Solubility Of Acetanilide In Pure And Mixed Solvents At 288.15 To 313.15 K And Its Correlation With Thermodynamic Model

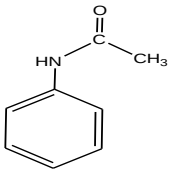
Ramesh R. Pawar and Atul S. Kale

Abstract: The solubility of Acetanilide in pure ethanol, water and ethanol + water solvents mixture were determined by using gravimetric method at the temperature ranging from (288.15 to 313.15) K. The solubility of acetanilide increases with increasing mole fraction of organic solvent and temperature. The solubility was correlated by using modified Apelblat equation. By using van't Hoff equation, the dissolution enthalpy, entropy and Gibbs free energy are predicted in aqueous co-solvent mixtures of ethanol.

Keywords: Acetanilide, Ethanol, Solubility, Enthalpy, Entropy.

1 INTRODUCTION

The chemical structure of acetanilide is as



Solid-liquid equilibrium (SLE) data are useful for the design and optimization of crystallization processes [1]. The acetanilide was the first aniline derivative has antipyretic as well as analgesic properties [2]. Y. Baena et.al. measured solubility of acetanilide in water, octanol, isopropyl myristate and chloroform at several temperatures [3] R.R. Pawar et.al. measured solubility and determined the thermodynamic functions of acetanilide in n-propanol + water at various mole fractions [4]. Y. Baena et.al. determined solubility of acetanilide in water and octanol at 25^0C [5]. However there is no data available for solubility of acetanilide in pure ethanol and water-ethanol solvent mixtures. In present work, systematic study of solubility of acetanilide in pure ethanol and water + ethanol solvent mixtures over the whole composition range at 288.15 to 313.15 K are reported.

2 MATERIALS AND METHODS

Material

Acetanilide were purchased from spectrochem (purity 99 %), Ethanol were purchased from fisher scientific (purity 99.5 %).MethodThe solubility of acetanilide was measured using an apparatus similar to that described as in the literature [6-8].

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An excess amount of acetanilide was added to the binary solvent mixture prepared by weight (Scale-Tec) with an accuracy of ± 0.1 mg, in a specially designed 100 ml double jacketed flask. Water was circulated between inner and outer walls of the flask. The temperature of the circulating water was controlled by thermostat within (± 0.1) K. The solution was continuously stirred using a magnetic stirrer for long time so that equilibrium is assured, and the temperature of solution is same as that of circulating water; the stirrer was switched off; and the solution was allowed to stand for 1 hour. Then a fixed quantity of the supernatant liquid was withdrawn from the flask in a weighing bottle with the help of pipette which is hotter than the solution. By using electronic balance the mass of solution were weighed and kept in an oven at 343 K until the whole solvent was evaporated and the residue was completely dry. This was confirmed by weighing two or three times until a constant weight was obtained after keeping the sample in an oven for another 30 minutes every time. The solubility has been calculated using weight of solute and weight of solution. The same procedure was repeated three times. The mean value of the three determinations was applied to calculate the mole fraction solubility(x_B). The mole fraction solubility (x_B), and is as the initial mole fraction of solvent mixture (x_C^0) is calculated by Eq. 1 and 2.

$$x_B = \frac{\frac{m_s}{M_s}}{\frac{m_c}{M_s} + \sum_{i=1}^{n} \frac{m_i}{M_i}} \quad (1)$$

$$x_C^0 = \frac{M_2}{\frac{m_2}{m_3} \cdot m_3} \quad (2)$$

Where, m_s= mass of the solute, M_s= molecular weight of solute, m_i= mass of the solvent, Mi= molecular weight of solvent, in this n=2 for single solvent and 3 for mixed solvent. m_2 & m_3= mass of water and alcohol, respectively, M_2 & M_3= molecular weight of water and alcohol, respectively [9].

3 RESULTS AND DISCUSSION

Solubility data

Table 1 show the experimental and calculated (using Apelblat

equation) values of solubility (x_B) of acetanilide at 288.15 to 313.15 K in water + ethanol. Variation of solubility with x_C^0 is visually shown in Figures 1.

Table 1: *Experimental $x_{B(exp.)}$ and calculated $x_{B(cal.)}$ values of mole fraction solubility of acetanilide for various initial mole fractions, x_C^0, of ethanol at temperatures (288.15 to 313.15) K*

T/K	x_C^0	$x_{B(exp.)} \times 10^{-2}$	$x_{B(cal.)} \times 10^{-2}$	RD
288.15	0.0000	0.0566	0.0566	0.0006
	0.0416	0.0860	0.0854	0.0077
	0.0891	0.1445	0.1440	0.0036
	0.1436	0.3317	0.3266	0.0153
	0.2068	0.8061	0.8117	-0.0069
	0.2812	1.6859	1.6944	-0.0050
	0.3698	2.9628	2.9672	-0.0015
	0.4772	4.5300	4.5496	-0.0043
	0.6100	6.1432	6.1451	-0.0003
	0.7788	7.5224	7.4927	0.0040
	1.0000	7.7583	7.7597	-0.0002
291.15	0.0000	0.0626	0.0632	-0.0092
	0.0416	0.0971	0.0983	-0.0120
	0.0891	0.1687	0.1692	-0.0029
	0.1436	0.3781	0.3874	-0.0246
	0.2068	0.9574	0.9521	0.0055
	0.2812	1.9513	1.9486	0.0014
	0.3698	3.3808	3.3728	0.0024
	0.4772	5.1086	5.1035	0.0010
	0.6100	6.8662	6.8625	0.0005
	0.7788	8.2462	8.2906	-0.0054
	1.0000	8.5330	8.5392	-0.0007
293.15	0.0000	0.0687	0.0679	0.0118
	0.0416	0.1055	0.1077	-0.0206
	0.0891	0.1882	0.1885	-0.0020
	0.1436	0.4356	0.4347	0.0019
	0.2068	1.0626	1.0609	0.0016
	0.2812	2.1527	2.1442	0.0039
	0.3698	3.6751	3.6813	-0.0017
	0.4772	5.5556	5.5207	0.0063
	0.6100	7.4071	7.3917	0.0021
	0.7788	8.8863	8.8740	0.0014
	1.0000	9.1282	9.1060	0.0024
296.15	0.0000	0.0761	0.0753	0.0104
	0.0416	0.1259	0.1232	0.0221
	0.0891	0.2223	0.2219	0.0018
	0.1436	0.5189	0.5178	0.0020
	0.2068	1.2566	1.2510	0.0044
	0.2812	2.4999	2.4836	0.0065
	0.3698	4.2215	4.2104	0.0026
	0.4772	6.2494	6.2292	0.0032
	0.6100	8.2741	8.2709	0.0004
	0.7788	9.8221	9.8342	-0.0012
	1.0000	10.0189	10.0337	-0.0015
298.15	0.0000	0.0806	0.0805	0.0010
	0.0416	0.1371	0.1344	0.0198
	0.0891	0.2481	0.2475	0.0024
	0.1436	0.5806	0.5827	-0.0036
	0.2068	1.4041	1.3986	0.0040
	0.2812	2.7503	2.7455	0.0018
	0.3698	4.6026	4.6136	-0.0024
	0.4772	6.8055	6.7638	0.0061
	0.6100	8.8938	8.9198	-0.0029
	0.7788	10.5166	10.5366	-0.0019
	1.0000	10.6962	10.7083	-0.0011
301.15	0.0000	0.0866	0.0888	-0.0255
	0.0416	0.1522	0.1528	-0.0035
	0.0891	0.2860	0.2918	-0.0204
	0.1436	0.6989	0.6969	0.0029
	0.2068	1.6428	1.6571	-0.0087
	0.2812	3.1763	3.2012	-0.0078
	0.3698	5.3007	5.3066	-0.0011
	0.4772	7.4947	7.6731	-0.0238
	0.6100	9.9299	9.9985	-0.0069
	0.7788	11.6798	11.6931	-0.0011
	1.0000	11.7833	11.8128	-0.0025
303.15	0.0000	0.0941	0.0946	-0.0052
	0.0416	0.1650	0.1660	-0.0061
	0.0891	0.3283	0.3258	0.0078
	0.1436	0.7943	0.7862	0.0102
	0.2068	1.8593	1.8582	0.0006
	0.2812	3.5509	3.5536	-0.0008
	0.3698	5.8544	5.8359	0.0032
	0.4772	8.3857	8.3604	0.0030
	0.6100	10.8315	10.7952	0.0034
	0.7788	12.5748	12.5392	0.0028
	1.0000	12.6548	12.6162	0.0030
306.15	0.0000	0.1007	0.1038	-0.0301
	0.0416	0.1849	0.1876	-0.0145
	0.0891	0.3924	0.3846	0.0198
	0.1436	0.9422	0.9437	-0.0016
	0.2068	2.2055	2.2113	-0.0026
	0.2812	4.1502	4.1688	-0.0045
	0.3698	6.7600	6.7477	0.0018
	0.4772	9.5809	9.5318	0.0051
	0.6100	12.1672	12.1201	0.0039
	0.7788	13.9820	13.9330	0.0035
	1.0000	13.9310	13.9317	0.0005
308.15	0.0000	0.1172	0.1102	0.0599
	0.0416	0.2026	0.2032	-0.0030
	0.0891	0.4288	0.4297	-0.0020
	0.1436	1.0696	1.0670	0.0024
	0.2068	2.4834	2.4867	-0.0013
	0.2812	4.6512	4.6458	0.0012
	0.3698	7.4196	7.4456	-0.0035
	0.4772	10.4783	10.4189	0.0057
	0.6100	13.1428	13.0990	0.0033
	0.7788	14.9867	14.9529	0.0023
	1.0000	14.9184	14.8888	0.0020
311.15	0.0000	0.1281	0.1268	0.0010
	0.0416	0.2299	0.2283	0.0067
	0.0891	0.5018	0.5078	-0.0121
	0.1436	1.2758	1.2850	-0.0072
	0.2068	2.9611	2.9711	-0.0034
	0.2812	5.4894	5.4808	0.0016
	0.3698	8.6074	8.6505	-0.0050
	0.4772	11.9013	11.9335	-0.0027
	0.6100	14.6944	14.7279	-0.0023
	0.7788	16.5553	16.6336	-0.0047
	1.0000	16.3972	16.4562	-0.0036
313.15	0.0000	0.1367	0.1368	-0.0004
	0.0416	0.2470	0.2464	0.0024
	0.0891	0.5696	0.5679	0.0031
	0.1436	1.4578	1.4560	0.0012
	0.2068	3.3688	3.3496	0.0057
	0.2812	6.1394	6.1301	0.0015
	0.3698	9.6196	9.5746	0.0047
	0.4772	13.0763	13.0825	-0.0005
	0.6100	15.9114	15.9320	-0.0013
	0.7788	17.8712	17.8638	0.0004
	1.0000	17.6196	17.5967	0.0013

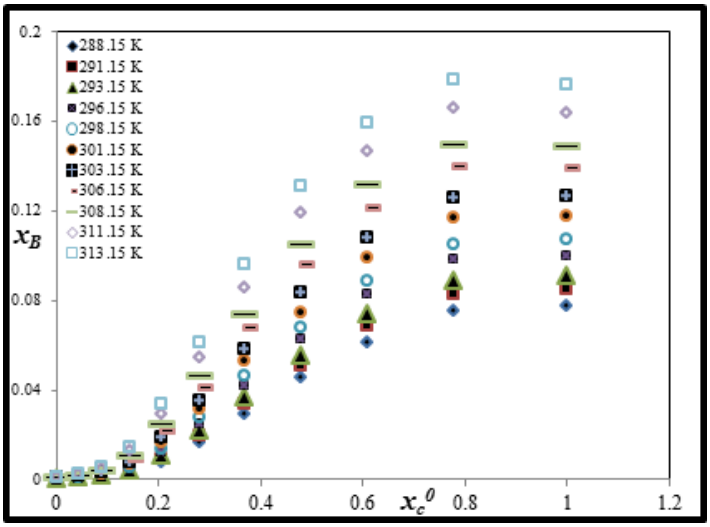

***Fig 1**: Variation in mole fraction solubility (x_B) of acetanilide with initial mole fraction (x_C^0) of ethanol.*

The solubility of acetanilide increases with increasing temperature. Acetanilide is an organic compound; naturally the solubility is more in ethanol as compared with water. In mixed solvents with water as the proportion of organic solvent increases, as expected the solubility also increases. Modified Apelblat EquationThe modified Apelblat equation can be used to correlate the solubility and temperature as follows [10].

$$lnx_{B=} A + \frac{B}{T} + ClnT \qquad (3)$$

A, B, and C are empirical constant and T is temperature in Kelvin. The value A and B represents the variation in the solution coefficient and the C value represents the effect of temperature on the fusion enthalpy [11]. Relative deviation (RD) [12] was calculated using equation 4.

$$RD = \frac{x_B - x_B}{x_{exp.}} \qquad (4)$$

From table 1 it can be seen that there is an excellent agreement between experimental and calculated values of mole fraction solubility. The values of parameters A, B and C along with co-relation coefficient (R^2) are listed in table 2.

***Table 2**: Parameters (A, B, C) and correlation coefficient (R^2) of Apelblat equation*

	x_C^0	A	B	C	R^2
E + W	0.0000	-293.970	10182.1	44.3492	0.9939
	0.0416	73.8902	-6856.09	-10.0932	0.9985
	0.0891	-266.895	7476.91	41.3887	0.9994
	0.1436	-378.908	12156.1	58.4439	0.9995
	0.2068	-397.964	13285.5	61.2773	0.9998
	0.2812	-448.284	15973.2	68.6454	0.9999
	0.3698	-394.588	13942.3	60.5077	0.9999
	0.4772	-367.121	13082.8	56.2601	0.9994
	0.6100	-211.563	6445.47	32.9134	0.9998
	0.7788	-184.290	5488.54	28.7193	0.9998
	1.0000	-167.334	4883.37	26.1023	0.9999

Thermodynamics functions of dissolution

According to the van't Hoff equation, the standard molar enthalpy change of solution ΔH_{sol}^0 is generally obtained from the slope of the $\ln x_B$ versus ($1/T - 1/T_{hm}$) plot. Average temperature T_{hm} is introduced to obtain a single value of ΔG_{sol}^0 and ΔS_{sol}^0 in the temperature range studied

$$T_{hm} = \frac{n}{\sum (1/T)} \qquad (5)$$

In the work, T_{hm} = 300.8773 K. The values of ΔH_{sol}^0 are derived using equation 6.

$$\Delta H_{sol}^0 = -R\left(\frac{\partial \ln x_B}{\partial (1/T)}\right) = -R\left|\frac{\partial \ln x_B}{\partial (1/T - 1/T_{hm})}\right| \qquad (6)$$

The values of slope and intercept of $\ln x_B$ versus ($1/T - 1/T_{hm}$) plot for different solutions including pure solvents and binary solvent mixtures are listed in Table 3. The ΔG_{sol}^0, can be calculated in the way similar to Krug et al [13] as

$$\Delta G_{sol}^0 = -RT_{hm} \times intercept \qquad (7)$$

The standard molar entropy change ΔS_{sol}^0 is obtained from

$$\Delta S_{Sol}^0 = \frac{(\Delta H_{sol}^0 - \Delta G_{sol}^0)}{T} \qquad (8)$$

Both ΔG_{sol}^0 and ΔS_{sol}^0 pertain to the mean temperature T_{hm} = 300.8773 K.

The results are shown in table 4 and 5, along with relative contribution of enthalpy (% ζH) and entropy (% ζTS) given by equation 9 and 10 respectively [14].

$$\% \zeta_H = \frac{|\Delta H_{sol}^0|}{|\Delta H_{sol}^0| + |T\Delta S_{sol}^0|} * 100 \qquad (9)$$

$$\% \zeta_{TS} = \frac{|T\Delta S_{sol}^0|}{|\Delta H_{sol}^0| + |T\Delta S_{sol}^0|} * 100 \qquad (10)$$

The values of ΔH_{sol}^0 and ΔS_{sol}^0 for all the solutions are positive indicating the solution process as endothermic. The contribution of enthalpy to positive molar Gibbs energy is more as compared to entropy for all solutions.

***Table 3**: Slope (m) and intercept (c) of the $\ln x_B$ versus ($1/T - 1/T_{hm}$) plot along with R^2.*

Acetanilide + Ethanol + Water			
x_c^0	m	c	R2
0.0000	-3144	-7.025	0.991
0.0416	-3823	-6.499	0.998
0.0891	-4959	-5.837	0.998
0.1436	-5405	-4.962	0.998
0.2068	-5127	-4.094	0.998
0.2812	-4653	-3.432	0.997
0.3698	-4239	-2.928	0.997
0.4772	-3822	-2.559	0.996
0.6100	-3444	-2.301	0.998
0.7788	-3141	-2.145	0.998
1.0000	-2959	-2.136	0.999

***Table 4**: Thermodynamic parameters of Acetanilide at T_{hm} = 300.8773 K*

x_C^0	ΔH_{sol}^0/kJ ·K−1·mol−1	ΔG_{sol}^0/kJ ·K−1·mol−1	ΔS_{sol}^0/kJ ·K−1·mol−1	$T\Delta S_{sol}^0$/kJ ·K−1·mol−1
Acetanilide + Ethanol + Water				
0.0000	26.1392	17.5730	0.0285	8.5662
0.0416	31.7844	16.2572	0.0516	15.5272
0.0891	41.2291	14.6012	0.0885	26.6279
0.1436	44.9372	12.4124	0.1081	32.5248
0.2068	42.6259	10.2411	0.1076	32.3848
0.2812	38.685	8.5851	0.1000	30.0999

0.3698	*35.2430*	*7.3244*	*0.0928*	*27.9187*
0.4772	*31.7761*	*6.4013*	*0.0843*	*25.3748*
0.6100	*28.6334*	*5.7559*	*0.0760*	*22.8775*
0.7788	*26.1143*	*5.3657*	*0.0690*	*20.7486*
1.0000	*24.6011*	*5.3432*	*0.0640*	*19.2579*

Table 5: *Relative contribution of enthalpy (% ζH) and entropy (% ζTS)*

x_C^0	*% ζH*	*% ζTS*
0.0000	*75.3174*	*24.6807*
0.0416	*67.1810*	*32.8190*
0.0891	*60.7588*	*39.2412*
0.1436	*58.0119*	*41.9881*
0.2068	*56.8264*	*43.1736*
0.2812	*56.2406*	*43.7594*
0.3698	*55.7981*	*44.2019*
0.4772	*55.6004*	*44.3996*
0.6100	*55.5871*	*44.4129*
0.7788	*55.7249*	*44.2751*
1.0000	*56.0913*	*43.9087*

4 CONCLUSIONS

This paper reports experimental data for the solubility of acetanilide in pure water, ethanol and binary mixtures of water-ethanol from (288.15-313.15) K. the solubility of acetanilide was increase with increasing temperature. The thermodynamic aspects of the solubility process of acetanilide in binary mixtures were studied in order to select the best solvent and optimize its solubility.

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