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Selective Solvent Extraction of Trioxane from Formaldehyde Solution

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Two solvents, namely, dichlorobenzene and benzene, have been studied for extraction of 1,3,5-trioxane from formaldehyde solution. The ternary liquid equilibrium diagrams are presented for the systems trioxane–formaldehyde solution–solvents, at 50 and 60 °C. The tie line data matched well with the Othmer–Tobias correlation. Dichlorobenzene has been found to be the more selective solvent; it has less affinity for formaldehyde solution in the extract phase. The separation of trioxane and dichlorobenzene by distillation is also easier.

Trioxane is produced from formaldehyde, usually from its concentrated aqueous solution, by distillation in the presence of acid. The overhead stream thus obtained contains trioxane, water, and formaldehyde. Trioxane is recovered from this aqueous formaldehyde solution by extraction with a water-immiscible solvent. The extent of water and other organic impurities in the extracted trioxane depends mainly on the solvent and the operating conditions. Such impurities, even in traces, affect the polymer yield (*1*).

Little work has been published on the separation of trioxane from formaldehyde solution. Most of the literature data deal with its crystallization directly from the aqueous phase (*2–5*), or extraction by methylene chloride (*6–10*). Slivkin et al. (*11*) used benzene, toluene, and *o*-xylene as solvents at 50 °C and reported benzene as the best solvent if the trioxane is to be separated from the extract by rectification and toluene as the best if trioxane is to be crystallized from the extract. These studies were mainly based on the estimation of solubility and equilibrium relationships. The amounts of impurities of water and formaldehyde were, however, not considered in detail. The Meissner process (*12*) for trioxane production mentioned the use of monochloro-, dichloro-, or trichlorobenzene as solvent. They preferred the use of dichlorobenzene because of lower heat requirements and ease of separation of trioxane from the solvent by rectification. Selectivity and equilibrium data for these solvents were, however, not reported.

The present paper is concerned with the studies on the extraction of trioxane using benzene and dichlorobenzene as solvents at 50 and 60 °C. The phase-equilibrium relationships were determined, and the selectivities of the solvents as well as the solvent recovery data were examined for a general comparison.

Chemicals

The feed used was a mixture of pure trioxane, prepared in the laboratory, and aqueous formaldehyde solution in desired proportions. The solvents were of laboratory grade and were further purified by fractionation. For benzene, the fraction boiling at 80 °C and, for dichlorobenzene, the 172–179 °C fraction were collected and used.

Experimental Procedure

The solubilities of trioxane in the pure solvents and in the formaldehyde solution were determined in the conventional way, by finding out the temperatures of complete dissolution while varying the amounts of trioxane. The solubility of water in dichlorobenzene at different temperatures was determined by mixing the two liquids, maintaining the temperatures constant, and analyzing the solvent phase by Karl Fischer reagent.

The data for the phase equilibrium were collected in a conventional mixer–settler, consisting of a jacketed cylindrical glass vessel (75 mm i.d., 230 mm long) of 1-L capacity. It was provided with a two-bladed paddle agitator and a thermometer pocket. The speed of the agitator could be varied up to 800 rpm. The content of the mixer–settler was maintained at the desired temperature (±1 °C) by circulating oil through the jacket from a thermostatic bath. A measured amount (by weight) of the synthetic feed, containing trioxane in 25% formaldehyde solution, was first taken in the mixer–settler. A measured amount of solvent was then added and stirred for 1 h while maintaining constant temperature. The ratio of solvent to feed was varied from 1 to 5 in the different series of runs. After mixing, the contents were allowed to settle for 1 h. These periods were sufficient since preliminary experiments had shown that the phase equilibrium was established within 15 min of stirring and 0.5-h settling time was sufficient for phase separation.

The extract and the raffinate phases were separated and analyzed by GLC (*13*). Water contents in the extract phase were also determined by the Karl Fischer method. The benzene or the dichlorobenzene contents in the aqueous phase were analyzed by ultraviolet spectroscopy.

Results and Discussion

The system consisted of four components—water, formaldehyde, trioxane, and the solvent. But because of the high affinity of formaldehyde for water, the system appears to behave like a ternary system with formaldehyde and water together as a single component. This was confirmed by the observations that there was practically no difference in the solubility of trioxane in water and in 30% formaldehyde solution at various temperatures and that no phase separation occurred between formaldehyde and water (Figure 1). The solubilities of trioxane in benzene and dichlorobenzene were much higher than in the aqueous formaldehyde.

It is desirable that the water content in the trioxane product should be minimal since water affects the behavior of trioxane

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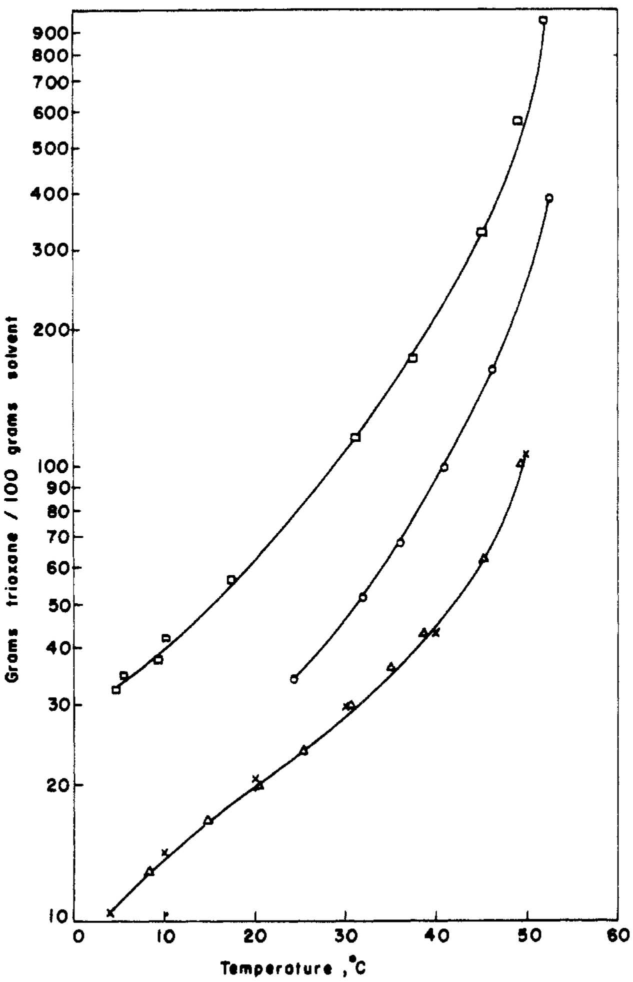

Figure 1. Solubility of trioxane in solvents: (X) water; (Δ) 30% formaldehyde solution; (O) dichlorobenzene; (□) benzene.

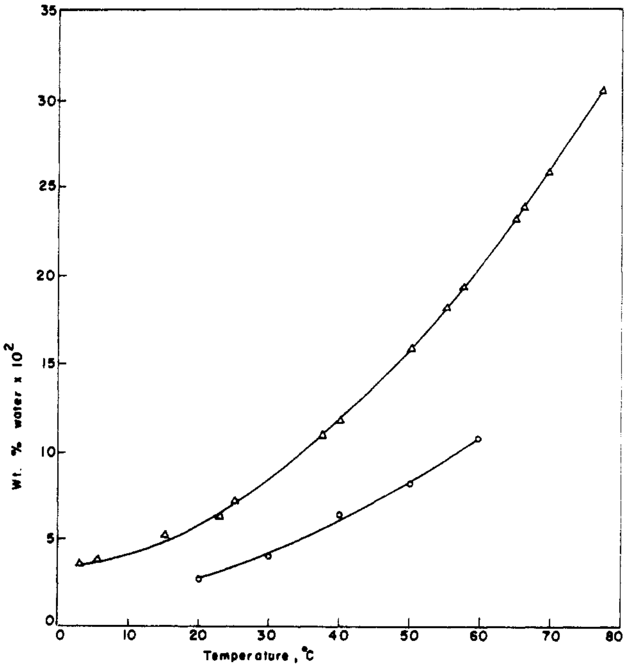

Figure 2. Solubility of water in solvents: (Δ) benzene; (O) dichlorobenzene.

as a monomer and decreases the polymer yield. This water content is dependent on the solubility of water in the solvent. Hence the solubilities of water in the two solvents were compared. This is shown in Figure 2; dichlorobenzene has less affinity for water than benzene.

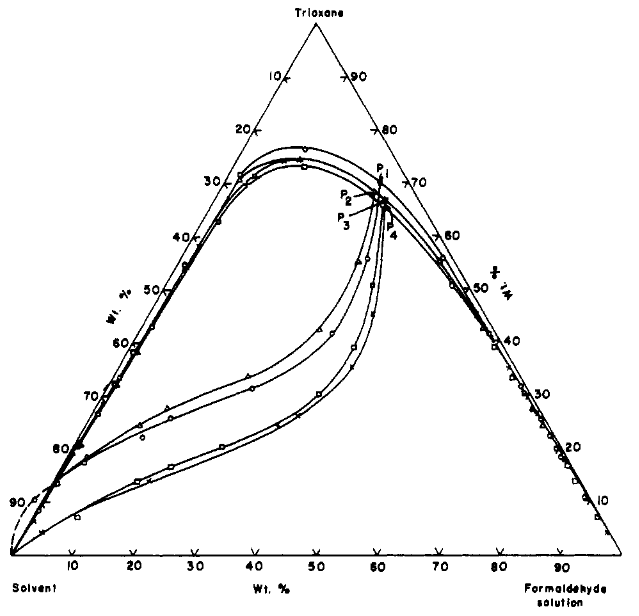

Figure 3. Phase equilibrium diagram of trioxane-formaldehyde solution and solvents: (O) dichlorobenzene at 50 °C; (Δ) dichlorobenzene at 60 °C; (X) benzene at 50 °C; (□) benzene at 60 °C.

Table I. Tie-Line Data for Trioxane-Formaldehyde Solution (25%)-Benzene at 50 °C[a]

aqueous layer			organic layer		
benzene	trioxane	formaldehyde soln	benzene	trioxane	formaldehyde soln
0.12	4.12	95.76	93.07	6.52	0.41
0.31	14.02	85.68	70.47	28.81	0.72
0.61	24.53	74.86	44.79	54.01	1.20
0.72	26.72	72.56	39.75	58.42	1.83
1.03	36.01	62.96	26.39	69.90	3.71
1.35	45.44	53.21	17.95	74.33	7.72

[a] Values expressed in wt %.

Table II. Tie-Line Data for Trioxane-Formaldehyde Solution (25%)-Benzene at 60 °C[a]

aqueous layer			organic layer		
benzene	trioxane	formaldehyde soln	benzene	trioxane	formaldehyde soln
0.21	7.01	92.78	85.88	13.51	0.61
0.40	13.97	85.63	72.51	26.77	0.72
0.47	16.71	82.82	65.57	33.61	0.82
0.56	20.12	79.22	55.42	43.27	1.31
0.82	30.18	69.00	34.60	62.92	2.48
1.12	39.14	59.74	24.36	71.50	4.14

[a] Values expressed in wt %.

Figure 3 shows the mutual solubility curves of the components in the systems: the dichlorobenzene-trioxane-formaldehyde solution and the benzene-trioxane-formaldehyde solution at 50 and 60 °C. The area of heterogeneity decreased with the rise of temperature, indicating that the mutual solubility of the solvent and the formaldehyde solution increases at higher temperatures in each case. At any given temperature, however, benzene showed higher mutual solubility with the formaldehyde solution.

The experimental tie-line data for the systems trioxane-formaldehyde solution-benzene at 50 and 60 °C and trioxane-formaldehyde solution-dichlorobenzene at 50 and 60 °C are given in Tables I-IV, respectively. The tie-line curves are

Table III. Tie-Line Data for Trioxane-Formaldehyde Solution (25%)-Dichlorobenzene at 50 °C

aqueous layer			organic layer		
dichlorobenzene	trioxane	formaldehyde soln	dichlorobenzene	trioxane	formaldehyde soln
0.10	2.97	96.93	97.84	2.06	0.10
0.15	6.26	93.59	95.25	4.59	0.16
0.20	10.73	89.07	90.95	8.84	0.21
0.25	18.20	81.55	78.69	20.90	0.41
0.28	22.31	77.41	67.07	32.23	0.70
0.30	26.02	73.48	60.66	38.53	0.81
0.33	31.71	67.96	44.05	54.66	1.29
0.70	41.89	57.41	26.24	71.97	1.79

[a] Values expressed in wt %.

Table IV. Tie-Line Data for Trioxane-Formaldehyde Solution (25%)-Dichlorobenzene at 60 °C[a]

aqueous layer			organic layer		
dichlorobenzene	trioxane	formaldehyde soln	dichlorobenzene	trioxane	formaldehyde soln
0.14	2.67	97.19	97.45	2.37	0.18
0.20	5.21	94.59	94.78	4.97	0.25
0.29	10.17	89.54	89.81	9.75	0.44
0.57	18.54	80.89	78.61	20.74	0.65
0.77	24.12	75.11	66.87	32.16	0.97
0.90	27.42	71.68	60.65	38.26	1.09
1.12	33.60	65.28	44.38	44.40	1.22
1.42	42.20	56.38	27.76	70.60	1.64

[a] Values expressed in wt %.

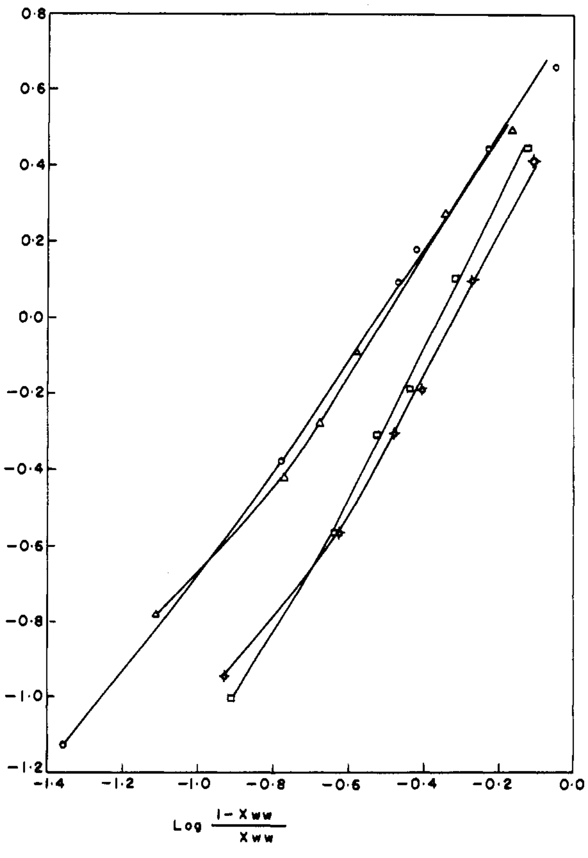

Figure 4. Othmer–Tobias plot of the tie-line data: (○) benzene at 50 °C; (△) benzene at 60 °C; (□) dichlorobenzene at 50 °C; (◇) dichlorobenzene at 60 °C.

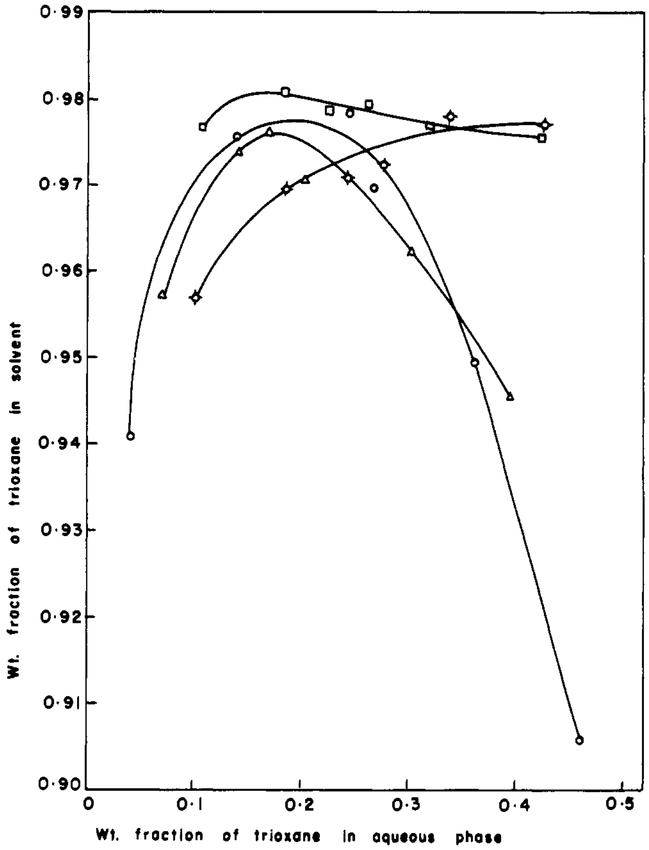

Figure 5. Selectivity diagram (all values on solvent-free basis): (○) benzene at 50 °C; (△) benzene at 60 °C; (□) dichlorobenzene at 50 °C; (◇) dichlorobenzene at 60 °C.

Table V. Theoretical Stages Required for Extraction of Trioxane by Benzene and Dichlorobenzene at 50 °C[a]

	benzene		dichlorobenzene	
solvent-to-feed ratio	formaldehyde soln in extract, wt %	no. of stages	formaldehyde soln in extract, wt %	no. of stages
1	0.80	2.4	0.60	5.1
2	0.52	1.8	0.40	2.7
3	0.49	1.6	0.29	2.0

[a] Feed: 35% trioxane in aqueous 25% formaldehyde.

plotted in Figure 3; the plait points were computed by using the method of Sherwood (*14*). The tie-line data satisfied the Othmer and Tobias correlation (*15*), shown in Figure 4. In the case of the system trioxane–formaldehyde solution–dichlorobenzene, the phenomenon of solutropy was observed; that is, at lower concentrations, the solute was more in the aqueous phase whereas at higher concentrations its affinity was more for the solvent phase.

The selectivities in the two solvents are shown in Figure 5. It can be seen clearly that the selectivity is maximal in the case of dichlorobenzene at 50 °C.

For assessing which of the two solvents would be economical to use, the number of theoretical stages required for trioxane extraction by the two solvents was calculated. Necessarily, the operating parameters and the thermal loads for the recovery of trioxane from these solvents were also calculated. The theoretical number of stages for the extraction of 95% trioxane from the aqueous formaldehyde solution containing 35% (w/w) of trioxane for three solvent-to-feed ratios is summarized in Table V. With dichlorobenzene, the number of stages required was higher than for the extraction with benzene at similar solvent-to-feed ratios. However, water and formaldehyde contents in the extract phase were less with dichlorobenzene. In the case of benzene extraction, the form-

Table VI. Comparison of Distillation Data for Separation of Trioxane and Solvent[b]

particulars	dichlorobenzene	benzene
important solvent properties		
boiling point, °C	172-179	80.1
specific gravity, d_4^{20}	1.299	0.879
change in enthalpy ($H_T - H_{298}$), kcal/kg-mol	5963 at 114.5 °C (l)	9960 at 80 °C (g)
toxicity (allowable limit), ppm	*o*-, 50 *p*-, 75	10
wt % trioxane in distillate or bottom product	99.9	99.9
min reflux ratio	0.5	1.0
operating reflux ratio	1.0	1.5
no. of theoretical stages	11.8	24.9
condenser duty,[a] kcal/h	2200	4700
reboiler duty,[a] kcal/h	2500	4900

[a] Calculated for processing extract, containing 10 kg/h trioxane.
[b] Trioxane bp 114.5 °C.

aldehyde and water contents being higher, the operating costs for purification of trioxane to bring it to the monomer grade would be more.

Finally, trioxane has to be separated from the extracts by distillation. The data for the distillation from the extracts obtained at a solvent-to-feed ratio of 1.0 at 50 °C were calculated and are given in Table VI. The boiling points of benzene, *o*-dichlorobenzene, and trioxane are 80.1, 179, and 114.5 °C, respectively. Therefore, in the case of benzene extract, benzene would be the overhead product (at 80 °C) whereas, from the dichlorobenzene extract, trioxane would be distilled over at 114.5 °C. But in the former case the entire quantity of the benzene has to be separated by rectification. This would require a higher number of theoretical stages as well as operation at a higher reflux ratio. The consumption of energy will thus be higher. For the recovery of trioxane from dichlorobenzene extract, the requirements of theoretical stages, operating reflux, and heat load would be considerably lower. Moreover, benzene is more toxic than dichlorobenzene, and the allowable limits are 10 and 50 ppm, respectively (*16*). Hence, the expenses for safety precautions would be higher for benzene.

Glossary

C	solute
P	plait point
S	solvent
W	formaldehyde solution
X_{ss}	weight fraction of solvent in solvent layer
X_{ww}	weight fraction of formaldehyde solution in aqueous layer

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Heat Capacity and Enthalpy of Phosphoric Acid

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Measurements of the heat capacity of phosphoric acid were made over the ranges of concentration of 61.8–83.0% and temperature of 25–367 °C. A possible transition was found at ~77 °C. Values for enthalpy were derived.

Previous studies (*1*) of the enthalpies of phosphoric acids and the derived heat capacities were made by using a high-temperature drop calorimeter. This study, using a Perkin-Elmer differential scanning calorimeter Model DSC-2, more precisely defines the heat capacities and entropies of the acids over a somewhat broader concentration range (61.8–83.0% P_2O_5) and temperature range (25–370 °C).

Materials and Procedure

The most concentrated superphosphoric acid (83.0% P_2O_5) was prepared by dissolving reagent P_2O_5 in reagent H_3PO_4 at 145 °C and filtering the hot solution through a coarse glass frit. Portions of this acid were diluted with reagent H_3PO_4 to form acids of the desired concentrations. All the solutions were held overnight at 100 °C to ensure equilibrium distribution of the phosphate species. Final concentrations of the acids were determined by chemical analyses.

The acid samples (17.56–29.87 mg) and a synthetic sapphire reference standard (40.09 mg) were hermetically sealed in weighed gold pans. The sample enclosure of the scanning calorimeter was cooled by an aluminum cold finger partially immersed in ice water and was purged continuously with dry nitrogen. The scanning rate for all measurements was 10 deg/min, and the sensitivity of the recorder was 2 mcal s^{-1}.

A weighed empty pan was placed in the sample holder and scanned over the desired temperature range. The empty pan was replaced with the pan containing the sapphire, and it was scanned over the same temperature range. The pan containing the sapphire was then replaced with the pan containing the acid