

SOLVENT-SOLUTE INTERACTIONS IN DIMETHYL SULFOXIDE REVEALED BY VAN'T HOFF FACTOR

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Van't Hoff factors for sixteen organic acids in DMSO have been determined using a simple cryoscopic method. The data indicate that oxalic acid, trichloroacetic acid and picric acid are completely ionized in DMSO while dichloroacetic acid is only 50% ionized. Other acids that show 10% ionization or less are salicylic, phenylacetic, tartaric, succinic, maleic, fumaric, monochloroacetic and phthalic acids. Benzoic, malonic and glutaric acids show almost no ionization.

Attempt has been made to sort out solvent-solute interactions by correlating the van't Hoff factor data in DMSO with similar data available for aqueous solutions.

DMSO has a number of properties that makes it useful as a solvent to chemists. It has a high b.p. (189°C) and its liquid range is considerable (m.p.=18.55°C). It has a large molal freezing point depression constant ($4.36^\circ \text{ mole}^{-1}$), and it dissolves a large number of organic and inorganic compounds.¹ Anions in diprotic solvent, like DMSO, have no general hydrogen-bonding interaction with the solvent, as is the case with protic solvents, and are thus much less solvated and more reactive in DMSO.² Although DMSO, contains six hydrogen atoms, it cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds with an appropriate species.

Attempt has been made here to sort out solvent-solute interactions by studying the behaviour of various organic acids in DMSO by a simple cryoscopic method. In such experiment, however, great care must be taken to exclude moisture from the reaction vessel for the simple reason that DMSO is a strong hydrogen acceptor. Simple cryoscopic data on DMSO-water system have revealed that intermolecular associations in aqueous DMSO are much stronger than those which exist in pure water or DMSO.^{3,4}

Experimental

Thirty ml of DMSO was added into clean and dry freezing-point tube containing flower of the magnetic stirrer in it. The Beckmann thermometer was set up at 18.5°C (m.p. of DMSO). The Beckmann thermometer was then inserted in the freezing point tube, so that the bulb of the thermometer was completely immersed into the liquid. The speed of the magnetic stirrer was adjusted for steady stirring. The outer vessel was filled with ice and water, so that a temperature of 13.1°C was obtained. The freezing point of DMSO was then determined. The tube was then withdrawn from the mantle and solid DMSO was melted by means of hand. In this operation the temperature of the liquid was raised more than about

1° above its freezing point. The tube was again placed directly in the cooling bath and the temperature was allowed to fall to within half a degree of the freezing point. The tube was then quickly dried and placed in the air mantle and the temperature was allowed to fall. Stirring was continued slowly all the while when the temperature was about 0.2° below the approximate freezing point, the speed of the stirrer was increased. The crystallization of DMSO was caused to commence, and the temperature began to rise. The highest temperature reached was noted. The solid DMSO was again melted and the freezing point was re-determined in the above manner. Four readings of the freezing point of DMSO were taken. Then weighed tablet of a given acid was introduced into the DMSO through the side tube. The tablet was dissolved and the freezing point of the solution was determined in exactly the same manner as described for pure solvent. Three more tablets of the acid were introduced and the freezing point was determined after each addition.

Calculation and Results

The van't Hoff factors for acids have been calculated using the following equation:

$$i = \frac{\Delta T_f MW}{K_f 1000 w}$$

where ΔT_f is the depression in freezing point caused by w g of the solute in W g of the solvent and K_f is the molal freezing point depression constant while M is the mol wt of the solute. i measures the number of particles produced by the solute through solvent-solute interaction. Therefore a complete dissociation of a monobasic acid at low molality (usually less than 0.1 molal) should give a value of 2. Any value between 1 and 2 measures the degree of dissociation of an acid from which its percentage ionization may be easily evaluated. The i values of sixteen organic acids along with

TABLE I

Acid	van't Hoff factor i	pK^* (in water)
Oxalic	3.00	$pK_1-1.19, pK_2-4.21$
Benzoic	1.00	4.2
Salicylic	1.18	$pK_1-2.97, pK_2-13.44$
Phenylacetic	1.08	4.31
Phthalic	1.16	$pK_1-2.89, pK_2-5.41$
Tartaric	1.17	$pK_1-3.02, pK_2-4.54$
Succinic	1.08	$pK_1-4.19, pK_2-5.57$
Maleic	1.06	$pK_1-2.0, pK_2-6.26$
Fumaric	1.06	$pK_1-3.03, pK_2-4.47$
Monochloroacetic	1.11	2.86
Dichloroacetic	1.50	1.3
Trichloroacetic	2.13	0.8×9
Malonic	1.00	$pK_1-2.85, pK_2-6.1$
Glutaric	1.04	4.34
Adipic	0.95	4.43
Picric	2.07	0.38

*N.A. Lange, *Handbook of Chemistry* (Handbook Publishers, Sandusky, Ohio, 1956).

their pK values in water have been tabulated in Table I.

Discussion

van't Hoff factors for acids given in Table I indicate that oxalic acid, trichloroacetic acid and picric acids are completely ionized in DMSO while dichloroacetic acid is only 50% ionized. Other acids that show 10% ionization or less are salicylic, phenylacetic, tartaric, succinic, maleic, fumaric, monochloroacetic and phthalic acids. Benzoic, malonic and glutaric acids show almost no ionization.

There is a marked difference, however, between the behaviour of DMSO and water as solvent in that oxalic acid ionizes to $(COO)^{-2}$ and $2H^+$ ions in DMSO while in water its pK value for the second hydrogen is only 4.2. It is noted that acids which yield large anions in DMSO show some ionization in comparison to water as solvent.

For example, the dissociation constant of picric acid is 500 times as great in DMSO as in water, but benzoic acid has a dissociation constant which is 10^6 times as great in water as in DMSO. Kolthoff and Reddy⁵ attributed this to the unusual stability of picrate ion in DMSO, but deferred explanation of 'abnormally small dissociation' of carboxylic acids in DMSO. An alternate explanation is that carboxylate anions are usually stabilized in water relative to DMSO by general hydrogen bonding to the negative charge localized on the oxygen atoms. A picrate ion may be similarly solvated in DMSO and water, but its hydrogen bonding interactions with water are small. This is because the negative charge on it is strongly dispersed over the aromatic system.

In general, if A is a small anion, HA is weaker in dipolar aprotic solvents than in protic solvents of comparable dielectric constants and basicity. This is because a positive charge localized on hydrogen, as in water, fits more closely about negative centre than would the positive charge localized on, for example, the sulphur in DMSO. The negative centre in DMSO is on a less hindered oxygen and interacts more strongly with positive centres.⁶

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