

ACIDIC DISSOCIATION CONSTANTS OF GLUTARIC ACID IN
AQUEOUS 1,3-DIMETHYL UREA FROM ELECTROMOTIVE
FORCE MEASUREMENTS

Lasgein Abdi Al-Sindy, Jalal M. Saleh and Mohammed Hashim Matloob
Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq

(Received: November 22, 1982)

يمكن إيجاد ثابتي التفكك الأول (K_1) والثاني (K_2) للحامض الكلوتاريك في مزيج يحتوي على 11.52٪ وزناً من ثنائي ميثيل اليوريا في الماء وذلك من قياسات القوة الدافعة الكهربائية لخلايا لا تشمل على الانتقال. وكانت أوتاً القيم المستحصلة للثابتين K_1 و K_2 في المدى الحراري من 278.15 إلى 318.15 كلفن هي القيم الخاصة بدرجة 298.15. وبلغت قيمة النسبة (K_1/K_2) للحامض في هذه الدراسة (27) وذلك مقارنة بالقيم (17) المعروفة للحامض في الماء وقد استخدمت نتائج البحث لحساب التغيرات القياسية في الانتالبي والانتروبي والسعة الحرارية بالنسبة لعملية التفكك في المزيج المائي لثنائي ميثيل اليوريا. وتدل نتائج هذه الحسابات على حصول استقرار أكبر لانيون الحامض في هذا المذيب قياساً باستقرار الأنيون في المحيط المائي.

The first (K_1) and second (K_2) acidic dissociation constants of glutaric acid in 11.52% by weight 1,3-dimethyl urea in water have been determined from e.m.f. measurements of cells without transference. The lowest K_1 and K_2 values, over the experimental temperature from 278.15 to 318.15 K, were those obtained at 298.15 K. The value of K_1/K_2 in the present work was ~27 as compared with ~12 in water. The results have also been used to calculate the standard changes of enthalpy, entropy and heat capacity for the two dissociation processes in the aqueous dimethyl urea. The evidence indicate a relatively greater acid-anion stabilization as compared with water.

INTRODUCTION

We have studied earlier⁽¹⁾ the transfer energies of HCl in 1,3-dimethyl urea + water mixtures and obtained some information regarding the specific ion-solvent interaction in such media. The study covered the temperature range 278.15 to 308.15 K using four different solvent compositions. The dielectric constant of the aqueous dimethyl urea containing 11.52% by weight of the latter was similar to that of water ranging from 88.3 at 278.15 K to 78.86 at 308.15K. A structure enhancement, due possibly to the formation of dimethyl urea + water complex, with a consequent high solvating capacity have been reported⁽¹⁾ to occur at such solvent composition.

The present paper aims to reveal the influence of such build-up in the structure on the ratios K_1/K_2 for a diprotic acid and, also, on the possible internal hydrogen bonding in the acid anion. Glutaric acid has been selected for our investigation as the thermodynamic quantities of the acid in water and many other solvents are well known⁽²⁻⁶⁾.

EXPERIMENTAL

Glutaric acid was obtained from B.D.H. and 1,2-dimethyl urea was supplied by Fluka, as pure samples (>99%). Both substances were subjected to a thorough purification operations before use. Sodium chloride (free of bromide), sodium hydroxide and hydrochloric acid were analar samples. Stock buffer solutions with the added NaCl were prepared from weighed amounts of glutaric acid, standard NaOH solution, NaCl, 1,3-dimethyl urea and water. They were diluted with 11.52% by weight dimethyl urea in water (solvent) to form the remainder of the cell solutions.

The cell vessel was similar to that used by others⁽⁷⁻⁸⁾ and the e.m.f. measurements were made as described before⁽⁹⁻¹⁰⁾. Using Tinsely Potentiometer which was accurate down to 10^{-6} volt. In general, the results at any temperature at the end of the run agreed within 0.1 mV with the initial data at the same temperature. The e.m.f. of the cells used in this investigation were corrected to a partial pressure of 1 atm. The stoichiometric molalities (m) of the glutaric acid, its sodium salt and sodium chloride, in the cells for the dissociation constants determination were equal. The dielectric constants of the solutions at different temperatures were measured with the aid of a universal dielectrometer; the error in any reading was <1%.

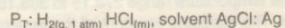
RESULTS

Activity Coefficient of HCl

The mean molal activity coefficient (γ_{\pm}) for any molal concentration (m) of HCl in 11.52% by weight 1,3-dimethyl urea in water was determined from the equation:

$$E = E_m^{\circ} - 2K \log m - 2K \log \gamma_{\pm} \quad (1)$$

where E is the electromotive force (Table 1), and E_m° is the standard potential on the molal scale, of the following cell (A):



where the "solvent" is the 1,3-dimethyl urea + water mixture and $K = 2.303 RT/F$. The values of E_m° were calculated as before^(1, 9-10) and are given at nine temperatures in Table 2. Using E and E_m° and the corresponding values of m , it was possible to estimate γ_{\pm} at the different temperatures and solvent compositions (Table 3). The activity

Table 1: The electromotive force E (volt) of the cell A at nine temperatures.

$m \times 10^2 / \text{mol Kg}^{-1}$	E volt at temperatures/K								
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
1.9782	0.4180	0.4253	0.4278	0.4320	0.4367	0.4363	0.4386	0.3393	0.4404
2.9673	0.4083	0.4098	0.4128	0.4168	0.4175	0.4198	0.4210	0.4216	0.4225
3.9564	0.3959	0.3992	0.4050	0.4071	0.4092	0.4117	0.4127	0.4135	0.4128
4.9455	0.3885	0.3897	0.3964	0.3976	0.3975	0.3982	0.4000	0.4001	4.4000
5.9347	0.3825	0.3883	0.3877	0.3896	0.3907	0.3903	0.3903	0.3897	0.3911
6.9238	0.3770	0.3798	0.3811	0.3835	0.3865	0.3881	0.3876	0.3866	0.3848
7.9129	0.3703	0.3760	0.3783	0.3787	0.3787	0.3779	0.3785	0.3788	0.3776
8.9020	0.3690	0.3710	0.3733	0.3753	0.3773	0.3775	0.3765	0.3760	0.3740
9.8911	0.3762	0.3683	0.3685	0.3687	0.3683	0.3676	0.3673	0.3671	0.3683

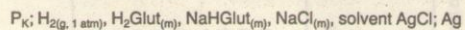
Table 2: The standard potential on the molal scale (E_m°) of the cell A at nine temperatures.

Temperature/K	E_m° /volt
278.15	0.2237
283.15	0.2251
288.15	0.2264
293.15	0.2274
298.15	0.2270
303.15	0.2252
308.15	0.2241
313.15	0.2214
318.15	0.2188

coefficient (γ_{\pm}) and E_m° data were then utilized to derive the concentration of hydrogen ions (m_H) in glutaric acid solutions as will be described later.

The First Dissociation Constant

The first dissociation constant (K_1) of glutaric acid in 11.52% by weight dimethyl urea in water was determined from the electromotive force (E_B) measurement of the cell (B):



using the equation:

$$p\bar{K}_1 = (E_B - E_m^\circ)/K + \log m (m - m_H)/(m + m_H) \quad \dots \dots \dots (2)$$

where K_1 is the "apparent" first dissociation constant of the acid. The concentration of the hydrogen ions (m_H) in the solution of the cell (B) was obtained from the equation:

$$-\log m_H = (E_B - E_m^\circ)/K + \log m + 2 \log \gamma_{\pm} (HCl) \quad \dots \dots \dots (3)$$

The mean activity coefficients were taken equal to $\gamma_{\pm} (HCl)$ in solutions of HCl in 11.52% by weight dimethyl urea in water (Table 3) at the appropriate molal concentration (m) of the acid. The values of E_B and $p\bar{K}_1$ at nine temperatures are given respectively in tables 4 and 5. The thermodynamic value pK_1 was derived from the linear extrapolation of the $p\bar{K}_1$ versus the ionic strength (I) to $I = 0$, where I is given by:

Table 3: The mean molal activity coefficient (γ_{\pm}) of HCl in 11.52% by weight 1,3-dimethyl urea in water at nine temperatures.

$m \times 10^3 / \text{mole Kg}^{-1}$	γ_{\pm} at temperatures/K								
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
1.9782	0.8766	0.8368	0.8774	0.8813	0.8539	0.8892	0.8902	0.8915	0.8884
2.9673	0.7170	0.7663	0.7912	0.7936	0.8272	0.8128	0.8268	0.8250	0.8209
3.9564	0.6965	0.7142	0.6942	0.7226	0.7291	0.7119	0.7249	0.7189	0.7349
4.9455	0.6501	0.6941	0.6604	0.6963	0.7325	0.7374	0.7367	0.7374	0.7423
5.9347	0.6166	0.5951	0.6555	0.6798	0.6963	0.7148	0.7369	0.7451	0.7276
6.9238	0.5903	0.6072	0.6418	0.6575	0.6480	0.6391	0.6647	0.6764	0.6997
7.9129	0.5940	0.5742	0.6942	0.6327	0.6599	0.6798	0.6902	0.6839	0.6981
8.9020	0.5425	0.5656	0.5840	0.6015	0.6028	0.6088	0.6371	0.6402	0.6627
9.8911	0.5069	0.5379	0.5789	0.6169	0.6464	0.6624	0.6819	0.6795	0.6618

Table 4: The electromotive force E_B (volt) of the cell B at nine temperatures.

$m=10^2/\text{mole Kg}^{-1}$	E (volt) at temperatures/K								
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
1.9782	0.5337	0.5421	0.5543	0.5603	0.5637	0.5687	0.5748	0.5759	0.5721
2.9763	0.5390	0.5399	0.5457	0.5570	0.5594	0.5599	0.5629	0.5628	0.5682
3.9564	0.5325	0.5394	0.5432	0.5443	0.5570	0.5579	0.5594	0.5620	0.5639
5.9347	0.5248	0.5324	0.5386	0.5394	0.5420	0.5431	0.5480	0.5500	0.5560
6.9238	0.5290	0.5290	0.5346	0.5368	0.5408	0.5425	0.5445	0.5475	0.5512
8.9020	0.5233	0.5266	0.5344	0.5351	0.5355	0.5372	0.5405	0.5435	0.5460
9.8911	0.5226	0.5246	0.5320	0.5364	0.5365	0.5375	0.5411	0.5411	0.5457

Table 5: The values of pK_1 at nine temperatures.

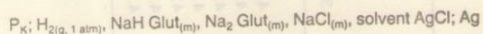
$m \times 10^2 / \text{mole Kg}^{-1}$	pK_1 at temperatures/K								
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
1.9782	3.9052	3.9300	4.0235	4.0137	3.9814	4.0015	4.0272	3.9966	3.8855
2.9573	4.1074	4.0696	4.0504	4.1352	4.0705	4.0327	4.0096	3.9627	4.0017
3.9564	4.1886	4.1870	4.1324	4.0414	4.1726	4.1252	4.0780	4.0758	4.0502
5.9347	4.2256	4.2390	4.2294	4.1347	4.0955	4.0543	4.0688	4.0600	4.1126
6.9238	4.2968	4.2459	4.2267	4.1573	4.1424	4.1131	4.0784	4.0868	4.1036
8.9020	4.3756	4.3128	4.3328	4.2376	4.1623	4.1346	4.1227	4.1320	4.1308
9.8911	4.4087	4.3230	4.3367	4.3062	4.2255	4.1859	4.1788	4.1395	4.1721

$$I = 2m + m_H \quad \dots \dots \dots (4)$$

The values of pK_1 are listed in Table 6. The thermodynamic deviation in each of the nine values was ± 0.0026 .

The Second Dissociation Constant

The second dissociation constant (K_2) of the glutaric acid in the aqueous dimethyl urea was determined from the electromotive force (E_2) measurements of the cell (c):



using the equation:

$$p\bar{K}_2 = pK_2 - B I = (E_c - E_a^0)/K + \log m + 2A\sqrt{I}/1 + Ba^*\sqrt{I} \quad \dots \dots \dots (6)$$

where \bar{K}_2 is the "apparent" second dissociation constant of the glutaric acid, A and B are the constants of the Debye-Huckel Theory, a^0 is the ion size parameter and B is an adjustable linear slope. The ionic strength $I = 5m$, and a^0 was obtained from the intercept of an appropriate plot⁽¹¹⁾. Tables 7 and 8 give respectively the values of E_c and $p\bar{K}_2$ at the nine different temperatures. Plots of pK_2 against I were linear, and the intercepts pK_2 are listed in Table 6; the standard deviation in the pK_2 values was ± 0.003 .

Table 6: Values of pK_1 , pK_2 , $\Delta pK(pK_2 - pK_1)$ and K_1/K_2 for Glutaric acid in 11.52% by weight 1,3-dimethyl urea in water at nine temperatures.

T/K	pK_1	pK_2	ΔpK	K_1/K_2
278.15	3.8997	5.3377	1.428	27.42
283.15	3.9346	5.3591	1.425	26.58
288.15	3.9495	5.3704	1.421	26.36
293.15	3.7643	5.3071	1.443	27.72
298.15	3.9964	5.4358	1.439	27.50
303.15	3.9858	5.4107	1.425	26.60
308.15	3.9791	5.4015	1.422	26.45
313.15	3.9494	5.3903	1.441	27.60
318.15	3.8973	5.3678	1.471	29.55

Table 7: The electromotive force E_c (volt) of the cell c at nine temperatures.

$m \times 10^2 / \text{mole Kg}^{-1}$	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
1.9782	0.6026	0.6154	0.6199	0.6318	0.6367	0.6380	0.6436	0.6491	0.6532
2.9673	0.5985	0.6027	0.6139	0.6178	0.6242	0.6273	0.6372	0.6396	0.6407
3.9564	0.6004	0.6084	0.6147	0.6177	0.6239	0.6308	0.6324	0.6322	0.6396
5.9238	0.5934	0.5980	0.6004	0.6081	0.6161	0.6153	0.6178	0.6245	0.6282
6.9238	0.5905	0.5946	0.6000	0.6011	0.6089	0.6052	0.6165	0.6199	0.6204
7.9129	0.5957	0.5968	0.5987	0.6057	0.6086	0.6151	0.6150	0.6159	0.6191
8.9020	0.5873	0.5852	0.5876	0.5974	0.6001	0.6042	0.6100	0.6153	0.6172
9.8911	0.5875	0.5934	0.5963	0.5958	0.5976	0.5963	0.6058	0.6087	0.6161

Table 8: The values of pK_a at nine temperatures.

$m \times 10^2 / \text{mole Kg}^{-1}$	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
1.9782	5.3895	5.4718	5.4067	5.4778	5.4524	5.3932	5.3927	5.4190	5.4107
2.9673	5.5288	5.4601	5.5158	5.4508	5.4550	5.4296	5.5025	5.4811	5.4277
3.9564	5.7170	5.7154	5.6837	5.5926	5.6039	5.6422	5.5785	5.5169	5.5647
5.9347	5.8098	5.7503	5.6537	5.6575	5.6920	5.6048	5.5603	5.6143	5.6046
6.9238	5.8414	5.7742	5.7311	5.6215	5.6547	5.5215	5.6237	5.6251	5.5657
7.9129	6.0089	5.8867	5.7817	5.7739	5.7230	5.7597	5.6728	5.6345	5.6186
8.9020	5.9217	5.9232	5.8275	5.6950	5.6443	5.6436	5.6562	5.6902	5.6537
9.8911	5.9834	5.9494	5.8629	5.7267	5.6602	5.5707	5.6459	5.6426	5.6947

The Thermodynamic Quantities

By the method of least squares, pK_1 and pK_2 were fitted in equations as:

$$pK_1 = -5772.945/T + 42.662 - 0.0648 T \quad \dots \quad (7)$$

and

$$pK_2 = -4354.734/T + 34.396 - 0.0482 T \quad \dots \quad (8)$$

where T is the thermodynamic temperature in K. The values of the constants were then substituted in the customary thermodynamic formulae⁽¹²⁻¹³⁾ to determine the standard enthalpy, entropy and heat capacity for the two dissociation processes (Table 9). The standard deviation for the fit of the data for the two dissociation constants were respectively ± 0.0006 and ± 0.0018 .

Table 9: The thermodynamic quantities for glutaric acid in 11.52% by weight 1,3-dimethyl urea in water at nine temperatures. The numbers (1) and (2) refer to the thermodynamic data corresponding to the first and the second dissociation processes.

T/K	$\Delta H^\circ/\text{KJ mol}^{-1}$		$\Delta S^\circ/\text{KJ}^{-1}\text{mol}^{-1}$		$\Delta C_p^\circ/\text{KJ}^{-1}\text{mol}^{-1}$	
	(1)	(2)	(1)	(2)	(1)	(2)
278.15	-14.59	-11.95	-126.94	-144.97	0.6896	0.5135
283.15	-11.11	-9.36	-114.56	-135.74	0.7021	0.5226
288.15	-7.57	-6.72	-102.17	-126.51	0.7145	0.5320
293.15	-3.97	-4.04	-89.75	-117.28	0.7269	0.5412
298.15	-0.30	-1.31	-77.36	-108.05	0.7393	0.5505
303.15	3.43	1.46	-64.98	-98.82	0.7517	0.5597
308.15	7.22	3.43	-52.59	-89.59	0.7641	0.5689
313.15	11.07	7.15	-40.17	-80.35	0.7765	0.5786
318.15	14.98	10.07	-27.78	-71.12	0.7889	0.5874

DISCUSSION

The values of K_1 in the present work (Table 6) are found to be somewhat greater than the corresponding values for the glutaric acid in purely aqueous medium. Moreover, the ratio K_1/K_2 in water^(6,14) at 298 K is ~12 as compared with ~27 in aqueous 1,3-dimethyl urea. The comparatively greater values of K_1 and K_1/K_2 in this work probably reflect a relatively higher stabilization of the acid anion in aqueous 1,3-dimethyl urea than in water.

It has been reported that in aqueous medium, the tendency of the water molecules for hydrogen bonding with the carboxylate is considerably greater than with the carboxyl group⁽⁶⁾. Such a medium effect is expected to decrease the strength of the internal hydrogen bond in the acid anion. In the presence of dimethyl urea such a behaviour is less likely to exist due to the strong tendency of the water molecules to form dimethyl urea + water complexes⁽¹⁾. Moreover, such solvent complexes are known to acquire a substantially high solvating capacity for the hydrogen ions. Aqueous urea compounds being more basic than water tend to attract the hydrogen ion from the solution in accordance with the acid-base theory of the ion solvation⁽¹⁵⁾. These two factors probably operate together in enhancing the extent of the first dissociation step of the acid and consequently resulting in a comparatively greater K_1/K_2 values than in water. This is likely to imply a relatively greater acid anion stabilization as compared with water.

Table 6 shows that there is a slow increase in the values of pK_1 and pK_2 with the increasing temperature from 278 to 298 K and this is, thereafter, followed by a slow decrease of the values on raising the temperature to 318 K; the lowest K_1 and K_2 values over the experimental temperature range are those at 298 K. This may be attributed to the structural changes in the solvent and the associated variations of its solvating capacity with the rise of the temperature⁽¹⁾. The changes in the values of K_1 and K_2 with temperature are also reflected in the thermodynamic quantities of the two main dissociation steps of the acid in the solutions. The values of ΔS° , ΔH° and ΔC_p° are shown in Table 9 to increase gradually with increasing temperature suggesting probably a slow shift towards a more disordered system involving some structure destructions.

REFERENCES

1. Ali Nori Lafta, Thesis, College of Science, University of Baghdad, 1979.
2. H. Milton Peak and T.L. Hill, *J. Amer. Chem. Soc.*, 1951, 73, 5304.
3. W. Simon, D. Meucle and E. Hellbronner, *Helv. Chim. Acta*, 1959, 39, 290.
4. C.A. Streuli and R.R. Miron, *Anal. Chem.*, 1958, 30, 1978.
5. I.M. Kolthof and M.K. Chantooni, Jr., *J. Amer. Chem. Soc.*, 1973, 95, 8579.
6. U.N. Dash and B. Nayak, *Aus. J. Chem.*, 1975, 28, 1377.
7. J.C. Halle and R.G. Bates, *J. Solution Chem.*, 1975, 4, 1033.
8. J.C. Halle and R.G. Bates, *J. Chem. Thermodynamics*, 1975, 7, 999.
9. K.S. Ahmad and J.M. Saleh, *Iraqi J. Sci.*, 1979, 20, 385.
10. J.M. Saleh and D.M. Mehdi, *Iraqi J. Sci.*, 1980, 21, 19.
11. R.G. Bates, *Determination of pH*, 2nd ed., John Wiley, New York, 1973, p. 222.
12. H.S. Harned and R.A. Robinson, *Trans. Faraday Soc.*, 1940, 36, 973.
13. R.N. Roy, J.J. Gibbons, G. Lacross, Jr. C.W. Krueger, *J. Solution Chem.*, 1976, 5, 339.
14. M.K. Chantoni, Jr. and I.M. Kolthof *J. Phys. Chem.*, 1975, 79, 1176.
15. W. Son, K.K. Kundu and M.N. Das, *J. Phys. Chem.*, 1967, 71, 3665.