

Isentropic Apparent Molal Compressibilities and Compressibilities of Ionization of Carboxylic Acids in Aqueous Solution

BY HARALD HØILAND* AND EINAR VIKINGSTAD

Department of Chemistry, University of Bergen, N-5000, Bergen, Norway

Received 28th July, 1975

Isentropic coefficients of compressibility of the homologous series of normal carboxylic acids and α -hydroxycarboxylic acids and their sodium salts have been determined from ultrasonic measurements. Isentropic apparent molal compressibilities at infinite dilution have been calculated.

Compressibilities of ionization have been calculated from the isentropic apparent molal compressibilities and also from conductance measurements at high pressures. Values from the two independent methods of measurement do not agree in a satisfactory manner, but both show a lower limiting value for the higher homologues in each acid series.

The apparent molal compressibility and the compressibility of ionization are thermodynamic quantities of particular interest in this work with respect to extending the information gained from studies of partial molal volumes and volumes of ionization of normal carboxylic acids and α -hydroxycarboxylic acids.^{1, 2}

The isothermal apparent molal compressibility, ϕ_K , is difficult to determine accurately. The isentropic coefficient of compressibility, however, can be obtained from ultrasonic measurements, and the isentropic apparent molal compressibility, $\phi_{K(s)}$, can then be calculated.³ It is possible to convert isentropic apparent molal compressibilities into isothermal values, but this requires a knowledge of molal heat capacities and expansibilities which are not known for carboxylic acids or their salts in aqueous solution.

The compressibilities of ionization can be obtained from two independent methods of measurement. The equations are ;

$$\frac{RT}{p-1} \ln \frac{K_p}{K_1} = -\Delta \bar{V}^0 + \frac{1}{2} \Delta \bar{K}^0 (p-1) \quad (1)$$

$$\Delta \bar{K}^0 = \phi_K^0(\text{NaA}) - \phi_K^0(\text{HA}) + \phi_K^0(\text{HCl}) - \phi_K^0(\text{NaCl}). \quad (2)$$

In eqn (1), K_p and K_1 are equilibrium constants at pressure p and 1 bar respectively (1 bar = 10^5 N m⁻²), $\Delta \bar{V}^0$ the volume of ionization and $\Delta \bar{K}^0$ the compressibility of ionization.⁴

In eqn (2), $\Delta \bar{K}^0$ is calculated from the apparent molal compressibilities at infinite dilution of the acid, HA, and its corresponding sodium salt, allowing for the difference in apparent molal compressibility between the hydrogen and sodium ions.

EXPERIMENTAL

The origin and the purity of the acids and their sodium salts have been described elsewhere^{1, 2}

Isentropic coefficients of compressibility were determined by the "sing-around" principle,⁵ which involves the passing of repeated pulses of ultrasonic radiation through the solution and measurement of the frequency of this radiation. The frequencies were measured by a Hewlett-Packard 5326A time-counter, averaging over periods of 10 s.

The ultrasonic cell was a stainless steel cylinder of length 10 cm. It was calibrated with water as the standard, using the data of Del Grosso and Mader.⁶

The cell was thermostatted in a water bath to better than $\pm 0.015^\circ\text{C}$. The error in the speed of sound was estimated to be $\pm 0.10 \text{ m s}^{-1}$.

EVALUATION OF $\phi_{K(s)}^0$

The isentropic apparent molal compressibilities of the salts were extrapolated to infinite dilution according to the equation³

$$\phi_{K(s)} = \phi_{K(s)}^0 + S_{K(s)} m^{\frac{1}{2}}. \quad (3)$$

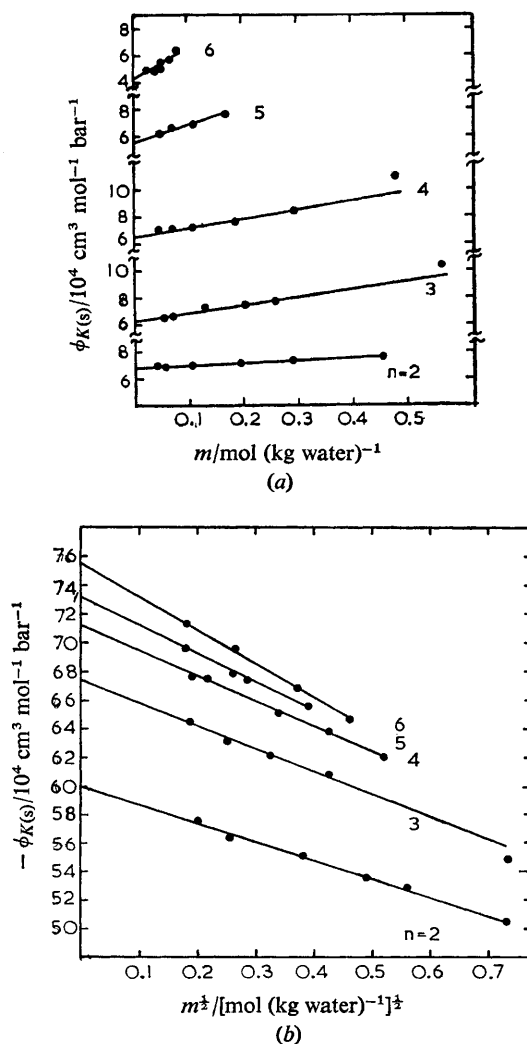


FIG. 1.—Isentropic apparent molal compressibilities as functions of concentration, (a) ordinary carboxylic acids from acetic acid, $n = 2$, to hexanoic acid, $n = 6$; (b) the corresponding sodium salts.

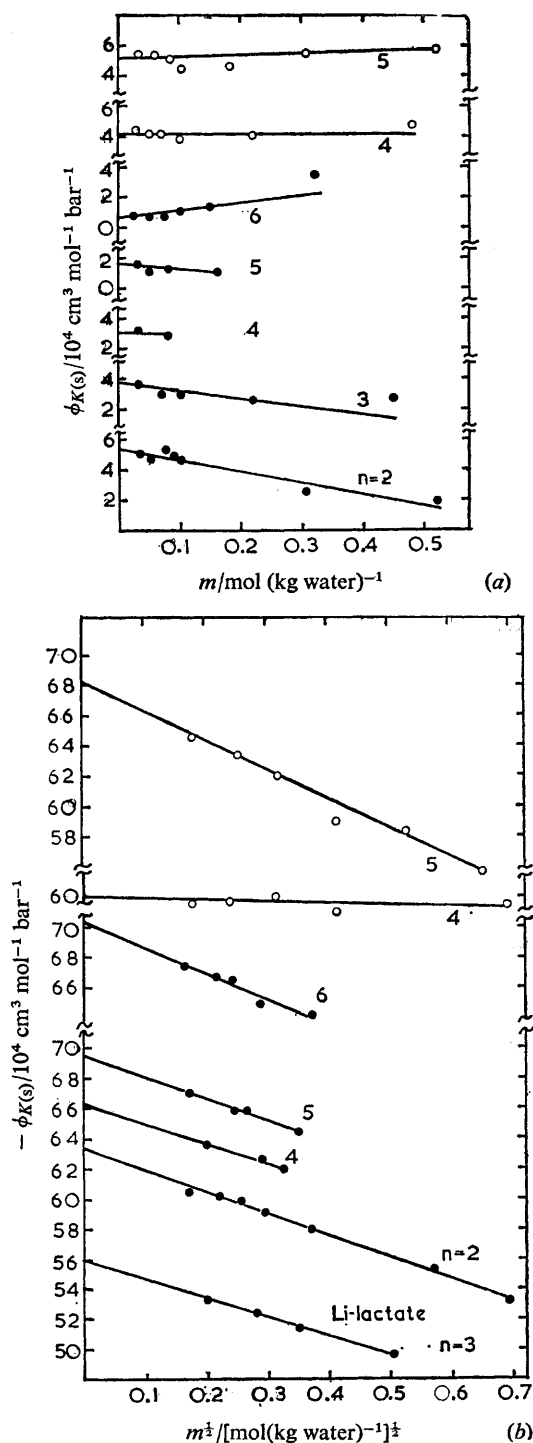


FIG. 2.—Isentropic apparent molal compressibilities as functions of concentration, (a) α -hydroxyacetic acid, $n = 2$, to α -hydroxyhexanoic acid, $n = 6$; (b) the corresponding sodium salts. The open circles represent α -hydroxyisobutyric and α -hydroxyisovaleric acid and their salts.

The densities and apparent molal volumes required for the calculation of $\phi_{K(s)}$ from isentropic coefficients of compressibility were taken from the literature.^{2, 7} Plots are shown in fig. 1.

The $\phi_{K(s)}$ values of the acids refer to a hypothetical state of purely undissociated acid molecules in solution; the measured values include dissociative effects for which corrections must be made. This may be done in the same way that apparent molal volumes were corrected for the effects of dissociation.⁸ The result is an equation which can be used both to

TABLE 1.—COMPRESSIBILITIES OF IONIZATION

acid	$T/^{\circ}\text{C}$	$\Delta\bar{K}^0 \times 10^4 / \text{cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$	
		from compressibility measurements	from conductance measurements
acetic	25	—23	—18
propionic	25	—30	—25
butyric	25	—33	—28
valeric	25	—35	—30
hexanoic	25	—35	—30
α -hydroxyacetic	25	—25	—20
	30		—20
	35		—20
α -hydroxypropionic	25	—26	—25
	30		—24
	35		—25
α -hydroxybutyric	25	—26	—26
	30		—26
	35		—25
α -hydroxyvaleric	25	—27	—27
	30		—28
	35		—26
α -hydroxyhexanoic	25	—27	—26
	30		—25
	35		—24
α -hydroxyisobutyric	25	—20	—21
	30		—21
	35		—21
α -hydroxyisovaleric	25	—29	—21
	30		—21
	35		—21

correct for dissociative effects and for extrapolation of $\phi_{K(s)}$ of the acids to infinite dilution;

$$\phi_{K(s)} - \alpha \Delta\bar{K}_s^0 = \phi_{K(s)}^0 + b_{K(s)} m \quad (4)$$

where α is the degree of dissociation calculated from equilibrium constants.^{2, 9} Plots at 25°C are shown in fig. 2.

The error in $\phi_{K(s)}^0$ is estimated to be $\pm 1 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ both for the acids and their salts.

EVALUATION OF $\Delta\bar{K}^0$

Equilibrium constants at various pressures for use in eqn (1) have previously been determined from conductance measurements.^{1, 2} Isothermal compressibilities of ionization have been calculated from these data, and are given in table 1.

The ultrasonic measurements make it possible to calculate isentropic compressibilities of ionization using eqn (2). The difference between isothermal and isentropic compressibilities of ionization may be estimated from the equation:

$$\Delta\bar{K}^0 = \Delta\bar{K}_s^0 + \delta^0 \left(\frac{2\Delta\phi_L^0}{\alpha_0} - \frac{\Delta\phi_R^0}{\sigma_0} \right). \quad (5)$$

This equation is derived from Desnoyers and Philip's equation for the conversion of isentropic to isothermal apparent molal compressibilities.¹⁰ $\Delta\phi_E^0$ is the expansibility of ionization and may be estimated from the temperature dependence of the volumes of ionization. $\Delta\phi_C^0$ is the heat capacity of ionization, and values of this quantity are given.¹¹ Values of δ^0 , α_0 and σ_0 are given by Mathieson and Conway.¹²

For the carboxylic acids studied in this work it is found that the difference between isentropic and isothermal compressibilities of ionization is less than the estimated experimental error, $\pm 2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$. Values of the compressibilities of ionization from conductance measurements may thus be compared directly with the values from the ultrasonic measurements.

DISCUSSION

The isentropic apparent molal compressibilities are presented in table 2. A literature value has been found only for acetic acid, $7.1 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$,¹² and isothermal values are reported for acetic acid and potassium acetate, 7×10^{-4} and $-47 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$.¹³

The $\phi_{K(s)}^0$ values are positive for all the acids and negative for all the salts. The negative isentropic apparent molal compressibilities of the salts can be explained by the electrostriction that makes the water near the charges considerably less compressible than the bulk water.¹⁴ The $\phi_{K(s)}^0$ values of the acids, though positive, are still less than the apparent molal compressibility of pure water at 25°C, $\phi_{K(s)} = 8.12 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$, and the more CH_2 groups the acid molecule contains, the lower is its isentropic apparent molal compressibility. This confirms that water in hydrophobic hydration sheaths is less compressible than bulk water at 25°C. However, at 30 and 35°C this is no longer so. Apparently, at 35°C the isentropic apparent molal compressibility increases with the length of the alkyl chain, while the values at 30°C seem to be intermediate, with very little change in isentropic apparent molal compressibility with solute size.

It is of interest to check if the increment in isentropic apparent molal compressibility per CH_2 group is constant, as is the case with partial molal volumes.⁷ The results, in table 1, show relatively large fluctuations, but the value of this isentropic methylene group molal compressibility is of the same magnitude as the experimental error.

The two independent methods of measuring compressibilities of ionization may now be compared. For the α -hydroxycarboxylic acids the agreement is good with the exception of α -hydroxyacetic acid, where a difference of $5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ appears, the same difference as for the normal carboxylic acids.

A literature value by the conductance method is given for acetic acid, $-17 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$,¹⁵ in agreement with our value from the conductance method $-18 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$. From isothermal compressibility measurements, Owen

and Brinkley¹³ report the compressibility of ionization of acetic acid, but their calculations were based on the difference $\phi_K^0(\text{HCl}) - \phi_K^0(\text{KCl}) = 37 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$, which according to recent measurement is too high.^{5, 12} Owen and Brinkley's data recalculated give $-21 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ for the compressibility of ionization of acetic acid, in good agreement with our value by the compressibility method.

This discrepancy between values from the two methods of measurement is most probably due to the conductance method. The compressibility of ionization calculated from conductance data is the second derivative of the equilibrium constant, and this probably involves larger uncertainties than the direct compressibility method.

The compressibility of ionization have a lower limiting value for butyric acid or α -hydroxybutyric acid and the higher homologues, regardless of the discrepancies mentioned above. The same was observed for the volumes of ionization.^{1, 2} It confirms that the negative charge from the dissociation reaction has no effect on the hydration sheath of the solute beyond the γ -carbon.

We thank Professor Dr. Thorvald Brun for his interest in this work.

TABLE 2.—ISENTROPIC APPARENT MOLAL COMPRESSIBILITIES AT INFINITE DILUTION OF CARBOXYLIC ACIDS AND SODIUM CARBOXYLATES

acid	$T/^{\circ}\text{C}$	$\phi_{K(a)}^0 \times 10^4 / \text{cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$	$[\phi_{K(a)}^0(n+1) - \phi_{K(a)}^0(n)] / 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$
acetic	25	6.9	-0.5
propionic	25	6.4	-0.2
butyric	25	6.2	-0.7
valeric	25	5.5	-1.3
hexanoic	25	4.2	
α -hydroxyacetic	25	5.4	(-1.8)
	30	5.9	(-0.2)
	35	6.0	(1.8)
α -hydroxypropionic	25	3.6	-0.6
	30	5.7	0.4
	35	7.8	2.0
α -hydroxybutyric	25	3.0	-1.6
	30	6.1	-0.2
	35	9.8	-0.2
α -hydroxyvaleric	25	1.4	-0.7
	30	5.9	1.0
	35	9.6	2.3
α -hydroxyhexanoic	25	0.7	
	30	6.9	
	35	11.9	
α -hydroxyisobutyric	25	4.2	
	30	8.2	
	35	12.2	
α -hydroxyisovaleric	25	5.2	
	30	8.2	
	35	12.0	

sodium salt			
acetate	25	−60.0	−7.5
propionate	25	−67.5	−3.7
butyrate	25	−71.2	−2.2
valerate	25	−73.4	−1.8
hexanoate	25	−75.2	
α -hydroxyacetate	25	−63.3	(−2.6)
	30	−59.3	(−2.1)
	35	−57.3	(−0.1)
α -hydroxypropionate	25	−65.9	−1.1
	30	−61.4	−0.1
	35	−57.4	0.1
α -hydroxybutyrate	25	−67.0	−2.5
	30	−61.5	−2.5
	35	−57.3	−0.5
α -hydroxyvalerate	25	−69.5	−1.1
	30	−64.0	0.2
	35	−57.8	−0.2
α -hydroxyhexanoate	25	−70.6	
	30	−63.8	
	35	−58.0	
α -hydroxyisobutyrate	25	−60.0	
	30	−56.5	
	35	−51.5	
α -hydroxyisovalerate	25	−68.1	
	30	−60.1	
	35	−56.4	

¹ H. Høiland, *J.C.S. Faraday I*, 1974, **70**, 1180.

² H. Høiland and E. Vikingstad, *J.C.S. Faraday I*, 1975, **71**, 2007.

³ H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold, New York, 3rd edn., 1967), pp. 386-388.

⁴ D. A. Lown, H. R. Thirsk and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1968, **64**, 2073.

⁵ R. Garnsey, R. J. Boe, R. Mahoney and T. A. Litovitz, *J. Chem. Phys.*, 1969, **50**, 5222.

⁶ V. A. Del Grosso and C. W. Mader, *J. Acoustical. Soc.*, 1972, **52**, 1442.

⁷ H. Høiland, *Acta Chem. Scand.*, 1974, **28A**, 699.

⁸ E. J. King, *J. Phys. Chem.*, 1969, **73**, 1220.

⁹ G. Kortüm, W. Vogel and K. Andrussov, *Dissociation Constants of Organic Acids in Aqueous Solution* (Butterworths, London, 1961).

¹⁰ J. E. Desnoyers and P. R. Philip, *Canad. J. Chem.*, 1972, **50**, 1094.

¹¹ J. W. Larson and L. G. Hepler, in *Solute-Solvent Interactions*, ed. J. F. Coetzee and C. D. Ritchie (Dekker, New York, 1969), p. 9.

¹² J. G. Mathison and B. E. Conway, *J.C.S. Faraday I*, 1974, **70**, 752.

¹³ B. B. Owen and S. R. Brinkley, *Chem. Rev.*, 1941, **29**, 461.

¹⁴ H. S. Frank, *J. Chem. Phys.*, 1955, **23**, 2023.

¹⁵ D. A. Lown, H. R. Thirsk and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1970, **66**, 51.