Enthalpies of Transfer of NaCl from Water to Aqueous Mono- and Dicarboxylic Acids at 25 °C

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Enthalpies of transfer of NaCl, $\Delta\bar{H}_2$, from water to seven aqueous mono- and dicarboxylic acids at low concentrations (X_3 = 0.01, m_3 = 0.56) were determined, with formic acid measurements extended to X_3 = 0.1803 (m_3 = 12.21). Values of $\Delta\bar{H}_2$ for the monoacids show the competing interaction effects of the carboxyl and alkyl groups, increasing with chain length from −100 to +60 cal/mol at X_3 = 0.01 for the series formic, acetic, propionic, and *n*-butyric acids. The diacid series, malonic, succinic, and glutaric, all have negative $\Delta\bar{H}_2$, with small positive increases with the number of methylene groups (−165 to −135 cal/mol). These results indicate that the end carboxyls shield the methylene groups from their polar environment. The low sensitivity of NaCl in distinguishing between the dicarboxylic acids may be related to the competitive inhibition of the enzyme succinic dehydrogenase by malonic and glutaric acids.

Introduction

Aqueous carboxylic acids are physicochemically important solutions and this contribution describes enthalpies of transfer of NaCl, $\Delta\bar{H}_2$, from water to aqueous formic, acetic, *n*-propionic, *n*-butyric, malonic, succinic, and glutaric acids. The majority of transfers were to acid concentration at mole fraction X_3 = 0.010 (m_3 = 0.56). Formic acid measurements were extended to X_3 = 0.1803 (m_3 = 12.21) in order to determine the range in which $\Delta\bar{H}_2$ remains a limiting linear function of X_3.

Previous related studies have shown the usefulness of NaCl as a probe for detecting changes in the solvent properties of water upon addition of hydrophilic solutes, including hydrogen peroxide (*1*), urea (*2*), and sucrose (*3*). Close values of $\Delta\bar{H}_2$ for all three systems as a linear function of X_3 were observed, indicating a rough colligative effect (to X_3 = 0.02 to 0.03), with $\Delta\bar{H}_2 = (-1 \times 10^4)X_3$ cal/mol. The present study will show the net result of opposing interaction effects of the carboxyl and alkyl groups in the various aqueous acids.

Experimental Section

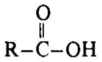
Two calorimeters were used. The Dewar calorimeter and experimental procedure have been described elsewhere (*4*). They were checked by measuring the enthalpy of neutralization of THAM, $(HOCH_2)_3CNH_2$, in HCl and the enthalpy of solution of NaCl in water. Both results agree within 1% of the literature values (*5*, *6*). The new submarine calorimeter was similar in design to Wadsö's (*7*). It consisted of a submersible stainless steel air jacket enclosing a 200-cm³ cylindrical glass vessel, with two separate wells for a thermistor and for a calibration heater, respectively. The glass vessel was attached to the top lid of the jacket by a stainless steel flange joint. A stainless steel shaft rotated a gold-plated stirrer with six blades which also served as a solute ampule holder. The spherical glass ampules were sealed with fluorocarbon or silicone rubber stoppers. During a run the rotating ampules were crushed against an anvil by a downward thrust of the stirrer shaft which passed through to an external concentric solenoid coil energized at 230 V. The heat of ampule breaking was negligible. The thermistor and calibration heater circuits were similar to those of the older calorimeter. The new calorimeter was checked by measuring the heats of solution of KCl and NaCl. Both results were within 1% of the "best" values recommended by Parker (*6*).

Table I. Enthalpies of Solution of NaCl in Aqueous Acids

acid system	X_3	no. of runs	ΔH_2, cal/mol
pure water	0.000	4	990 ± 10[b]
	0.000[a]	4	995 ± 10[b]
formic	0.0050	4	920 ± 10
	0.0098	3	880 ± 10
	0.0100[a]	3	895 ± 10
	0.0244	6	715 ± 10
	0.0309	5	670 ± 10
	0.0637	4	330 ± 20
	0.1002	3	140 ± 10
	0.1803	4	−100 ± 10
acetic	0.0100[a]	5	965 ± 10
	0.0108	4	960 ± 10
propionic	0.0100[a]	3	1010 ± 10
n-butyric	0.0100[a]	3	1055 ± 20
malonic	0.0100	4	825 ± 10
succinic	0.0100	6	840 ± 10
glutaric	0.0100[a]	3	860 ± 10

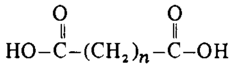
[a] Measured with new calorimeter. [b] $\Delta H_2°$.

Table II. Enthalpies of Transfer $\Delta\bar{H}_2$ at X_3 = 0.01



$R-C(=O)-OH$

R	$\Delta\bar{H}_2$,[a] cal/mol	$\Delta(\Delta\bar{H}_2)$,[b] cal/mol
H	−100	
CH_3	−30	70
CH_3CH_2	15	45
$CH_3CH_2CH_2$	60	45



$HO-C(=O)-(CH_2)_n-C(=O)-OH$

n	$\Delta\bar{H}_2$, cal/mol	$\Delta(\Delta\bar{H}_2)$, cal/mol
1	−165	
2	−150	15
3	−135	15

[a] Estimated uncertainty is ±15 cal/mol. [b] Estimated uncertainty is ±20 cal/mol.

All materials were high-quality commercial products. The monocarboxylic acids were prepared from concentrated stock solutions by dilution with distilled deionized water and assayed by titration with standard NaOH. The dicarboxylic acid solutions were prepared from the pure solids. The final overall concentrations of NaCl were ca. 0.02 in the old and 0.03–0.05 mol/1000 g of water or mixed solvent in the new calorimeter. The dissociation of all acids was negligible, except for malonic which was ca. 5%.

Results and Discussion

Table I shows enthalpies of solution of NaCl in the aqueous acids (ΔH_2) and in pure water ($\Delta H_2°$). Table II compares $\Delta\bar{H}_2$, given by $\Delta\bar{H}_2 = \Delta H_2 - \Delta H_2°$ in each of the series RCOOH and

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$HOOC(CH_2)_nCOOH$ and shows the changes in $\Delta\bar{H}_2$ $[\Delta(\Delta\bar{H}_2)]$ with increasing chain length.

The values of $\Delta\bar{H}_2$ for formic acid are the most exothermic of the monocarboxylic acids, and within experimental error fit into the roughly colligative series of hydrogen peroxide, urea, and sucrose, up to $X_3 = 0.0309$. At higher mole fractions $\Delta\bar{H}_2$ becomes nonlinear. As the carbon chain lengthens $\Delta\bar{H}_2$ becomes less exothermic for acetic acid, with positive values for propionic and butyric acids. The overall changes from formic to butyric acids show the inability of the terminal carboxyl to overcome the unfavorable interaction between the growing hydrocarbon chain and the aqueous environment. There may be a leveling effect as $[\Delta(\Delta\bar{H}_2)]$ decreases from 70 to 45 cal/mol; however, the experimental error makes this trend uncertain.

Enthalpies of transfer to the three diacids are the most negative. Insertion of methylenes between the carboxyls in going from malonic to succinic and to glutaric acid represents a less drastic change than the extension of a carbon chain by one methylene in the monoacids. It is likely that this is the net result of carboxyl group solvation reducing the methylene-water interactions, with the carboxyls providing a shielding effect between the methylenes and their polar aqueous environment. It may be noted that the diacids are very important in enzyme inhibition since all three combine with the enzyme succinate dehydrogenase (*8*). Malonic and glutaric acids thus competitively inhibit the enzyme by blocking the active center, which apparently is not selective between the three acids, just as the transfer of NaCl is relatively nonspecific.

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Solubility of O_2 in 2-Propanone, 2-Butanone, 2-Pentanone, and 2-Hexanone

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Experimental data for the solubility of O_2 in CH_3COCH_3, $CH_3COC_2H_5$, $CH_3COC_3H_7$, and $CH_3COC_4H_9$ within the temperature range 298–344 K are reported. For $T =$ 298.2 K the following values for Henry's constant were measured ($H_{O_2,1}^{(p_1^*)}$, bar/mole fraction): ketone C_3, 1190; C_4, 986; C_5, 904; C_6, 855. The data can be well correlated by using the semiempirical approach of Cysewski and Prausnitz. The prediction of Henry's constant of O_2 for higher ketones by the regular solution equation is tested and found applicable. A rapid technique for performing oxygen solubility measurements on a working sample is described and tested.

When making kinetic measurements for the autoxidation of hydrocarbons in the liquid phase, it is necessary to know the solubility of oxygen in the reaction mixture at elevated temperatures. There exist several experimental methods for determining gas solubility data (see, e.g., ref 1), but they are all rather cumbersome to use in this situation. A rather rapid working method, though not as precise as volumetric methods, consists of injecting a sample of small volume from a reaction mixture containing oxygen into a comparatively large volume of water with a fairly low, but known, concentration of oxygen. From the increase of the oxygen concentration the solubility of oxygen in the reaction mixture can be easily evaluated. This technique, as tested by comparison of oxygen solubility data for acetone with known data, is described herein. New solubility data for oxygen in 2-butanone, 2-pentanone, and 2-hexanone obtained by this technique within the temperature range from 298 to 344 K are reported.

To date there exists no theoretical approach for predicting solubility data of gases in industrially relevant solvents. A semiempirical approach for correlating the solubility of gases in polar solvents was given by Cysewski and Prausnitz (*2*). While one of the parameters of their model was physically interpreted by them and could therefore be well predicted, this was not tried for the second parameter. Further insight into this second parameter gained from new experimental results is an additional point treated in this contribution.

The polarity of ketones decreases with increasing chain length. So the prediction of Henry's constant of oxygen in ketones by the regular solution equation must yield more meaningful results for the higher ketones. This idea is being tested by comparing experimental and predicted solubility parameters for the different ketones.

Experimental Section

Apparatus. The apparatus (Figure 1) consisted of a 100-mL round-bottom flask (a) with SVL 15 and SVL 22 screw caps (b) and NS 14.5 and NS 29 ground joints (c). The upper cap was closed with a Teflon septum whereas in the lower one an oxygen electrode (Clark) with temperature compensation was built in. In the lower ground joint a glass capillary was fixed and on the upper one a storage flask (d) was mounted which could be separated from the round-bottom flask by closing stopcock NS 8 (e).

Preliminaries. Prior to the experiments the storage flask was filled up with bidistilled water with the stopcock closed. With the upper screw cap opened, the round-bottom flask was rinsed by N_2 via the capillary. After rinsing of the flask, the screw cap was closed and at the same moment the stopcock was partly opened so that the water was well gassed by N_2 without dropping into the round-bottom flask. After gassing of the water, the stopcock was closed for a short time and the capillary replaced

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