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Association Parameters for Paratoluic Acid in Binary Mixtures of Ethanol and Water at Different Temperatures

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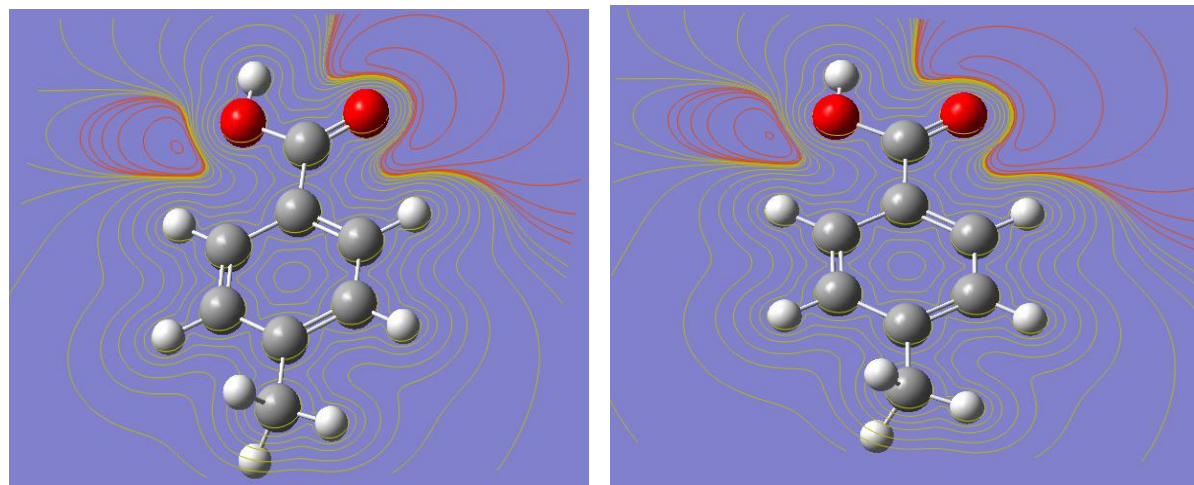
ABSTRACT

Different association parameters were evaluated for saturated paratoluic acid in the binary mixtures of ethanol-water at different temperatures by measuring the molal solubility and the mean activity coefficient. From the experimental solubility, pH, density data:- molar, Van der Waals, electrostriction, apparent molar volumes, dissociation constants, and association constants of paratoluic acid were estimated in order to estimate the contributions of solute-solvent interactions related to ion association. The saturated solution of paratoluic acid in the binary solvent mixtures of ethanol-water 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 paratoluic acid were increased by increasing ethanol content in the mixed solvent due mainly to the higher solvation. It was concluded that the solute-solvent interaction increased by increasing $\Delta\Delta G$ and ΔG_s due mainly to the increase in the association parameters in the corresponding solvents.

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Graphical Abstract



Mapping of the 2D electrostatic potential isosurface for (a) PTA in water (b) in ETOH as obtained from SMD/B3LYP/6-311G(d,p) calculations at a contour value of 0.2.

Introduction

Paratoluic acid is an intermediate in many industrial processes and has been produced in large quantities [1,2]. It is widely used as a vital intermediate for production of many alternative organic substances applied within the fields of resins, pharmaceuticals, dyes, plasticizers, preservatives and cosmetics[3,4].

Many publications have appeared on the behaviour of weak acids in anhydrous solvents. Interesting work has been done by Kolthoff et al.[5,6]. Aleksandrov et al.[7,8] studied the dissociation of salicylic acid in butane-2-one. Kreshkov et al.[9] studied the dissociation of amino acids (as weak acids) in mixtures of formic and ethylmethylketone and in mixtures of acetic acid-ethylmethylketone. Gomaa et al.[10-11] studied association, dissociation and hydrogen bonding of a weak acid in different solvent mixtures from solubility measurements. Thermo-physical properties of solutions are greatly helpful to the vitally known information onto the inter-molecular interactions of the systems. It is worth mentioning that thermodynamic properties are very important for the industrial processes. It is in this sense that careful investigation of a solution thermodynamic property has become very useful in applied and theoretical research.

The focus of this work is to study the effects of temperature and the addition of an ethanol in the association, dissociation and different molar volumes of paratoluic acid to evaluate the association parameters of solvation.

Experimental

2.1. Chemicals:

The paratoluic acid (PTA) and ethanol used in the experiments were purchased from Merck, they are analytical grade reagents and were used without any further purification.

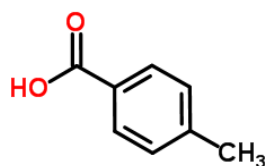


Fig. 1. The chemical structure of PTA

2.2. Solubility measurement:

The solubility of paratoluic acid in binary solvent mixtures of (ethanol–water) was determined using gravimetric method [12]. For each measurement, an excess mass of acid was added to about 30 mL binary solvent mixture. The equilibrium cell was heated to a desired temperature with continuous stirring for about 12 hours using a magnetic stirrer in order to fully mix the suspension and a condenser which was used to prevent the evaporation of solvent during the experiments. The temperature of the cell was controlled by circulating water from a thermostat (CF41, Julabo, Germany) through the jacket of the vessel and measured by a thermometer with accuracy of ± 0.02 K. After 12 hours, stirring was stopped and the solution was kept for 3 hours to approach equilibrium and allow the undissolved solid to settle down in the lower portion of the glass vessel. About 3 mL upper clear saturated solution was withdrawn by a syringe (10 mL) and filtered quickly with a membrane filter (0.22 μm) and poured into a pre-weighed glass dish. The total weight of the solution and the glass dish was measured immediately using an analytical balance (Mettler Toledo AB204-S, Switzerland) with an accuracy of ± 0.0001 g. When the mass of the residue reached at constant value, the final mass was recorded. At each temperature, the measurement was conducted three times, and the mean value was used to determine the molal solubility. The relative standard uncertainty of the solubility measurement based on the repeated observations is within 2%.

The pH readings of the saturated solutions were measured using a pH-meter of the type Tacussel/Minis 5000. The densities were measured using a weighing bottle of 1ml and analytical balance (4 digits) of the type Mettler Toledo DA.

Results and Discussion

The solubility values for saturated PTA at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15K) were listed in Table (1) and plotted graphically in Figure (2). The results show that

the solubility of acids depends on both solvent composition and temperature. It can be seen clearly from the figures that the solubility of PTA was increased by increasing the mole fraction of ethanol (X_s) due to the increase in the solvation. Moreover, solute-solvent interaction and also the solubility increased by increasing the temperature with a given composition in all solvent mixtures indicating that the dissolving process of acids is endothermic [13, 14].

Table (1): Molal solubility (S), Log activity coefficient ($\log \gamma_{\pm}$), Molar (V_M), Vander waal (V_w), Electrostriction (V_e) and Apparent (V_{ϕ}) volumes of PTA in (ETOH-H₂O) mixed solvents at different temperatures.

ETOH vol. %	X_s	S molal solubility (mol/kg. solvent)					V_M (Cm ³ / mole)				
		293.15K	298.15K	303.15K	308.15K	313.15K	293.15K	298.15K	303.15K	308.15K	313.15K
0	0	0.0053	0.0084	0.0107	0.0130	0.0146	137.73	139.75	140.10	141.16	141.87
20	0.0717	0.0084	0.0108	0.0148	0.0203	0.0229	141.58	142.71	143.63	145.15	146.54
40	0.1708	0.0448	0.0491	0.0529	0.0599	0.0681	144.26	145.44	147.54	148.44	150.74
60	0.3166	0.0574	0.0691	0.0756	0.0805	0.1357	153.06	157.34	160.70	162.53	163.82
80	0.5527	0.1267	0.1422	0.2108	0.2696	0.4616	165.21	169.28	171.32	173.90	174.21
100	1	0.4620	0.5339	0.6972	0.7520	0.8462	181.58	182.46	183.76	184.51	185.46
		V_w (Cm ³ / mole)					V_e (Cm ³ / mole)				
0	0	91.041	92.377	92.605	93.306	93.773	-44.17	-46.41	-46.673	-47.45	-47.75
20	0.0717	93.588	94.333	94.940	95.942	96.861	-47.80	-48.62	-48.373	-49.29	-49.75
40	0.1708	95.353	96.137	97.523	98.118	99.639	-48.67	-49.10	-49.559	-49.87	-50.76
60	0.3166	101.17	104.00	106.23	107.43	108.28	-51.16	-52.83	-54.26	-54.97	-55.50
80	0.5527	109.20	111.89	113.24	114.95	115.16	-55.79	-57.29	-57.97	-58.91	-59.01
100	1	120.02	120.60	121.47	121.96	122.59	-61.51	-61.82	-62.272	-62.53	-62.85
		V_{ϕ} (Cm ³ / mole)					r^0 in (Å)				
0	0	135.213	138.788	139.28	140.761	141.522	3.2037	3.2193	3.2219	3.2300	3.2354
20	0.0717	141.392	142.957	143.31	145.236	146.608	3.2333	3.2418	3.2488	3.2602	3.2705
40	0.1708	144.022	145.240	147.08	147.989	150.400	3.2535	3.2624	3.2779	3.2846	3.3015
60	0.3166	152.330	156.830	160.48	162.399	163.783	3.3184	3.3490	3.3727	3.3854	3.3943
80	0.5527	164.994	169.177	171.21	173.863	174.161	3.4039	3.4316	3.4454	3.4626	3.4647
100	1	181.538	182.42	183.74	184.484	185.436	3.5128	3.5185	3.5268	3.5316	3.5377

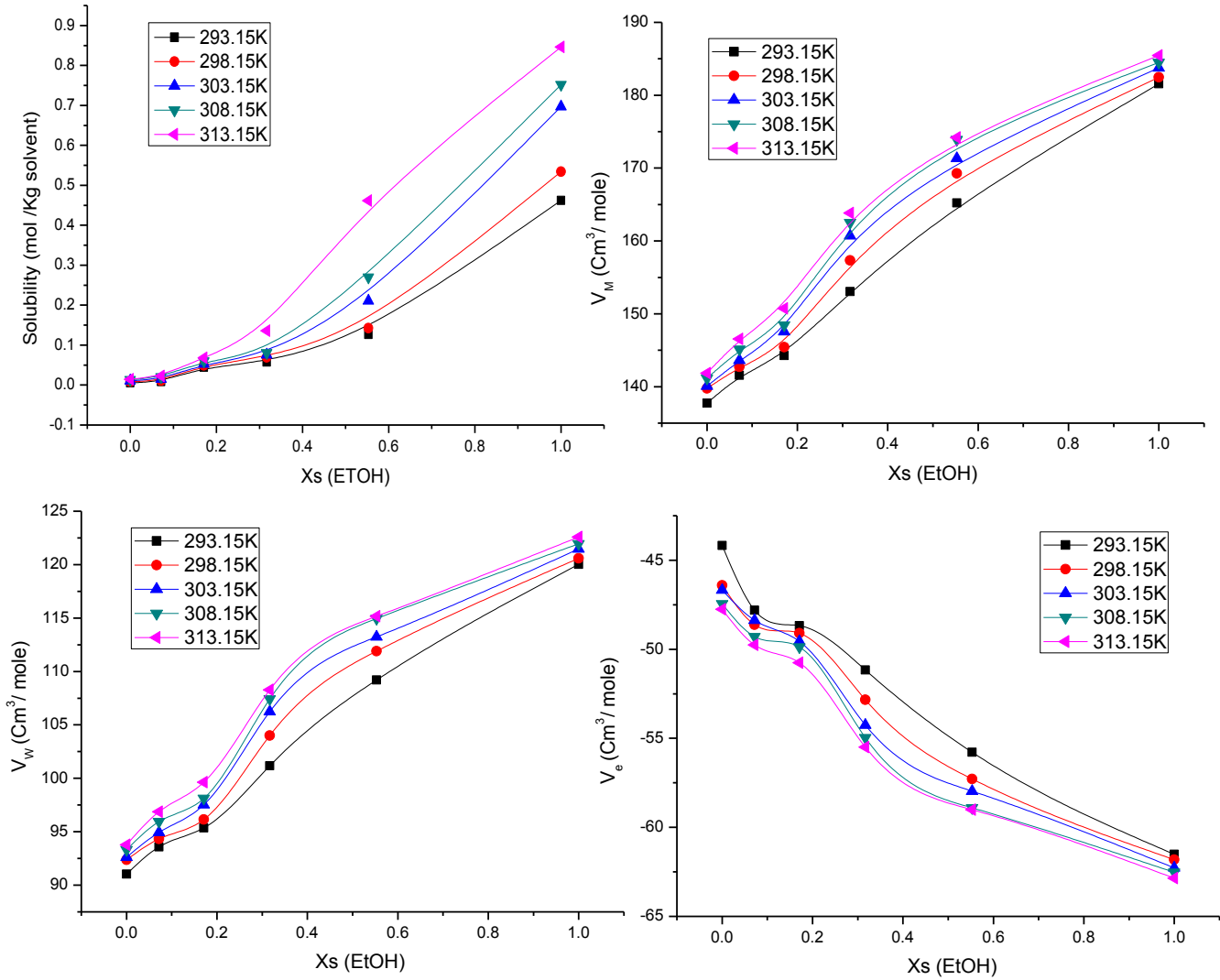


Fig (2). Relation between S, V_M, V_W and V_e of PTA acid and the mole fraction of EtOH (X_s) in (EtOH-H₂O) solvent mixtures at different temperatures.

The molar volumes (V_M) of PTA were obtained by dividing the molar mass and the densities. The packing density as reported by Kim et al. [15] was found to be a constant value and equal to 0.661. The Van der Waals (V_W) can be calculated from the equation (1)

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

The electrostriction volume (V_e), which is the volume compressed by the solvent was calculated using the following equation (2) (Gomaa et al. [16-17]):

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

The apparent molar volumes, V_ϕ , [18-19] were calculated using equation (3) [20]:

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

where M is the molar mass of PTA, m is the solubility, d and d_o are the densities of saturated solution and pure solvents, respectively, Table (2& 3).

Table (2): Density (d_o) of (EtOH-H₂O) mixed solvents at different temperatures.

EtOH vol. %	X_s	(EtOH -H ₂ O) mixtures (d_o)				
		293.15K	298.15K	303.15K	308.15K	313.15K
0	0	0.9757	0.9666	0.9636	0.9597	0.9551
20	0.0717	0.9601	0.9564	0.9437	0.9396	0.9305
40	0.1708	0.9346	0.9275	0.9027	0.8951	0.8847
60	0.3166	0.8575	0.8396	0.8355	0.8306	0.8280
80	0.5527	0.8061	0.7954	0.7806	0.7765	0.7670
100	1	0.7393	0.7360	0.7322	0.7286	0.7222

Table (3): Density (d) of paratoluic acid in (EtOH-H₂O) mixed solvents at different temperatures.

EtOH vol. %	X_s	Saturated soltion denisty (d)				
		293.15K	298.15K	303.15K	308.15K	313.15K
0	0	0.9885	0.9742	0.9718	0.9645	0.9597
20	0.0717	0.9616	0.954	0.9479	0.938	0.9291
40	0.1708	0.9438	0.9361	0.9228	0.9172	0.9032
60	0.3166	0.8895	0.8653	0.8472	0.8377	0.8311
80	0.5527	0.8241	0.8043	0.7947	0.7829	0.7815
100	1	0.7498	0.7462	0.7409	0.7379	0.7341

The solvated radii (r) of PTA in (EtOH-H₂O) mixtures at different temperatures were calculated using equation (4) by considering the spherical form of the solvated molecules [21].

$$V_M = \frac{1}{6} \pi N r^3 \quad \dots\dots\dots(4)$$

The values of V_M , V_W , V_e and V_ϕ for PTA are listed in Table (1). In comparing the data of solvation of PTA, it was observed that the values of V_M and V_W were increased by increasing the organic solvents content in the mixtures (Fig.2) due to the increase in the solubility and the volume of organic solvent compared to water. All the electrostriction volumes V_e calculated for PTA have negative values. The V_e increase in negativity on increasing the percentages of the organic solvent (Fig.2) indicates that the more work (energy) can be done by the solvent on the solvation sheaths of the acid. All PTA volumes V_M , V_w , V_e , and V_ϕ are increased by increasing the temperature and ETOH percentage due to increasing the solubility which favors more solvation interactions. Van der Waals radii, as tabulated by Bondi, have been used for a wide range of applications. [22-27]. Bondi radii result from a refinement of the work of Pauling [28] who determined standard values of atomic radii from contact distances between nonbonded atoms in molecular crystals. Van der Waals radii (r) are also increased by increasing the temperature and ETOH percentage due to increasing Van der Waals volume.

The activity coefficient was calculated using the relation [29].

$$\log \gamma_{\pm} = -0.5062 \sqrt{I} \quad (5)$$

K_{ass} values were calculated [30] from the ratios of association constant to dissociation constant (i.e. K_1/K_2) for the dimers of paratoluic acid which form a complex ion (HA_2^-) and hydrogen ion (H^+). Moreover, the values of K' (where K' is the dissociation constant of the associated acid complex, H_2A_2) are given by the following equations

$$K' = a^2 H^+ / m^2 \quad (6)$$

$$p a_{H^+} = \frac{1}{2} \log \frac{K_1}{K_2} - \log m = pH - \log \gamma_{\pm} \quad (7)$$

$$\frac{K_1}{K_2} = K' K_{ass} \quad (8)$$

In the above equation a is the activity. The values obtained K' , K_{ass} and $\frac{K_1}{K_2}$ are reported in Table (4).

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 PTA saturated solutions in various solvents were calculated using the following equations and listed in Table (4).

$$\Delta G_d = -RT \ln K' \quad (9)$$

$$\Delta G_A = -RT \ln K_{ass} \quad (10)$$

$$\Delta \Delta G = \Delta G_{ass} - \Delta G_d \quad (11)$$

$$\Delta G_s = -RT \ln K_{sp} \quad (12)$$

$$pK_{sp} = -(\log 4S^3 \cdot \gamma_{\pm}^3) \quad (13)$$

Table (4): Dissociation (K'), association (K_{ass}), free energies (ΔG_d), solvation free energies (ΔG_s), dissociation free energies (ΔG_d), association free energies (ΔG_A), and difference free energies ($\Delta \Delta G$) for PTA in (ETOH-H₂O) mixed solvents at different temperatures.

ETOH vol. %	Xs	K'					K _{ass}				
		293.15K	298.15K	303.15K	308.15K	313.15K	293.15K	298.15K	303.15K	308.15K	313.15K
0	0	1.21 x10 ⁻⁴	1.16 x10 ⁻⁴	6.9x10 ⁻⁵	7.18x10 ⁻⁵	5.6x10 ⁻⁵	6.87 x10 ⁶	7.47 x10 ⁷	2.10x10 ⁸	1.94x10 ⁸	3.19x10 ⁸
20	0.0717	7.19x10 ⁻⁵	4.29x10 ⁻⁵	3.44x10 ⁻⁵	2.75x10 ⁻⁵	3.37x10 ⁻⁵	1.93x10 ⁸	5.44x10 ⁸	8.43x10 ⁸	1.32x10 ⁹	8.81x10 ⁸
40	0.1708	3.04x10 ⁻⁶	2.47x10 ⁻⁶	3.31x10 ⁻⁶	2.50x10 ⁻⁶	2.95x10 ⁻⁶	1.08x10 ¹⁰	1.63x10 ¹⁰	9.10x10 ¹⁰	1.6x10 ¹¹	1.15x10 ¹¹
60	0.3166	1.74x10 ⁻⁶	7.16x10 ⁻⁷	1.46x10 ⁻⁶	2.00x10 ⁻⁶	5.78x10 ⁻⁷	3.31x10 ¹¹	1.95x10 ¹²	4.69x10 ¹²	2.49x10 ¹²	3.01x10 ¹³
80	0.5527	1.72x10 ⁻⁷	8.17x10 ⁻⁸	3.07x10 ⁻⁸	2.59x10 ⁻⁸	6.08x10 ⁻⁹	3.40x10 ¹³	1.50x10 ¹⁴	1.06x10 ¹⁵	1.49x10 ¹⁵	2.71x10 ¹⁶
100	1	3.83x10 ⁻⁹	1.6x10 ⁻⁹	4.66x10 ⁻¹⁰	3.71x10 ⁻¹⁰	4.11x10 ⁻¹⁰	6.83x10 ¹⁶	3.88x10 ¹⁷	4.61x10 ¹⁸	7.26x10 ¹⁸	9.52x10 ¹⁸
		ΔG _s					ΔG _d				
0	0	25.931	24.166	23.394	22.815	22.615	21.986	22.474	24.152	24.451	25.493
20	0.0717	23.742	22.984	21.838	20.681	20.451	23.255	24.935	25.905	26.907	26.817
40	0.1708	16.04	15.893	15.813	15.551	15.231	30.965	32.006	31.806	33.057	33.158
60	0.3166	14.983	14.386	14.222	14.361	12.271	32.332	35.081	33.872	33.622	37.404
80	0.5527	11.717	11.407	9.822	9.369	7.214	37.975	40.461	43.605	44.765	49.264
100	1	9.772	9.4652	8.632	8.647	8.657	47.247	50.206	54.167	55.641	56.279
		ΔG _A					ΔΔG				
0	0	-43.973	-44.949	-48.305	-48.902	-50.987	-65.959	-67.423	-72.457	-73.353	-76.480
20	0.0717	-46.509	-49.871	-51.810	-53.814	-53.634	-69.764	-74.806	-77.715	-80.721	-80.451
40	0.1708	-61.931	-64.011	-63.612	-66.114	-66.317	-92.896	-96.017	-95.417	-99.170	-99.475
60	0.3166	-64.664	-70.163	-67.743	-67.244	-74.809	-96.996	-105.24	-101.62	-100.87	-112.21
80	0.5527	-75.950	-80.923	-87.211	-89.530	-98.529	-113.92	-121.38	-130.82	-134.29	-147.79
100	1	-94.493	-100.413	-108.335	-111.283	-112.56	-141.74	-150.62	-162.50	-166.92	-168.84

The Gibbs free energies of solvation (ΔG_s) for PTA are decreased in positivity with increase of ethanol content indicating more solvation process and less endothermic character reaction which increases its solvation behaviours. The K' dissociation for PTA are decreased by increasing the mole fraction of ethanol in the mixed ethanol – water mixtures at all the used temperatures while the association constant (K_{ass}) and the Gibbs free energies differences ($\Delta\Delta G$) are increased in negativity favouring with rise of both the mole fraction of ethanol in the mixtures and temperatures indicating more solvation by association.

Conclusions

The saturated solution of paratoluic acid in the binary solvent mixtures of ethanol–water 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 paratoluic acid were increased by increasing ethanol 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 adding more 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. Finally, increasing ethanol percentage is achieved by increasing the association parameters in the mixture used.

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