in situ oil followed trends similar to those found for hydrocracked gas-combustion shale oil. It also resembled trends previously reported for raw shale oil.

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Synthesis of N,N-Dimethylaniline from Aniline and Methanol

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A systematic study has been made on the synthesis of dimethylaniline from aniline and methanol using various acids as catalysts under pressure. Sulfuric, hydrochloric, hydrobromic, and hydroiodic acids are almost equally effective with regard to the catalytic activity for the formation of the compound. Phosphoric acid is inferior to all above mentioned acids. Sulfuric and hydrochloric acids were used as catalysts for detailed studies of the reaction. Under optimum conditions, the conversion of aniline to dimethylaniline offers yields of 86% in both cases.

Introduction

Dimethylaniline, an important chemical, is widely used in various fields of chemical industries although its major use is for the preparation of vauable dye-intermediates and a large variety of important dyes. It has been manufactured on a large scale by the liquid phase methylation of aniline since 1866 (Poirrier and Chappat, 1866). A large number of catalysts have been used by various workers for the synthesis of dimethylaniline from aniline and methanol (for references, see Bhattacharyya and Nandi, 1975). The vapor phase preparation of dimethylaniline at higher temperatures was studied earlier by Hill et al. (1951), who indicated that the conversion of over 92% to tertiary amines was possible. The production of alkylated amines such as dimethylaniline by high pressure liquid phase reaction of alcohols and aniline has been well established for many years. A wide variety of catalysts has been advocated for this reaction by a number of workers (Mailhe and Godon, 1918; Brown and Reid, 1924; Inoue, 1926; Roy, 1928; Shuikin, 1936; Andrew, 1937; Goshorn, 1944; Maxted, 1944; Earl and Hills, 1947). However, a systematic study on the various aspects of the production of dimethylaniline from aniline and methanol is lacking. The present authors have previously investigated the reactions in detail regarding the syntheses of diethylaniline (Bhattacharyya and Nandi, 1975), dipropylaniline (Nandi and Bhattacharyya, 1975b) and dibutylaniline (Nandi and Bhattacharyya, 1975a) through the alkylation of aniline by ethanol, 1-propanol and 1-butanol respectively, in the presence of various acids as catalyst under pressure. The purpose of the present study is to determine the effects of various process variables on the

alkylation of aniline with methanol under pressure in the presence of different acids as catalysts in order to find out the optimum conditions for the reactions involved in the synthesis of dimethylaniline.

Thermodynamics of the Reactions

The values of the standard heats of formation and entropies of the reactants and products of the reactions

$$C_6H_5NH_2(g) + CH_3OH(g) \rightleftharpoons C_6H_5NHCH_3(g) + H_2O(g)$$
(1)

and

$$C_6H_5NH_2(g) + 2CH_3OH(g) \rightleftharpoons C_6H_5N(CH_3)_2(g) + 2H_2O(g)$$
(2)

are available (Stull et al., 1969). The standard enthalpy and entropy changes of the above reactions are expected to be independent of temperature for the negligible ΔC_p values (Vriens and Hill, 1952) and the equilibrium constants may be represented by the equation

$$\ln K^{\circ}{}_{p} = -\Delta H^{\circ}{}_{298}/RT + \Delta S^{\circ}{}_{298}/R \tag{3}$$

The equilibrium constants and hence the standard free energy changes of the above reactions at different temperatures were calculated by eq 3 and the results are reported in Tables I and II. As the reactions proceed with no change in volume, the equilibrium conversion may remain independent of pressure. As high pressure may influence the fugacity coefficients of the

Table I. Thermodynan (b) Equilibrium Consta	nic Table of the Reac ants at Various Press	ctions. Free Energy (ures for a Constant ¹	Changes and Equilib Temperature of 225	rium Constants of R °C. (Reaction 1: Me	eactions 1 and 2, (a) thylation of Aniline	at Various Tempers to N-Methylaniline)	atures and a Pressure μ	of 1 Atm, and
(a) Temperature, °C $K^{\rm p}_{\rm C}$, kcal/mol (b) Pressure, atm $K^{\gamma}_{\rm D}$	$\begin{array}{c} 25\\ 77.98\times10^{4}\\ -8.0347\\ 1\\ 1.0000\\ 8.395\times10^{2} \end{array}$	$\begin{array}{c} 100\\ 25.47\times10^{3}\\ -7.5204\\ 10\\ 0.9634\\ 8.713\times10^{2} \end{array}$	$\begin{array}{c} 180\\ 23.07\times10^{2}\\ -6.9713\\ 25\\ 0.8863\\ 9.471\times10^{2} \end{array}$	$\begin{array}{c} 200\\ 14.39\times10^{2}\\ -6.8354\\ 40\\ 0.8292\\ 10.124\times10^{2} \end{array}$	$\begin{array}{c} 225\\ 83.95\times10'\\ -6.6634\\ 50\\ 0.9084\\ 9.241\times10^2\end{array}$	$\begin{array}{c} 250\\ 51.52\times10^{1}\\ -6.4905\\ 75\\ 0.9566\\ 8.775\times10^{2}\end{array}$	$\begin{array}{c} 300\\ 22.18\times10^{1}\\ -6.1487\\ 100\\ 0.9631\\ 8.716\times10^{2} \end{array}$	$350 \\ 10.86 \times 10^{1} \\ -5.8044$
$\int_{a}^{a} K_{p} = K_{p}^{\circ}/K_{\gamma}$ where [$\gamma c_{s} H_{s} NH(CH_{3}) \times \gamma H_{s} C$	$K_0^{\circ} = \text{equilibrium }$	constant for reaction ,0H J. γ = <i>f/p</i> where	f is the fugacity of the fugac	hullibrium constant f he gas and γ is the fi	or different pressure igacity coefficient of	s at constant tempe I the gás.	rature for reaction 1	. K _Y =
Table II. Reaction 2: N	Methylation of Anilir	ne to N,N-Dimethyla	niline ^a					
(a) Temperature, °C K_{p}° , ΔF° , kcal/mol	$25 \\ 31.77 imes 10^{10} \\ -15.684$	$100 \\ 40.93 \times 10^{7} \\ -14.699$	$180 \\ 38.37 \times 10^{5} \\ -13.648$	$200 \\ 15.28 imes 10^{\circ} \\ -13.385$	$225553.58 imes 10^4$ -13.055	$250 \\ 20.80 \times 10^{4} \\ -12.727$	$300 \\ 40.09 \times 10^{3} \\ -12.069$	$350 \\ 10.09 \times 10^{3} \\ -11.414$

compounds, the effect of pressure on the equilibrium constant at 225 °C was determined by the method of Dodge (1944). using a fugacity coefficient chart (Smith, 1956). Tables Ib and IIb show that the values of the equilibrium constants for both the reactions should increase up to a pressure of 40 atm and then decrease with further increase of pressure. Thus the optimum pressure for maximum conversion at 225 °C, the optimum temperature (see Table IV) is expected to be about 40 atm.

Experimental Section

Apparatus. The runs were carried out in a high-pressure, rocking-bomb-type autoclave having a capacity of 300 ml. The apparatus which was used to study the reaction was the same as described previously (Bhattacharyya and Nandi, 1975).

Reactants. Aniline and methanol of B.D.H. quality were used as reactants. Aniline was distilled before use.

Catalyst. Sulfuric acid (92%, sp. gr. 1.824), hydrochloric acid (32%, sp. gr. 1.1593), hydrobromic acid (35%, sp. gr. 1.315), hydroiodic acid (45%, sp. gr. 1.475), and phosphoric acid (90%, sp. gr. 1.746) of chemically pure quality were used to investigate the reaction.

Procedure. Requisite quantities of aniline, methanol, and catalyst were placed in a glass liner to decrease the corrosion in the autoclave. The glass liner and the materials were put into the autoclave. Nitrogen gas was pumped to the desired pressure, if necessary, and the reactor was heated to the reaction temperature. At the end of the reaction period, the autoclave was cooled to room temperature and opened after releasing the gas pressure. The liquid product in the reactor was collected and analyzed.

Analysis of the Product. The method of analysis of the product was similar to that described by the authors earlier (Bhattacharyya and Nandi, 1975). The amines were separated by the Hinsberg method (Vogel, 1951). The primary, secondary, and tertiary amines were identified as aniline, methylaniline, and dimethylaniline, respectively, from their boiling points and refractive indices. The identity was confirmed by preparing derivatives.

Results and Discussion

 ${}^{d}K_{p}^{*} = K_{p}^{\circ} * |K_{\gamma}^{*}|_{Y}^{*}$ where $K_{p}^{\circ} = \text{equilibrium constant at 1 atm for reaction 2. <math>K_{p}^{*} = \text{equilibrium constant for different pressures at constant temperature for the reaction 2. <math>K_{\gamma}^{*}$

 $6.358 \times 10^{\circ}$

 $0.7903 \\ 6.779 imes 10^{5}$

 $\begin{array}{c} 0.7870 \\ 6.808 \times 10^{5} \end{array}$

 $0.7371 \\ 7.269 imes 10^{\circ}$

 $0.8011 \\ 6.688 \times 10^{5}$

 $5.858 \times 10^{\circ}$

1.0000 5.358×10^{5}

(b) Pressure, atm

10 0.9146

40

50

100 0.8427

> Performance and Catalysts. The results from various acids as catalysts show that (Table III) all the strong acids are almost equally effective with respect to the total conversions of aniline to dimethylaniline and methylaniline. A lower conversion is achieved with phosphoric acid. It is observed that when water is added to hydrochloric acid its catalytic activity goes down, so it appears that the discrepancies among the strong acids regarding their catalytic activities may be due to the presence of varying amounts of water in the acids. Though the ratio of water is at a minimum in sulfuric acid, the maximum conversion of aniline to the products was not obtained, which is probably due to the weak secondary ionization of sulfuric acid. From the results it is evident that in the absence of acid the formation of methylaniline and dimethylaniline is not possible, although in an earlier publication by Vriens and Hill (1952) dealing with this reaction no mention of any catalyst was made, suggesting that the reaction can proceed in the absence of a catalyst. The present observations are nevertheless in conformity with the results reported earlier in the literature which indicate the need of a catalyst to achieve the reaction. All the strong acids are equally effective to catalyze the reaction involving the total conversion of aniline to dimethylaniline and methylaniline. However, comparatively better results are obtained with sulfuric and hydrochloric acids regarding the synthesis of dimethylaniline and hence subsequent detailed study has been made using sulfuric acid and hydrochloric acid as catalysts.

Effect of Reaction Temperature. In the temperature

	Volof	Amount	Mole vetic	Theoretical mole ratio of aniline	% conver aniline (on of aniline	sion of the basis fed) to:	Total conversion of aniline to di- methyl- aniline	Uncon	Tarry
Catalyst	catalyst, ml	in catalyst,	of aniline to catalyst	from catalyst	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	verted aniline, %	mate- rials, g
Phosphoric acid	1.0	0.17	1:0.053	1:0.16	24.04	29.10	53.14	46.57	
Sulfuric acid	1.5	0.22	1:0.08	1:0.16	53.53	27.20	80.73	18.49	
Hydrochloric acid	4.5	3.54	1:0.15	1:0.15	51.22	31.09	82.31	17.10	
Hydrobromic acid	8.5	7.27	1:0.15	1:0.16	45.96	34.93	80.89	18.01	
Hydroiodic acid	9.0	7.29	1:0.15	1:0.15	45.10	32.74	77.84	18.94	
Hydrochloric acid ^b	9.5	8.54	1:0.15	1:0.15	42.55	26.12	68.67	29.75	
Nil	Nil		_	_	_		—	100.00	—

^{*a*} Volume of aniline = 27.35 ml; amount of aniline = 27.95 g; volume of methanol = 24.30 ml; amount of methanol = 19.23 g; reaction temperature = 225 °C; reaction pressure = 540 psi; residence period = 1 h; mole ratio of aniline to methanol = 1:2. ^{*b*} 4.5 ml of hydrochloric acid diluted with 5 ml of distilled water.

Table IV. Influence of Reaction Temperature on the Conversion of Aniline to Dimethylaniline in Presence of Sulfuric Acid and Hydrochloric Acid Catalysts^a

	Max	Volof	Amount of	Mole ratio	% conver aniline (on of aniline	sion of the basis fed) to:	Total conversion of aniline to di- methyl- aniline and	Uncon-	Tarry
Reaction temp, °C	pressure, psi	catalyst, ml	catalyst,	of aniline to catalyst	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	verted aniline, %	materials, g
				Catalyst:S	ulfuric Acid				
180	360	1.5	2.5170	1:0.0855	6.95	15.92	22.87	76.81	
200	520	1.5	2.5170	1:0.0855	30.21	48.81	79.02	19.89	
225	700	1.5	2.5170	1:0.0855	76.27	17.91	94.18	5.54	
245	880	1.5	2.5170	1:0.0855	74.42	18.96	93.38	3.64	Trace
265	1040	1.5	2.5170	1:0.0855	71.59	20.52	92.11	2.79	2.12
				Catalyst:Hyd	rochloric Acid	1			
210	600	4.5	1.6695	1:0.1525	48.74	38.24	87.98	12.30	
225	700	4.5	1.6695	1:0.1525	73.10	21.51	94.61	4.79	
240	820	4.5	1.6695	1:0.1525	72.20	23.81	96.01	2.32	Trace
250	920	4.5	1.6695	1:0.1525	70.63	24.59	95.12	1.21	1.50

^{*a*} Volume of aniline = 27.35 ml; amount of aniline = 27.95 g; volume of methanol = 36.45 ml; amount of methanol = 28.85 g; mole ratio of aniline to methanol = 1:3; residence period = 1 h.

range of 180-265 °C in the case of sulfuric acid and 210-250 °C in the case of hydrochloric acid and a constant mole ratio of aniline to methanol of 1:3, the maximum conversion of dimethylaniline was obtained at 225 °C with both sulfuric and hydrochloric acids as catalysts (Table IV). Above and below this temperature, the conversion was lower. At 225 °C and a pressure of 700 psi, the yields of dimethylaniline were 76% with sulfuric acid and 73% with hydrochloric acid at a residence period of 1 h. The corresponding yields of methylaniline were 18% and 22% with sulfuric acid and hydrochloric acid, respectively, at the same temperature. Maximum conversions of aniline to methylaniline were 49% with sulfuric acid at 200 °C and 38% with hydrochloric acid at 210 °C. It is observed that with sulfuric acid the total conversion of aniline to amines is comparatively low at reduced temperature (180 °C). The catalytic activity of sulfuric acid is improved considerably at a temperature above 180 °C which might be due to the enhanced secondary ionization of the acid (i.e., $HSO_4^- \rightarrow H^+$ + SO₄²⁻). A reaction temperature above 225 °C resulted in an increased amount of tarry materials with both acids.

Effect of Mole Ratio of Aniline to Methanol. The effect of mole ratio of aniline to methanol on the conversion of aniline to dimethylaniline was investigated at aniline to methanol mole ratios between 1:1 to 1:3.5 with both sulfuric and hydrochloric acids (Table V). Decreasing mole ratios of aniline to methanol resulted in an improvement in the yield of dimethylaniline. However, the optimum yields of dimethylaniline were found to be 76% and 73%, respectively with sulfuric acid and hydrochloric acid at a mole ratio of 1:3. The yield of methylaniline decreased as mole ratio of aniline to methanol was decreased. With the mole ratio of 1:3, the yields of methylaniline were 18% with sulfuric acid and 22% with hydrochloric acid.

Effect of Mole Ratio of Aniline to Catalysts. The results on the effect of mole ratio of aniline to catalysts on the conversion of aniline to dimethylaniline tabulated in Table VI show that the yield of dimethylaniline increased with the decreasing mole ratio of aniline to catalyst. The best conversion of aniline to dimethylaniline (79%) was obtained with a mole ratio of aniline to sulfuric acid of 1:0.1140 and the cor-

Table V. Influence of Mole Ratio of Aniline to Methanol (Aniline Volume Constant) on the Conversion of Aniline to Dimethylaniline in Presence of Sulfuric Acid and Hydrochloric Acid Catalysts^a

Webof	Amount of	Mole ratio	Penation	% conversion (on the l aniline f	n of aniline pasis of ed) to:	Total conversion of aniline to dimethyl- aniline and		Torny
methanol, ml	methanol,	of aniline to methanol	pressure, psi	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	Unconverted aniline, %	materials,
			Ca	talvst:Sulfuric	acid			
12.15	9.61	1:1.0	420	22.13	39.95	62.08	37.81	Trace
24.30	19.23	1:2.0	540	53.53	27.20	80.73	18.49	
30.35	24.06	1:2.5	620	69.23	21.42	90.65	9.08	—
36.45	28.85	1:3.0	700	76.27	17.91	94.18	5.54	—
42.55	33.68	1:3.5	720	77.83	18.09	95.92	3.52	
			Catal	yst:Hydrochlo	ric Acid			
12.15	9.61	1:1.0	420	20.51	43.50	64.01	35.13	Trace
24.30	19.23	1:2.0	540	51.22	31.09	82.31	17.10	
30.35	24.06	1:2.5	620	65.21	26.11	91.32	7.79	—
36.45	28.85	1:3.0	700	73.10	21.51	94.61	4.78	
42.55	33.68	1:3.5	720	74.59	21.89	96.48	3.00	_

^{*a*} Volume of aniline = 27.35 ml; amount of aniline = 27.95 g; reaction temperature = 225 °C; residence period = 1 h; volume of sulfuric acid = 1.5 ml; amount of sulfuric acid = 2.5170 g; mole ratio of aniline to sulfuric acid = 1:0.0855; volume of hydrochloric acid = 4.5 ml; amount of hydrochloric acid = 1.6695 g; mole ratio of aniline to hydrochloric acid = 1:0.1525.

Table VI. Influence of Mole Ratio of Aniline to Catalysts on the Conversion of Aniline to Dimethylaniline in Presence of Sulfuric Acid and Hydrochloric Acid Catalysts^a

Volof	Amount of	Mole ratio	% conversior (on the k aniline fo	of aniline basis of ed) to:	Total conversion of aniline to dimethyl- aniline and		Tarry
catalysts, ml	catalyst,	of aniline to catalyst	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	Unconverted aniline, %	materials,
			Catalyst:Sulf	uric Acid			
0.5	0.839	1:0.0285	16.41	34.54	50.95	48.94	
1.0	1.678	1:0.0570	39.51	40.60	80.11	19.67	
1.5	2.517	1:0.0855	76.27	17.91	94.18	5.54	
2.0	3.356	1:0.1140	79.15	18.19	97.34	1.89	
3.0	5.034	1:0.1711	76.79	20.49	97.28		Trace
			Catalyst:Hydro	chloric Acid			
1.5	0.5565	1:0.0508	15.20	38.21	53.41	45.79	
3.0	1.1130	1:0.1017	36.59	42.52	79.11	20.39	
4.5	1.6695	1:0.1526	73.10	21.51	94.61	4.78	_
6.0	2,2260	1:0.2034	76.11	22.51	98.62	1.10	
9.0	3.3390	1:0.3051	75.80	23.22	99.02	-	Trace

^a Volume of aniline = 27.35 ml; amount of aniline = 27.95 g; volume of methanol = 36.45 ml; amount of methanol = 28.85 g; reaction temperature = 225 °C; residence period = 1 h; mole ratio of aniline to methanol = 1:3; reaction pressure = 700 psi.

responding yield of methylaniline was 18%. Below this mole ratio of aniline to sulfuric acid the yield of dimethylaniline decreased resulting in the formation of small amount of tarry materials. A maximum conversion of aniline to methylaniline was obtained (41%) at a mole ratio of aniline to sulfuric acid of 1:0.0570. The same trend in the result was observed with hydrochloric acid as catalyst. A mole ratio of aniline to hydrochloric acid of 1:0.2034 was optimum for the best conversion of aniline to dimethylaniline (76%) and the corresponding yield of methylaniline being 23%. The highest yield of methylaniline (43%) was observed at a mole ratio of aniline to hydrochloric acid of 1:0.1017.

Effect of Residence Period. From Table VII, with both catalysts, the bulk of the reaction involved in the conversion of aniline to dimethylaniline took place at a residence period of 2 h. Further increase in the residence period had little improvement over the yields of dimethylaniline. It is observed that with both the catalysts the conversions of aniline to methylaniline decreased progressively with increase in residence period. A slight amount of tarry matter was produced in the course of the reaction when the residence period was more than 2 h.

Effect of Pressure. The effect of high pressure, developed with nitrogen gas, on the reaction system on the conversion of aniline to dimethylaniline was studied under various initial pressure of nitrogen and the experimental results (Table VIII) showed that increasing the pressure on the reaction system did not help in increasing the yield of dimethylaniline and methylaniline. The ratio of tarry materials in the reaction product increased with increasing pressure. This may be due to the fact that the pressures used in these experiments were much higher than the optimum pressure referred to in the previous section.

From the thermodynamic calculation it was found that a reaction pressure of 40 atm, i.e., about 600 psi, is favorable for methylation of aniline with methanol and this pressure is attainable from the total vapor pressure of the mixture of aniline (27.95 g) and methanol (28.85 g) of mole ratio of 1:3 at 225 °C (see Table IV). However, the reactant mixture having aniline and methanol in the mole ratio of 1:3 gave maximum yield at

Table VII. Influence of Residence Period on the Conversion of Aniline to Dimethylaniline in Presence of Sulfuric Acid and Hydrochloric Acid Catalysts^a

	Volume of	Amount of	Mole ratio	% conversior (on the b aniline fo	n of aniline pasis of ed) to:	Total conversion of aniline to dimethyl- aniline and	Uncon-	Towy
Residence period, h	catalyst, ml	catalyst,	of aniline to catalyst	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	verted aniline, %	materials,
			Cat	alyst:Sulfuric A	cid			
1	1.5	2.5170	1:0.0855	76.27	17.91	94.18	5.54	
2	1.5	2.5170	1:0.0855	87.81	10.10	97.91	1.89	
4	1.5	2.5170	1:0.0855	89.49	7.83	97.32	0.42	Trace
6	1.5	2.5170	1:0.0855	90.21	6.40	96.61		1.40
		· · ·	Cataly	st:Hvdrochloric	Acid			
1	4.5	1.6695	1:0.1525	73.10	21.51	94.61	4,79	
2	4.5	1.6695	1:0.1525	85.92	12.09	98.01	1.39	
4	4.5	1.6695	1:0.1525	89.11	8.89	98.00		Trace
6	4.5	1.6695	1:0.1525	90.12	7.52	97.64		Trace

^{*a*} Volume of aniline = 27.35 ml; amount of aniline = 27.95 g; reaction temperature = 225 °C; reaction pressure = 700 psi; volume of methanol = 36.45 ml; amount of methanol = 28.85 g; mole ratio of aniline to methanol = 1:3.

Table VIII. Effect of High Pressure (Developed by Nitrogen Gas) on the Conversion of Aniline to Dimethylaniline Using Sulfuric Acid and Hydrochloric Acid Catalysts^a

Initial	Maximum	Vol of	Amount of	Mole ratio	% conver aniline (on of aniline	sion of the basis fed) to:	Total conversion of aniline to di- methyl- aniline and	Uncon	Torry
of N ₂ , psi	pressure, psi	catalyst, ml	catalyst,	of aniline to catalyst	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	verted aniline, %	materials,
				Catalyst:Su	lfuric Acid				
Nil	700	1.5	2.5170	1:0.0855	76.27	17.91	94.18	5.54	
100	780	1.5	2.5170	1:0.0855	75.99	17.63	93.62	4.92	
500	1360	1.5	2.5170	1:0.0855	75.41	17.10	92.51	4.77	Trace
1000	2260	1.5	2.5170	1:0.0855	74.70	16.41	91.11	4.58	1.20
				Catalyst: Hydi	cochloric Acid				
Nil	700	4.5	1.6695	1:0.1525	73.10	21.51	94.61	4.79	_
100	780	4.5	1.6695	1:0.1525	72.91	21.39	94.30	4.68	
500	1360	4.5	1.6695	1:0.1525	72.42	21.01	93.43	4.10	Trace
1000	2260	4.5	1.6695	1:0.1525	71.78	20.21	91.99	3.50	0.80

^a Volume of aniline = 27.35 ml; amount of aniline = 27.95 g; reaction temperature = 225 °C; residence period = 1 h; volume of methanol = 36.45 ml; amount of methanol = 28.85 g; mole ratio of aniline to methanol = 1:3.

Table IX. Influence of Input Volume of Aniline (Mole Ratio of Aniline to Methanol Constant)^a

							% conver	sion of	Total conversion of aniline to di-		
Vol of	Amount of	Volume of	Amount of	Volume of	Amount of	Reac- tion pres-	basis of fed)	aniline to:	methyl- aniline and	Uncon- verted	Tarry
aniline, ml	aniline, g	methanol, ml	methanol, g	catalyst, ml	catalyst, g	sure, psi	Dimethyl- aniline	Methyl- aniline	methyl- aniline, %	aniline, %	materials,
				C	Catalyst: Su	lfuric Ac	id				
18.20	18.65	24.30	19.23	1.00	1.678	620	69.50	23.08	92.58	7.09	
27.35	27.95	36.45	28.85	1.50	2.5170	700	76.27	17.91	94.18	5.54	
36.50	37.30	48.60	38.47	2.00	3.3560	720	71.50	19.62	91.12	6.91	Trace
				Cat	alyst:Hydr	ochloric	Acid				
18.20	18.65	24.30	19.23	3.00	1.1130	620	68.09	25.51	93.60	6.18	
27.35	27.95	36.45	28.85	4.50	1.6695	700	73.10	21.50	94.60	4.79	
36.50	37.30	48.60	38.47	6.00	2.2260	720	67.42	23.30	90.72	6.51	1.12

^a Reaction temperature = 225 °C; residence period = 1 h; mole ratio of aniline to methanol = 1:3; mole ratio of aniline to sulfuric acid = 1:0.0855; mole ratio of aniline to hydrochloric acid = 1:0.1525.

this temperature at a pressure of 700 psi, which is slightly different from the theoretically expected pressure.

To find the optimum charge of reactants in a fixed reactor volume, reaction was carried out at the constant optimum mole ratio of aniline to methanol. Table IX shows that the best yield of dimethylaniline was obtained with an aniline volume of 27.35 ml (0.3 mol). Increasing or decreasing the volume of aniline has a lowering effect on the yield of dimethylaniline. The amount of tarry matter was found to be greater at a higher input volume of aniline.

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Acid–Base Interaction in Filler–Matrix Systems

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The mechanical properties of solution-cast films of filled polymers are found to be very much enhanced when the polymer is strongly adsorbed on the filler in the casting solution. Acid-base interactions between polymer and filler promote such adsorption, subject to the acidic or basic nature of the solvent. (-Potential measurements were used as a measure of acid-base interaction between filler and polymer in solvents of low dielectric constant. Thin films containing up to 60 vol % filler were cast from both acidic and basic solvents. Relative values of Young's modulus and tensile strength were compared for each system using the equations of Kerner and Nielsen as a basis for the cases of good and poor adhesion. In a system with acidic polymer (post-chlorinated PVC) and basic filler (CaCO3 or BaTiO3) cast from an acidic solvent (CH2CI2), both adhesion and mechanical properties were improved over the same system cast from a basic solvent (THF); adsorption measurements showed no polymer adsorption from THF, but rapid and strong adsorption from CH₂Cl₂. For the most part, in systems where both polymer and filler were either acidic or basic, brittle films (or none at all) were obtained.

Introduction

It is well known that many properties of polymers are markedly changed by the incorporation of a filler as a second phase (Fowkes, 1972; Fowkes and Hielscher, 1972; Nielsen, 1975; Manson and Sperling, 1976). For example, at least for the case of good filler-matrix adhesion, the modulus and dimensional stability are increased, and the permeability to penetrants decreased (Nielsen, 1967; Manson and Chiu, 1973). Such effects are of great interest in engineering plastics and pigmented coatings, respectively. However, these improvements must be balanced against tendencies of the filler to decrease the elongation, toughness, and tensile strength (Nielsen, 1966). In order to optimize the balance of properties in filled plastics, and to make possible the use of even larger concentrations of cheap and non-energy-intensive inorganic fillers, much attention is being given to the control and modification of filler-matrix interaction (Modern Plastics, 1975).

Examples of fortuitous or deliberate modification or selection of filler-matrix interactions abound, for example, the use of silane treatments on glass and of organic titanates on calcium carbonate. While many of these treatments may involve either an improvement in compatibility or actual reaction with the matrix, polar interactions must also be important. Following earlier work by Fowkes et al. (1970, 1972) and Anderson et al. (1975) with effects of electrostatic (acid-base) interaction, a program was begun to investigate in detail the role of such interactions in optimizing mechanical and permeability behavior in particulate fillers. Results should also be of interest to the general question of adhesion between polymers and substrates. In particular, with a suitable match between an acidic filler and a basic matrix, or vice versa, it should be possible to obtain a strong but ductile filler-matrix bond, thus permitting the use of high filler contents without sacrifice of toughness. It should also be possible to thus minimize undesirable particle-particle aggregation, and also reduce the penetration of deleterious ions, such as chloride, through a protective coating.

For this study, polycarbonate (PC) and chlorinated poly-(vinyl chloride) (CPVC) were selected as intrinsically basic electron donors (+) and acidic electron acceptor (-) polymers, and silica, barium titanate, and calcium carbonate as nominally acidic and basic fillers. (It may be noted that both acidic and basic sites undoubtedly exist on the surface of any filler, whether it be basic or acidic overall.)

Films were cast from basic and acidic solvents (tetrahydrofuran and methylene chloride, respectively, for several filler concentrations). Mechanical properties (Young's modulus and ultimate tensile strength and elongation) were determined, ζ potentials measured in some cases to indicate