type of the solute.
R	the general gas-constant.
S	solubility of the solute salt; it is identical to C as identified above.
T	the absolute temperature.
z_+	the cationic valence in the solute salt, identically η.
z_-	the anionic valence in the solute salt; it is identical to $-\nu$.

Special Premises

Throughout the subsequent reasoning, the following assumptions are included as reasonable premises:

1. It is expressly assumed, *ab initio*, that the following interaction effects are absent from the system to which the reasoning applies:

a) any common-ion effects, and

b) all substance-specific interactions, such as chelations or special complex-formations between any species of solute ion and any component of the mixed-solvent.

2. It is implicitly assumed that the saturated solution contains no ions other than those arising from dissociation of the principal solute salt, which is presumed to be wholly ionized in the saturated solution.

These assumptions are deemed necessary, both to render the result of the derivation sufficiently general to provide an adequate description of the relationship between most salt solubilities and solvent polarity, and also with special respect to assumption # 2, to lead to such a descriptive function able to afford a reasonably respectable test of alternative hypotheses concerning the presence or absence of full ionization by a solute salt, such as the curious question concerning K*OBz* which has been noted above in the introduction. Anyone who may find these assumptions unacceptable for any reason is always at liberty to reject any or all of them and independently to develop whatever consequent special cases may appear relevant to any particular system or systems for which such rejection should seem advisable.

Convention and Definitions

It is convenient to employ the following convention and definitions:

1. The parameter, A, is defined as

$$A = e^3[\pi N/500(DkT)^3]^{1/2}. \tag{1}$$

2. According to customary practice, the chemical activity of any component (*e.g.* a solute salt) in a solution is defined as

$$a = Cf. \tag{2}$$

3. The parameter, B, is defined as

$$B = e(\pi N/125\, DkT)^{1/2}. \tag{3}$$

4. The mean dielectric constant, D, of a binary mixed solvent is easily computed from the weight-composition of the solvent mixture and the known dielectric constants (whose variations with changes in temperature are well-known to be negligible) of the respective components of that mixture by means of the well-known function for estimation of a weighted mean which, in the case of a binary mixture, has the specific form,

$$D = D_i F_i + D_j F_j. \tag{4}$$

5. According to the unrestricted result of the well-known *Debye-Hückel* theory of electrolytes in solution, the mean activity coefficient of any solute salt at any concentration can be expressed by

$$\ln f = -Az_+ z_- i^{1/2}/(l + b\, B i^{1/2}). \tag{5}$$

6. The proportionality coefficient, g, is defined as

$$g = \frac{1}{2}(\eta^2 \nu + \eta \nu^2) \tag{6}$$

because, inasmuch as the respective cationic and anionic concentrations in terms of total salt concentration are $C_+ = \nu C$ and $C_- = \eta C$, whilst the corresponding ionic valences are $z_+ = \eta$ and $z_- = -\nu$, the customary definition of ionic strength is to be written as

$$i = \frac{1}{2}(\eta^2 \nu + \eta \nu^2) C. \tag{6 b}$$

7. The parameter, K, is defined as

$$K = Q/RT. \tag{7}$$

8. The parameter, m, is defined as

$$m = be\,(g \pi N/125\,kT)^{1/2}. \tag{8}$$

9. The parameter, n, is defined as

$$n = -beK\,(g \pi N/125\,kT)^{1/2}. \tag{9}$$

10. Since every "standard" chemical potential (in the present cases, the respective μ^0 and μ_0^0) is commonly regarded as a peculiarly constrained "constant" characteristic of both the temperature and the pressure, it readily follows that the differences between two such "constants" pertaining to the same chemical system must also be a similarly constrained "constant", so that one may legitimately define a "standard" partial molar free energy of solution, Q, as

$$Q = \mu_0^0 - \mu^0. \tag{10}$$

11. The parameter, q, is defined as

$$q = \eta \nu e^3 \,[g \pi N/500\,(kT)^3]^{1/2}. \tag{11}$$

12. By well-known customary convention, the chemical activity, a_0, of any pure substance, especially in the solid state, may be arbitrarily fixed at unity, so that one may write

$$a_0 = 1. \tag{12}$$

Method of Reasoning

It is both advisable and most feasible to commence with the well-known fact that the so-called solubility of any solid substance in a liquid medium is but a measure of that solid's concentration in the liquid phase when its solid and dissolved conditions exist in dynamic equilibrium with one another. This equilibrium can be most generally stated in terms of the chemical thermodynamic condition of equilibrium applied to such a solute, namely

$$\mu = \mu_0. \tag{13}$$

Since these chemical potentials are thermodynamically defined as

$$\mu = \mu^0 + RT \ln a \tag{14 a}$$

and

$$\mu_0 = \mu_0^0 + RT \ln a, \tag{14 b}$$

their explicit introduction into the equilibrium condition immediately expands eqn. (13) to

$$\mu_0^0 + RT \ln a_0 = \mu^0 + RT \ln a, \tag{15 a}$$

in which obvious transpositions and collections of terms leads to the form,

$$\mu_0^0 - \mu^0 = RT (\ln a - \ln a_0). \tag{15 b}$$

Now, the introduction of definitions (10) and (7), together with the convention (12), alters (15 b) to the simple form,

$$K = \ln a, \tag{15 c}$$

which by substitution for a according to eqn. (2) becomes expanded to

$$K = \ln C + \ln f. \tag{15 d}$$

Further substitution for ln$f$ according to eqn. (5) again expands (15 d) to

$$K = \ln C - A z_+ z_- i^{1/2} / (l + b B i^{1/2}), \tag{15 e}$$

which readily becomes

$$K = \ln C + q (C/D^3)^{1/2} / [l + m (C/D)^{1/2}] \tag{15 f}$$

when one recalls that $z_+ = \eta$ and $z_- = -\nu$ and also takes account of the respective definitions of A, B, i, m and q given above in equations (1), (3), (6), (8) and (11). If the foregoing reasoning be correct, eqn. (15 f) basically provides a methematically implicit function to describe the relationship at constant temperature between the saturation concentration (*i.e.* the solubility, since $S = C$) of any strong-electrolyte salt and the dielectric constant of any solvent into which its dissolution to a saturation equilibrium may occur. For the practical case of any given system of salt solubilities, all that remains necessary to complete the description is to make a corresponding empirical determination of the respective parameters, K, m and q pertaining to the system in question. These determinations can be facilitated by converting eqn. (15 f) to a linear form which is well suited to the conventional procedure of curve fitting by the method of least squares. Such a conversion is readily accomplished when one multiplies eqn. (15 f) through by the denominator of its final term to clear it of the fractional character peculiar to that term, and then transposes selected terms to obtain the result,

$$\ln S = K - m/S/D) \ln S/D)^{1/2} - q (S/D^3)^{1/2}; \tag{16}$$

after having introduced the notational fact that $S = C$. Used in this form, eqn. (16) is best to be considered simply as an isothermal descriptive expression of the functional relationship between salt solubilities and solvent polarity, of which eqn. (15 f) is the directly derived theoretical form.

Experimental

Materials

1. *Potassium acetate* used in this work was "Baker-Analyzed" reagent-grade material (assayed at 99.0% pure) obtained from the J. T. Baker Company.

2. *Potassium benzoate* used here was prepared by the stoichiometric neutralization of aqueous "Baker-Analyzed" reagent-grade benzoic acid by standardized aqueous KOH, and the resulting aqueous salt solution was evaporated to dryness.

3. *1,4-Dioxane* was purified by distillation of the J. T. Baker technical-grade material over metallic sodium according to *Vogel*[5].

4. *Tetrahydrofuran* was "Baker-Analyzed" reagent-grade material having a density of 0.881 gm per ml and a boiling range of 65.8-66.4 °C.

5. Standard *Karl-Fischer* reagent was obtained from the Allied Chemical Co.

Procedures

Separate stock solutions of each of the respective potassium salts (*vide supra*) were prepared in CO_2-free distilled water, and each such solution was standardized[6] against standard perchloric acid in glacial acetic acid, using methyl violet as the indicator.

In a typical trial, a measured volume of the selected standard aqueous salt solution (*vide supra*) was magnetically stirred in a stoppered, jacketed reaction flask maintained at 25 °C by constantly circulating water from a thermally regulated reservoir through the jacket. From a buret penetrating the stopper, the selected cyclic ether (Diox. or *THF*) was slowly dropped into the stirred solution until appearance of the *Tyndall* effect indicated that an inhomogeneity had been produced in the mixture. (When the solute was KO*Bz*, this indication coincided with the commencement of that salt's precipitation; but when the solute was KO*Ac*, the indication often showed the first appearance of a second liquid phase, and during the subsequent equlibration period, the salt generally became deposited in the solid state.) Upon the appearance of the *Tyndall* effect, the volume of cyclic ether delivered to reach that point was recorded, and the mixture was stirred at the same constant temperature for eight hours to assure the attainment of equilibrium composition amongst all phases present, and at the end of that period, the mixture was filtered at the equilibrium temperature to remove all precipitated salt. The filtrate from the system containing KO*Ac* was separated to segregate the principally aqueous phase which, as well as the filtrate from the system containing KO*Bz*, was divided into equal portions, each of which was weighed and its density was determined before they were subjected to the following analytic determinations. One of the respective foregoing aliquot portions was analyzed to determine its content of potassium salt by the same method already indicated (*supra*) for the standardizations of the respective aqueous stock solutions. The second such portion from each system was titrated with standard *Karl-Fischer* reagent to determine its content of water. Each of these analytic results was converted to the respective weights of water and potassium salt in the saturated solution, and the sums of these weights were used, together with the previously determined weight of each sample, to estimate the weight of cyclic ether in the saturated solution.

Duplications of the foregoing procedures, using in each case the same proportions of the respective aqueous salt solutions and the cyclic ethers, were performed to assure the accuracy of each reported solubility datum within one percent. Literature values for the respective dielectric constants of the pure solvent-components were used, together with the respective mixed-solvent weight-compositions estimated from the analytical results (*supra*) in the saturated solutions to calculate the mean dielectric constant of the mixed-solvent corresponding to each solubility datum reported in the first two Tables.

Results and Discussion

The solubilities at 25°, determined for KO*Ac* in the respective aqueous cyclic ethers, 1,4-dioxane and tetrahydrofuran, are listed, together with the mean dielectric constants of the solvent corresponding to each solubility datum, in Table 1. Similarly, Table 2 presents the same kinds of associated data found for KO*Bz* in the same types of solvent mixtures at 25 °C.

Table 1. *Solubilities of* KO*Ac at 25 °C in aqueous cyclic ethers in relation to the mean dielectric constants of the solvents*

Mean Dielectric Constant	Solubility (mol/l) in Water/Dioxan	Water/*THF*
12.94	0.034	
14.51	0.057	
27.01		0.0035
30.29	1.699	
34.05		0.0819
38.37	0.967	
45.45		0.1807
48.84	1.844	
53.26		0.417
55.76	3.3	
62.19		0.496
62.54	4.39	
74.32		5.307
76.50		8.234

Data Treatment

Each of the respective sets of associated data shown in Tables 1 and 2 was fitted to equation (16) by the method of least squares with the aid of the electronic computer to make empirical determinations of the

Table 2. *Solubilities of* K*OBz at 25 °C in aqueous cyclic ethers in relation to the mean dielectric constants of the solvents*

Mean Dielectric Constant	Solubility (mol/l) in Water/Dioxan	 Water/*THF*
2.1	0.0067	
9.32		0.0028
12.71		0.227
16.9	0.007	
17.1	1.769	
17.4	0.4	
17.86		0.638
24.8		1.311
26.5	0.167	
33.09		2.092
44.05	2.802	
49.72	2.802	
55.56	3.539	
58.64	4.671	

Table 3. *Empirical parameters required to fit all data of Table 1 to Eqn. (16)*

Parameter	Value
K	-5.173
m	7.611
n	45.214
q	495.838

several parameters respectively listed in Tables 3 and 5, and the results of the empirical fits so obtained were thoroughly tested to evaluate both their statistical significance and the reliabilities of the respective correlations thus established. The results of these tests are included in the following discussion. Using the empirical parameters summarized in Table 3, eqn. (16) has a statistical significance of 96.79% in describing the relationship between all the K*OAc* solubilities and the corresponding mean dielectric constants of the mixtures comprising the solvent media in the saturated solutions at 25 °C regardless of the nature of the cyclic ether in any given mixture, and also the multiple correlation coefficient corresponding to that fitting of the data is 0.984 upon a scale ranging from zero (no correlation) to unity (perfect correlation). These statistical measures show that the combined solubility data for K*OAc*

Table 4. *Empirical parameters to fit* K*OAc solubilities at 25 °C in water/1,4-dioxane to Eqn. (16)*

Parameter	Value
K	—4.6914
m	6.295
n	39.764
q	433.364

Table 5. *Empirical parameters required to fit data of Table 2 to Eqn. (16)*

Parameter	Value
K	—0.16565
m	0.32026
n	—0.40043
q	—0.001046

at 25 °C and the corresponding polarities of the respective saturated solvents fit the description offered by eqn. (16) sufficiently well in this particular case to indicate quite well both that eqn. (16) provides a reasonably valid empirical function to describe the isothermal relationship between salt solubility and solvent polarity, and also that this relationship is not significantly influenced by the specific nature of the cyclic ether present in these respective solvent mixtures. In order to gain, at the least, a minimal conception of the degree of confidence to which this latter indicated conclusion may be entitled, we have also segregated from Table 1 the data pertaining only to the K*OAc* solubilities in aqueous 1,4-dioxane, and have similarly fitted them to eqn. (16) to determine the admittedly less general set of empirical parameters shown in Table 4. Equivalent statistical analysis of these latter results shows that these parameters fit the segregated data to eqn. (16) with a statistical significance of 99.9% and also that the corresponding multiple correlation coefficient (*vide supra*) is 0.999. Both of the foregoing multiple correlation coefficients approach to unity closely enough to afford strong support to the conclusion that the solubilities of K*OAc* at 25 °C are indeed much more effectively a function of the mean solvent polarity, as measured by the mean dielectric constant, than they might be of the specific natures of the respective organic components in the mixed solvents studied here, and the measures of statistical significance stated above to have been found for the respective fittings of both the complete set of data in Table 1 and only the segregated data pertaining specifically to the solubilities in aqueous dioxane to eqn. (16) are both high enough and in sufficiently good agreement with each other to indicate not only that the foregoing conclusion concerning the relative unimportance of the mixed-solvent's cyclic ether component as any other than a modifier of the bulk dielectric constant is most probably correct, but also that eqn. (16) is indeed a valid empirically descriptive isothermal function worth testing both with the isothermal solubilities of other salts and at temperatures significantly divergent from the one chosen for the present work, and further that its immediate precursor, namely eqn. (15f), has been correctly derived, including the special premises which have been made part of that derivation. Although we should have preferred further to test eqn. (16) as an empirical descriptive isothermal function with other solute salts of more complex valence-types than the simple 1—1 type represented by KO*Ac* and hope eventually to do so unless anticipated by other workers, the data here reported in Table 2 for the solubilities of KO*Bz* in the same kinds of mixed-solvent media used as solvents for KO*Ac* do indeed afford material for a further test of the function, despite the regrettably obvious fact that, like KO*Ac*, KO*Bz* has the 1—1 valence-type, the simplest one possible. Inasmuch as the obviously best procedure for a systematic investigation of this question is to work progressively from the simplest cases toward the more complex, it appears both desirable and fortuitously expedient to begin that procedure here by making maximum possible use of the pragmatic information already in hand. Toward that end, the complete set of data given in Table 2 has been fitted to eqn. (16) in the same manner as before to obtain the corresponding empirical parameters shown in Table 5. Using these parameters, eqn. (16) has been found to reproduce the parent data from Table 2 with a statistical significance of 45.54%, and the corresponding multiple correlation coefficient for that data-fit is found to be 0.675. Although these statistical measures obviously do not precisely agree with the values found for their counterparts when the solute is KO*Ac* in the same kinds of mixed-solvent media, it is the more useful course to let them speak only for themselves rather to expect perfect agreement, especially because the obvious differences in the behaviours of the respective salts which have already been mentioned in the introduction must surely indicate substantial differences between the relative conditions of the two salts in their respective saturated solutions. With regard to the KO*Bz* solubilities,

Table 6. *Mean minimum interionic separations of* KO*Ac and* KO*Bz at 25 °C in saturated water/dioxane and water/THF*

Solute Salt	Mean Minimum Separation (Å)
KO*Ac*	2.6
KO*Bz*	0.11

the foregoing multiple correlation coefficient is still large enough to indicate that eqn. (16) provides a reasonably correct, through distinctly less than perfect, isothermal summary of the relationship between the measured KO*Bz* solubilities at 25 °C and the corresponding gross solvent polarities. Moreover, not only does this indication tend to show that KO*Bz* is indeed a fully ionized electrolyte in the saturated solutions investigated here, despite its failure to exert any perceptible salting-out influence upon any component of the respective solvent mixtures, but also further inquiry to compute the respective mean minimum interionic separations for the two salts in their saturated solutions reveals an apparently good reason for the marked difference between their behaviours with respect to the presence or absence of a salting-out effect—a reason which will be seen to be not inconsistent with the total ionization of KO*Bz* in the solvent media studied here. These mean minimum interionic separations can easily be estimated by means of eqn. (8) with the aid of the respective empirical parameters, m, listed in Tables 3 and 5. The results of those respective calculations are presented together for convenient comparison in Table 6. The fact that the mean minimum interionic separation so found for KO*Bz* in its saturated solutions at 25 °C turns out to be only about $^1\!/_9$ Å an exceedingly short distance even upon the scale normally expected of interionic distances, both greatly helps to explain the otherwise astonishing observation that the presence of KO*Bz* wholly fails to induce any salting-out effect in these mixed-solvent media whilst that effect is quite strong when the solute is KO*Ac* or any of several other simple "strong" electrolytes, and when considered in light of the final clause of assumption #2 among the premises to the derivation of eqn. (15 f), also tends to refute the too-obvious hypothesis, likewise remarked in the introduction, that KO*Bz* in these media displays an extraordinarily unique property by failing to dissociate ionically as a "strong" electrolyte should. In this context, it is also of interest to notice that the minimum interionic separations summarized in Table 6 indicate that, on the average, the ions of KO*Ac* in their

Table 7. *"Standard" partial molar free energies of solution for* KO*Ac and* KO*Bz in water/dioxane and water/THF*

Solute Salt	"Standard" Partial Molar Free Energy of Solution (cal/mol)
KO*Ac*	—3065.021
KO*Bz*	—98.148

respective saturated solutions at 25 °C, are more than twenty times as widely separated than are those of KO*Bz* in its saturated solutions at 25 °C. One may remark in passing that it would doubtless be more interesting to learn how such interionic distances may compare amongst solute salts of more complex valence-types than the extremely simple, symmetric cases considered here. To the extent that the general derivation culminating in eqn. (15 f) permits a relatively simple estimation, by aid of the "empirical" function (16), of such distances through the results of further suitably systematic solubility determinations, it seems reasonable to suggest that the methods presented here offer a new way to obtain information about the characters of electrolytes in solution, which has previously been inaccessible except by aid of equipments too costly for many laboratories to acquire merely for application to so special a purpose.

Yet a further apparently useful feature of the foregoing theory is the means offered by eqn. (7) to make an isothermal calculation of "standard" partial molar free energy of solution for any salt by aid of the corresponding empirically determined parameter, K, which can be found by fitting an appropriate set of systematic solubility determinations to eqn. (16). As an illustration of that feature, Table 7 compares the respective values of that property so computed for KO*Ac* and KO*Bz* in the solvent systems studied here. Here, it is of somewhat more than passing interest to notice that the magnitude of this quantity for KO*Ac* is considerably more than thirty-fold its magnitude for KO*Bz*. At present, we suspect that this marked disparity may be related, in a way we cannot yet specify, to the previously noted large ratio between the mean minimum interionic separations found for the same salts at saturation in the same types of medium. Of course, it is well understood that any such partial molar free energy of solution should not become accepted as definitive until it has been independently confirmed more directly by calorimetric measurements which always remain the standard approach in that area.

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