Monatshefte für Chemie 115, 1039—1045 (1984)

Monatshefte für Chemie
Chemical Monthly

Influence of Solvent Polarity upon Salt Solubilities, II**: Solubilities of Two Potassium Carboxylates at 85 °C in Aqueous 1,4-Dioxane

John A. McNaney**, **Franz M. Zimmerman**,
and **Howard K. Zimmerman***

Department of Chemistry, University of the Pacific,
Stockton, CA 95204, U.S.A.

(Received 22 February 1984. Accepted 1 March 1984)

The solubilities of potassium acetate and benzoate in aqueous 1,4-dioxane at a temperature of 85 °C are reported together with a quasi-thermodynamic general treatment of the experimental results.

(Keywords: Free energy of solution; Interionic separations; Quasi-thermodynamic)

Einfluß der Lösungsmittelpolarität auf die Löslichkeit von Salzen, 2. Mitt.: Die Löslichkeit zweier Kaliumcarboxylate in wäßrigem 1,4-Dioxan bei 85 °C

Die Löslichkeit von Kaliumacetat und Kaliumbenzoat in wäßrigem 1,4-Dioxan bei einer Temperatur von 85 °C wird zusammen mit einer quasithermodynamischen generellen Behandlung der experimentellen Daten diskutiert.

Our initial report upon the solubilities of potassium carboxylates, namely the acetate (KO*Ac*) and the benzoate (KO*Bz*) respectively in the aqueous cyclic ethers, 1,4-dioxane (Diox.) and tetrahydrofuran (*THF*), has presented evidence to indicate both that the solubilities of these salts at 25 °C in those mixed-solvent media appear to be much more strongly affected by the overall solvent polarity as reflected in the average dielectric constant of the solvent mixture than by the nature of the organic component in the mixed media, and also that the relationship

---

** This brief contribution is a second report upon the results of systematic solubility measurements, commenced with Ref.[1], which have been performed by Dr. *John A. McNaney* during his abruptly truncated lifetime.

between the salt solubilities (S) at constant temperature and the mean dielectric constant (D) of the mixed-solvent appears to be adequately summarized by the mathematically implicit isothermal function *,

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

for which the immediately previous contribution[1] has offered a quasi-thermodynamic derivation, during the course of which the several empirical parameters, K, m, n and q, have been respectively defined as

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

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

$$n = beK\sqrt{g\pi N/125\,kT}, \tag{4}$$

and

$$q = \eta\,\nu\,e^3\sqrt{g\pi N/500\,(kT)^3}, \tag{5}$$

where g is defined quite generally in terms of the absolute values, η and ν, respectively, for the cationic and anionic valences in the solute salt to be

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

whilst b represents the "mean distance of closest interionic approach" (i.e., mean minimum interionic separation) among the solute ions in saturated solution at the temperature for which the isothermal function, eq. (1), has been applied, e represents the electronic charge, k is the *Boltzmann* constant, N is the Avogadro number, Q indicates the isothermal "standard" partial molar free energy of solution for the solute salt in the aqueous cyclic ether, R signifies the general gas-constant, and T is absolute temperature.

As a result of the foregoing findings that eq. (1) satisfactorily summarizes the respective solubility data at a constant temperature of 25 °C, one is fairly entitled to ask whether the same empirical function serves equally well to summarize a relevant set of mutually consistent data of the same nature determined at any other constant temperature, more especially one quite substantially different from 25 °C. Since we have chosen for the present work a thermal difference as great as 60 °C, namely the temperature of 85 °C where the comparatively high volatility of *THF* renders a fixed binary mixed-solvent composition

---

* This is the correct form of eq. (16) in Ref.[1] where it has been erroneously printed as a result of faulty proof-correction by the author.

containing *THF* extremely difficult, if not wholly impossible, to maintain, we have become obliged here to rely upon the aforementioned findings that the exact nature of the organic constituent in a binary mixed-solvent consisting of an aqueous cyclic ether (Diox. or *THF*) is of much lesser consequence to the solubilities of each of the respective subject salts in such a solvent than is the average bulk dielectric constant of that solvent, so that it consequently has appeared that the question, indicated above, to be investigated as the subject of this brief communication can quite feasibly be examined through measurements at 85 °C of the respective solubilities of KO*Ac* and KO*Bz* in aqueous 1,4-dioxane, a mixed-solvent whose composition is relatively free of uncontrollable fluctuations that may result from any selective evaporation of either solvent constituent at the working temperature.

Table 1. *Solubilities of* KO*Ac in water/diox. at 85 °C in relation to solvent polarity (D)*

Mean D (solvent)	Solubility, mol/l
14.14	0.038
15.95	0.0626
33.33	0.622
41.92	1.072
51.65	1.959
56.48	3.326

The determinations here reported used, *inter alia,* a standard aqueous KO*Bz* solution (as well as standard aqueous KO*Ac*) and 1,4-dioxane, both prepared in precisely the ways which have already been described[1], and the KO*Ac* used here was of the same high-assay reagent-grade material specified for use in our immediately previous communication[1]. Excepting the present significantly higher saturation temperature at 85 °C, the practical methods employed in making the present solubility determinations were substantially identical to those which have already been sufficiently described in detail in our first communication[1]. The respective sets of solubilities at 85 °C so established for KO*Ac* and KO*Bz* in aqueous 1,4-dioxane are separately listed as functions of the average overall mixed-solvent dielectric constants in Tables 1 and 2.

The adequacy with which eq. (1) serves as an isothermal descriptive summary at 85 °C for the latter respective sets of data has been tested by fitting each such set to eq. (1) to make empirical determinations of the several parameters noted above, using the same straightforward methods employed in the earlier work[1], to obtain the values summarized

Table 2. *Solubilities of* KO*Bz in water/diox. at 85° C in relation to solvent polarity (D)*

Mean D (solvent)	Solubility, mol/l
2.1	0.0067
16.9	0.0070
17.1	1.769
17.4	0.4
26.5	0.167
44.05	2.802
55.56	3.539
58.64	4.671
63.1	3.884
68.3	4.327
70.57	3.78
74.32	3.78
78.56	3.687

Table 3. *Empirical parameters required to fit data of Table 1 to eq. (1)*

Parameter	Value
K	-5.4623
m	8.7037
n	45.778
q	-441.732

in Tables 3 and 4 respectively. The corresponding statistical analyses of these results have shown that the data for the KO*Ac* solubilities fit eq. (1), using the corresponding empirical parameters from Table 3, with a statistical significance of 99.97 percent, and also that the equivalent statistical significance for the fit of the KO*Bz* data, using the parameters from Table 4, is 93.71 percent. The same analyses have shown that the corresponding multiple correlation coefficients, upon the usual scale ranging from zero (no correlation) to unity (perfect correlation) for the KO*Ac* data and the KO*Bz* data are 0.9999 and 0.968 respectively. Considered altogether, these respective statistical measures are distinctly good enough to indicate both that eq. (1) provides an excellent correlation of the data for both of the subject solute salts at 85 °C, and that the statistical significance of both these correlations is very good indeed. Upon these grounds, it strongly appears that eq. (1) serves very well as an empirical isothermal descriptive function to express the

Table 4. *Empirical parameters required to fit data of Table 2 to eq. (1)*

Parameter	Value
K	-3.996
m	0.8424
n	24.1792
q	-114.5839

Table 5. *Estimated "standard" partical molar free energy of solution and mean interionic separation for* K*OAc and* K*OBz at saturation in aqueous 1,4-dioxane at 85 °C*

Property	Value for KO*Ac*	Value for KO*Bz*	Units
Mean minimum interionic separation	3.28	0.32	Ångstrom
"standard" partial molar free energy of solution	$-3\,887.72$	$-2\,844.1$	cal/mol

isothermal dependence of salt solubilities upon solvent polarity as it is reflected in the mean bulk dielectric constant of the latter. Despite the foregoing statistical indications, it must of course be acknowledged that the case in favor of eq. (1) should never be considered as fully proven solely upon the basis of data limited only to the solubilities of simple salts of the 1-1 valence-type, of which both KO*Ac* and KO*Bz* constitute obvious representatives. Clearly, such "proof" will surely require the eventual testing of eq. (1) in connection with the solubilities of several salts of more complex valence-types, yet to be determined in a form suitable for such testing. We prefer to regard both the present work and its immediate predecessor[1] merely as constructive beginnings of a systematic attack upon the general problem.

The respective empirical parameters, m, listed in Tables 3 and 4 can be used to make secondary empirical estimations of the respective mean minimum interionic separations for KO*Ac* and KO*Bz* in their saturated solutions at 85 °C through solutions of eq. (3) to find the values of b corresponding to those respective parameters. The results of both those estimations are included in Table 5, together with the corresponding "standard" partial molar free energies of solution for the respective salts at 85 °C, which have been similarly calculated from eq. (2) by aid of the respective empirically determined parameters, K, from Tables 3 and 4. For the purpose of easy comparison, Table 6 lists together these respective derived properties as estimated from the present data and also from the previously reported[1] solubilities for the same salts in the same types of mixed-solvent media at 25 °C. In light of the marked differences, very similar at both 25 °C and 85 °C, between the salting-out effects attributable to both of these salts in the aqueous cyclic ethers, it is not wholly unexpected to notice that the mean minimum interionic separations for K*OBz* are both very short upon a normally expected interionic scale (only about one-ninth Ångstrom at 25 °C and somewhat less than three-ninths of an Ångstrom at 85 °C). So marked an evident close "packing" of the K*OBz* ions in the saturated solutions would clearly seem to encourage that salt's precipitation at both temperatures long before its presence could have an opportunity to induce any significant salting-out effect upon the components of either mixed solvent. At present it is tempting to speculate about what may be the limit of interionic separations required to differentiate those respective behaviors, but it is common experience that speculations usually are not notably instructive by themselves until they may lead to the formulation of testable hypotheses. While refraining from fruitless speculation on this subject for the present, one is surely permitted to wonder precisely how, and why, the obvious difference in energy concentrations between the saturated solutions at 25 °C and at 85 °C respectively affects the interionic separations of solute in general. In the latter context, it may be pragmatically relevant to notice from Table 6 that the thermal difference of sixty degrees is associated with a ratio of only about 1.27 between the interionic separations found for KO*Ac*, while the analogous ratio between the corresponding separations found

Table 6. *Comparison of mean minimum interionic separations and of the corresponding "standard" partial molar free energies of solution for* KO*Ac and* KO*Bz in saturated aqueous cyclic ethers at 25 °C and 85 °C*

Solute salt	Mean minimum interionic separation (Ångstroms) at		"Standard" partial molar free energy of solution (cal/mol) estimated at	
	25 °C	85 °C	25 °C	85 °C
KO*Ac*	2.6	3.3	−3 065.02	−3 887.72
KO*Bz*	0.11	0.32	−98.15	−2 844.1

for KO*Bz* is about 2.91. Since both of these solutes are of the identical simple 1-1 valence-type, it seems very probable that an answer to the foregoing general query will turn out to be considerably more complex than a simple electromagnetic function. Perhaps the greater than tenfold ratio between the isothermal interionic separations found for these respective salts in their saturated solutions at each of the different temperatures now being considered suggests that specific chemical differences (of a yet undetermined character) make a contribution no less important to the eventual outcome than do customarily acknowledged physico-chemical generalities.

Further pertinent to our previously acknowledged caution[1] about hasty acceptance of isothermally estimated "standard" partial molar free energies of solution without their independent confirmation by a recognized standard method is the comparison of this isothermally estimated property for the subject solutes as found from the solubility data at 25 °C and 85 °C respectively. Whereas the theoretical background[1] to eq. (1) might lead one to expect the value so found for this property to be the same for any given kind of chemical system, the comparative values indicate that its magnitude for KO*Ac* at 85 °C is some 1.27 times that at 25 °C, and the corresponding ratio for KO*Bz* is about 28.98. Inasmuch as it has previously[1] been pointed out in the definition of this property by chemical thermodynamic theory that this property is a constrained conditional "constant" characteristic of both pressure *and* temperature, it comes as no great surprise now to observe that its value has turned out to be so markedly dependent upon the temperature as these ratios so emphatically show.

References

[1] *McNaney J. A., Zimmerman F. M., Zimmerman H. K.*, Monatsh. Chem. **114**, 1321 (1983).
[2] *Debye P., Häckel H.*, Physikal. Z. **24**, 185 (1923).