Technology and Metallurgy, University of Beograd, Beograd (1977).

Mihajlov-Duduković, A. N., B. D. Djordjevic, and A. Z. Tasić, "Calculation of the Thermodynamic Properties of Real Gases and Liquids by Modified Redlich-Kwong Equation of State," paper presented at Advances in Separation Science, p. 200-209, Trieste, Italy (1978).

Nothnagel, K. H., D. S. Abrams and J. M. Prausnitz, "Generalized Correlation for Fugacity Coefficient in Mixtures at Moderate Pressures. Application of Chemical Theory of Vapor Imperfections," *Ind. Eng. Chem. Process Design Develop.*, **12**, 25-35 (1973).

O'Connell, J. P., and J. M. Prausnitz, "Empirical Correlation of Second Virial Coefficients for Vapor-Liquid Equilibrium Calculations," *ibid.*, **6**, 245-250 (1967).

Polak, J., and B. C.-Y. Lu, "Second Virial Coefficients of Polar Gases—A Correlation with Stockmayer Potential Function," *Can. J. Chem. Eng.*, **50**, 553-556 (1972).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions," *Chem. Rev.*, **44**, 233 (1949).

Rosenbrock, H. H., and C. Storey, *Computational Technique for Chemical Engineers*, Pergamon Press, Oxford, England (1966).

Santis, R., G. J. F. Breedveld and J. M. Prausnitz, "Thermodynamic Properties of Aqueous Gas Mixtures at Advanced Pressures," *Ind. Eng. Chem. Process Design Develop.*, **13**, 374-377 (1974).

Simonet, R., and E. Behar, "A Modified Redlich-Kwong Equation of State for Accurately Representing Pure Components Data," *Chem. Eng. Sci.*, **31**, 37-43 (1976).

Tarakad, R. R., and R. P. Danner, "An Improved Corresponding States Method for Polar Fluids: Correlation of Second Virial Coefficients," *AIChE J.* **23**, 685-695 (1977).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *ibid.*, **20**, 263-272 (1974).

————, "Second Virial Coefficients of Polar Haloalkanes," *ibid.*, **21**, 827-829 (1975).

————, "Second Virial Coefficients of Water Pollutants," *ibid.*, **24**, 1112-1115 (1978).

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The Separation of Ethylbenzene from *p*- and *m*-Xylene by Extractive Distillation Using Mixtures of Polychloro Compounds

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The use of a single compound as the agent in modifying the apparent relative volatility in extractive distillation is well known. In the separation of ethylbenzene from para- and meta-xylenes by extractive distillation, it was found that mixtures containing from two to four components were more effective than any known single compound. Hundreds of combinations of extractive agents were investigated in vapor-liquid equilibrium stills, and from these, twenty-seven different combinations of chlorinated organic compounds showed merit. The relative volatility of ethylbenzene to *p*-xylene is 1.06 and to *m*-xylene 1.08. The promising combinations were investigated in three glass perforated plate extractive distillation columns containing twelve, fifteen and nineteen theoretical plates, respectively. Of the twenty-seven different extractive agents tested in the columns, sixteen yielded a relative volatility greater than 1.20. The best one, a mixture of pentachlorophenol, benzene hexachloride and 1,2,4-trichlorobenzene, gave a relative volatility of 1.27. Other combinations approaching this relative volatility are pentachlorophenol, benzene hexachloride and 2,4-dichlorotoluene giving 1.25 and polychlorobenzene, pentachlorophenol, benzene hexachloride and 1,2,4-trichlorobenzene giving 1.26, when used in the ratio of two parts of extractive agent to one part of ethylbenzene-xylene mixture. All the extractive agents boil sufficiently above xylene to make their recovery by distillation easy and complete. Life studies showed no excessive decomposition of any of them while in use.

The separation of ethylbenzene (boiling point 136.15°C.) from *p*-xylene (boiling point 138.4°C.) and *m*-xylene (boiling point 139.2°C.) presents considerable difficulty by reason of the proximity of their boiling points and the accompanying similarity of their vapor pressures as to require the use of fractioning columns containing a great number of plates and high reflux ratios in order to assure effective separation thereof. A major end use for these compounds is in plastics, where high purity is essential; for example, ethylbenzene is converted to styrene and much of *p*-xylene is made into dimethyl terephthalate. As a result, the cost of accomplishing such a separation by conventional rectification is relatively uneconomical. Since ethylbenzene, *p*-xylene and *m*-xylene are all isomers of C_8 aromatic hydrocarbons, their chemical properties are almost identical, and separation by chemical means does not appear to be an attractive route.

Although extractive distillation has fairly wide acceptance in some hydrocarbon separations, toluene from similar boiling nonaromatic hydrocarbons for example, this technique has not been widely investigated in the separation of ethylbenzene from the xylenes. Most of the previous investigators in this field have looked at single compounds as the extractive agent without marked success (Chu, 1954). The relative volatility of ethylbenzene to *p*-xylene is 1.06; to *m*-xylene it is 1.08. To be considered attractive, we believe that the extractive agent should be capable of increasing this value to about 1.20. Amir (1963) reported that *p*-dichlorobenzene increased the relative volatility to 1.116, 2,4,5-trichlorophenol to 1.147 and 2,3,4,5,6-pentachloro-1-butoxybenzene to 1.26. Nixon (1950, 1953) reported that antimony trichloride gave 1.15.

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Anstey (1966) reported on the use of tris-(o-phenylene dioxy) cyclophosphazene, tris-(2,3-napthyl dioxy) cyclotriphospazene, tris-(o-phenylene dioxy) cyclotriphosphazene and tris-(o-phenylene diamino) cyclotriphosphazene as extractive agents. Smith, Black and Hickman (1973) have reported 1,2,4-trichlorobenzene as 1.11. Thus we have a situation where individual compounds used as extractive distillation agents are either ineffective or unstable and costly.

We have found that if proper mixtures of compounds are used as the extractive distillation agent, relative volatilities can be achieved which are not possible with the components of the mixture when used alone. Amir (1963) stated that improved yield and purity of ethylbenzene may be obtained from mixtures with xylenes by distilling the mixtures in the presence of extractive solvents including various polychlorinated benzenes. While he stated that mixtures of two or more of the compounds may be used as the extractive distillation solvent, no examples of such mixtures are cited. In actual practice, it has been found that unless the particular polychlorinated benzenes are carefully selected and combined, the relative volatility of such a mixture may be no higher and sometimes is lower than that of the individual polychlorinated benzenes when used alone. Thus, for example, the value of the relative volatility for *o*-dichlorobenzene used in distilling a mixture containing equal parts by weight of ethylbenzene and *p*-xylene is 1.10. When *p*-dichlorobenzene is used to effect this separation, the relative volatility is 1.11. On the other hand, when the extractive solvent contains equal parts of ortho and paradichlorobenzenes and the ratio of these compounds used in distilling a mixture of ethylbenzene and *p*-xylene is one part ethylbenzene, one part *p*-xylene, one part *o*-dichlorobenzene and one part *p*-dichlorobenzene, the value of the relative volatility is only 1.05. When the mixture being distilled contains one part of ethylbenzene, one part of *p*-xylene, one half part of *o*-dichlorobenzene and one half part of *p*-dichlorobenzene, the value of the relative volatility is increased to 1.08. Even when the mixture is reduced to one part of ethylbenzene, one part of *p*-xylene, one third part of *o*-dichlorobenzene, and one third part of *p*-dichlorobenzene the relative volatility holds at 1.08.

The value of the relative volatility for mixtures of polychlorinated benzenes used as extractive solvents also varies with the ratio of the solvent to the two hydrocarbons and with the ratio of the ethylbenzene to the xylene in the hydrocarbon mixture being distilled.

One of the best extractive agents for the separation of ethylbenzene from para- and/or meta-xylene is pentachlorophenol when it is admixed with one or more additional solvents such as polychlorophenol, polychlorinated benzene and/or glycol ethers. Such mixtures are found to possess unexpectedly high relative volatilities, they maintain their value throughout the changing ethylbenzene-xylene concentration range in the rectifying column and the ratio of the extractive agents to the material being distilled is relatively moderate.

Table 1 shows the relative volatility of ethylbenzene and *p*-xylene or *m*-xylene with a number of solvents which, when properly combined, gives attractive relative volatilities. In Table 1, hydrocarbon means the sum of the weights of ethylbenzene and *p*- or *m*-xylene. Extractive agent means the sum of the weights of the chlorinated compound(s). Thus, when one part by weight of ethylbenzene-*p*-xylene mixture is distilled in the presence of one one part of 2,3,4,6-tetrachlorophenol, the apparent relative volatility of ethylbenzene to *p*-xylene is 1.20. When the mixture is one part of ethylbenzene-*m*-xylene mixture to one part of 2,3,4,6-tetrachlorophenol, the apparent relative volatility of ethylbenzene to *m*-xylene is 1.16. When two parts by weight of ethylbenzene-*p*-xylene

TABLE 1. RELATIVE VOLATILITIES OF PURE COMPOUNDS AND TWO-COMPONENT MIXTURES AS DETERMINED IN A VAPOR-LIQUID EQUILIBRIUM STILL

	Ratio: hydrocarbon	Relative volatility	
Extractive agent	to extractive agent	EtBn-p-xylene	EtBn-m-xylene
Pentachlorophenol	—	solid, melts too high	
Polychlorobenzene	1 : 1	1.16	
	2 : 3	1.14	
1,2,4-trichlorobenzene	1 : 1	1.11	1.08
	2 : 1	1.11	1.09
1,2,3-trichloropropane	1 : 1	1.11	
	1 : 2	1.10	
2,4-dichlorotoluene	1 : 1	1.06	
	1 : 2	1.06	
Benzene hexachloride	1 : 1	1.07	
	2 : 1	1.13	
2,3,4,6-tetrachlorophenol	1 : 1	1.20	1.16
	2 : 1	1.12	1.17
n-butoxyethanol	2 : 1	1.04	
1,2,4,5-tetrachlorobenzene	—	Melts too high	
50% pentachlorophenol	2 : 1	1.12	
50% polychlorobenzene	1 : 1	1.14	
50% pentachlorophenol	2 : 1	1.09	
50% 1,2,4-trichlorobenzene	1 : 1	1.16	
75%Pentachlorophenol	2 : 1	1.04	
25% 1,2,3-trichloropropane	1 : 1	1.03	
25% pentachlorophenol	2 : 1	1.10	
75% 2,4-dichlorotoluene	1 : 1	1.14	
85% pentachlorophenol	2 : 1	1.18	
15% benzene hexachloride	1 : 1	1.08	
50% pentachlorophenol	2 : 3	1.23	1.27
50% 2,3,4,6-tetrachlorophenol	1 : 2	1.25	1.21
50% pentachlorophenol	2 : 1	1.09	
50%*n*-butoxyethanol	1 : 1	1.14	
50% pentachlorophenol	2 : 1	1.10	
50% 1,2,4,5-tetrachlorobenzene	1 : 1	1.13	

mixture are distilled in the presence of three parts of a 50-50 wt% mixture of 2,3,4,6-tetrachlorophenol and pentachlorophenol, the apparent relative volatility of ethylbenzene to *p*-xylene becomes 1.23 and for ethylbenzene to *m*-xylene becomes 1.27. None of these compounds by themselves or in most pairs are particularly attractive in regards to their separation capability. However, when these are combined in the following way, as shown in Table 2, the results of the combination far exceed those of the individual components.

The data presented in Table 1 were obtained in a glass vapor-liquid equilibrium still of the Othmer design. The data in Table 2 were obtained from either a 2.5 cm diameter glass perforated plate Oldershaw column or a 5 cm diameter perforated plate glass rectifying column in the following manner. A column consisting of two twenty-plate sections of 2.5 cm diameter glass perforated plates equipped with a vacuum jacket was employed. The column was fitted with a Corad constant reflux ratio distilling head. Between the Corad head and the top of the column, a feed line from a constant flow pump was introduced. The stillpot was equipped with a sampling tube. The column was calibrated with a test mixture of ethylbenzene and *p*-xylene, which mixture possesses a relative volatility of 1.06. At total reflux, this column calibrated twelve theoretical plates. Then a run was made with a charge of approximately 20 wt % ethylbenzene, 80 wt. % *p*-xylene in the stillpot. The column was operated at total reflux for about 1 hr, and then the pump started at a rate to deliver about one part of extractive agent to one part of ethylbenzene-*p*-xylene being boiled up. The extractive agent in this example was 33.3 wt % pentachlorophenol, 33.3 wt % benzene hexachloride, 33.3 wt % 1,2,4-trichlorobenzene. The following data were obtained:

Time,hr	Overhead composition, %EtBn	Stillpot composition, %EtBn	Rel. vol.
1	46.67	13.64	1.15
2	72.15	12.16	1.28
3	71.03	11.95	1.27

It will be noted that after about 2 hr equilibrium appears to have been achieved, and the relative volatility remains essentially constant at about 1.27. Without the extractive agent, it would have been 1.06.

A second column consisting of a forty-plate section of 5 cm diameter glass perforated plates and equipped with two outer glass tubes, one with a heating element, was also used. A feed tube connected to a constant volume pump was placed above the forty-plate section, and above that is a 1 m section of a packed column. On top of the packed column was a Corad constant reflux ratio distilling head. The stillpot was equipped with a sampling tube. The purpose of the packed section above the pump feed inlet is to fractionate out any of the extractive agent that might have otherwise been carried off with the overhead distillate. The column was calibrated with ethylbenzene-*p*-xylene, and with 1.06 used as the relative volatility of this mixture, the forty-plate section was found to have fifteen theoretical plates and the packed section 4.5 theoretical plates at total reflux. The pump was started up, and an extractive agent comprising 50 wt % pentachlorophenol, 25 wt % benzene hexachloride, 25 wt % polychlorobenzenes was fed at a rate such that the extractive agent

TABLE 2. RELATIVE VOLATIVITIES OF ETHYLBENZENE-P-XYLENE WITH MULTICOMPONENT EXTRACTIVE AGENTS AS DETERMINED IN MULTIPLATE RECTIFICATION COLUMNS

Extractive agent	Ratio: hydrocarbon to extractive agent	Relative volatility EtBn- *p*-xylene
38% pentachlorophenol 24% 2,3,4,6-tetrachlorophenol 38% 1,2,4-trichlorobenzene	2 : 1	1.24
38% pentachlorophenol 24% 2,3,4,6-tetrachlorophenol 38% 2,4-dichlorotoluene	2 : 1	1.23
33% pentachlorophenol 33% benzene hexachloride 33%2,4-dichlorotoluene	2 : 1	1.25
25% pentachlorotoluene 25% polychlorobenzenes 25% 1,2,4,5-tetrachlorobenzene 25% *n*-butoxyethanol	2 : 1	1.19
26.7% pentachlorophenol 26.7% polychlorobenzenes 26.6% 1,2,4,5-tetrachlorobenzene 20% 2,4-dichlorotoluene	2 : 1	1.18
25% pentachlorophenol 25% polychlorobenzenes 25% benzene hexachloride 25% 1,2,4-trichlorobenzene	2 : 1	1.26
33.3% pentachlorophenol 33.3% polychlorobenzenes 33.4% 1,2,4-trichlorobenzene	2 : 1	1.20
26% pentachlorophenol 52% polychlorobenzenes 22% 1,2,3-trichlorobenzene	2 : 1	1.18
33.3% pentachlorophenol 33.3% benzene hexachloride 33.4% 1,2,4-trichlorobenzene	2 : 1	1.27
50% pentachlorophenol 25% benzene hexachloride 25% polychlorobenzenes	2 : 1	1.22

was about equal to the volume of the hydrocarbon boil up rate. The following data were obtained:

Time,hr	Overhead composition, %EtBn	Stillpot composition, %EtBn	Rel. vol.
1	75.30	20.48	1.18
2	81.08	20.64	1.21
3	83.14	20.47	1.22

Again, it will be noted that it takes about 2 hr for this equipment to attain equilibrium and that this extractive agent raises the relative volatility from 1.06 to 1.22.

In order for extractive distillation to be economically attractive, the agents must be chemically stable and capable of continual recycle. The combinations of agents shown in Table 2 were allowed to boil at atmospheric pressure in the equilibrium still for periods of time ranging from 24 to 96 hr with no evidence of decomposition.

LITERATURE CITED

Amir, E. M., and W. R. Edwards, "Separation of Ethylbenzene with Di- and Tri-chlorobenzenes," *U.S. Patent 3,105,017* to Esso Research & Engr. Co., (Sept. 24, 1963).

Anstey, R. H., H. J. Naylor and P. T. Davis, "Extractive Distillation of Ethylbenzene using Phosphazenes," *Brit. Patents 1,257,024-5* (Sept., 1966).

Chu, J. C., O. P. Kharbanda, R. F. Brooks and S. L. Wang, "Vapor-Liquid Equilibrium," *Ind. Eng. Chem.*, **46**, 754 (1954).

Nixon, A. C., C. H. Deal and R. J. Evans, "Separation of Ethylbenzene with Antimony Trichloride," *U.S. Patent 2,532,031* to Shell Dev. Co. (Nov. 28, 1950).

----------, and C. H. Deal, "Extractive Distillation of Ethylbenzene with Antimony Trichloride," *U.S. Patent 2,638,441* to Shell Dev. Co., (May 12, 1953).

Smith, B. D., B. Black and K. C. D. Hickman, *Extractive Distillation*, p. 21, McGraw-Hill, New York (1973).

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Influence of Condensable Vapor on Strength of Powders

Diametrically different influences of small moisture contents upon strength are often measured in beds of different kinds of particles. Here we explain such opposing trends in terms of capillary forces exerted by condensed liquid rings at the points of particle contact. The effects of such rings are opposite for different particle shapes at the point of contact, namely, at spherical or at sharp angular contact points. In addition to the theoretical development, data are given for two different illustrative types of particles.

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Increasing moisture content of beds of powders influences their strength in diverse ways, depending on the nature of the particulate powders. In some instances, strength increases, and in some it decreases as moisture concentration grows. Such converse behavior has been a theoretical problem for years; we propose a possible resolution of this difficulty. Haines (1925) laid down the early theoretical foundations for such effects of moisture by considering the capillary forces acting upon nonporous, insoluble, identical spherical particles as a result of liquid (water) condensed in the form of rings at the points of contact of the spheres. Following Haines (1925), Fisher (1926) was the first to deduce theoretically that both the tension in the air-liquid interface and the pressure deficiency in the capillary condensed liquid rings must be considered together in computing the net force effect. This theory predicts a monotonic decrease in strength with increasing liquid content, a behavior actually observed in practice only for some nonporous insoluble powders. Other powders can behave very differently.

More recently, Dietl and Coughlin (1976) presented a simplified one-dimensional model based on capillary condensation at points of particle contact that was used to explain quantitatively the bizarre influence of humidity on the electrical conductivity of flyash; this model relied upon the conduction pathway provided by the capillary condensed liquid and did not consider the capillary forces which are very sensitive to the curvature of the liquid surface.

According to the spherical model, and assuming the solid is perfectly wet by the liquid (liquid-solid contact angle = 0 deg), we can approximate the air-liquid interface (before coalescence of the liquid rings) as having two radii of circular curvature t_0 and y as shown in Figure 1. With respect to radius t_0, the liquid surface is concave, whereas with respect to radius y, it is convex. The curvature of the liquid surface is such as to decrease the internal pressure of the liquid by an amount $\gamma(1/t_0 - 1/y)$. In addition to this hydrostatic suction, the liquid surface will exert a tension also tending to hold the particles together. The total force acting to hold the spheres together is readily computed at the plane tangent to each sphere at the point of contact; the intersection of this plane with the liquid surface is the circle of circumference $2\pi y$ at which the surface tension force $2\pi y\gamma$ acts, whereas the capillary suction force within the liquid at this plane acts across the surface area πy^2. The total force is

$$F_{\text{tot}} = \pi y^2\gamma\left(\frac{1}{t_o} - \frac{1}{y}\right) + 2\pi y\gamma = \pi y\gamma\left(\frac{y + t_o}{t_o}\right) \tag{1}$$

The foregoing expression can also be written in terms of the central angle ϕ, as illustrated in Figure 1, by expressing y and t_o in terms of ϕ and substituting them into the above equation. It can be shown that t_o and y are given by

$$t_o = r \tan\phi \tan\frac{\phi}{2} \tag{2a}$$

and

$$y = r \tan\phi\left[1 - \tan\frac{\phi}{2}\right] \tag{2b}$$
