Phase Equilibrium and Interfacial Tension

System: Ethylene Glycol—Acetic Acid—Ethyl Acetate

ALUF ORELL
Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, Israel

The equilibrium phase diagram and interfacial tension of the ternary system ethylene glycol—acetic acid—ethyl acetate were determined at 25° C. The two-phase region of this nonaqueous system was restricted to acetic acid concentrations below 5.2 wt %. The equilibrium distribution of acetic acid was successfully correlated by a two-suffix ternary van Laar equation.

THE EQUILIBRIUM phase diagram and interfacial tension of the ternary system ethylene glycol–acetic acid–ethyl acetate were determined in the course of mass transfer studies of liquid–liquid systems exhibiting spontaneous interfacial activity (*6*). No such data could be found in the literature.

The investigated nonaqueous ternary system is a fairly complex one, as acetic acid undergoes association in both phases. The acid, in addition, is susceptible to chemical reaction with ethylene glycol. The extent of the reaction at room temperature, however, is negligible. This was ascertained by measuring the change with time of acetic acid concentration in various acid-glycol solutions.

EQUILIBRIUM PHASE DIAGRAM

Experimental. MATERIALS. Ethylene Glycol. Certified reagent (Fisher Scientific Co.). $n_D^{25} = 1.42956$. Literature value: $n_D^{25} = 1.43063$ (*7*).

Ethyl Acetate. Analytical reagent (Merck), conforming to A.C.S. specifications. $n_D^{25} = 1.36882$. Literature value: $n_D^{25.2} = 1.37012$ (*7*).

Acetic Acid. Glacial, reagent grade (Du Pont). $n_D^{25} = 1.36933$. Literature value: $n_D^{25} = 1.3698$ (*7*).

All the materials were used without further purification.

Determination of Solubility Curve. The composition of the solubility curve was determined by the turbidity method. The quantity of each component was measured by weighing it up to the nearest 0.1 mg. All work was carried out in glass-stoppered bottles in order to minimize the evaporation of the volatile ethyl acetate.

The composition of the binodal curve was determined by titrating a turbid mixture of ethyl acetate and ethylene glycol with acetic acid up to the clearing point. First, known volumes of glycol and ethyl acetate were weighed successively in a glass-stoppered bottle. The total mixture weight ranged from 90 to 120 grams. The bottle was then immersed for several hours in a constant temperature bath kept at 25° ± 0.1° C. The mixture was finally titrated with acetic acid. Since rather small quantities were involved, the acid was dispensed from a 25-ml. weighing bottle with an eye dropper.

The end point was determined by comparing the clearing mixture with a slightly overtitrated ternary solution of a similar composition. The end point appeared sharpest in the central region of the solubility curve, becoming less distinct in the region of low acid concentrations. The reproducibility of the solubility data was checked by making a duplicate run at an acid concentration of 4.2%. The results agreed within 2%.

The mutual solubility of the pair ethylene glycol–ethyl acetate was evaluated by titrating a given weight of one component with the other up to the cloud point. For instance, the solubility limit of ethyl acetate was measured by titration of 100 grams of the glycol. The ethyl acetate was stored in a bottle equipped with a glass-stoppered eye dropper. As a check, both the glycol and ethyl acetate bottles were weighed before and after the titration. The weights checked within 15 mg. The end point was reached when the turbidity persisted more than half an hour.

All the samples used for establishing the ternary solubility curve were utilized also for construction of tie line composition calibration curves. The stoppered titration bottles were returned to the constant temperature bath and kept there until reaching thermal equilibrium. The refractive index of the clear mixtures was determined in a Bausch and Lomb Precision Refractometer at 25° ± 0.1° C. Calibration curves were then constructed by plotting the composition of each of the three components against the refractive index of the mixture.

Determination of Tie Lines. Three component mixtures of about 100 grams were weighed to the nearest 0.1 mg. in sealed bottles, agitated for at least 1 hour in a mechanical shaker, and left to equilibrate in the constant temperature bath for a period of 16 hours. Two samples were then withdrawn from each phase for refractive index measurement. Reproducibility was usually better than 1%. The equilibrium composition of the glycol and acetate phases was finally read from the proper calibration curves.

RESULTS

Table I lists the solubility curve and tie line compositions. The ternary phase diagram of the system is presented in Figure 1.

The consistency of the tie line composition data was checked by the correlations of Othmer-Tobias (*4*), Bachman (*1*), and Hand (*3*). All data fell on good straight lines. The Hand plot, reproduced in Figure 2, was also used to locate the plait point graphically.

CORRELATION OF THE DISTRIBUTION CURVE

Thermodynamic prediction of the equilibrium distribution of a solute in a ternary system, based on binary and, if necessary, ternary experimental data, is highly desirable. Rigorous prediction of the equilibrium distribution of acetic acid in the studied ternary system is impossible, since experimental vapor-liquid data for the binary acetic acid–ethylene glycol are lacking. Furthermore, association constants for acetic acid in the glycol and acetate phases are not known. An attempt was made, however, to correlate the experimental distribution data by a thermodynamic expression based on the following assumptions:

Table I. Phase Diagram Composition Data

Ethylene Glycol Phase Weight Fraction			Ethyl Acetate Phase Weight Fraction		
Acetic acid X_{CB}	Ethylene glycol X_{BB}	Ethyl acetate X_{AB}	Acetic acid X_{CA}	Ethylene glycol X_{BA}	Ethyl acetate X_{AA}
Solubility Curve Composition					
0	0.816	0.184	0	0.079	0.921
0.016	0.767	0.217	0.009	0.108	0.883
0.034	0.687	0.279	0.015	0.131	0.854
0.036	0.685	0.279	0.024	0.164	0.812
0.048	0.591	0.361	0.037	0.226	0.737
0.051	0.528	0.421	0.042	0.280	0.678
0.050	0.456	0.494	0.048	0.362	0.590
0.050[a]	0.386	0.564	0.050[a]	0.386	0.564
Tie Line Composition					
0.009	0.789	0.202	0.006	0.097	0.897
0.012	0.779	0.209	0.008	0.103	0.889
0.020	0.753	0.227	0.011	0.117	0.872
0.021	0.750	0.229	0.013	0.123	0.864
0.029	0.719	0.252	0.020	0.150	0.830
0.035	0.683	0.282	0.026	0.177	0.797
0.042	0.636	0.322	0.034	0.214	0.752
0.049	0.565	0.386	0.040	0.266	0.694

[a] Estimated plait point.

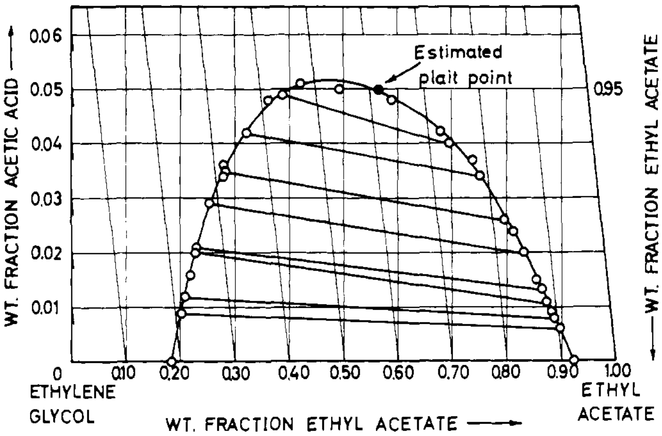

Figure 1. Phase diagram of the system ethylene glycol–acetic acid–ethyl acetate at 25° C.

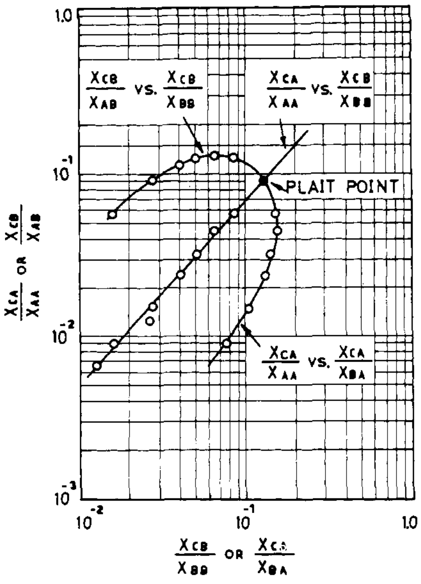

Figure 2. Hand tie line correlation

That the ternary activity coefficients could be calculated by an equation containing experimental constants determined by binary data only.

That the two lacking binary constants could be evaluated by a trial and error procedure.

That acetic acid was completely associated in both the glycol and ethyl acetate phases.

A two-suffix van Laar equation containing six binary constants (*9*) was chosen for the calculation of ternary activity coefficients of acetic acid in each phase. The constants for the binary acetic acid–ethyl acetate were evaluated from the data of Garner, Ellis, and Pearce (*2*). The mutual solubility data of the ethylene glycol–ethyl acetate pair, determined in the present investigation, were used to calculate the binary constants by the appropriate form of the van Laar equation (*8*).

The binary constants of the system acetic acid–ethylene glycol were established by a trial and error procedure guided by Wohl's restricting condition (*9*):

$$\frac{A_{CB}}{A_{BC}} = \left(\frac{A_{CA}}{A_{AC}}\right)\left(\frac{A_{AB}}{A_{BA}}\right) \qquad (1)$$

Initial trial values were generated from the data of Rius, Oter, and Macarron (*5*) for the system acetic acid–ethyl alcohol. Adjustment of these initial values resulted in a satisfactory final correlation.

The values of the six binary constants are presented in Table II. Substitution of these constants in the ternary van Laar equation resulted in the final equation:

$$\log \gamma_C = \frac{-\,0.0745x_A{}^2 - 0.211x_B{}^2 - 0.549x_Ax_B}{[x_C + 0.532x_A + 0.680\ x_B]^2} \qquad (2)$$

Activity coefficients of acetic acid in the two phases were calculated by Equation 2 and the experimental ternary solubility data listed in Table I. The mole fractions of the various components were computed using an acetic acid molecular weight of 120.1. The activities and activity coefficients calculated from the experimental data are listed in Table III. The activity of acetic acid in each phase is plotted in Figure 3.

Equilibrium concentrations of acetic acid at a given activity value were read off Figure 3. The predicted distribution curve along with the experimental values are plotted in Figure 4. Equation 2 correlates the experimental data extremely well, the maximum deviation being 5%.

INTERFACIAL TENSION

Interfacial tension between the ethylene glycol and the ethyl acetate phases was determined at 25° C. by a Cenco Du Nouy Interfacial Tensiometer.

Procedure. A Petri dish, thoroughly cleaned with chromic acid, was placed in a shallow pan of water kept at 25° ± 0.5° C. An equilibrated ternary mixture was poured then into the dish from a glass-stoppered bottle taken out of the constant temperature bath. Care was taken to prevent the evaporation and cooling of the ethyl acetate phase by immediately covering the dish with a Lucite sheet, slotted to accommodate the tensiometer ring.

Table II. Six Binary Constants for van Laar Equation

Ethyl Acetate–Acetic Acid	Ethylene Glycol–Ethyl Acetate	Acetic Acid–Ethylene Glycol
$A_{AC} = -0.140$	$A_{AB} = 1.089$	$A_{CB} = -0.46$
$A_{CA} = -0.263$	$A_{BA} = 1.178$	$A_{BC} = -0.31$

Table III. Activity of Acetic Acid in Glycol and Acetate Phases

Ethylene Glycol Phase			Ethyl Acetate Phase		
Mole fraction x_{CB}	Activity coefficient γ_{CB}	Activity a_{CB}	Mole fraction x_{CA}	Activity coefficient γ_{CA}	Activity a_{CA}
0.0089	0.3095	0.00276	0.0065	0.3998	0.00260
0.0195	0.3103	0.00605	0.0105	0.3761	0.00395
0.0207	0.3114	0.00645	0.0166	0.3587	0.00595
0.0285	0.3093	0.00881	0.0251	0.3358	0.00843
0.0310	0.3065	0.00950	0.0281	0.3242	0.00911
0.0312	0.3051	0.00952	0.0308	0.3107	0.00957
0.0319	0.3090	0.00980	0.0319	0.3088	0.00985

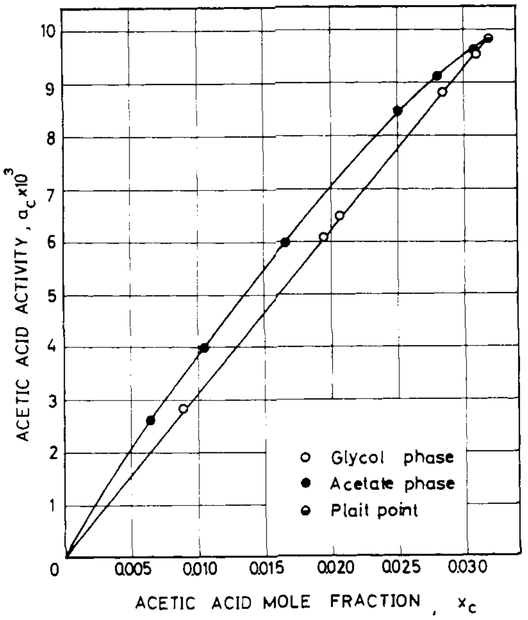

Figure 3. Acetic acid activity in the glycol and ethyl acetate phases

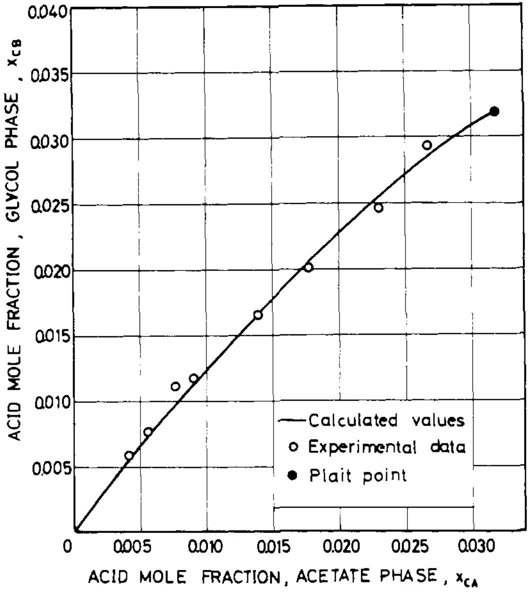

Figure 4. Experimental and predicted acetic acid distribution curves

Interfacial tension then was measured. The reported values are an average of at least 10 readings and are reproducible within ±0.1 dyne per cm.

Results. The interfacial tension readings were appropriately corrected by the tensiometer constant and the Zuidema factor (*10*). Interfacial tension as a function of acetic acid equilibrium concentration data are given in Table IV and plotted in Figure 5. The surface tensions of the ternary systems are extremely low. Consequently, the accuracy of the results varied from 6% for the lowest acid concentration to 30% for the highest concentration.

CONCLUSIONS

The ternary system is highly miscible at 25° C. as the two-phase region is restricted to acetic acid concentrations below 5.2 wt. %. The system exhibits extremely low interfacial tensions over the acetic acid concentration range corresponding to the two-phase region. The acetic acid distribution is correlated by a two-suffix ternary van Laar equation to better than ±5%.

Table IV. Interfacial Tension of Ternary System

Interfacial Tension, Dynes/Cm.	Acetic Acid Concentration, Wt. Fraction	
	Glycol phase	Acetate phase
1.5	0	0
1.0	0.012	0.008
0.8	0.021	0.013
0.5	0.035	0.026
0.3	0.042	0.034
0.2	0.049	0.040

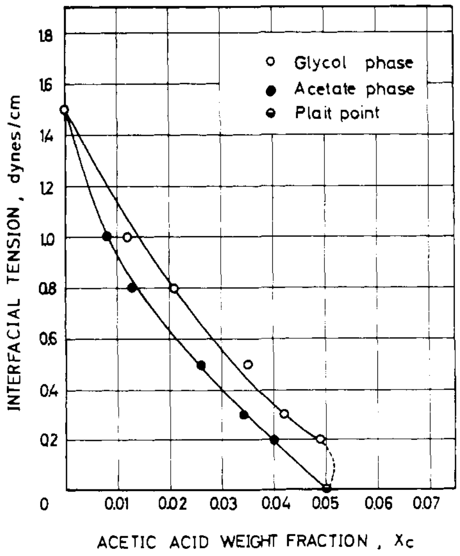

Figure 5. Interfacial tension of the ternary system

ACKNOWLEDGMENT

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NOMENCLATURE

a = Activity
A = Limit of log γ as $x \to 0$ in a binary solution
x = Mole fraction, based on acetic acid molecular weight of 120.1
X = Weight fraction
γ = Activity coefficient

SUBSCRIPTS

A = Ethyl acetate, component or phase
B = Ethylene glycol, component or phase
C = Acetic acid

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Dielectric Behavior of Some Alcohol and Carbon Tetrachloride Mixtures

PHILLIP I. GOLD and RICHARD L. PERRINE
University of California, Los Angeles, Calif.

Dielectric constant data are presented for a number of alcohol and carbon tetrachloride mixtures obtained at 22°, 30°, and 40° C. Densities and the Fröhlich correlation parameter also are included.

A NUMBER of progressively more detailed theories have been developed to describe the dielectric behavior of fluids whose molecules possess a permanent dipole moment. The simplest theories, those of Clausius-Mosotti and Debye (*7*), neglect intermolecular forces. These yield satisfactory results only for gases at low pressures.

The Onsager theory (*13*) recognizes that when a molecule having a permanent dipole moment is surrounded by other molecules, the field of the dipole polarizes the surrounding molecules, since they have a polarizability, even if no permanent moment. This polarization of the environment of a molecule gives rise to a field at the location of the molecule. The theory is limited by the assumption that the molecule occupies a spherical cavity in the dielectric. A more limiting factor is the treatment of the entire surroundings of each molecule as a homogeneous continuum, making no distinction between interactions of closely neighboring molecules and those relatively far apart. Just this distinction is needed for an effective treatment of associated liquids.

By using classical statistical mechanics, Fröhlich (*8, 9*) showed that the dielectric constant of a fluid can be related to the dipole moment of a free molecule of the fluid by the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon}\,\frac{M}{d} = \frac{n_*^2 - 1}{n_*^2 + 2}\,\frac{M}{d}\left[\frac{(n_*^2 + 2)(2\epsilon + 1)}{(n_*^2 + 2\epsilon)}\right] + \frac{4\pi N_A}{3}\,\frac{g\mu_0^2}{9kT}\left[\frac{(n_*^2 + 2)(2\epsilon + 1)}{(n_*^2 + 2\epsilon)}\right]^2 \tag{1}$$

where ϵ is the dielectric constant, M the molecular weight, d the density in grams per cm.^{3}, and n_* the refractive index of the fluid. μ_0 is the dipole moment of a free molecule, N_A is Avogadro's number, and k is the Boltzmann constant. n_* refers to the refractive index measured at frequencies high enough so that orientational polarization effectively has ceased.

The parameter g represents the influence of hindered molecular rotation due to close range intermolecular forces such as occur in liquids which exhibit hydrogen bonding. g is called the correlation parameter. It is defined by the expression

$$g = [1 + n\,\overline{\cos\gamma}] \tag{2}$$

where n is the number of molecules in a sphere of the fluid surrounding a molecule with dipole moment μ and $\overline{\cos\gamma}$ is the average value of the cosine of the angle between the dipole moments of an arbitrary pair of dipoles. Clearly, in the absence of specific close range interactions—such as hydrogen bonding—$\overline{\cos\gamma} = 0$. In this limit, the Fröhlich equation is identical to that of Onsager.

The Fröhlich equation can be extended to consider the case of binary mixtures of polar liquids in nonpolar solvents.

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon}\,\frac{M}{d} = \left[\frac{(n_*^2)_1 - 1}{(n_*^2)_1 + 2}\cdot\frac{M_1}{d_1}\right] \times \left[\frac{\{(n_*^2)_1 + 2\}\{2\epsilon + 1\}}{\{(n_*^2)_1 + 2\epsilon\}}\right] x_1 + \left[\frac{(n_*^2)_2 - 1}{(n_*^2)_2 + 2}\cdot\frac{M_2}{d_2}\right]\left[\frac{\{(n_*^2)_2 + 2\}\{2\epsilon + 1\}}{\{(n_*^2)_2 + 2\epsilon\}}\right] x_2 + \frac{4\pi N_A}{3}\,\frac{g(\mu_0^2)_1}{9kT}\left[\frac{\{(n_*^2)_1 + 2\}\{2\epsilon + 1\}}{\{(n_*^2)_1 + 2\epsilon\}}\right]^2 x_1 \tag{3}$$

where x_1 and x_2 are the mole fractions of the polar and nonpolar components, respectively.