Liquid–Liquid Equilibria of Water + Acetic Acid + Phthalic Esters (Dimethyl Phthalate and Diethyl Phthalate) Ternaries

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Experimental liquid–liquid equilibria of water + acetic acid + dimethyl phthalate and water + acetic acid + diethyl phthalate systems were investigated at 293.16 ± 0.20 K. The reliability of experimental tie-line data was ascertained through an Othmer–Tobias plot. Distribution coefficients and separation factors were evaluated over the immiscibility region. It is concluded that the high-boiling solvents dimethyl phthalate and diethyl phthalate are suitable separating agents for dilute aqueous acetic acid solutions.

Introduction

Various methods of recovering acetic acid from aqueous mixtures have been reviewed by several researchers (1–4). The outstanding advantages of high-boiling solvents for the extraction of acetic acid from its dilute aqueous solutions have been recently reported (5,6). The objective of this study was to determine the experimental solubility and tie-line data of water + acetic acid + dimethyl phthalate and water + acetic acid + diethyl phthalate ternaries at 293.16 ± 0.20 K, under atmospheric pressure. Complete phase diagrams were obtained by evaluating the solubility and the tie-line data simultaneously for each ternary. In addition, the thermodynamic consistency of the tie-line data was ascertained by making an Othmer–Tobias plot (7) and applying the independent material balance check. In order to compare the selectivity advantages of dimethyl phthalate and diethyl phthalate, solvent-free based selectivity diagrams were plotted.

Experimental Section

Chemicals. Acetic acid (100%), dimethyl phthalate (99%), and diethyl phthalate (99%) were furnished by Merck. The acetic acid was redistilled, with the middle 80% collected. The refractive index n_D^{20} at 293.16 ± 0.20 K measured with an Abbe refractometer was 1.3718 ± 0.0001. The density at the same temperature measured with a Westphal apparatus was found to be 1050 ± 1 kg/m³. Dimethyl phthalate and diethyl phthalate reagents were also redistilled under a moderate vacuum, with approximately the middle 70% collected. The refractive index and density values at 293.16 ± 0.20 K for dimethyl phthalate were 1.5155 ± 0.0001 and 1192 ± 1 kg/m³ and for diethyl phthalate 1.5018 ± 0.0001 and 1120 ± 1 kg/m³, respectively. The gas chromatografic analysis showed that the major peak area exceeds 99.6%. The measured physical properties were found in good agreement with literature data (8, 9). Deionized water was further distilled before use.

Procedure. Solubility curve data determinations were performed in an equilibrium cell equipped with magnetic stirrer and isothermal fluid jacket. The mixture temperature was regulated by a thermostated bath with an accuracy of ±0.2 K. The inner temperature of the cell was measured within an accuracy of ±0.1 K by a certified Fischer thermometer. The cell designed to contain a solution of 50–200 cm³ was filled with homogeneous water + acetic acid mixtures prepared by weighing. An electronic Sauter balance accurate to ±0.1 mg was used. The solvent was added by means of an automatic microburet with an accuracy of ±0.005 cm³. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. This pattern was convenient to provide the water-rich side of the curves. The data for the solvent-rich side of the curves were therefore obtained by titrating homogeneous acetic acid + solvent binaries with water until the turbidity had appeared. Composition determinations for solubility curve data were accurate to ±0.0005 mass fraction.

The mutual solubilities of water + solvent were determined by applying a synthetic method. A weighed amount of one pure substance was filled into the cell; the other was added until a permanent heterogeneity had been observed. An ultraaccurate titrator of ±0.001 cm³ was used. Then the content of the solute for all determinations was generally accurate to ±0.0002 mass fraction.

The tie-line data determinations were obtained by using the equilibrium apparatus as described above. Seven different weighed ternary mixtures with compositions within the heterogeneous gap were prepared for each ternary. Each of these mixtures was filled into the cell and vigorously stirred for 1 h under isothermal conditions. After the stirrer was turned off, the contents were immediately allowed into the vertical settler equipped also with an isothermal jacket; after the complete break of the phases, a suitable amount of each layer was withdrawn for analysis. The acid contents of the samples were determined by volumetric titration with $^1/_{10}$ N NaOH solutions to the ethanolic phenolphthalein end point. Several check determinations on known samples showed that the accuracy of the method was ±0.001 mass fraction.

Results

The experimental tie lines and solubility curves of water + acetic acid + dimethyl phthalate and water + acetic acid + diethyl phthalate ternaries at 293.16 ± 0.20 K are plotted in Figures 1 and 2, respectively. Distribution coefficients D_i for acetic acid ($i = 2$) and water ($i = 1$) and separation factors S were determined as follows:

$$D_i = W_{i3}/W_{i1} \qquad (1)$$

$$S = D_2/D_1 \qquad (2)$$

W_{i3} and W_{i1} are the mass fractions in the solvent and aqueous phases, respectively. The results are listed in Tables I and II. The measured values for the solubility curves and experimental mutual solubilities are reported in Tables III and IV. The tie-line data are given in Tables V and VI.

Reliability of Data. The reliability of experimentally measured tie-line data is ascertained by making a Othmer–Tobias plot for each ternary. The linearity of the plot indicates the degree of consistency of the related data. The plots are shown in Figures 3 and 4.
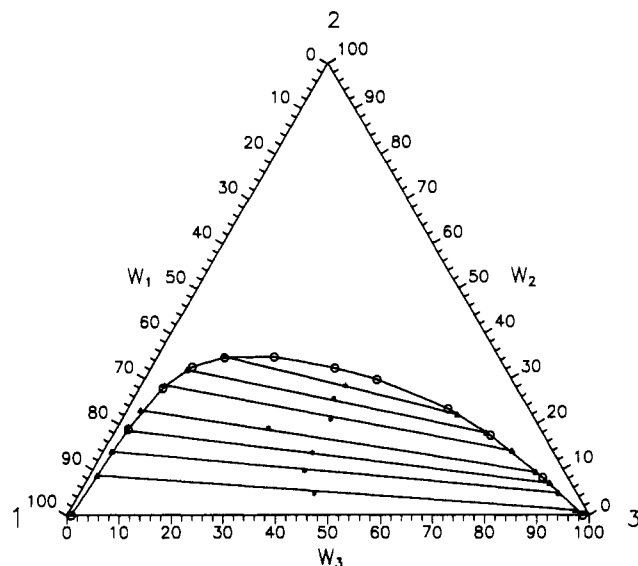
Figure 1. Ternary diagram for experimental liquid–liquid equilibria (LLE) of water (1) + acetic acid (2) + dimethyl phthalate (3) at 293.16 ± 0.20 K: O, solubility curve data; Δ, tie-line data; *, overall composition for tie line (concentrations are expressed in W_i).
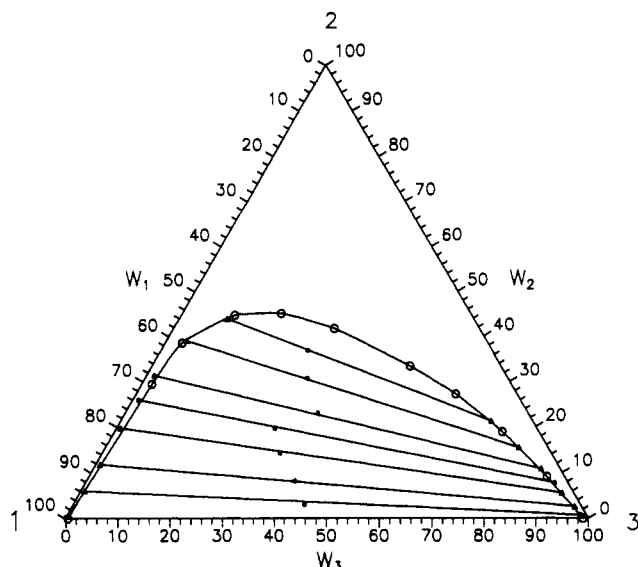
Figure 2. Ternary diagram for experimental LLE of water (1) + acetic acid (2) + diethyl phthalate (3) at 293.16 ± 0.20 K: O, solubility curve data; Δ, tie-line data; *, overall composition for tie line (concentrations are expressed in W_i).

Table I. Mass Fraction Distribution Coefficients D_i of Water (1) + Acetic Acid (2) and Separation Factors, $S = D_2/D_1$, with Dimethyl Phthalate as Solvent, at 293.16 ● 0.20 K

D_2	D_1	S
0.138	0.022	6.27
0.342	0.040	8.55
0.376	0.051	7.37
0.407	0.074	5.50
0.494	0.115	4.30
0.559	0.176	3.18
0.631	0.270	2.34

Selectivity. Selectivity diagrams on a solvent-free basis are plotted for each ternary in Figure 5.

Conclusions

It is concluded that both of the solvents, showing extremely low solubilities against water, may serve as adequate solvents to extract acetic acid from its dilute aqueous solutions.

Table II. Mass Fraction Distribution Coefficients D_i of Water (1) + Acetic Acid (2) and Separation Factors, $S = D_2/D_1$, with Diethyl Phthalate as Solvent, at 293.16 ± 0.20 K

D_2	D_1	S
0.117	0.011	10.64
0.221	0.015	14.73
0.283	0.028	10.11
0.299	0.034	8.79
0.345	0.054	6.39
0.396	0.096	4.13
0.483	0.168	2.88

Table III. Solubility Values for Water (1) + Acetic Acid (2) + Dimethyl Phthalate (3), at 293.16 ● 0.20 K[a]

W_1	W_2	W_3
0.0120		0.9880 (ms)
0.0475	0.0817	0.8708
0.1020	0.1740	0.7240
0.1533	0.2329	0.6138
0.2581	0.2977	0.4442
0.3253	0.3232	0.3515
0.4283	0.3480	0.2237
0.5240	0.3462	0.1298
0.5972	0.3258	0.0770
0.6766	0.2786	0.0448
0.7880	0.1896	0.0224
0.9920		0.0080 (ms)

[a] ms = mutual solubility.

Table IV. Solubility Values for Water (1) + Acetic Acid (2) + Diethyl Phthalate (3), at 293.16 ± 0.20 K[a]

W_1	W_2	W_3
0.0095		0.9905 (ms)
0.0338	0.0904	0.8758
0.0694	0.1895	0.7411
0.1174	0.2726	0.6100
0.1733	0.3339	0.4928
0.2378	0.3832	0.3792
0.2756	0.4176	0.3068
0.3595	0.4510	0.1895
0.4515	0.4470	0.1015
0.5829	0.3864	0.0307
0.6912	0.2948	0.0140
0.9960		0.0040 (ms)

[a] ms = mutual solubility.

**Table V. Tie-Line Values for Water (1) + Acetic Acid (2) + Dimethyl Phthalate (3), at 293.16 ± 0.20 K**

water-rich phase			solvent-rich phase		
W_1	W_2	W_3	W_1	W_2	W_3
0.9000	0.0870	0.0130	0.0200	0.0120	0.9680
0.8450	0.1399	0.0151	0.0341	0.0478	0.9181
0.7930	0.1860	0.0210	0.0401	0.0699	0.8900
0.7441	0.2309	0.0250	0.0550	0.0939	0.8511
0.6700	0.2552	0.0448	0.0770	0.1410	0.7820
0.6100	0.3205	0.0695	0.1073	0.1793	0.7134
0.5255	0.3491	0.1254	0.1418	0.2204	0.6378

Distribution coefficients greater than 0.25 and separation factors varying between 70 and 2 make the solvent a candidate as a separating agent. Distribution coefficients varying from 0.138 to 0.631 (for dimethyl phthalate) and from 0.117 to 0.483 (for diethyl phthalate) require relatively larger amounts of solvent. However, for dilute extract, using a high-boiling solvent may be one of the economic advantages since the recovery of the solvent necessitates the solute to be volatilized.

Another noteworthy observation is that the complete break of the conjugate phases was never hindered by density-, viscosity-, and interfacial tension-related phenomena during the settling process. Sedimentation and coalescence of dispersed phases were so rapid that less than 10 min was

Table VI. Tie-Line Values for Water (1) + Acetic Acid (2) + Diethyl Phthalate (3), at 293.16 ± 0.20 K

water-rich phase			solvent-rich phase		
W_1	W_2	W_3	W_1	W_2	W_3
0.9330	0.0601	0.0069	0.0101	0.0070	0.9829
0.8750	0.1180	0.0070	0.0130	0.0261	0.9609
0.7950	0.1980	0.0070	0.0220	0.0560	0.9220
0.7310	0.2588	0.0102	0.0250	0.0774	0.8976
0.6726	0.3134	0.0140	0.0361	0.1081	0.8558
0.5710	0.3910	0.0380	0.0550	0.1549	0.7901
0.4706	0.4383	0.0911	0.0791	0.2115	0.7094
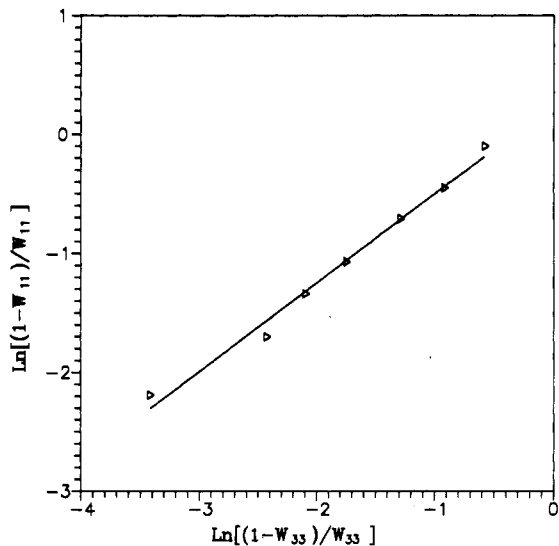
Figure 3. Othmer–Tobias plot for the water (1) + acetic acid (2) + dimethyl phthalate (3) ternary at 293.16 ± 0.20 K.
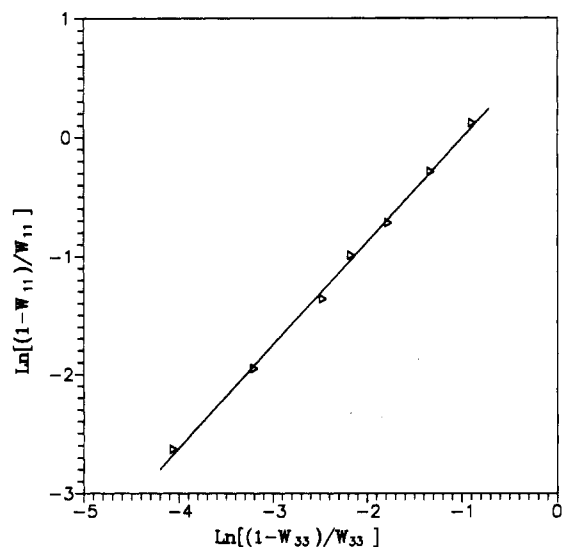
Figure 4. Othmer–Tobias plot for the water (1) + acetic acid (2) + diethyl phthalate (3) ternary at 293.16 ± 0.20 K.

sufficient to obtain absolutely clear layers with very thin dispersion bands for both solvents.

It is observed that the values of the distribution coefficients are higher for dimethyl phthalate, while the opposite is
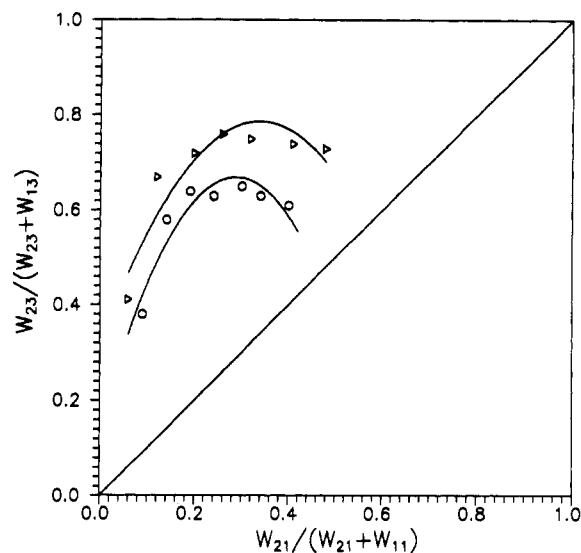
Figure 5. Selectivity diagrams of both ternaries at 293.16 ± 0.20 K: O, water (1) + acetic acid (2) + dimethyl phthalate (3); △, water (1) + acetic acid (2) + diethyl phthalate (3) (solvent-free basis).

observed in the case of comparing the separation factor values and selectivity.

Glossary

D_i	distribution coefficient of the ith component, eq 1
S	separation factor, eq 2
W_i	mass fraction of the ith component
W_{11}	mass fraction of water (1) in the aqueous phase
W_{21}	mass fraction of acetic acid (2) in the aqueous phase
W_{31}	mass fraction of solvent (3) in the aqueous phase
W_{13}	mass fraction of water (1) in the solvent-rich phase
W_{23}	mass fraction of acetic acid (2) in the solvent-rich phase
W_{33}	mass fraction of solvent (3) in the solvent-rich phase

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