

GENERATING YOUR OWN VLE DATA

When engineers need to separate one chemical from another, they first decide on the process concept: whether to employ distillation, extraction, crystallization, or some other unit operation. To determine this, however, it is necessary to know the relevant physical properties – molecular weight, normal boiling point, vapor pressure (as a function of temperature), solubility (in water), liquid density, melting point, and so on – of the various components.

In addition, the engineers need to know the relationships between the pairs of compounds that are to be separated. Information that is useful for determining these relationships include:

- Vapor-liquid equilibrium (VLE) data. For example, the Dechema series of VLE data provides a compilation of much of the data in the open literature
- Binary azeotrope data for all pairs of compounds, and any ternary azeotrope data that are available. The American Chemical Soc.'s *Azeotropic Data* is a very good source for this data
- Liquid-liquid equilibrium (LLE) data. This is necessary if one of the compounds in the mixture is water, or if there is a large difference in the water

G. Schlowsky, A. Erickson,
T. Schafer
Modular Process Systems, Inc.

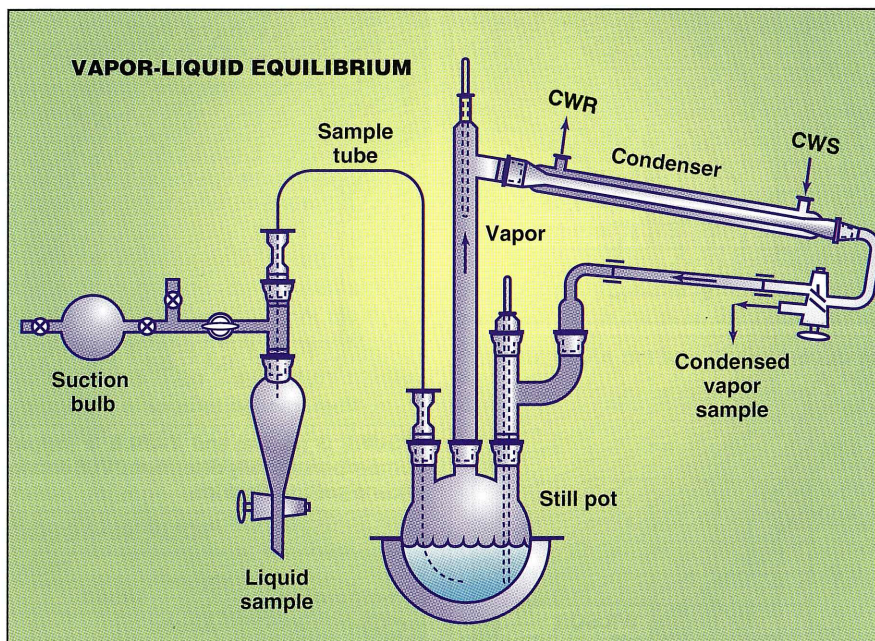


FIGURE 1. Experimental setup for determining the vapor-liquid equilibria of compounds prior to designing a process

PHYSICAL PROPERTIES		
PROPERTY	COMPONENT	
	Toluene	Acetic anhydride
Molecular weight	92.0	102.0
Boiling point, at 760 torr, °C	110.8	139.6
Antoine constants: A	16.0137	16.3982
$\ln(VP) = A - B/(T+C)$: B	3,096.52	3,287.56
VP(=)mm Hg, T(=) K: C	-53.67	-75.11
Water solubility, g/100 g H ₂ O	0.05	12.0
Liquid density, g/cm ³	0.866	1.082
Melting point, °C	-95.0	-73.0

TABLE 1. The first step in generating VLE data: Locating the physical properties of the components, as shown here

How to design a separations system when no data are available

solubilities of the key components. Again, the Dechema series has an excellent compilation of binary and ternary LLE data

Starting off

In general, distillation should be evaluated first for making a desired separation. If relative volatilities between the key components are 2.0 or greater, then distillation will probably result in the most economic process.

For compounds with relative volatilities less than 2.0, compounds that form azeotropes, or dilute

aqueous systems where water is the most volatile component, other process alternatives should be explored. Some alternatives include azeotropic distillation, extractive distillation, liquid-liquid extraction and fractional crystallization.

There are times, however, when no VLE data can be found for important component pairs. Here, engineers have to choose among one or more of the following alternatives:

1. Assume that the compounds form an ideal solution. This means that component vapor pressure vs. temperature

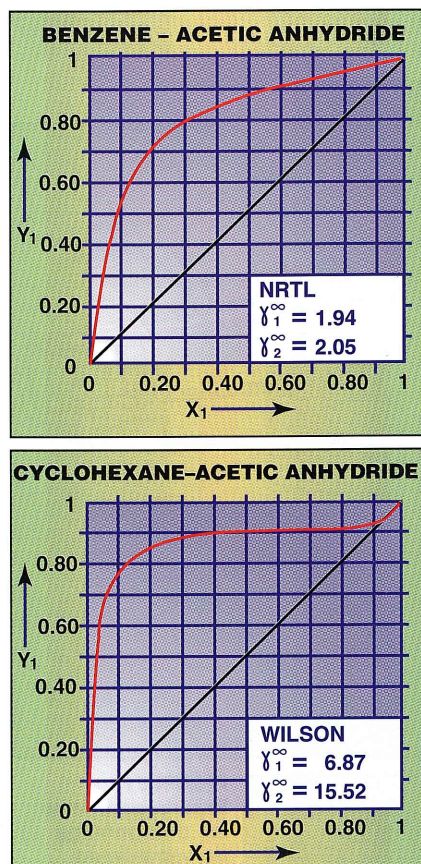


FIGURE 2. Data from Dechema for benzene-acetic anhydride (top) and cyclohexane-acetic anhydride

data can be used to predict the VLE numbers, and to calculate relative volatilities. This option is generally acceptable when the compounds in question are closely related, such as members of a homologous series. Examples include linear alcohols, paraffinic hydrocarbons, aliphatic substituted benzene (benzene, toluene, xylene), polymeric glycols, and so on

2. Find VLE data for an analogous system, one that contains one of the compounds of the pair. The second compound of the analogous system should be closely related to the other compound of the pair, containing the same or similar structure and functional groups. An example of this approach would be to use liquid activity coefficient data for ethanol and benzene to predict the vapor-liquid equilibrium for propanol and benzene

3. Develop VLE data for all key pairs of components in the laboratory. Many process engineers choose to run a pilot test in a batch distillation column when

ETHANOL-WATER SYSTEM				
Experimental		Reference	Experimental	Reference
Ethanol In liquid m.f.	Ethanol In vapor m.f.	Ethanol In vapor m.f.	K value	K value
0.1414	0.5095	0.4911	3.60	3.47
0.1598	0.5049	0.5055	3.16	3.16
0.2414	0.5627	0.5466	2.33	2.26

TABLE 2. Test data for the ethanol-water system

m.f. = mole fraction

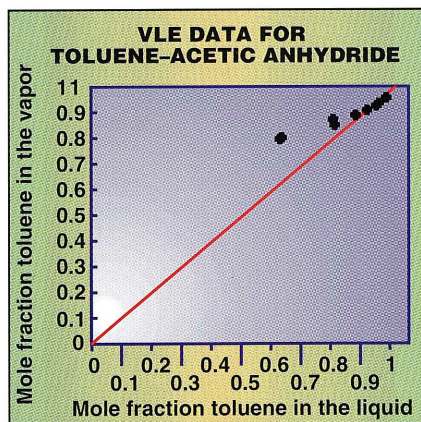


FIGURE 3 (above) and **TABLE 3** (below). Some experimentally determined VLE data for toluene-acetic anhydride

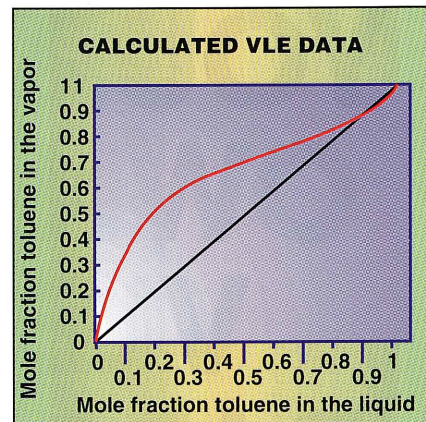


FIGURE 4. The NRTL-derived VLE curve for the toluene-acetic anhydride system

TOLUENE-ACETIC ANHYDRIDE SYSTEM					
Temperature (°C)	Mole fractions				Relative volatility
	Liquid		Vapor		
	Acetic anhydride	Toluene	Acetic anhydride	Toluene	
107.5	0.02835	0.97165	0.03010	0.96990	0.94030
107.5	0.05673	0.94327	0.05278	0.94722	1.07926
108.0	0.08502	0.91498	0.07973	0.92027	1.07253
108.1	0.12518	0.87482	0.10000	0.90000	1.28777
108.5	0.19692	0.80308	0.13114	0.86886	1.62467
111.0	0.37074	0.62926	0.18605	0.81395	2.57750

not enough data can be found. This is appropriate *only* after a design has been developed – for confirmation, or to make samples

To generate useful information the pilot test must use the correct number of stages and operate at the correct reflux ratio. Even if both requirements are met, the results only provide information at one set of conditions. Optimizing or predicting results at other reflux ratios and number of stages is very difficult at best, and, often, not possible based on pilot plant data.

The preferred approach is to set up a VLE apparatus to test each key component pair, using a setup such as that shown in Figure 1. This can be readily accomplished at pressures from a few mm Hg absolute to one atmosphere and at temperatures up to 250°C.

Data developed this way can be regressed to provide interaction coefficients (NRTL, Uniquac, and so on). The interaction coefficients can then be

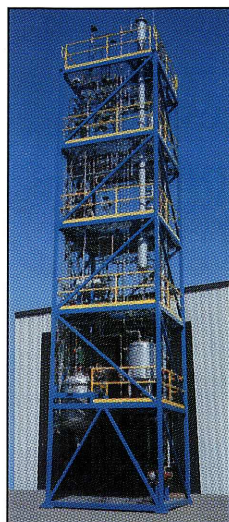
used in most process simulation computer programs to explore a wide range of design alternatives. For example, it is possible to calculate relative volatilities, predict whether there is an azeotrope and provide the basis for an optimized process design.

A typical example

The procedure for determining VLE data is best illustrated via an example. For instance, the authors recently faced the problem of having to design a process for separating toluene and acetic anhydride.

To begin, no VLE data on this system could be found in the literature, nor could it be determined whether this pair of compounds forms an azeotrope. So, as a first step in the development of a solution, the physical properties of the components were located (Table 1).

The literature was then searched for VLE data for analogous systems. For example, data for benzene-acetic anhy-



DESIGN PARAMETERS			
COMPONENT	FEED	DISTILLATE	BOTTOMS
Toluene, wt. %	40	91	1
Acetic anhydride, wt. %	60	9	99
Theoretical stages: 19			
Packing type: Koch Flexipac			
Packed height: 33 ft			
Reflux ratio: 1.85			

TABLE 4. Design and operating parameters for a toluene-acetic anhydride distillation column, illustrated in the photo

dride and cyclohexane-acetic anhydride are found in Dechema (Figure 2). These data clearly indicate non-ideality.

Since toluene boils closer to acetic anhydride than both benzene and cyclohexane, an engineer should expect that the toluene-acetic anhydride system will exhibit similar, but more severe, non-ideality. Thus, it is not prudent to use either ideal assumptions or data from analogous systems to design this system.

As a result, in this case, generating laboratory data is the only alternative available to serve as a basis for design. To generate the data, a simple, inexpensive apparatus was constructed of glass and polytetrafluoroethylene components, similar to the design in Figure 1. Most of the parts can be found in a typical laboratory, or can be purchased from a laboratory-equipment supply company for about \$2,000.

After assembly, the apparatus is checked by testing a known system. This ensures that the apparatus will yield exactly one equilibrium stage. The known system should boil close to the temperature of the experimental system, to be certain that the apparatus operates adiabatically. For example, internal condensation due to heat loss can result in up to two theoretical stages in the test apparatus.

For the experimental setup, an ethanol-water system was chosen for the test. Data from the testing of the apparatus is presented in Table 2, along with a comparison to literature results. As can be seen, the test system results in almost exactly one theoretical stage.

Using the experimental VLE apparatus, toluene-acetic anhydride data was generated over the range of compositions required in the separation equipment. Analogous systems indicate that it would be easy to remove toluene from acetic anhydride in high concentrations of anhydride, but difficult to separate acetic anhydride from high concentrations of toluene. Thus, it becomes necessary to obtain more data points in the toluene-rich portion of the curve (Table 3 and Figure 3). As can be seen, this binary system forms a minimum boiling azeotrope of 8 mole% acetic anhydride.

Based on the VLE data points, NRTL coefficients were derived for the toluene-acetic anhydride binary pair. Using the calculated NRTL coefficients a smooth curve was developed for the system. Figure 4 presents the NRTL-derived VLE curve along with the experimental data points, and shows excellent agreement between the two.

Because the two components form an azeotrope, it is not possible using simple distillation to separate a toluene-acetic anhydride mixture into pure toluene and pure acetic anhydride. When two components form a minimum boiling azeotrope, only one pure component can be produced by distillation, and always as a bottoms product.

Thus, if the feed is richer in toluene than the azeotrope, only pure toluene can be produced. Similarly, feeds richer in acetic anhydride than the azeotrope will allow the production of relatively pure acetic anhydride. In both cases, the azeotrope (92% toluene-8% acetic anhydride) will be approached as the distillate product in a single fractionation column.

In this specific example, the goal is to separate a feedstream that is 60 wt.% acetic anhydride and 40 wt.% toluene. Given the composition, a single distillation column is adequate to recover high-purity acetic anhydride as bottoms and the toluene-acetic anhydride azeotrope as distillate. Fortunately, the acetic anhydride is recovered with approximately 93 wt.% yield in one pass through the distillation column.

The toluene in the distillate is recovered - for recycling - by water extraction, to remove the small amount of acetic anhydride. Here, the water not only acts as an extraction agent, but also reacts with the acetic anhydride to form aqueous acetic acid.

Some of the distillation column design and operating parameters (Table 4) were used to fabricate the modular system (photo). The resulting process recovers 92% of the acetic anhydride and 99+% of the toluene from a stream that was previously incinerated. ■

The authors

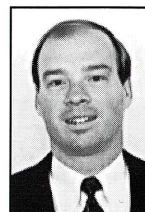
George Schlowsky is vice president of Modular Process Systems, Inc. and principal of Schlowsky Engineers, Inc., 45 Eisenhower Drive, Paramus NJ 07652; Tel: 201 368-9299. He has more than 25 years' experience designing separation processes, with a special emphasis on distillation, extractive distillation, and solvent extraction. He has a B.S. from Columbia University School of Engineering, and an M.S. from Virginia Polytechnic Institute in chemical engineering. He is a registered Professional Engineer and a member of AIChE.



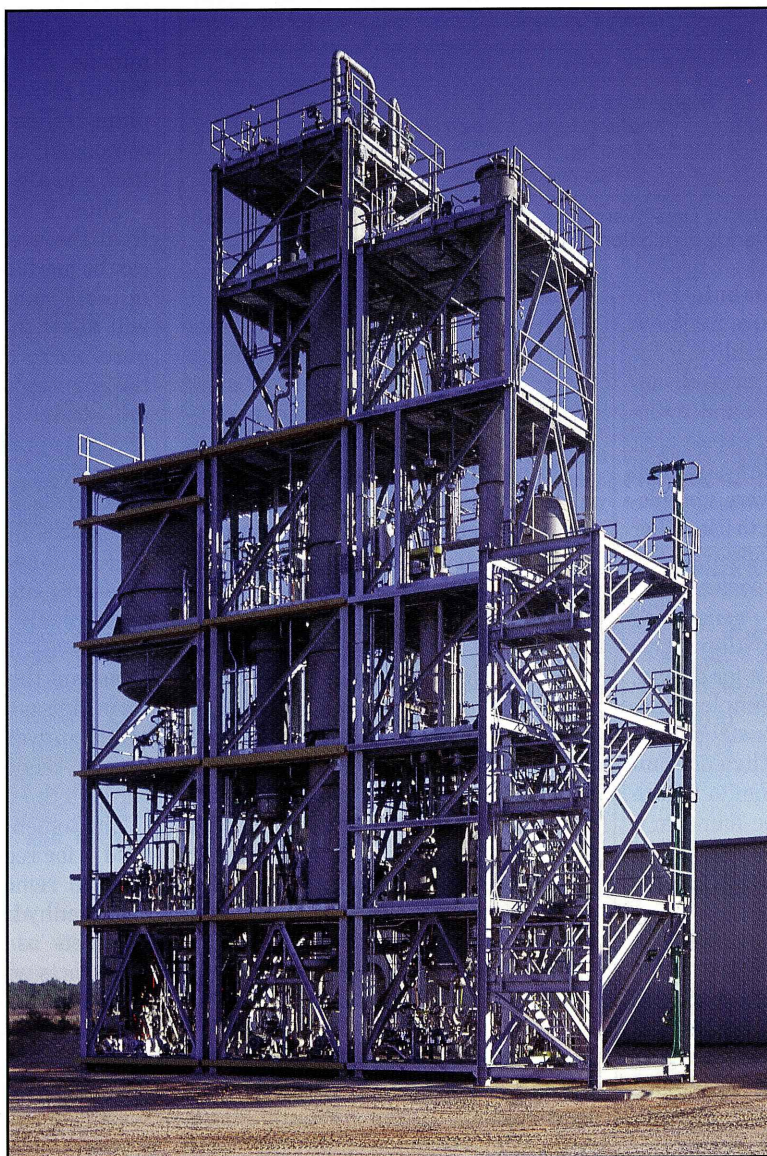
Alan Erickson is vice president of Modular Process Systems, Inc. and principal of Schlowsky Engineers, Inc., 45 Eisenhower Drive, Paramus NJ 07652; Tel: 201 368-9299. Previously, he was a senior process engineer at Glitsch, Inc., following which he was an independent consultant specializing in design, construction and start-up of separation equipment. He is a registered Professional Engineer and a member of AIChE. He has a B.S. degree from Rutgers University.



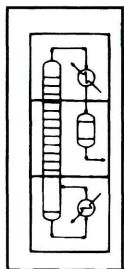
Thomas A. Schafer is president of Modular Process Systems, Inc. 45 Eisenhower Drive, Paramus NJ 07652; Tel: 201 368-2929. As a practicing engineer since 1976, Mr. Schafer has been responsible for marketing and development of modular separations systems, and the design of mass transfer equipment. He has specific experience in distillation, solvent drying, and heat exchanger design. A holder of B.S. and M.S. degrees in chemical engineering from Manhattan College, he is a member of the International Society for Pharmaceutical Engineering.



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Modular Process Systems, Inc.

45 Eisenhower Drive, Paramus, NJ 07652 USA

Phone (201) 368-2929 • Fax (201) 368-8989

Website www.modular-process.com