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Non Isothermal Solvation Parameters for Saturated Adipic Acid in Mixed Methanol –Water Solvents

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Abstract
The molal solubilities for saturated adipic acid solutions were determined at different temperatures 298.15, 303.15, 308.15 and 313.15K in mixed methanol-water (MeOH-H_2O) solvents. Different thermodynamic parameters were evaluated for the adipic acid like Gibbs free energies, enthalpies and entropies of solvation. From the experimental solubility, pH and density data, the different free energies, dissociation constants, association constants and other solvation parameters were estimated. The results were discussed.

1. Introduction

Adipic acid is very important dicarboxylic acid. About 2.5 billion kilograms white crystalline powder are produced mainly as precursor for the production of Nylon [1] polycondensation reaction was used with hexamethylenediamine forming 6.6 naylon. Other major applications involve polymers, it is a monomer for production of polyurethane and its esters are plastirizers, especially PVC [1]

In medicine adipic acid has been incorporated into controlled-release formulation matrix tablets to obtain pH-independent release for both weakly basic and weakly acid drugs [2]. In foods is used in small amount as flavour and gelling acid. Therefore more results needed about the solubility of adipic acid and its behaviour in mixed solvents.

Many publications have appeared on the behaviour of weak acids in anhydrous solvents. Interesting work has been done by Kolthoff et al. [3,4]. Aleksandrov et al. [5,6] studied the dissociation of salicylic acid in butane-2-one. Kreshkovet al. [7] studied the dissociation of amino acids (as weak) acids) in mixtures of formic and ethylmethyl ketone and in mixtures of acetic acid-ethylmethyl ketone. Gomaa et al. [8-11] studied association, dissociation and hydrogen bonding of a weak acid in different solvent mixtures from solubility measurements.

The aim of this work is to evaluate the solubility of adipic acid in (MeOH-H_2O) mixed solvents at different temperature and discuss in details the salvation parameters for the solubility process. Also, study the effect of mole fraction of MeOH in (MeOH-H_2O) mixed solvents on the solubility and the physical behaviour accompanied is very important for the biochemical analyzers. Also apply a theoretical model for evaluating different a microscopic interaction of adipic acid is necessary.

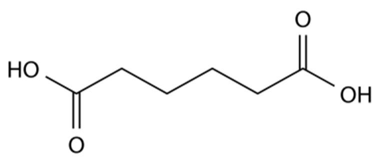
2. Experimental

The adipic acid and solvents used, methanol and water, were supplied from Merck. The saturated solutions of adipic acid were prepared by dissolving it in the solvents used. The solutions were saturated with N_2 gas in closed test tubes. The tubes were placed in a shaking water bath for a period of 4 days, followed by another 2 days without shaking to reach the necessary equilibrium .The solubility of adipic acid in each solution was determined gravimetrically by taking 1ml of the saturated solution and subjecting it to complete evaporation using small aluminium disks heated by an infrared lamp. The pH readings of the saturated solutions were measured using a pH-meter of the type Tacussel /Minis 5000. The densities were measured by using a weighing bottle of 1ml and analytical balance (4 digits) of the type Mettler Toledo DA.

2.1. Chemical Identity

Brand names: Rhodiacid AA - Adipic acid
Chemical name (IUPAC): Hexanedioic acid
Molecular formula: $C_6H_{10}O_4$

2.2. Structure



2.3. Physical/Chemical Properties

Property	Value
Physical state	Solid at 20°C and atmospheric pressure
Form	Crystalline powder
Colour	White
Odour	Slight odour
Molecular weight	146.14 g/mol
Melting Point	150.85°C at atmospheric pressure
Boiling Range	337.5°C at atmospheric pressure
Vapour pressure	0.097 hPa at 18.5°C
Water solubility	23 g/l at 25°C
Octanol/Water partition	0.09 at 20°C

2.4. Uses and Applications

Adipic acid is used as a monomer, for the production of Nylon 6-6. It is used also as a monomer orienter mediate for the synthesis of polyurethanes, mono- or polyesters for plasticizers, lubricant additives, coatings, foams or shoe soles applications [13].It is also used in formulation, for a wide number of specific applications, such as:

- tanning agent for pre-treatment of leather
- pH regulator in several processes such as the production of detergents and cleaning agents
- polluting agent in disinfection pills for drinking water
- additive in flue gas desulphurisation
- additive in the coatings of dish washing machine tablets
- additive in laboratory chemicals.

This technical grade is not intended to be used as an additive for human or animal foodstuff.

2.5. Calculations

The calculated molal solubilities (m) for adipic acid saturated solution are given in Table 1. The molar volumes (V_M) of adipic acid were obtained by dividing the molar mass by the densities and their values are listed in Table 2. The packing density as reported by Kim et al. [14] and Gomaa et al. [15], i.e. the relation between the Van der Waals volume (V_W) and the molar volume (V_M) of relatively large molecules(above 40) was found to be a constant value and equal to 0.661.

$$\text{Packing density } (P) = \frac{V_w}{V_M} = 0.661 \pm 0.017 \quad (1)$$

The electrostriction volume (V_e), which is the volume compressed by the solvent, was calculated using the following (Gomaa et al. [16-36]):

$$V_e = V_W - V_M \quad (2)$$

The molar, Van der Waals and electrostriction volumes of adipic acid in various solvents at 298.15K are tabulated in Table 2. The apparent molar volumes, V_ϕ, [37-38] were calculated using the following equation (3) [39]:

$$V_\phi = M/d - (d-d_o/dd_o)\ 1000/m \quad (3)$$

where M is the molar mass of adipic acid, m is the concentration, d and d_0 are the densities of saturated solution and pure solvents, respectively.

The values of V_ϕ for adipic acid in various solvents at 298.15K are presented in Table 2.

The activity coefficient was calculated using the relation [40].

$$\log \gamma_\pm = -0.5062\sqrt{m} \quad (4)$$

K_{ass} values were calculated [41, 42] from the ratios of association constant to dissociation constant (i.e. K_1/K_2) for the dimmers of adipic acid which form a complex ion (HA_2^-) and hydrogen ion(H^+)and the values of K` (where K` is the dissociation constant of the associated acid complex, H_2A_2)) are given by the following equations

$$K` = a^2H^+/m^2 \quad (5)$$

$$pa_{H^+} = \frac{1}{2}\log\frac{K_1}{K_2} - \log m = pH - \log\gamma_\pm \quad (6)$$

$$\frac{K_1}{K_2} = K\grave{}\ K_{ass} \quad (7)$$

Where a is the activity. The values obtained $\frac{K_1}{K_2}$, $K\grave{}$ and K_{ass} are reported in Table 3.

The free energies of dissociation (ΔG_d), free energies of association (ΔG_A), difference free energies ($\Delta\Delta G$), and free energies of solvation (ΔG_s) for adipic acid saturated solutions in various solvents were calculated by using the following equations and tabulated in Table 4 (see Fig. 3).

$$\Delta G_d = -RT \ln K\grave{} \quad (8)$$

$$\Delta G_{ass} = -RT \ln K_{ass} \quad (9)$$

$$\Delta\Delta G = \Delta G_{ass} - \Delta G_d \quad (10)$$

$$\Delta G_s = -RT\, pK_{sp} \quad (11)$$

$$pK_{sp} = -(\log 4S^3.\gamma_\pm^3) \quad (12)$$

3. Results and Discussion

Table 1. Molal solubilities (m) for saturated adipic acid solution in (MeOH-H_2O) mixed solvents at different temperature.

MeOH vol.%	m (g.mol/kg solvent)			
	298.15K	303.15K	308.15K	313.15K
0	0.1235	0.1445	0.1726	0.1870
20	0.1893	0.1969	0.2116	0.2259
40	0.3677	0.3761	0.4355	0.4872
60	0.7417	0.7671	0.8002	0.9153
80	1.1337	1.1626	1.2321	1.3584
100	1.3639	1.5554	1.6617	1.7652

Table 2. Molar volumes (V_M), Van der Waals volumes (V_W), electrostriction volumes (V_e) and apparent molar volumes (V_ϕ) for saturated solutions of adipic acid in (MeOH-H_2O) mixed solvents at 298.15K (in cm^3/ mol).

MeOH vol.%	V_M	V_W	$-V_e$	V_ϕ
0%	144.98015	95.83188	49.14827	144.89
20%	147.17019	97.27949	49.8907	147.08
40%	154.15611	101.89719	52.25892	154.16
60%	159.54148	105.45692	54.08456	159.54
80%	162.01773	107.09372	54.92401	161.97
100%	165.69161	109.52215	56.16946	165.59

Table 3. Log activity coefficients ($\log \gamma_\pm$), dissociation constants ($K\grave{}$) and association constants for adipic acid saturated solutions in (MeOH-H_2O) mixed solvents at 298.15 K

MeOH vol.%	$\log \gamma_\pm$	pa_{H^+}	$K\grave{}$	$\frac{K_1}{K_2}$	K_{ass}
0%	-0.17792	3.377921	$1.15\text{x}10^{-5}$	86987.67	$7.57\text{x}10^{9}$
20%	-0.22023	3.420228	$4.03\text{x}10^{-6}$	248117	$6.16\text{x}10^{10}$
40%	-0.30693	3.606933	$4.52\text{x}10^{-7}$	2211836	$4.89\text{x}10^{12}$
60%	-0.43596	3.735962	$6.13\text{x}10^{-8}$	16309059	$2.66\text{x}10^{14}$
80%	-0.53898	3.838983	$1.36\text{x}10^{-8}$	61231880	$3.75\text{x}10^{15}$
100%	-0.59116	3.691163	$2.23\text{x}10^{-8}$	44860563	$2.01\text{x}10^{15}$

Table 4. Free energies of dissociation (ΔG_d), free energies of association (ΔG_A), difference free energies ($\Delta\Delta G$) and free energies of solvation (ΔG_s) for adipic acid saturated solutions in (MeOH-H_2O) mixed solvents at 298.15K (in k Joule/mole)

MeOH vol.%	ΔG_d	ΔG_A	$\Delta\Delta G$	ΔG_s
0%	28.1979	-56.396	-84.594	12.117
20%	30.797	-61.593	-92.389	8.9435
40%	36.220	-72.441	-108.661	4.0053
60%	41.174	-82.348	-123.521	-1.215
80%	44.454	-88.907	-133.361	-4.370
100%	43.682	-87.365	-131.047	-5.745

Table 5. Mole fraction (X_s), mixed volumes of (MeOH-H_2O), Van der Waals volumes (V_W), difference in different Van der Waals volumes (ΔV_w) and solvation numbers (n_s) for adipic acid a saturated solutions in (MeOH-H_2O) mixed solvents at 298.15 K

MeOH vol.%	X_s MeOH	V_{mixed}	V_w	ΔV_w	n_s
0%	0	19.8773	95.831	99.77223	5.0194
20%	0.0999	23.8759	97.279	98.32423	4.1181
40%	0.2284	29.0194	101.897	93.70623	3.2290
60%	0.3976	35.7919	105.456	90.14723	2.5287
80%	0.6397	45.4824	107.093	88.51023	1.9460
100%	1	59.9041	109.522	86.08123	1.4369

Carboxylic acids are polar, and form hydrogen bonds with themselves, especially in non-polar solvents; since they contain both hydroxyl and carbonyl functional groups. It usually exist as dimeric pairs in nonpolar media due to their tendency to “self-associate.” Lower carboxylic acids (1 to 4 carbons) are soluble in water, whereas higher carboxylic acids (like adipic acid) are less soluble due to the increasing hydrophobic nature of the alkyl chain. These longer chain acids tend to be rather soluble in less-polar solvents such as ethers and alcohols [43]. And, the molal solubility of saturated solution of adipic acid in (MeOH – H_2O) mixed solvents found to increase with the increase the mole fraction of MeOH in the mixed solvent (see Fig. 1). This indicates that, the addition of an organic solvent to water favoured the solubilisation of adipic acid.

Van der Waals radii, as tabulated by Bondi have been used for a wide range of applications [44-53]. Bondi radii result from a refinement of the work of Pauling, [54] who determined standard values of atomic radii from contact distances between non bonded atoms in molecular crystals. The solvation volumes for adipic acid were evaluated from the difference between Van der Waals of adipic acid in absence and given before in various solvents. The Van der Waals volume was calculated from Bondi method [54, 57] and found to be 195.603 cm^3/mole. Subtracting this value from V_w in solvents and divide the results by the molar volumes of the solvents taken from ref. [58], n_s (the solvation number) was obtained and given in Table 5 (see Fig. 4).

The Gibbs free energies of solvation of adipic acid in mixed solvents found to decrease with the increase the mole fraction of MeOH in the mixed solvent and the transfer Gibbs free energies from water to mixed solvents found to increase with negative value. These indicate that, adding more organic solvent to the mixture, significant changes in adipic acid solubility in mixtures of methanol-water were verified. Therefore, the addition of an organic solvent to water favored the solubilisation of adipic acid.

And, the data in Table 2 shows an increase in the values of V_M and V_W and decrease at the values of the third V_e (see Fig. 1). A negative increase of electrostriction values was observed for adipic acid solutions by increasing the proportions of methanol in the mixtures. It was observed from the different volume values, that all volumes for adipic acid increased by increasing methanol content in the mixed solvent due mainly to the higher solvation. Also the electrostriction volumes increase in negativity confirming the increase in solvent effect by more adding ethanol to the mixtures. The maximum value of K_{ass} was found 80% MeOH-H_2O where water is the least association parameters.

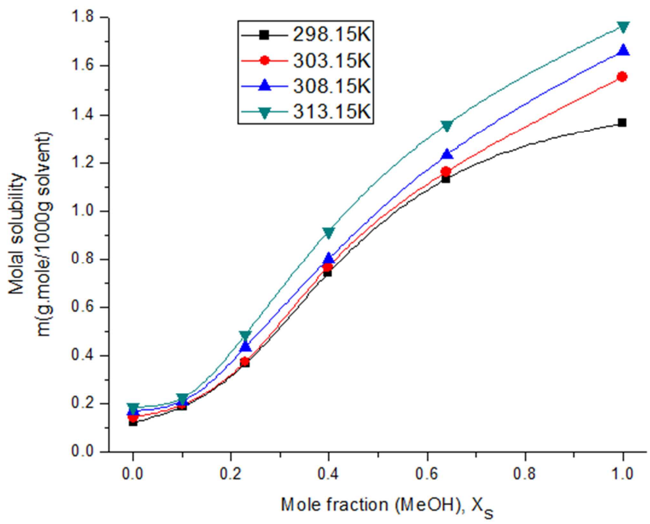


Fig 1. *Relation between molal solubility (m) of saturated solutions of adipic acid with mole fraction (x_s) of methanol in mixed MeOH -H_2O solvents at different temperature.*

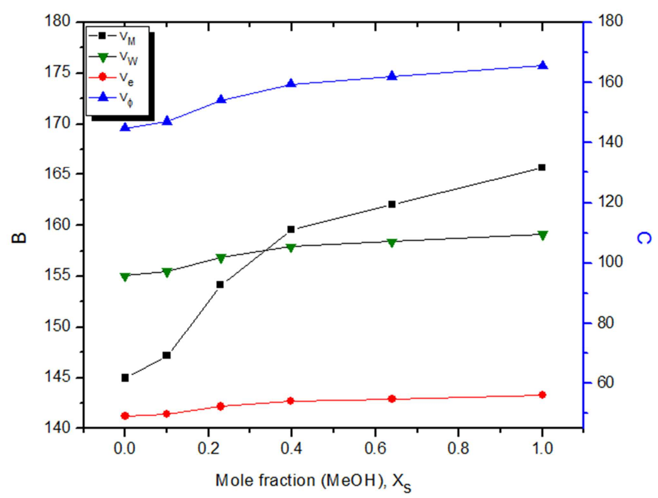


Fig 2. *Relation between change in Molar volumes (V_M), Van der Waals volumes (V_W), electrostriction volumes (V_e) and apparent molar volumes (V_ϕ) for saturated solutions of adipic acid with mole fraction (x_s) of methanol in mixed MeOH -H_2O solvents at 298.15 K.*

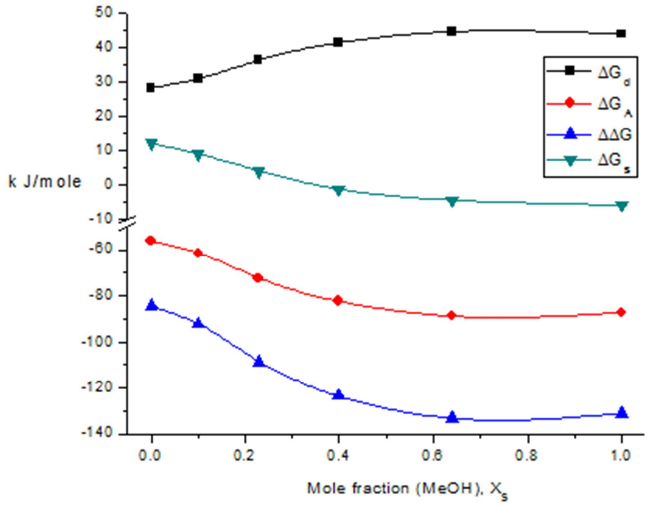


Fig 3. *Relation between change in free energies of dissociation (ΔG_d), free energies of association (ΔG_A), difference free energies ($\Delta\Delta G$) and free energies of solvation (ΔG_s) for adipic acid saturated solutions with mole fraction (x_s) of methanol in mixed MeOH -H_2O solvents at 298 K.*

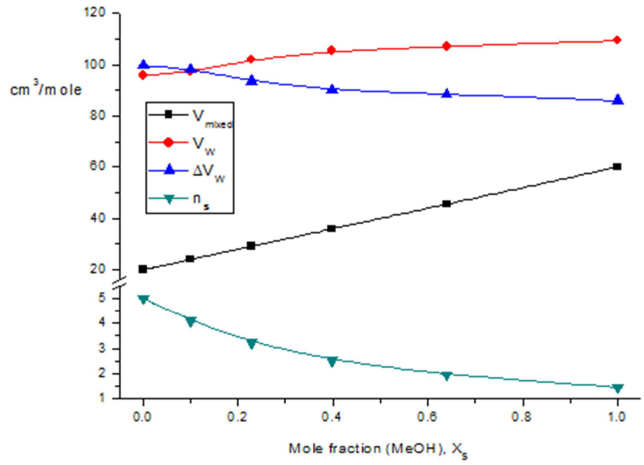


Fig 4. *Relation between mixed volumes (V_{mixed}) of (MeOH-H_2O), Van der Waals volumes (V_W), difference in different Van der Waals volumes (ΔV_w) and solvation numbers (n_s) for saturated solutions of adipic acid with mole fraction (x_s) of methanol in mixed MeOH -H_2O solvents at 298.15 K.*

4. Conclusions

The solubility of saturated solution of adipic acid in mixed solvents found to increase with the increase the mole fraction of MeOH in the mixed solvent. In addition, Gibbs energy, for the solution processes were also calculated in order to estimate the contributions solute-solvent interactions related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium. The saturated solution of adipic acid in the mixed solvent is perfectly non-ideal due to the mean activity coefficient of ions in the solution and partly due to the ion association phenomenon. It was observed from the different volume values, that all volumes for adipic acid increased by increasing methanol content in the mixed solvent due mainly to the higher solvation. Also the electrostriction volumes increase in negativity confirming the increase in solvent effect by more adding ethanol to the mixtures. It was concluded that the solute-solvent interaction increased by increasing $\Delta\Delta G$ and ΔG_s due mainly to the increase of the association parameters in the corresponding solvents. Also it was observed that increasing methanol percentage is achieved by increase in all the association parameters in the mixture used. Consequently, increasing of the salvation numbers favor more solute-solvent interactions between adipic acid and solvents. Also, small solvation numbers favour more solute -solute interaction or ion pair formation resulting in the decrease of the solute – solvent interactions in the mixed (MeOH-H_2O) solvent under discussion. Big positive values for $\Delta\Delta G$ and big negative values for ΔG_s indicate also more solute –solvent interactions.

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