Liquid−Liquid Equilibria for the Epichlorohydrin + Water + Methanol and Allyl Chloride + Water + Methanol Systems

Pravin S. Vaidya and Raghavendra V. Naik*

Process Development Division, National Chemical Laboratory, Pune 411 008, India

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Isothermal liquid−liquid equilibrium data for two ternary systems of epichlorohydrin + methanol + water and allyl chloride + methanol + water were experimentally determined at 273.15 K ± 0.1 K. These two systems exhibit the type-I behavior of LLE. These systems have not been previously investigated at this temperature, but there was motivation to study these as part of a novel process, which is under development. These systems were studied in order to develop separation strategies for a novel epoxidation process for the manufacture of epichlorohydrin. The experimental equilibrium data of ternary systems were used to regress the interaction parameters for the nonrandom two-liquid (NRTL) model and UNIQUAC model.

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1. Introduction

In a novel catalytic epoxidation process[1] methanol is used as a solvent to carry out epoxidation of allyl chloride to epichlorohydrin at room temperature. This process has potential to replace the current chlorohydrin process, which generates a lot of aqueous waste. The two ternary systems studied here were chosen to develop separation schemes for this novel process. Epichlorohydrin is a highly reactive intermediate; in its pure form epichlorohydrin is a clear, colorless liquid. The presence of both an epoxide ring and chlorine in the molecule allows epichlorohydrin to readily undergo a variety of chemical reactions with many types of compounds. This versatility earns it wide use as a chemical intermediate. The four components covered in this article are, therefore, industrially relevant.

Two ternary systems are chosen for study, epichlorohydrin + water + methanol and allyl chloride + water + methanol. In this work, an equilibrium cell was used and liquid−liquid-phase equilibrium data are determined for the two ternary systems. The plait points were determined using the tie lines and binodal curve data and the method of Treybal.[2] The experimental data were correlated using the UNIQUAC[3] and NRTL[4,5] equations, and the interaction energy parameters of these models were obtained.

2. Experimental Section

2.1. Chemicals. Epichlorohydrin used in this study was of 99% purity and was supplied by Loba Chemie Ltd., and methanol was supplied by S. D. Fine-Chem Ltd., with purity 99.5%. These materials were used as received without any purification. Commercial grade allyl chloride was received from Tamilnadu Petro Ltd. with purity 97% and was distilled twice and made free from color and rust. It was found to be 99.9% pure by GC. Water used throughout all experiments was deionized and distilled. The purities of all the materials were verified by gas chromatography and by measurement of densities and refractive indices, and they were checked periodically during the experiments. Table 1 compares experimental densities and refractive indices with literature data.

Table 1. Densities (ρ) and Refractive Indices (n) of the Pure Components at 293 K and Atmospheric Pressure

	ρ/g·cm^{-3}		n	
component	exp	lit.[6]	exp	lit.[6]
epichlorohydrin	1.1820	1.1812	1.4363	1.4361
allyl chloride	0.9375	0.9376	1.4155	1.4157
water	0.9990	0.9970	1.3331	1.3330
methanol	0.7915	0.7914	1.3289	1.3288

2.2. Apparatus. The experimental values that define the solubility curves were determined by using a 100 mL jacketed glass cell. The temperature of the glass cell was controlled by circulating methanol using a cryostat, model-FP50 JULABO Labortechnik GMBH, Seelbach, Germany, and the cell temperature was measured with a T-type copper constantan thermocouple estimated to be accurate within ±0.05 K. The refractive indices of all solutions were determined at 297.15 K with a refractometer, Model Mark II Plus, ABBE, Leica, OH, with an error <0.0001 units.

2.3. Procedure. (A) A set of solutions of epichlorohydrin (ECH) and methanol (MeOH) were prepared by mass with various chosen compositions. Each solution was placed in the equilibrium cell and cooled to 273.15 K. The saturation limit determined by the cloud point method was obtained by dropwise addition of cold water to the solution, which was maintained in stirred condition by means of a magnetic stirrer. The saturated solution was weighed accurately, and thus, data of the binodal curve were obtained. All solutions were prepared by mass. The refractive indices of the saturated solutions were determined at 297.15 K with a refractometer. Calibration of the instrument was performed by measuring the RI value of distilled water. An average of two measurements was taken for each sample mixture. In the same fashion, a set of solutions of water and methanol were prepared. Epichlorohydrin was added to its saturation point, and refractive indices of these solutions were determined at 297.15 K. For the allyl chloride (ALC), methanol, and water system too, the same procedure was followed and data on the binodal curve covering aqueous and organic phases were generated along with the corresponding refractive indices.

Calibration curves of RI versus composition data, two for aqueous layers and two for organic layers, were prepared.

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* Corresponding author. Telephone: +91-20-5893300 (Ext. 2316). Fax: +91-20-5893359. E-mail: rvnaik@pd.ncl.res.in.

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Table 2. Experimental Solubility Data for the Epichlorohydrin (1) + Water (2) + Methanol (3) (Mole Fraction) System at 273.15 K

aqueous phase				organic phase			
x_1	x_2	x_3	n	x_1	x_2	x_3	n
0.0129	0.9638	0.0233	1.3385	0.1476	0.5088	0.3436	1.3693
0.0130	0.9404	0.0466	1.3412	0.2151	0.4532	0.3317	1.3760
0.0130	0.9142	0.0728	1.3414	0.3174	0.3670	0.3156	1.3915
0.0141	0.8863	0.0996	1.3425	0.3859	0.3172	0.2969	1.4000
0.0165	0.8545	0.1290	1.3438	0.4629	0.2693	0.2678	1.4080
0.0192	0.8221	0.1587	1.3450	0.5653	0.2046	0.2301	1.4176
0.0283	0.7482	0.2235	1.3482	0.6757	0.1479	0.1766	1.4262
0.0570	0.6500	0.2930	1.3538	0.8193	0.0797	0.1010	1.4315
0.1407	0.5126	0.3467	1.3685	0.9352	0.0196	0.0452	1.4335
				0.9576	0.0189	0.0235	1.4340

Table 3. Experimental Solubility Data for Allyl Chloride (1) + Water (2) + Methanol (3) (Mole Fraction) System at 273.15 K

aqueous phase				organic phase			
x_1	x_2	x_3	n	x_1	x_2	x_3	n
0.0014	0.9710	0.0276	1.3366	0.1287	0.2913	0.5798	1.3444
0.0014	0.9484	0.0502	1.3370	0.1850	0.2650	0.5500	1.3537
0.0015	0.8970	0.1015	1.3378	0.2598	0.2329	0.5072	1.3623
0.0016	0.8672	0.1311	1.3384	0.3750	0.1750	0.4500	1.3717
0.0021	0.8357	0.1622	1.3398	0.4585	0.1485	0.3930	1.3786
0.0046	0.7650	0.2304	1.3408	0.5164	0.1270	0.3566	1.3827
0.0095	0.6832	0.3074	1.3415	0.6100	0.0950	0.2952	1.3883
0.0218	0.5884	0.3897	1.3423	0.6647	0.0753	0.2599	1.3927
0.0586	0.4623	0.4790	1.3430	0.7506	0.0500	0.2004	1.3997
				0.8756	0.0279	0.0965	1.4083

Table 4. Experimental LLE Data for the Epichlorohydrin (1) + Water (2) + Methanol (3) (Mole Fraction) System at 273.15 K

aqueous phase			organic phase		
x_1	x_2	n	x_1	x_2	n
0.0130	0.9142	1.3414	0.9450	0.0188	1.4337
0.0148	0.8780	1.3429	0.9352	0.0196	1.4335
0.0192	0.8221	1.3450	0.8750	0.0500	1.4323
0.0250	0.7750	1.3472	0.8050	0.0850	1.4320
0.0283	0.7482	1.3482	0.7700	0.1000	1.4305
0.0350	0.7100	1.3500	0.7025	0.1350	1.4279
0.0725	0.6225	1.3560	0.6250	0.1730	1.4225
0.0944	0.5798	1.3605	0.5750	0.2025	1.4185
0.1355	0.5260	1.3677	0.4950	0.24625	1.4113

(B) For the determination of tie line data of the epichlorohydrin + water + methanol system, a mixture with partial miscibility was prepared by addition of the individual components by mass. The heterogeneous mixture was placed in the equilibrium cell, where it was cooled to 273.15 K with stirring for 1 h. This mixture was transferred to a specially prepared separating funnel and held in the cryostatic bath at 273.15 K for the next 2 h. The organic phase and aqueous phase were separated, and their refractive index values were determined at 297.15 K. The compositions of both the layers were found by using the calibration curves and the mixture rule.[2]

3. Results and Discussion

The experimental solubility data for the two ternary systems are presented in Tables 2 and 3. Corresponding tie line data (LLE data) are presented in Tables 4 and 5. Concentrations of components in aqueous and organic phases are expressed in mole fractions.

Liquid−Liquid Equilibria. In multicomponent liquid−liquid equilibrium, the equation of equilibrium, for every component i, is[8]

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \tag{1}$$

Table 5. Experimental LLE Data for the Allyl Chloride (1) + Water (2) + Methanol (3) (Mole Fraction) System at 273.15 K

aqueous phase			organic phase		
x_1	x_2	n	x_1	x_2	n
0.0015	0.9235	1.3374	0.949	0.020	1.4146
0.0021	0.8357	1.3397	0.935	0.020	1.4131
0.0095	0.6832	1.3415	0.931	0.024	1.4133
0.0218	0.5884	1.3423	0.928	0.022	1.4118
0.0420	0.5000	1.3426	0.918	0.022	1.4120
0.0750	0.4000	1.3433	0.899	0.026	1.4100
0.1340	0.2900	1.3446	0.860	0.032	1.4063
0.1750	0.2700	1.3523	0.709	0.061	1.3959

Here, γ_i^{I} and γ_i^{II} are the corresponding activity coefficients of component i in phases I and II, and x_i^{I} and x_i^{II} are the mole fractions of component i in phases I and II, respectively. Equation 1 holds only when, for every component i, the same standard state fugacity is used in both liquid phases. Since we make the simplifying assumption that the partial molar volumes are functions only of temperature, we assume that pressure has no effect on liquid−liquid equilibria. The activity coefficients depend only on temperature and composition.[8] The UNIQUAC[3] model developed by Abrams and Prausnitz (1975) and the nonrandom two-liquid (NRTL[4,5]) model by Renon and Prausnitz (1968) give a set of equations for representing liquid-phase activity coefficients.

UNIQUAC Model. The UNIQUAC equation $g \equiv G^{\mathrm{E}}/RT$ is composed of two additive parts, a combinatorial term g^{C} to account for molecular size and shape differences and a residual term g^{R} to account for molecular interactions.[8]

$$g \equiv g^{\mathrm{C}} + g^{\mathrm{R}} \tag{2}$$

g^{C} contains pure species parameters only, wheras g^{R} incorporates two binary parameters for each pair of molecules. For a multicomponent system,

$$\frac{G^{\mathrm{E}}}{RT} = \sum_{i=1}^{c} x_i \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2}\sum_{i=1}^{c} q_i x_i \ln\left(\frac{\theta_i}{\phi i}\right) - \sum_{i=1}^{c} q_i x_i \ln\left(\sum_{j=1}^{c}\theta_j \tau_{ji}\right) \tag{3}$$

Differentiation gives

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \tag{4}$$

where

$$\ln \gamma_i^{\mathrm{C}} = \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2}\sum_{i=1}^{c} q_i \ln\left(\frac{\theta_i}{\phi i}\right) + l_i - \frac{\phi_i}{x_i}\left(\sum_{j=1}^{c} x_j l_j\right) \tag{5}$$

here

$$l_i = \left(\frac{Z}{2}\right)(r_i - q_i) - (r_i - 1) \tag{6}$$

and

$$\ln \gamma_i^{\mathrm{R}} = q_i\left[1 - \ln\left(\sum_{j=1}^{c}\theta_j \tau_{ji}\right) - \sum_{j=1}^{c}\left(\frac{\theta_j \tau_{ij}}{\sum_{k=1}^{c}\theta_k \tau_{kj}}\right)\right] \tag{7}$$

Here γ_i^{C} is the combinatorial part of the activity coefficient, and γ_i^{R} is the residual part of the activity coefficient. Subscript i denotes a species, and j is a dummy index. All sums are over all species. Note that $\tau_{ji} \neq \tau_{ij}$; however, when $i = j$, then $\tau_{ii} = \tau_{jj} = 1$. The variable τ_{ij} is an adjustable

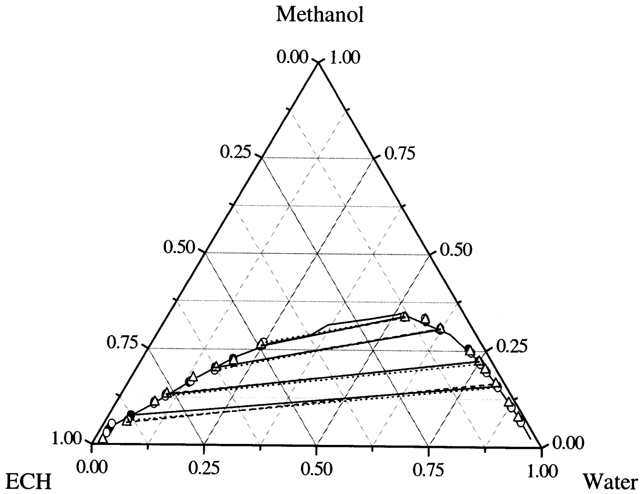

Figure 1. Ternary liquid−liquid equilibria (mole fraction) for the system epichlorohydrin (1) + water (2) + methanol (3) at 273.15 K: binodal curve (solid line); experimental tie lines (●, solid line); UNIQUAC correlation (○, dotted line); NRTL correlation (Δ, dashed line).

Table 6. UNIQUAC Structural Parameters for Components[13]

component	r	q
ECH	2.8306	2.272
ALC	2.8108	2.440
water	0.9200	1.400
methanol	1.4311	1.432

parameter in the UNIQUAC equation, x_i is the equilibrium mole fraction of component i, and $Z = 10$ is the lattice coordination number. The average area fraction θ and segment fraction ϕ are defined by

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{8}$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \tag{9}$$

Here x_i is the mole fraction, and r_i (a relative molecular van der Waals volume) and q_i (a relative molecular surface area) are pure species parameters.

The influence of temperature on g enters through the interaction parameters τ_{ij} of eq 7, which are temperature dependent.[10−12]

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{jj}}{RT}\right) \tag{10}$$

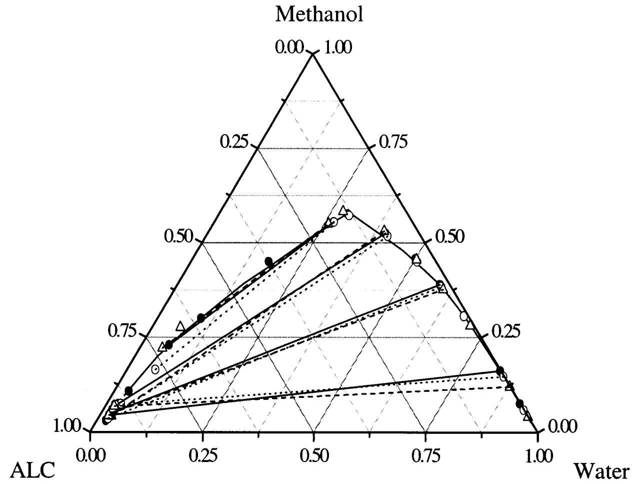

Figure 2. Ternary liquid−liquid equilibria (mole fraction) for the system allyl chloride (1) + water (2) + methanol (3) at 273.15 K: binodal curve (solid line); experimental tie lines (●, solid line); UNIQUAC correlation (○, dotted line); NRTL correlation (Δ, dashed line).

The UNIQUAC structural parameters r and q were calculated from the group contribution data that have been previously reported.[13] The values of r and q used in the UNIQUAC equation are presented in Table 6. Optimum interaction parameters a_{ij} between each component were determined using the observed liquid−liquid equilibrium data, where the interaction parameters describe the interaction energy between each pair of compounds. Table 7 lists the UNIQUAC and NRTL binary interaction parameters for both the systems. These parameters were obtained by regression of observed LLE data using CHEMCAD 5.0 simulation software. The root-mean-square deviation (rmsd) is a measure of the agreement between the experimental data and the calculated values. It is defined as

$$\text{rmsd} = 100\left[\sum_i^3\sum_j^2\sum_k^N\left(\frac{x_{ijk} - x_{ijk}{}^{c}}{4N}\right)^2\right]^{1/2} \tag{11}$$

Here, N is number of tie lines and x_{ijk} and $x_{ijk}{}^{c}$ are the experimental and calculated mole fractions of component i in phase j for the tie line k, respectively.[14] Figures 1 and 2 are the phase diagrams which compare graphically the measured and calculated phase behavior (LLE data) for the ternary systems of epichlorohydrin + methanol + water and allyl chloride + methanol + water, respectively. The UNIQUAC and NRTL models were used to correlate the experimental LLE data.[7] As can be seen from Figures 1 and 2, the predicted tie lines are in good agreement with the experimental data.

Table 7. UNIQUAC and NRTL Binary Interaction Parameters at 273.25 K, the Calculated Root-Mean-Square Deviation (rmsd), and the Nonrandomness Parameter (α) for the NRTL Model for the Systems (I) Epichlorohydrin (1) + Water (2) + Methanol (3) and (II) Allyl Chloride (1) + Water (2) + Methanol (3)

		UNIQUAC			NRTL			
i	j	a_{ij}/K	a_{ji}/K	rmsd	a_{ij}/K	a_{ji}/K	α	rmsd
I								
1	2	1145.121	271.4335	1.45	482.6104	1473.710	0.2000	1.39
1	3	−437.4045	1189.140		−12.53867	126.3058	0.1042	
2	3	306.0060	−641.1900		747.5396	−537.0938	0.3001	
II								
1	2	940.6016	−48.7354	2.32	−164.6617	584.1211	0.2000	3.35
1	3	1438.079	679.7304		971.3814	1287.746	0.4126	
2	3	−488.6593	478.2310		−199.9525	−706.6366	0.3001	

4. Conclusions

The solubility data and liquid−liquid equilibrium of the ECH + water + methanol and ALC + water + methanol systems have been investigated at 273.15 K. Both the ternary systems studied were type-I LLE systems. The experimental LLE data were used to calculate optimum UNIQUAC and NRTL binary interaction parameters of the ternary systems, using the regression program in the simulation software, CHEMCAD 5.0. The experimental equilibrium data can be satisfactorily correlated using the UNIQUAC and NRTL models.

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