995. *Hydration Equilibria of Aliphatic Aldehydes in* H_2O *and* D_2O.

By L. C. GRUEN and P. T. McTIGUE.

Hydration equilibrium constants for acetaldehyde, propionaldehyde, n- and iso-butyraldehyde, and chloral in H_2O and D_2O have been measured in the temperature range 25—90°. The equilibrium constant for formaldehyde has been determined in H_2O over the same temperature range. The effects of added electrolytes on the activity coefficients of the hydrates and free aldehydes have also been investigated.

OTHER workers have estimated spectrophotometrically the hydration equilibrium constants for formaldehyde,[1] acetaldehyde,[2-4] propionaldehyde,[2] n- and iso-butyraldehyde,[2] and chloral.[2,5] However, only in the work of Bell and Clunie [4] with acetaldehyde, and of Bell and McDougall [5] with chloral, has proper attention been given to temperature control, or care been taken in estimating the extinction coefficient of the unhydrated form in an aqueous medium. There are virtually no data for solvent isotope effects for these hydrations (see, however, ref. 6), and only scattered values of heats and entropies of hydration. The present investigation provides information on these quantities and we discuss some implications of the results.

EXPERIMENTAL

The technique was essentially the spectrophotometric one used by earlier workers.[4] A manually operated Hilger Uvispek spectrophotometer was used with an electrically heated, brass cell-block. Temperatures were measured and controlled with an S.T.C. F23 thermistor (resistance ~1500 Ω) which formed one arm of an a.c. bridge, the out-of-balance current of which operated a switch in the cell-block heating circuit.

The optical-density scale of the spectrophotometer was checked at 300 mμ with standard solutions of potassium nitrate. The scale was accurate to at least ±1%.

D_2O of 99·75% nominal purity was supplied by the Australian Atomic Energy Commission. Aldehydes, except formaldehyde and chloral, were laboratory-grade reagents purified by fractional distillation under nitrogen. Formaldehyde was supplied as aqueous solution and used unchanged; chloral was prepared by the action of concentrated sulphuric acid on chloral hydrate, then distilled in the same manner as the other aldehydes. Aldehyde solutions of known concentration were made up by weight, except for formaldehyde solutions which were analysed by treating a known volume of the solution with an excess of sodium sulphite and titrating the liberated alkali with standard acid.[7]

RESULTS

Experiments consisted of measuring the extinction coefficients of aqueous solutions of an aldehyde, at various concentrations, in matched, stoppered silica cells, of 1 or 10 mm. path-length as convenient. We express our hydration equilibrium constants in the form

$$K_{\mathrm{h}}(T)\ \{\text{or } K_{\mathrm{d}}(T)\} = [\mathrm{H}]y_{\mathrm{H}}/[\mathrm{A}]y_{\mathrm{A}}, \qquad (1)$$

where $K(T)$ is an equilibrium constant at temperature T and the subscripts h and d refer to H_2O and D_2O, respectively. H represents the aldehyde hydrate, A the free aldehyde, and y_{H} and y_{A} are molar acitivity coefficients. If we let the extinction coefficient of free aldehyde in water be ε_{∞} at the wavelength of maximum absorption (~280 mμ), then $[\mathrm{A}]_{\mathrm{T}} \propto \varepsilon_T$, where ε_T

---

[1] Bieber and Trumpler, *Helv. Chim. Acta*, 1947, **30**, 1860.
[2] Herold, *Z. phys. Chem.*, 1932, *B*, **18**, 265.
[3] Lombardi and Sogo, *J. Chem. Phys.*, 1960, **32**, 635.
[4] Bell and Clunie, *Trans. Faraday Soc.*, 1952, **48**, 439.
[5] Bell and McDougall, *Trans. Faraday Soc.*, 1960, **56**, 1281.
[6] Pocker, *Proc. Chem. Soc.*, 1960, 17.
[7] Walker, "Formaldehyde," Reinhold, New York, 1944, p. 256.

is the extinction coefficient of the aldehyde solution at temperature T, and therefore $[\mathrm{H}]_T \propto \varepsilon_\infty - \varepsilon_T$. Thus

$$K(T) = (\varepsilon_\infty - \varepsilon_T)y_{\mathrm{H}}/\varepsilon_T y_{\mathrm{A}}. \qquad (2)$$

ε_∞ has usually been estimated by assuming that it is identical with the $\varepsilon_{\mathrm{max.}}$ determined in a hydrocarbon solvent. Bell and Clunie,[4] however, used a curve-fitting procedure to determine this quantity for acetaldehyde, and we similarly chose ε_∞ values such that our plots of log $K(T)$ against 10^3T^{-1} are linear over the temperature range 25—90°. Such a procedure requires that $\Delta H°$ and $\Delta S°$ for hydration remain constant within the quoted temperature range, and although this is almost certainly not exact, the error involved should be within the accuracy of the $\Delta H°$ values so determined (*i.e.*, about $\pm 0{\cdot}2$ kcal. mole^{-1}). In writing equation (2) it is also assumed that ε_∞ is independent of temperature, an assumption shown to be valid for acetone which is known to be unhydrated in water: the extinction coefficient of acetone at 280 mμ in aqueous solution varied by $\ngtr 1\%$ in the temperature range 25—90°. Further, we have assumed that in all dilute solutions of aldehydes in pure water, the molar activity coefficients y_{H} and y_{A} are equal to unity.

We have ignored any possible effects of the polymerisation equilibria of these aldehydes. The similarity of the K-values obtained at different aldehyde concentrations eliminates the possibility of significant errors from this source, except in the case of formaldehyde (see below).

An attempt was made to obtain a direct estimate of ε_∞ in one case, by breaking a bulb containing propionaldehyde in a known volume of water at pH 7 at 25° with continuous rapid stirring. The change in the transmitted intensity of a beam of light of wavelength 280 mμ passing through the solution was followed as a function of time, with a photomultiplier connected to a microammeter. A first-order extrapolation ($t_{\frac{1}{2}}$ was ~5 sec.) to zero time gave the extinction coefficient of the free aldehyde. Uncertainties, in part caused by glass fragments in the light beam, rendered the accuracy of the method inadequate and we could merely say that within error limits of about 25% the ε_∞ values obtained by this method agreed with those given in Table 1.

Table of ε *Values* (*Table* 1).—$\lambda_{\mathrm{max.}}$ is the wavelength in mμ of maximum absorption in spectroscopically pure cyclohexane; ε_{h} is the extinction coefficient in cyclohexane at this wavelength; $\lambda_{\mathrm{max.}}$ (aq.) is the wavelength of maximum absorption obtained for these aldehydes in aqueous solutions; ε_∞ has been obtained by the curve-fitting method described above. We have assumed that ε_∞ is the same in both H_2O and D_2O for any given aldehyde.

TABLE 1.

R in R·CHO	$\lambda_{\mathrm{max.}}$	ε_{b} Found	ε_{b} Lit.	$\lambda_{\mathrm{max.}}$ (aq.)	ε_∞	R in R·CHO	$\lambda_{\mathrm{max.}}$	ε_{h} Found	ε_{h} Lit.	$\lambda_{\mathrm{max.}}$ (aq.)	ε_∞
H ………	310	—	5 *	310	7	$\mathrm{Pr^n}$ ……	295	21·5	20·4 ‡	285	17·0
Me ……	290	16·1	16·2 [4]	278	14·5	$\mathrm{Pr^i}$ ……	295	21·6	18·4 ‡	285	17·7
Et ……	293	20·4	20·9 †	280	17·7	$\mathrm{CCl_3}$……	290	36·9	38·3 [5]	290	37

* Value from Reid and Cohen (*J. Chem. Phys.*, 1956, **24**, 85) for solution in isopentane at −70°.
† Hershenson, " Ultraviolet and Visible Absorption Spectra," Academic Press Inc., New York, 1956; Kamlet, " Organic Electronic Spectral Data," Vol. I, Interscience Publ., Inc., New York, 1960.
‡ Conrad-Billroth, *Z. phys. Chem.*, 1933, *B*, **23**, 318.

The equilibrium constant determinations are presented graphically in Figs. 1—3. The K values were calculated from equation (2); the ε_∞ values in water given in Table 1, were obtained by assuming $y_{\mathrm{H}}/y_{\mathrm{A}} = 1$. Smaller ε_∞ values give plots concave to the T^{-1} axis, while higher ε_∞ values give graphs with plots convex to the T^{-1} axis. To ensure that evaporation of either the aldehydes or the solvent was not important at high temperatures, measurements of optical density were made while solutions were being both heated and cooled. This procedure was followed at least once for each aldehyde; optical densities were the same under the same physical conditions during both the heating and the cooling periods. The K values for the aldehydes dealt with in Figs. 1 and 2 were determined at the following molar concentrations (the number of experiments is given in brackets after each concentration): acetaldehyde in H_2O 0·03(2), 0·4(1), 0·5(2); in D_2O 0·07(3), 0·3(3), 0·5(1). Propionaldehyde in H_2O 0·04(2), 0·4(2); in D_2O 0·03(2), 0·06(1), 0·3(2). n-Butraldehyde in H_2O: 0·04(2), 0·05(2), 0·5(1); in D_2O 0·05(4), 0·5(2). Isobutyraldehyde in H_2O 0·03(1), 0·05(3), 0·3(1); in D_2O: 0·05(1), 0·4(2). Measured optical densities were in the range 0·05—0·90.

Table of Thermodynamic Quantities (*Tables* 2 *and* 3).—Values of $\Delta H°$ and $\Delta S°$, obtained from Figs. 1—3, are given in Tables 2 and 3 for the hydration:

$$\mathrm{R{\cdot}CHO + H_2O\ (D_2O) \rightleftharpoons R{\cdot}CH(OH)_2\ [R{\cdot}CH(OD)_2]}$$

The results for formaldehyde and chloral are presented in Fig. 3. These aldehydes are hydrated to a much greater extent than those of Figs. 1 and 2, and higher concentrations of these aldehydes were studied in order that the optical densities measured would be sufficiently large. Concentrations (molar) studied, together with the number of experiments (in parentheses), were: Formaldehyde in H_2O 3·4(1), 5·7(1), 8·7(1), 13·3(1). Chloral in H_2O 1·2(3), 1·7(1), 6·8(1); in D_2O 1·4(3), 6·5(1), 7·7(2). In all these cases there was a very weak carbonyl

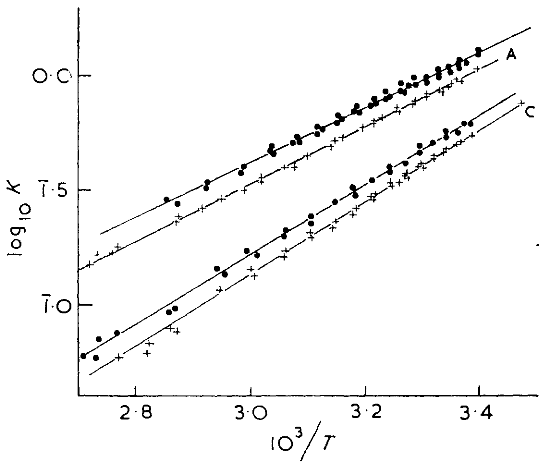


FIG. 1.

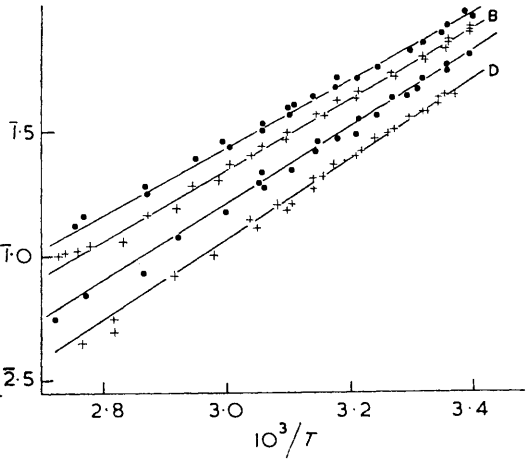


FIG. 2.

FIGS. 1 and 2. Variation of the equilibrium constant (K) with temperature: (A) Acetaldehyde; (B) propionaldehyde; (C) n-butryraldehyde; and (D) isobutyraldehyde. [×—× indicate results in water; ·—· indicate results in D_2O.]

TABLE 2.

Hydration in H_2O.

R in R·CHO	$-\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta H°$ (kcal. mole^{-1})		K_h at 25°	
		Found	Lit.	Found	Lit.
H	5·4	5·7	14·6[1]	1000	10,000[1]
Me	19·2	5·7	5·1[4]	0·93	1·5,[4] 1·9[2]
Et	22·5	6·5	—	0·69	1·4[2]
Pr^n	25·3	7·1	—	0·48	1·2[2]
Pr^i	26·0	7·3	—	0·44	0·9[2]
CCl_3	26·6	14·0	14 *	28,000	500,[5] † >2500[2]

* "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Circular No. 500, Washington, 1952, p. 586. † Calc. for unit water activity in cyclohexane.

TABLE 3.

Hydration in D_2O.

R in R·CHO	$-\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta H°$ (kcal. mole^{-1})	K_d at 25°	R in R·CHO	$-\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta H°$ (kcal. mole^{-1})	K_d at 25°
Me	18·4	5·5	1·11	Pr^i	25·6	7·0	0·55
Et	21·3	6·2	0·80	CCl_3	26·2	14·0	33,000
Pr^n	24·2	6·9	0·57				

band detectable in aqueous solutions at 25°. Its intensity increased with increasing temperature, as for the weakly hydrated aldehydes. Optical densities measured in a typical run with chloral (6·8M) in H_2O were:

Temp.	25°	35°	45°	55°	65°	70°
O.D.	0·116	0·136	0·176	0·26	0·38	0·41

To obtain the contribution of the carbonyl groups to these optical densities we must subtract from the total optical density at 290 mμ the contribution at this wavelength due to the band ($\lambda_{max.}$ 210 mμ) associated with the CCl_3 grouping. This was done by trial and error until the chloral line in Fig. 3 remained straight over the temperature range studied when using a value of ε_∞ identical with that obtained in cyclohexane. In this way we estimate the extinction coefficient at 290 mμ due to the CCl_3 grouping to be ~0·015. This value has been used in all the calculations involving chloral.

Figs. 1—3 show points taken from all the experiments performed at different concentrations. Only in the case of formaldehyde was a concentration effect on K_h noted. In this case the lowest (3·4M) formaldehyde concentration (represented by crosses) used gave a line of slope close to that obtained at higher concentrations, but falling below the line obtained at the higher concentrations (represented by the closed circles) (see Fig. 3) and giving a $K_h(25°)$ value of about 1000. This concentration effect is probably due to the well-known polymerisation of formaldehyde and we feel that the lower line in Fig. 3 is more truly representative of the behaviour of the hydration equilibrium and that a value of 1000 cannot be far wrong for $K_h(25°)$ for formaldehyde. The extinction coefficients of aqueous formaldehyde measured by Bieber and Trumpler [1] at 54° (0·021) and 64° (0·040) agree fairly well with our values of 0·028 and 0·035, respectively, obtained for ~3M-formaldehyde solutions. Since their results were obtained with 0·87M-solutions it seems that at concentrations around 1—3M the effects of the polymerisation are not large at ~60°. In view of the thermochemical evidence discussed below we feel that our quoted value of $\Delta H°$ for hydration must be approximately correct. For >8M formaldehyde the measured extinction coefficients are about one-half those for the more dilute solutions, reflecting the importance of polymerisation in these solutions. Owing to these uncertainties, our value of 7 for ε_∞ of formaldehyde is not as accurate as our estimates for the other aldehydes.

Variations of Extinction Coefficients of Aldehyde Solutions in Electrolyte Solutions in H_2O *at* 25° (*Tables* 4 *and* 5).—Table 4 refers to the effects of varying concentrations of three salts on the extinction coefficient of propionaldehyde. Table 5 shows the salt effects in sodium chloride solutions on the extinction coefficients of the aliphatic homologous series. Within experimental error, all the aldehydes studied behave similarly and the results of the more detailed study of propionaldehyde (Table 4) probably apply equally to the aldehydes dealt with in Table 5. The results may be used to afford y_H/y_A ratios in the salt solutions by the application of equation (2), the $K_h(25°)$ values obtained in pure water being used ($y_H/y_A = 1$). These results are discussed in section B below.

TABLE 4.

Extinction coefficients of 0·05M-propionaldehyde in presence of salts.

Molality	0	1	2	3	4	5
NaCl	10·5	12·1	12·9	—	14·3	15·7
NaBr	10·5	12·3	12·9	13·7	14·8	—
$NaClO_4$	10·5	11·0	—	12·9	13·6	14·8

TABLE 5.

Effect of sodium chloride on the extinction coefficients of 0·05M-solutions of aldehydes at 25°.

	Molality of NaCl					
R in R·CHO	0	1·0	2·0	3·0	4·0	5·0
Me	7·7	—	9·6	—	11·7	12·8
Et	10·5	12·1	12·9	—	14·3	15·7
Pr^n	11·3	—	12·7	13·3	14·2	14·6
Pr^i	12·3	14·3	15·3	—	15·6	16·2

DISCUSSION

(*A*) *Comparison with Earlier Work.*—Where the results obtained in this paper can be compared with those of previous workers, agreement is fair. The two greatest discrepancies occur with formaldehyde and chloral, the reasons for this being clear.

The previous estimate of 10^4 for K_h for formaldehyde [1] at 25° was obtained from a spectroscopic estimate of the equilibrium constant in the temperature range 55—65°, and subsequent extrapolation to 25°, a thermochemical value [8] of —14·8 kcal. mole^{-1} being used for the heat of hydration. This extrapolation is invalid since the thermochemical work measured ΔH for the process

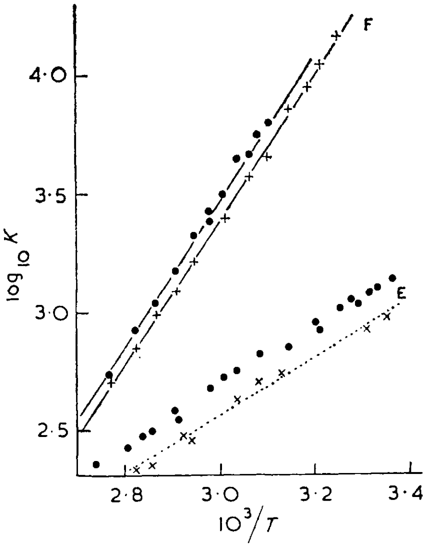


FIG. 3. Variation of the equilibrium constant (K) with temperature for (E), formaldehyde, and (F) chloral.

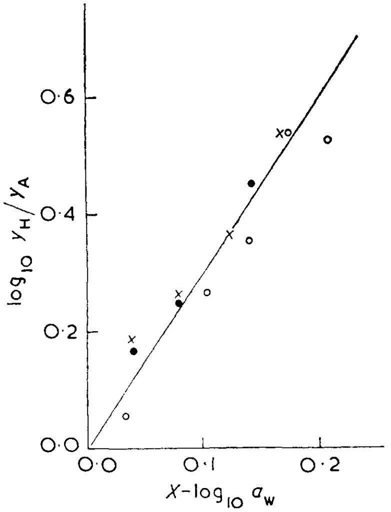


FIG. 4. Variation of the activity coefficients in concentrated electrolyte solutions (× NaBr, ● NaCl, ○ $NaClO_4$) with solution properties.

$$H{\cdot}CHO\ (gas) + H_2O\ (liq.) \longrightarrow H{\cdot}CH(OH)_2(aq):\ \Delta H_1^\circ = -14{\cdot}8\ \text{kcal mole}^{-1}.$$

The value used for extrapolation should be that for the reaction

$$H{\cdot}CHO\ (aq) + H_2O\ (liq.) \longrightarrow H{\cdot}CH(OH)_2(aq.):\ \Delta H_2^\circ = -5{\cdot}7\ \text{kcal. mole}^{-1},$$

where ΔH_2° is taken from our own work. ΔH_1° and ΔH_2° will differ by the sum of the ΔH's for the reactions:

$$H{\cdot}CHO\ (gas) \longrightarrow H{\cdot}CHO\ (liq.):\ \Delta H_3^\circ = -5{\cdot}5\ \text{kcal. mole}^{-1}\ \text{(ref. 9)}$$

$$H{\cdot}CHO\ (liq.) + H_2O\ (liq.) \longrightarrow H{\cdot}CHO\ (aq.):\ \Delta H_4^\circ \sim -2\ \text{kcal. mole}^{-1}.$$

Using our experimental value of ΔH_2 we obtain

$$\Delta H_1^\circ = \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ \sim -13{\cdot}3\ \text{kcal. mole}^{-1}.$$

In view of the uncertainties involved in ΔH_4°, where we have taken a value close to that obtained for the heats of solutions of liquid acetone [10] and acetaldehyde,[4] we feel that this

---

[8] Walker, *J. Amer. Chem. Soc.*, 1933, **55**, 2821.

[9] " Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular No. 500, Washington, 1952, p. 586.

[10] " International Critical Tables," Vol. V, McGraw-Hill, New York, 1929, p. 148.

agreement is satisfactory. In the case of chloral we have a discrepancy of a factor of 60. However, the K_h value obtained by Bell and McDougall[5] was obtained in a hydrocarbon solvent. It is reasonable to expect that in aqueous solution the hydrate will be stabilised relative to the free aldehyde owing to the extra hydrogen-bonding possibilities of the diol group. Our work in electrolyte solutions supports this view. Our experimental value of $-14{\cdot}0$ for the heat of hydration of chloral may be compared with the thermochemical[11] ΔH° for the reaction

$$\mathrm{CCl_3{\cdot}CHO\ (liq.) + H_2O\ (liq.) \longrightarrow CCl_3{\cdot}CH(OH)_2(aq.)}: \ \Delta H^\circ = -11{\cdot}9 \text{ kcal. mole}^{-1}.$$

This differs from the required ΔH° by the heat of solution of liquid chloral, which is unknown. Our value of -14 kcal. mole^{-1} for ΔH° for the reaction

$$\mathrm{CCl_3{\cdot}CHO\ (aq.) + H_2O\ (liq.) \longrightarrow CCl_3{\cdot}CH(OH)_2\ (aq.)}$$

suggests a value of about $+2$ kcal. mole^{-1} for this reaction, which in the absence of any direct evidence seems reasonable.

(*B*) *Hydration Equilibria in Electrolyte Solutions.*—The results in Tables 4 and 5 show that the ratio [H]/[A] decreases with increasing electrolyte concentration. We suggest that this is due largely to the decrease in water activity accompanying the increase in electrolyte concentration. We may express this quantitatively by using the model of a solution developed by Gluekauf,[12] and by Robinson and Stokes,[13] wherein we apply volume-fraction statistics to our aqueous solution containing both electrolyte and non-electrolyte. Such treatment has correctly predicted the activity coefficients of concentrated electrolyte solutions and when applied to our case yields:

$$\log\,(y_{\mathrm{H}}/y_{\mathrm{A}}) = (h' + 1)\{X - \log a_{\mathrm{w}}\},$$

where $X = 0{\cdot}018\ m_1(r_1 + h_1 - 2)/2{\cdot}3(1 + 0{\cdot}018 m_1 r_1)$ for 1 : 1 electrolytes; $h' = (h_{\mathrm{H}} - h_{\mathrm{A}})$, h_{H} and h_{A} being the hydration numbers of H and A, respectively; m_1 is the molality of the electrolyte; $r_1 = \phi_1/v_{\mathrm{w}}$ where ϕ_1 is the apparent molar volume of the electrolyte and v_{w} is the apparent molar volume of water; h_1 is the hydration number of the electrolyte, and a_{w} is the water activity. In Fig. 4 we plot $\log\,(y_{\mathrm{H}}/y_{\mathrm{A}})$ against $(X - \log a_{\mathrm{w}})$. The values for r_1 and h_1 for the three salts have been taken from the tabulation in ref. 12*a*, a_{w} from Robinson and Stokes.[13b] Apart from the assumptions inherent in Gluekauf's model, we have assumed that electrostatic effects due to the dipolar characters of H and A will cancel in the ratio $y_{\mathrm{H}}/y_{\mathrm{A}}$; we have also assumed that the difference in the apparent molar volumes of H and A is v_{w}, the apparent molar volume of a water molecule.

The straight line in Fig. 4 corresponds to a value of $(h' + 1) = 3$. This suggests that the solvation difference between H and A is two water molecules, and we represent the equilibrium as

$$\mathrm{R{\cdot}CHO(H_2O)}_n + \mathrm{3H_2O} \rightleftharpoons \mathrm{R{\cdot}CH(OH)_2(H_2O)}_{n+2}$$

n is unlikely to be greater than one or two. If both lone pairs of the carbonyl-oxygen atom were to accept hydrogen bonds, n would be 2, but since the aliphatic aldehydes are weaker bases than water we should not expect water molecules to form stronger hydrogen bonds with the carbonyl-oxygen atom than with each other. Thus, although the aldehydes must certainly form short-lived hydrogen-bonded complexes with water molecules, such weak associations should not be regarded as entities with independent

---

[11] Ref. 9, p. 134.

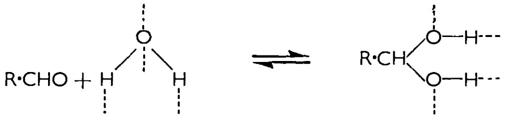
[12] (*a*) Gluekauf, *Trans. Faraday Soc.*, 1955, **51**, 1235; (*b*) " The Structure of Electrolytic Solutions," ed. Hamer, John Wiley and Sons Inc., New York, 1959, p. 97.

[13] (*a*) Stokes and Robinson, *Trans. Faraday Soc.*, 1957, **53**, 301; (*b*) Robinson and Stokes, " Electrolyte Solutions," 2nd edn., Butterworths, London, 1959.

existence (like, *e.g.*, the hydrogen-bonded $H_9O_4^+$ complex). Hence we suggest $n = 0$. The presence of two water molecules of solvation for the aldehyde hydrates may be plausibly explained since the two water molecules may be attached to the hydroxy groups of the *gem*-diol.

(*C*) *Equilibrium Constants in* H_2O.—The relative sizes of the equilibrium constants are as expected. However, the trend of the $\Delta H°$ values for hydration (decreasing) as we ascend the homologous series is surprising. A wrong choice of ε_∞'s in water would perhaps account for this, although to obtain a value of $-5{\cdot}7$ for the $\Delta H°$ for hydration of n-butyraldehyde in the vicinity of 25°, we must use an ε_∞ close to 21 and it is then found that the experimental points (cf. Figs. 1—3) in the temperature range 55—90° lie well away from the extrapolation of the " straight " line at low temperatures. It seems then that the observed trend is a real effect, and that the parallel trend in $\Delta S°$ values also reflects a real effect. It is difficult to avoid the conclusion that these $\Delta H°$ and $\Delta S°$ effects are closely related to the changes in solvent structure on passing from the free aldehyde to the aldehyde hydrate. The ordering effect of this change seems to be least in the case of formaldehyde ($\Delta S° = -5{\cdot}4$ cal. deg.$^{-1}$), and greatest for chloral, and the two butyraldehydes ($\Delta S° \sim -26$ cal. deg.$^{-1}$).

(*D*) *Solvent Isotope Effects*.—It is clear from our results that $K_h/K_d \approx 0{\cdot}85$ for all the aldehydes examined. The $\Delta H°$ and $\Delta S°$ parameters suggest that the heavier hydration of aldehydes in D_2O is not the result of a smaller $\Delta H°$ value (if anything, $\Delta H°$ is a few hundred calories larger in D_2O), but to a larger $\Delta S°$ value. The model used by Bunton and Shiner [14] to calculate isotope effects may be applied to this equilibrium. Thus, using their notation of broken lines to represent hydrogen bonds, we write:



noting that their empirical rules for determining hydrogen-bonding sites accord well with our findings on solvation numbers. Applying the Bunton–Shiner formula,

$$K_h/K_d = \text{antilog}\,[(\textstyle\sum\nu_H - \sum\nu_H')/12{\cdot}53T],$$

we obtain a value of $\sim 1{\cdot}1$ for K_h/K_d, where we have taken 13·5 as the pK_a of *gem*-diol hydrogen grouping,[15] and 15·7 as the pK_b of the *gem*-diol oxygen atoms. This latter choice is guided by Taft's observation that an α-hydroxyalkyl group has similar electron-attracting qualities to H.[16] Obviously the predicted isotope effect is in the wrong direction, although the predicted change in $\Delta H°$ on going from H_2O to D_2O is a few hundred calories per mole positive, which appears to be roughly correct in both sign and magnitude.

It is tempting to suggest that, while large solvent isotope effects tend to be due to zero-point energy differences and are predictable in approximate terms from rough models, small solvent isotope effects such as those reported in this paper, are difficult to predict, since entropy effects may outweigh energy effects when the latter are small.

One of us (L. C. G.) gratefully acknowleges a Commonwealth Postgraduate Award during the tenure of which this work was carried out.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF MELBOURNE, AUSTRALIA.

[*Received, February* 19*th*, 1963.]

---

[14] Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 42.
[15] Bell and McTigue, *J.*, 1960, 2983.
[16] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 3120.