J. Chem. Eng. Data 1995, 40, 927−930

Liquid−Liquid Equilibrium for the Propylene Oxide + Water + Propylene Dichloride System†

Balakrishnan Srinivasa,* Madan G. Parande, and Raghavendra V. Naik

National Chemical Laboratory, Pune 411 008, India

Ternary liquid−liquid equilibrium (LLE) is presented for propylene oxide + water + propylene dichloride at 27 °C. Activity coefficients of the three components are correlated with the Margules three-suffix equation. The parameters of the equation are evaluated by the Nelder−Mead optimization procedures using two different objective functions. LLE predictions are found to be better using the optimized parameters rather than those obtained from independent binary data.

Introduction

Propylene oxide, water, and propylene dichloride are encountered in streams in the process for propylene oxide by the chlorohydrin route. While propylene oxide and water form a partially miscible system, propylene dichloride and water form an immiscible pair. Temperature seems to have only a marginal effect on the solubility of the binary mixtures. Separation schemes involving distillation of the three components pose some problems due to the formation of two liquid phases, the high relative volatility of propylene dichloride, and the conversion to propylene glycol. The first two problems necessitated the study of ternary liquid−liquid equilibrium for propylene oxide separation. Purification by the extractive distillation process using chlorinated hydrocarbons and other solvents has been reported in patented literature (*5*, *14*) through different manufacturing routes.

Experimental Section

The chemicals used were of 99.9% purity and were further redistilled to ensure purity. Some of the physical properties measured are reported in Table 1. The corresponding values reported in the literature are also given in the table. The experiment consists of the determination of the binodal curves by the titration method and the determination of tie lines. The tie lines were obtained by preparing heterogeneous mixtures of known composition, separating the two coexisting phases, and then measuring the refractive indices (RI) of the layers. Calibration curves prepared earlier for the binodal curves were used to determine the ends of the tie lines (Figures 1 and 2).

Binodal Curves

For the determination of the organic portion of the binodal curve, a known mass of a propylene oxide + propylene dichloride mixture was placed in a conical flask and distilled water was added from a micropipet till the solution turned just turbid. The conical flask was maintained at a constant temperature of (27 ± 0.5) °C.

A freshly prepared propylene oxide + propylene dichloride mixture was used for the above purpose. The aqueous portion of the binodal curve was obtained by adding propylene dichloride to a known mixture of propylene oxide + water till turbidity was reached. Due to the low solubility of propylene dichloride in these mixtures, large amounts of propylene oxide + water mixtures were used to minimize experimental error. After each titration, the refractive indices of the saturated solutions were measured using an Abbe refractometer. Table 2 gives the compositions determined by this procedure and the corresponding RI. The results are shown in the triangular diagram in Figure 3. The ratio of propylene oxide in each phase is shown in Figure 4.

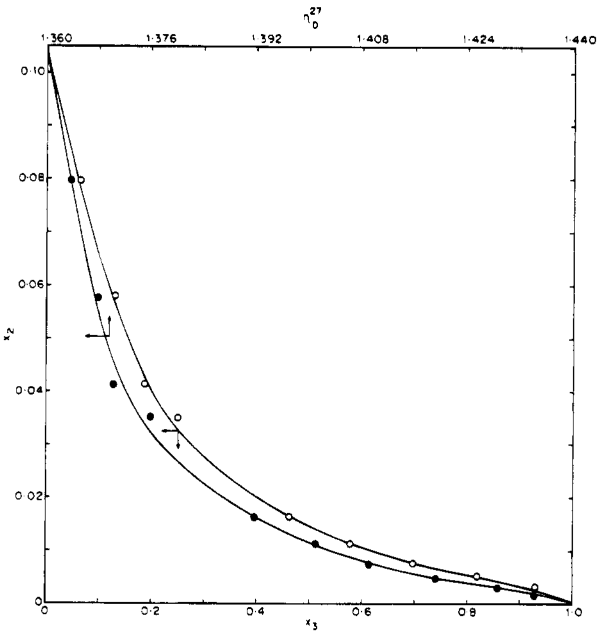


Figure 1. Calibration curves for organic layer: (outer curve) n_D^{27} vs x_2, (inner curve) x_2 vs x_3, x_2 = mass fraction of water in organic layer, x_3 = mass fraction of propylene dichloride in organic layer, n_D^{27} = refractive index at 27 °C.

The binodal curve is a typical type II system of two immiscible (or partly miscible) pairs. A total of 17 points were determined on the binodal curve, including four corresponding to binary solubility points which are tabulated separately together with literature data (Table 3). The two calibration curves are used in the determination of tie line data.

Tie Lines

Synthetic heterogeneous ternary mixtures were prepared by thoroughly mixing accurately known masses of each component in a stoppered separatory funnel. The layers were allowed to separate, and the RI values were deter-

---

* To whom correspondence should be addressed.

† NCL Communication No. 6200.

0021-9568/95/1740-0927$09.00/0

Table 1. Densities (ρ) and Refractive Indices (n_D) of Pure Components

	ρ/(g·cm^{-3})		n_D	
component	obsd at 27 °C	lit.	obsd at 27 °C	lit.
propylene oxide	0.8175	0.8540 (0 °C) (*3*) 0.8300 (20 °C) (*3*) 0.8040 (40 °C) (*3*)	1.3615	1.366 10 (20 °C) (*3*) 1.363 35 (25 °C) (*2*) 1.360 60 (30 °C) (*2*)
propylene dichloride	1.1490	1.1554 (20 °C) (*2*) 1.1161 (50 °C) (*2*)	1.4340	1.439 4 (20 °C) (*12*) 1.437 0 (25 °C) (*12*)
water	0.9966	0.996545 (27 °C) (*10*)	1.3322	1.332 29 (27 °C) (*1*)

Table 2. Experimental Binodal Curve for Propylene Oxide (1) + Water (2) + Propylene Dichloride (3) at 27 °C^a

x_1	x_2	n_D	x_1	x_2	n_D
		Organic Layer			
0.0662	0.0031	1.4285	0.7139	0.0353	1.3760
0.1751	0.0048	1.4190	0.7769	0.0411	1.3705
0.2970	0.0074	1.4090	0.8150	0.0577	1.3680
0.4111	0.0111	1.4010	0.8570	0.0797	1.3640
0.5237	0.0162	1.3915			
		Aqueous Layer			
0.0831	0.9144	1.3345	0.2591	0.7397	1.3410
0.1693	0.8285	1.3385	0.3297	0.6701	1.3425

^{a} x_i = mass fraction of component i.

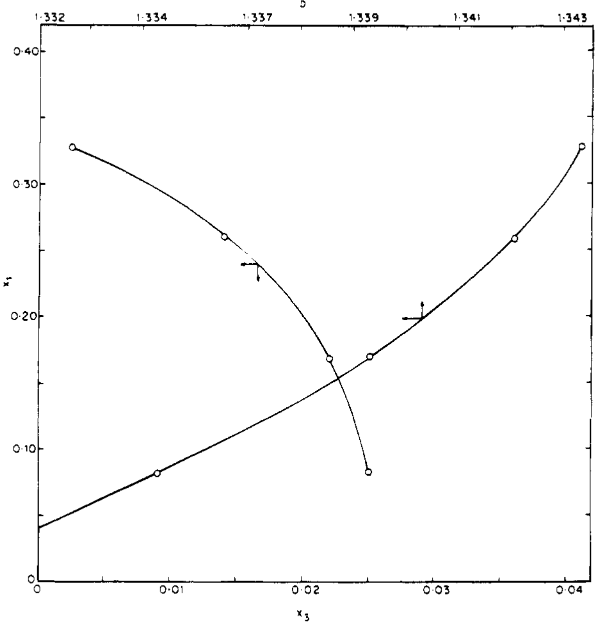


Figure 2. Calibration curves for aqueous layer: (right side curve) n_D^{27} vs x_1, (left side curve) x_1 vs x_3, x_1 = mass fraction of propylene oxide in aqueous layer, x_3 = mass fraction of propylene dichloride in aqueous layer, n_D^{27} = refractive index at 27 °C.

mined by using an Abbe refractometer. The compositions were fixed with the help of the calibration curves (Figures 1 and 2). The data obtained are presented in Table 4. The time for equilibration was restricted to 1 h due to the conversion of propylene oxide to propylene glycol by the action of water. The first seven values in Table 4 have the organic layer as the top layer, and the remaining have the aqueous layer as the top layer, indicating a reversal in density of two phases. There were some points in the two-phase region corresponding to the above which gave stable globules which did not settle or float easily. Such points are not reported in the table.

Data Correlation and Determination of Optimal Margules Constants

From the experimental tie line data, we propose to obtain values of the constants of the Margules three-suffix equation given in Table 5. We also propose to obtain a smoothened fit for the experimentally observed ternary LLE data. For similar systems, viz., two partially miscible pairs, and a third totally miscible pair, Prausnitz et al. (*11*) recommend the use of binary mutual solubility data as a starting point for parameter estimation. The ternary interaction parameter is generally calculated from experimental data.

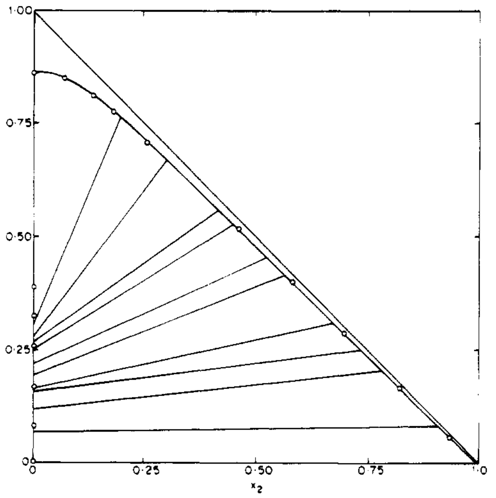


Figure 3. Equilibrium data for propylene oxide (1) + water (2) + propylene dichloride (3): x_1 = mass fraction of propylene oxide, x_2 = mass fraction of water.

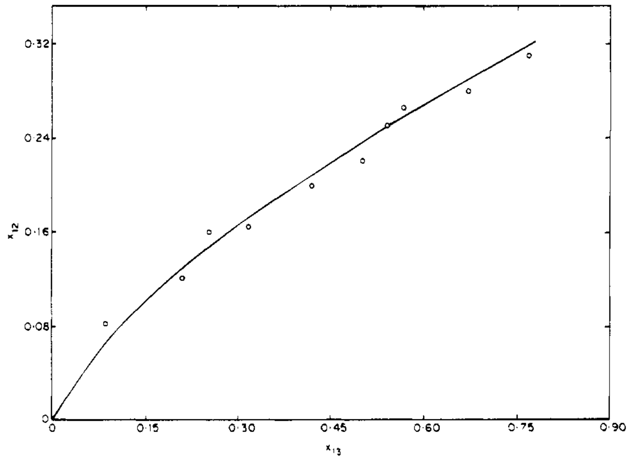


Figure 4. Distribution diagram for propylene oxide (1) + water (2) + propylene dichloride (3): x_{13} = mass fraction of propylene oxide in organic layer, x_{12} = mass fraction of propylene oxide in aqueous layer.

The basic features of the procedure adopted here consist of calculation of the activities of the three components in the two equilibrium phases for an assumed set of values for Margules constants and solution of two nonlinear algebraic equations arising from the relation

$$x_i\gamma_i - \bar{x}_i\bar{\gamma}_i = 0 \qquad (1)$$

where x_i and $\bar{x}_i$ are mole fractions of component i and γ_i

Table 3. Binary Solubility Data for the Propylene Oxide + Water + Propylene Dichloride System

	solubility of A in B (mass fraction)		solubility of B in A (mass fraction)	
component	obsd at 27 °C	lit.	obsd at 27 °C	lit.
propylene oxide (A) + water (B)	0.3960	0.399 (24.5 °C) (*15*) 0.3920 (35 °C) (*15*)	0.135	0.134 (24.5 °C) (*15*) 0.154 (35 °C) (*15*)
propylene dichloride (A) + water (B)	0.0028	0.0025 (25 °C) (*2*) 0.0029 (30 °C) (*6*) 0.0032 (40 °C) (*6*)	0.0013	0.0016 (20 °C) (*2*)

Table 4. Equilibrium Data for Propylene Oxide (1) + Water (2) + Propylene Dichloride (3) at 27 °C[a]

aqueous phase composition		organic phase composition	
x_1	x_2	x_1'	x_2'
0.3100	0.6895	0.7640	0.0400
0.2800	0.7191	0.6715	0.0275
0.2670	0.7319	0.5655	0.0195
0.2520	0.7467	0.5345	0.0175
0.2220	0.7764	0.4589	0.0131
0.1980	0.8001	0.4185	0.0115
0.1640	0.8338	0.3158	0.0082
0.1600	0.8378	0.2555	0.0065
0.1200	0.8756	0.2095	0.0055
0.0835	0.9150	0.0865	0.0035

[a] x_i = mass fraction of component i in the aqueous phase. x_i' = mass fraction of component i in the organic phase.

and $\bar{\gamma}_i$ are activity coefficients for component i in the corresponding phases ($i = 1-3$). Generally the two steps mentioned above do not result in the best fit for all the tie line data. In order to obtain a better fit for the entire concentration range, the method suggested by Prausnitz et al. (*11*) and Sorenson and Arit (*13*) for multicomponent systems is adopted. The Nelder–Mead (*8*, *9*) optimization technique of parameter estimation, applicable to multivariable, nonlinear relations, is used. Unlike the other optimization techniques, this method does not demand differentiations of functions involving activity coefficients, and it does not have problems of convergence due to arbitrary initial values.

Two types of objective functions are chosen for this optimization exercise (*13*):

OF 1 Minimum

$$\sum_{k=1}^{n}\sum_{i=1}^{3}[(x_{ik})_{\text{exptl}} - (x_{ik})_{\text{calcd}}]^2 \tag{2}$$

OF 2 Minimum

$$\sum_{k=1}^{n}\sum_{i=1}^{3}[(x_{ik}\log\gamma_{ik})_{\text{exptl}} - (x_{ik}\log\gamma_{ik})_{\text{calcd}}]^2 \tag{3}$$

In the above, k = the number of data points and the other symbols have the same meanings as in eq 1. For the purpose of initialization, the six Margules constants (Table 7) are chosen from the binary data determined from mutual solubility data (for propylene oxide (1) + water (2) and water (2) + propylene dichloride (3)) from Table 3 and from vapor–liquid equilibrium data for propylene oxide (1) +

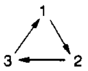
Table 5. Equations for Evaluating Margules Constants (*4*)

nature of available data	equations used	glossory
binary vapor–liquid equilibrium	$A_{ij} = \dfrac{(x_j - x_i)}{x_j^2}\log\gamma_i + \dfrac{2\log\gamma_j}{x_i}$	x = mole fractions of components
	$A_{ji} = \dfrac{(x_i - x_j)}{x_i^2}\log\gamma_j + \dfrac{2\log\gamma_i}{x_j}$	γ = activity coefficients A = Margules constants
mutual solubilities of components	$\dfrac{A_{ij}}{A_{ji}} = \dfrac{2\log(x_j'/x_j)(M-N) + \log(x_i'/x_i)(U-2V)}{2\log(x_i'/x_i)(U-V) + \log(x_j'/x_j)(M-2N)}$	i,j = components x_i = mole fraction of component i in one phase
	$A_{ij} = \dfrac{\log(x_i'/x_i)}{[(2(A_{ji}/A_{ij}) - 1)M] - [2(A_{ji}/A_{ij} - 1)N]}$	x_i' = mole fraction of component i in conjugate phase
	$M = x_j^2 - x_j'^2;\ U = x_i^2 - x_i'^2$	j = second component
	$N = x_j^3 - x_j'^3;\ V = x_i^3 - x_i'^3$	

Table 6. Ternary Margules Three-Suffix Equations for Activity Coefficients (*4*)

$\log\gamma_1 = x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] + x_2x_3[A_{21} + A_{13} - A_{32} + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23}) - C(1 - 2x_1)]$

$\log\gamma_2$ and $\log\gamma_3$ can be obtained by the method shown below:



x_1, x_2, x_3 = mole fractions of components 1, 2, and 3, respectively, in the liquid phase

$A_{12}, A_{21}, A_{23}, A_{32}, A_{31}$, and A_{13} = binary Margules constants for component 1 + 2, 2 + 3, and 3 + 1, respectively

C = ternary constant

an estimate of the ternary constant is given by $C = (1/2)[A_{21} - A_{12} + A_{31} - A_{13} + A_{23} - A_{32}]$

Table 7. Margules Constants from Binary Data

system	Margules constants
propylene oxide (1) + water (2)	$A_{12} = 1.074, A_{21} = 0.7733$
water (2) + propylene oxide (3)	$A_{23} = 2.167, A_{32} = 3.351$
propylene oxide (1) + propylene dichloride (3)	$A_{13} = -0.0630, A_{31} = -0.1310$

Table 8. Optimized Values of the Margules Constants[a]

constant	objective function 1	objection function 2
A_{12}	1.047	1.058
A_{21}	0.778	0.876
A_{23}	2.176	1.840
A_{32}	3.358	3.275
A_{13}	0.002	0.041
A_{31}	−0.199	−0.171
C	0.496	0.594

[a] Objective function 1 minimum: $\sum_{k=1}^{n}\sum_{i=1}^{3}[(x_{ik})_{\mathrm{exptl}} - (x_{ik})_{\mathrm{calcd}}]^2$. Objective function 2 minimum: $\sum_{k=1}^{n}\sum_{i=1}^{3}[(x_{ik} \log \gamma_{ik})_{\mathrm{exptl}} - (x_{ik} \log \gamma_{ik})_{\mathrm{calcd}}]^2$.

propylene dichloride (3) (7). The equations used are given in Table 6.

Table 8 gives the salient results of the optimization exercise. The Margules constants for the propylene oxide + propylene dichloride system A_{13} and A_{31} do not conform to the usual observation of having the same sign.

Results and Conclusions

Experimental ternary LLE data for propylene oxide + water + propylene dichloride are reported. Margules constants for the propylene oxide + water + propylene dichloride systems are obtained by an optimization procedure using the data. Due to the combined effect of a given experimental error in measuring small concentrations of a given component and the possibility of association, one of the constants for the propylene oxide + propylene dichloride system does not conform to the usual observation of having the same sign as the conjugate constant. The prediction, however, is better when constants are optimized simultaneously.

Literature Cited

(1) Dean, J. A. *Lange's Hand Book of Chemistry*; McGraw-Hill Co.: New York, 1979.
(2) Gerhartz, W., Exec. Ed. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH Publishers: New York, 1986; Vol. A 6.
(3) Gerhartz, W., Exec. Ed. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH Publishers: New York, 1986; Vol. A 22.
(4) Hala, E.; Pick, J.; Fried, V.; Vilim, O. *Vapor-liquid equilibrium*; Pergamon Press: London, 1957.
(5) Kageyama, O.; Kai, M.; Yakoo, H. Purifying alkylene oxides. Ger. Offen 2,258,521, June 7, 1973.
(6) Kirk, R. E.; Othmer, D. F. *Encyclopedia of Chemical Technology*; Interscience Publishers: New York, 1965; Vol. 8.
(7) Kolodziej, E. J.; Jin, Z.-L.; Greenkorn, R. A.; Chao, K.-C. Vapor-liquid equilibrium in binary mixture of propylene oxide with 1,2 dichloropropane and with tert-butanol. *AIChE Symp. Ser. No. 244* **1985**, *81*, 80–85.
(8) Kuester, J. L.; Mize, J. H. *Optimisation techniques with Fortran*; McGraw-Hill Co.: New York, 1973.
(9) Nelder, J. A.; Mead, R. A simplex method for function minimisation *Comput. J.* **1964**, 308–313; **1965**, *8*, 27.
(10) Perry, J. H. *Chemical Engineer's Hand Book*; McGraw-Hill Co.: New York, 1963.
(11) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for multicomponent vapor-liquid and liquid-liquid equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.
(12) Snell, F.; Dee, H.; Clifford, L. *Encyclopedia of Industrial Chemical Analysis*; Interscience Publishers: New York, 1971; Vol. 13.
(13) Sorenson, J. M.; Arit, W. *Liquid-Liquid equilibria collection*; Chemistry Data Series; DECHEMA: Frankfurt, 1979; Vol. 5, Part 2.
(14) Suzuki, K.; Miura, K. Separation of olefin oxides. Japan 72,37,603 Sept 22, 1972.
(15) Wickert, J. N.; Tamplin, W. S.; Shank, R. L. Phase equilibria in the system propylene oxide–water. *Chem. Eng. Prog. Symp. Ser. No. 2* **1958**, *48* (2), 92–96.

Received for review January 12, 1995. Accepted April 20, 1995.[⊗]

JE950010T

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1995.