

## Conductometric Studies of Dissociation Constants of Benzoic Acid in Water and 2-Propanol Mixtures at Different Temperatures

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**Summary:** The molar conductance of dilute solutions of benzoic acid in binary mixtures of water and 2-propanol has been measured at temperatures ranging from 298.15 K to 313.15 K. The experimental data were analyzed by means of the Fuoss-Kraus equation (1933) for the derivation of the thermodynamic dissociation constants and limiting molar conductance. The results were compared with those available in literature pertaining to analogue media.

Key Words: Benzoic Acid, 2-Propanol, Conductance, Dielectric Constant, Walden Product.

### Introduction

There has been much recent attention on the use of binary solvent systems for many purposes and practical applications. These mixtures have also been used as solvents in the study of various physicochemical properties of electrolyte solutions. Quite a number of papers on the conductometric studies of different electrolytes in both water and mixed solvent mixtures have recently been published [1-8]. The cosolvent can both be organic and aqueous. The dissociation of solutes in mixed solvents depends primarily on the solvation of solutes or their constituent ions by the components of solvent mixtures [9].

The thermodynamic dissociation constants of benzoic acid are available in water with acetone [10] and water with tetrahydrofuran [11] mixtures which were derived from conductometric data. The pK<sub>a</sub> values for benzoic acid are also available in the literatures in a few acetone-water [12, 13], dioxan-water [14] and water-formamide [15] mixtures derived potentiometrically.

The present paper is on the study of the dissociation of benzoic acid in binary mixtures of water with 2-propanol. The molar conductance of dilute solutions of benzoic acid have been measured in 2-propanol-water binary mixtures ranging in composition from 0-40 wt% 2-propanol at temperatures ranging from 298.15 K to 313.15 K. The conductance-concentration data have been analyzed for the derivation of thermodynamic dissociation constants, pK<sub>a</sub> and limiting molar conductance,  $\Lambda_0$  values. Normalized Walden Product (NWP) is also reported for the system. The dependence of pK<sub>a</sub> values on the composition of the

solvent mixtures is investigated in order to assess solute-solvent interaction.

### Result and Discussion

A conductometric method has been applied to measure the molar conductance of dilute solutions of benzoic acid. The corresponding values of the molar conductance for solutions of different concentrations of the acid are given in Table-1.

The values were analyzed using the equation of Bray-Kraus (1913),

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda \times C}{K_a \times \Lambda_0^2} \quad (1)$$

where,  $\Lambda_0$  is limiting molar conductance of the solute in the particular solvent at the particular temperature,  $K_a$  is dissociation constant of the monobasic acid. This equation was initially used to obtain the limiting molar conductance,  $\Lambda_0$ . The values of  $\Lambda_0$  of the acid in different solvent mixtures at different temperatures obtained from the least square fitting of the plot  $1/\Lambda$  vs. ( $\Lambda \times C$ ) of the Bray-Kraus equation were used to calculate  $K_a$  values of the monobasic acid by applying Fuoss-Kraus equation,

$$\frac{F_{(z)}}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda \times C \times f_{\pm}^2}{K_a \times \Lambda_0^2 \times F_{(z)}} \quad (2)$$

where,  $F_{(z)}$  called the Fuoss function is expressed as

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$$F_{(c)} = \frac{4}{3} \cos^2 \left[ \frac{1}{3} \left\{ \cos^{-1} \left( -3^{\frac{3}{2}} \times \frac{Z}{2} \right) \right\} \right] \quad (3)$$

$$Z = \frac{(\alpha \wedge_0 + \beta)}{(\wedge_0)^{\frac{3}{2}}} \times \sqrt{\wedge \times C} \quad (4)$$

$$\log f_{\pm} = -\frac{A\sqrt{\mu}}{1+\sqrt{\mu}} \quad (5), \quad \sqrt{\mu} = \sqrt{\alpha' C}$$

For weak electrolyte, and  $\alpha' = \frac{\wedge}{\wedge_0}$

Here  $\alpha$ ,  $\beta$ , A and B are characteristic solvent properties,

where  $\alpha = 0.8204 \times 10^6 / (DT)^{\frac{3}{2}}$ ,  $\beta = 82.501 / \eta (DT)^{\frac{1}{2}}$ ,

$A = 1.8246 \times 10^6 / (DT)^{\frac{3}{2}}$ ,

$B = 50.29 \times 10^8 (DT)^{\frac{1}{2}}$ ,

The values of the solvent parameters are summarized in Table-2.

The values of  $pK_a$  and  $\wedge_0$  of benzoic acid in 2-propanol-water mixtures at different temperatures derived from the slopes and intercepts of Fuoss-Kraus equation respectively are summarized in Table-3. The dependence of  $pK_a$  values for benzoic acid on the inverse of dielectric constants of 2-propanol-water mixtures at different temperatures is shown in Fig. 1.

#### Thermodynamic Dissociation Constants

The  $pK_a$  values of benzoic acid reported in Table-3 indicate an increase with the increase in concentration of the alcohol in the solvent mixtures at a particular temperature. The values of  $pK_a$  as a function of dielectric constant of the media (100/D) are represented by the Fig. 2. Niazi *et al* [16] have reported similar trend for benzoic acid in ethanol-water and 1-propanol-water mixtures.

Table-1: Molar Conductance,  $\wedge$  for Solutions of Benzoic Acid in 2-Propanol-Water Mixtures at Different Temperatures and Varying Concentration of Cosolvent.

S. No	% solution 2-Propanol	Concentrations $\times 10^4$ (Mole litre <sup>-1</sup> )	Molar conductance ( $\wedge$ ) (ohm <sup>-1</sup> cm <sup>2</sup> )			
			Temperature 298.15 K	Temperature 303.15 K	Temperature 308.15 K	Temperature 313.15 K
1		6.1971	91.656	91.174	90.687	90.203
2		5.7381	94.631	94.197	93.677	93.236
3		5.3423	97.523	97.087	96.588	96.026
4		4.9977	100.246	99.846	99.346	98.845
5		4.6127	103.518	103.193	102.585	102.218
6		4.3426	106.158	105.697	105.241	104.776
7	0 Wt%	4.0938	108.579	108.207	107.730	107.268
8		3.8824	110.756	110.497	110.108	109.726
9		6.4472	56.614	55.838	55.063	54.287
10		5.6887	59.768	59.064	58.185	57.306
11		5.3727	61.235	60.491	59.746	58.816
12		4.6051	65.634	64.711	63.842	63.113
13		3.7195	71.729	70.977	70.171	69.095
14		3.0221	78.091	77.430	76.437	75.444
15	10 Wt%	2.6863	81.897	81.152	80.408	79.291
16		2.4177	85.618	84.791	83.964	83.137
17		6.7420	28.330	27.737	26.698	27.791
18		6.3206	29.206	28.636	27.529	29.538
19		5.6183	30.828	30.117	29.119	31.184
20		5.0565	32.374	31.642	30.555	32.730
21		4.2137	35.147	34.411	33.225	35.527
22		3.8896	36.456	35.736	34.451	36.816
23	20 Wt%	3.3710	38.861	38.119	36.784	39.276
24		2.9744	41.017	40.277	38.831	41.487
25		10.1423	12.127	10.510	10.964	11.477
26		9.4661	12.536	10.860	11.335	11.874
27		8.8745	12.936	11.212	11.685	12.248
28		7.8884	13.653	11.878	12.360	13.013
29		7.0996	14.353	12.427	13.029	13.620
30		6.4542	15.029	13.046	13.603	14.238
31	30 Wt%	5.9163	15.652	13.606	14.181	14.840
32		5.4612	16.260	14.136	14.723	15.418
33		4.7331	17.409	15.127	15.761	16.501
34		14.0069	4.790	4.983	5.204	5.469
35		12.6729	5.0344	5.232	5.468	5.737
36		11.0888	5.366	5.582	5.835	6.122
37		10.2358	5.578	5.803	6.057	6.370
38		9.5047	5.787	6.018	6.283	6.597
39	40 Wt%	8.8711	5.986	6.222	6.493	6.809
40		7.8274	6.362	6.605	6.899	7.231
41		6.6533	6.869	7.139	7.440	7.816

Table-2: Solvent Parameters for 2-Propanol-Water Mixtures

S. No	% of 2-Propanol	Temperature (K)	Characteristic properties of 2-propanol			
			$\alpha$	$\beta$	$\Lambda$	$B \times 10^{-8}$
1	0 Wt%	298.15 K	0.2289	60.3260	0.5092	0.3286
2		303.15 K	0.2311	67.5450	0.5140	0.3297
3		308.15 K	0.2327	75.0221	0.5174	0.3304
4		313.15 K	0.2357	82.9811	0.5241	0.3318
5	10 Wt%	298.15 K	0.2640	38.9909	0.5872	0.3446
6		303.15 K	0.2673	43.3378	0.5946	0.3461
7		308.15 K	0.2706	49.1430	0.6019	0.3475
8		313.15 K	0.2740	59.0142	0.6095	0.3489
9	20 Wt%	298.15 K	0.3104	29.3933	0.6903	0.3637
10		303.15 K	0.3137	33.2661	0.6976	0.3650
11		308.15 K	0.3178	38.5513	0.7068	0.3666
12		313.15 K	0.3221	46.8291	0.7163	0.3682
13	30 Wt%	298.15 K	0.3713	25.3364	0.8257	0.3861
14		303.15 K	0.3758	29.7188	0.8358	0.3877
15		308.15 K	0.3820	35.5245	0.8495	0.3898
16		313.15 K	0.3869	41.9706	0.8604	0.3914
17	40 Wt%	298.15 K	0.4548	23.2901	1.0115	0.4131
18		303.15 K	0.4613	28.2554	1.0260	0.4151
19		308.15 K	0.4684	33.8833	1.0418	0.4172
20		313.15 K	0.4767	39.5655	1.0602	0.4196

Table-3: Summary of  $pK_a$  and  $\Lambda_0$  of Benzoic Acid in Different 2-Propanol-Water Mixtures at Different Temperatures.

Wt% of 2-Propanol	298.15 K		303.15 K		308.15 K		313.15 K	
	$\Lambda_0$	$pK_a$	$\Lambda_0$	$pK_a$	$\Lambda_0$	$pK_a$	$\Lambda_0$	$pK_a$
0	332.732	4.195 [16]	343.197	4.232	353.379	4.267	364.793	4.305
10	265.470	4.438	277.664	4.494	289.836	4.550	297.326	4.589
20	210.834	4.860	216.164	4.903	225.197	4.976	205.788	4.826
30	159.524	5.208	167.693	5.381	164.313	5.325	163.195	5.277
40	122.452	5.663	116.801	5.586	103.443	5.439	97.092	5.338

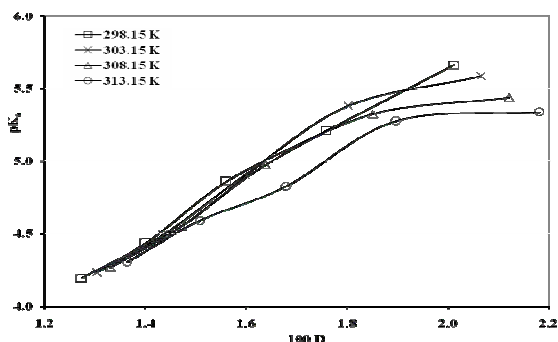
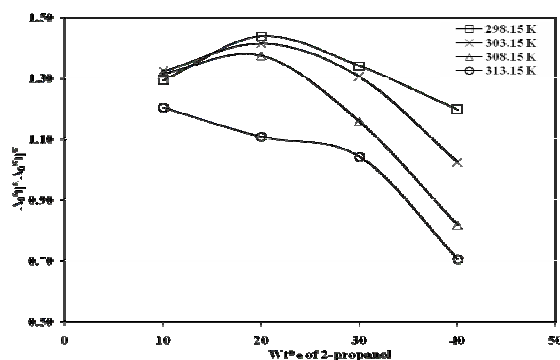
Fig. 1: Plots of  $pK_a$  of benzoic acid against inverse of dielectric constants ( $D$ ) for 2-propanol-water mixtures at different temperatures.

Table-3 shows an interesting variation of  $pK_a$  with temperature. The maximum in  $pK_a$  shifts to lower temperatures on passing from 20 wt% of 2-propanol-water mixtures to that of 30 wt%, whereas curves for 0-10 wt% of the alcohol concentration show a continuous increase as the temperature increases. A close similarity in present work was observed with the works of earlier workers [15, 17]. A possible explanation of the behavior of the solvent system under study may be found due to by considering the selective solvation [17] which occurs when the composition of the solvent components in the neighborhood of the charged species is different from the composition of 10 wt% of 2-propanol, the

concentration of the solvent component with higher dielectric constant increases around the charged species. In the system under study it is possible that solvation shell probably changes, passing from a prevalence of 2-propanol ones. The observance of decrease in  $K_a$  with the increase of temperature may also be due to the negative temperature coefficient of the dielectric constant of the media.

Fig. 2: Plots of Normalized Walden Product ( $\Lambda_0^s \eta^s / \Lambda_0^w \eta^w$ ) vs. wt% composition of 2-propanol-water mixtures at different temperatures.

#### Normalized Walden Products

The ratio of the Walden product of the acid in the solvent mixture to that in water is termed as normalized Walden product, nwp ( $\Lambda_0^s \eta^s / \Lambda_0^w \eta^w$ ). The values of nwp as a function of solvent composition

for the acid studied as mentioned at different temperatures are shown in Fig. 2. At the highest studied temperature the values gradually decreases but at the other temperatures a systematic trend is found to occur and the values pass through a maximum at about 10 to 20 wt.% of 2-propanol concentration in the solvent mixtures. A close similarity in present work was observed with the works of earlier workers [8, 16, 18]. This trend of the normalized Walden product values might not only due to the  $\eta$  or D changes, but also to an altering proton transfer mechanism as solvent is enriched with organic component.

### Experimental

Benzoic acid was a BDH product of high purity (99.9% pure). The melting point of benzoic acid was observed 122.4 °C [19]. 2-propanol of 99.7% purity was obtained from E. Merch and used as such. KCl used for calibration of electrode, was recrystallized from doubly distilled water, dried in an oven at 170 °C for several days and kept in a desiccator over P<sub>2</sub>O<sub>5</sub>. Double distilled water with the specific conductance 1.2-1.3 × 10<sup>-6</sup> ohm<sup>-1</sup>cm<sup>-1</sup> was used for the preparation of binary mixtures and as an aqueous medium. Conductance measurements were carried out using a conductivity meter, Model DDS-307 with dip type cell. The accuracy of the cell was ± 1.0% (F. S). Thermostatic water bath having a temperature accuracy of ± 0.05 °C was used for equilibrating all solutions before conductance measurement. The extrapolated values of dielectric constants (D) and viscosities ( $\eta$ ) of 2-propanol-water mixtures taken from the literatures [20, 21] were used for the calculation of solvent parameters and are shown in Table-4.

Table-4: Values of Dielectric Constant (D) and Viscosity ( $\eta$ ) of 2-Propanol-Water Mixtures at Different Temperatures

Wt% of 2-Propanol	Property	298.15	303.15	308.15	313.15 K
		K	K	K	K
0	D	78.54	76.76	75.18	73.35
	$\eta$	8.937	8.007	7.225	6.560
10	D	71.42	69.66	67.97	66.33
	$\eta$	14.5	13.1	11.6	9.7
20	D	64.12	62.62	61.07	59.56
	$\eta$	20.3	15.9	13.9	11.5
30	D	56.90	55.51	54.02	52.71
	$\eta$	25.0	21.4	18.0	15.3
40	D	49.70	48.42	47.15	45.86
	$\eta$	29.1	24.1	20.2	17.4

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### References

- P. A. Sonkar, P. S. Suryavanshi, S. H. Sutar and S. T. Shukla, *Journal of Chemical Pharmaceutical Research*, **4**, 1978 (2012).
- J. I. Bhat and M. N. Manjunatha, *Indian Journal of Chemical Technology*, **17**, 462 (2010).
- I. Tominic, R. Tomas, M. Visic and V. Sokol, *Croatica Chemica Acta*, **77**, 537 (2004).
- Y. P. Handa and G. C. Benson, *Journal of Solution Chemistry*, **10**, 291 (1981).
- A. A. Ansari and M. R. Islam, *Canadian Journal of Chemistry*, **66**, 1720 (1988).
- M. M. Sanchez, C. Moran, C. Quintana and A. Vivo, *Journal of Solution Chemistry*, **18**, 993 (1989).
- M. S. K. Niazi and M. Z. I. Khan, *Journal of Solution Chemistry*, **22**, 437 (1993).
- M. A. Rauf, M. Ikram, U. Ehsan and A. Iqbq, *Journal of Chemical Society Pakistan*, **20**, 275 (1998).
- Y. Marcus, *Pure and Applied Chemistry*, **62**, 2069 (1990).
- J. F. J. Dippy, S. R. C. Hughes, B. C. Kitchiner, *Journal of the Chemical Society (Resumed)*, 1275 (1964)
- M. S. K. Niazi, A. Hassan, M. Z. I. Khan, S. S. Shah, J. Ali, *Journal of Chemical Engineering Data*, **37**, 470 (1992)
- R. Reynaud, *Comptes Rendus Acad. Sciences Paris*, **260**, 693 (1965).
- S. R. Singh, A. K. Tendon and S. P. Rao, *Journal of Physical Chemistry*, **255**, 109 (1974).
- U. N. Das, *Journal of Indian Chemical Society*, **72**, 453 (1995).
- U. N. Das, *Journal of Indian Chemical Society*, **71**, 65 (1994).
- M. S. K. Niazi, S. S. Shah, J. Ali and M. Z. I. Khan, *Journal of Solution Chemistry*, **19**, 623 (1990).
- G. C. Franchini, L. Tassi and G. Tosi, *Journal of Chemical Society, Faraday Transaction*, **1**, **83**, 3129 (1987).
- L. E. Strong, D. J. Blubaugh, J. B. Kallmyer and S. P. Taylor, *Journal of Physical Chemistry*, **89**, 1318 (1985).
- L. D. Hughes, D. S. Palmer, F. Nigsch and J. B. O. Mitchell, *Journal of Chemical Information and Modeling*, **48**, 220 (2008).
- Y. Y. Akhadov, *Dielectric Properties of Binary Solutions*; Pergamon Press, London, p. 277 (1981).
- S. Akhtar, M. M. H. Bhuiyan, M. S. Uddin, B. Sultana, M. Nessa and M. A. Saleh, *Physics and Chemistry of Liquids*, **37**, 215 (1999).