Liquid Phase Equilibria for Mixtures of (Water + Morpholine + Ethyl Nonanoate, Dimethyl Phthalate, or Isoamyl Alcohol) at 298.15 K

Lutfullah M. Sevgili, Mehmet Bilgin,* and Selin Şahin

Istanbul University, Engineering Faculty, Chemical Engineering Department, 34320 Avcilar, Istanbul, Turkey

---

This work reports liquid−liquid equilibrium (LLE) data for the mixtures {water (1) + morpholine (2) + ethyl nonanoate, dimethyl phthalate, or isoamyl alcohol (3)} at 298.15 K and 101.3 kPa. The solubility curves and tie-line end compositions were examined for the related mixtures. The reliability of the experimental tie-line data was verified by using the Othmer−Tobias correlation. Distribution coefficients and separation factors were evaluated for the immiscibility region. Although all of the proposed solvents show low distribution coefficients, they can be served as convenient agents for extracting morpholine from aqueous medium, since they exhibit high separation factors. The experimental tie-line data were correlated by universal quasichemical activity coefficient (UNIQUAC) model representing the LLE data for these systems with respect to tie-line slopes only.

Introduction

Morpholine, having both amine and ether functional groups, is a conventional additive in parts per million concentration ranges for pH adjustment in fossil oil and nuclear power plant steam systems. It has a volatility close to water, and if added to water, it distributes rather evenly in both water and steam phases. Adjusting the pH in the whole steam system, it protects the system against corrosion and decomposes reasonably slowly with oxygen even at the high temperature and pressures. It is also used as an auxiliary agent in some separation operations by forming selective complexes with some compounds.[1] The low cost and high polarity of morpholine lead to its common use as an agent in organic synthesis commonly used to generate enamines.[2] Newly, it is used in extremely small amounts as a chemical emulsifier in the synthetic fruit waxing process, when fruits lost its naturally available coating wax shellac.[3] Morpholine derivatives are also of great interest in the petroleum industry because of their high efficiency for the extraction of aromatic hydrocarbons from petroleum products.[4−7]

There are some papers published in literature serving the chemical properties of morpholine to facilitate the use of it, such as the thermodynamic properties of the ionization,[4] the vapor pressures,[5] the densities, and excess or partial molar volumes of aqueous morpholine,[6] the surface thermodynamics of aqueous solutions of morpholine,[7] and the excess volumes for alkanol + morpholine systems.[8] On the other hand, liquid−liquid equilibrium (LLE) data of systems including morpholine is crucial for the design and operation of required extraction systems.[9−12] The recovery of morpholine from water is also an important process for environmental reasons, and there are no studies so far which investigate the LLE data of systems containing water, morpholine, and solvent. In this paper, LLE results were reported for three ternary systems, (water + morpholine + ethyl nonanoate), (water + morpholine + dimethyl phthalate), and (water + morpholine + isoamyl alcohol) at 298.15 K, for which no such data have previously been published.

Experimental Section

Materials. Morpholine, dimethyl phthalate, and isoamyl alcohol were supplied by Merck and were of > 0.99, 0.99, and > 0.98 mass fraction purity, respectively. Ethyl nonanoate was purchased from Aldrich and was of 0.97 mass fraction purity.

Procedure. The solubility curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions.[13,14] The temperature in the cell was kept constant by circulating water from a water bath (model: NUVE BS 302), which was equipped with a proportional−integral−derivative (PID) temperature controller capable of maintaining the temperature within ± 0.1 K. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of (water + solvent) with morpholine until the turbidity had disappeared. For the raffinate-side and solvent-side, binary mixtures of either (water + morpholine) or (solvent + morpholine) were titrated against the third component until the transition from homogeneity to heterogeneity was observed. All initial mixtures were prepared by weighting with Sartorious CP224S accurate to within $\pm 10^{-7}$ kg. Mutual solubility values of the binary mixture (water + solvent) were also measured using the method based on the detection of the cloud point. The transition point between the homogeneous and the heterogeneous zones was determined visually. The reliability of the method depends on the precision of the Metrohm microburet with an accuracy of $\pm 3 \cdot 10^{-9}$ m^3 and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting for about 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least twice to acquire high accuracy. To ensure the detection in an acceptable uncertainty, the absolute differences between the results of repeated experiments did not exceed 3 %.

End-point determinations of the tie-lines were carried out by the independent analysis of the conjugate phases that were

---

* Corresponding author. E-mail: mbilgin@istanbul.edu.tr. Phone: 0090-212-4737070 (17662). Fax: 0090-212-4737180.

10.1021/je1000022

regarded as being in equilibrium. A mixture in known masses of water, morpholine, and solvent lying within the heterogeneous gap were introduced into the extraction cell, stirred for 4 h, and then left for 6 h (the time necessary to attain equilibrium was established in preliminary experiments) to settle down into the two layers. The solvent used did not create any problem related to phase separation-like forming foam or emulsions.

Analysis. The liquid samples were analyzed by a gas chromatograph (HP 6890 model) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). A 15 m long HP-Innowax polyethylene glycol capillary column (30 m × 0.32 mm × 0.5 μm) for the FID and HP Plot Q column (0.32 mm i.d., 0.2 μm film thickness) for the TCD were utilized to separate components of samples at programmed oven programs suitable for each ternary. The two columns and detectors are operated in a parallel way. The FID is used for the detection of morpholine and solvents (isoamyl alcohol, ethyl nonanoate, dimethyl phthalate) and TCD for water. Injections were performed on the split 70/1 mode. Nitrogen was used as a carrier gas; the flow rate of which is 6 $\text{mL}\cdot\text{min}^{-1}$. Injection volumes of the liquid samples were 0.3 μL. Isopropanol is used as the internal standard for each column. The detector temperature was kept at 543.15 K. The oven temperature program was as follows: the initial temperature was set to 343 K. It was held at that temperature for 1 min. It is followed by a heating rate of 2 $\text{K}\cdot\text{min}^{-1}$ until the final temperature of 543.15 K was acquired. The calculation of the concentrations of each component is performed via a software program, which is based on the separate calibration for FID and TCD. The samples of each phase were analyzed twice, and the average values were used. The greatest errors in the determination of mole fraction composition using the calibration curves were ± 0.002 in both of the water-rich and solvent-rich phases.

Results and Discussion

Experimental Data. The compositions of mixture on the binodal curve as well as the mutual binary solubility of water and solvent at 298.15 K are given in Table 1, in which w_i denotes the mass fraction of component i. The measured equilibrium tie-line data are given in Table 2. The experimental solubility curve and tie-line data are plotted in Figures 1 to 3. The reliability of the experimental tie-line data is verified by using the Othmer−Tobias correlation.[15] This correlation is stated by the equation below;

$$\ln\left(\frac{1 - w_{33}}{w_{33}}\right) = a + b \ln\left(\frac{1 - w_{11}}{w_{11}}\right) \qquad (1)$$

where w_{33} refers to the mass fraction of the solvent in the solvent-rich phase and w_{11} refers to mass fraction of the water in the water-rich phase; a and b are the constants of this equation. Othmer−Tobias plots constructed of the $\ln((1 - w_{11})/w_{11})$ versus $\ln((1 - w_{33})/w_{33})$ are shown in Figure 4. The correlation being linear indicates the degree of consistency of the related data.

Figures 1 to 3 exhibit the area of heterogeneous gap change in the ethyl nonanoate > dimethyl phthalate > isoamyl alcohol order. This can be explained by the fact that the mutual solubility of water in these solvents depends on the polarity of them. Water is the least soluble in the system with ethyl nonanoate.

The distribution coefficient, d_i, and separation factor, S, are evaluated for the immiscibility region and also given in Table 2. These parameters represent the extraction performance of the solvent. The distribution coefficient, the capacity of solvent for the extracted component, is calculated as follows:

$$d_i = w_{i3}/w_{i1} \qquad (2)$$

w_{i1} and w_{i3} are the mass fractions of component i in the water-rich phase and in the solvent-rich phase, respectively. Higher

Table 1. Experimental Solubility Curve Data for {Water (1) + Morpholine (2) + Solvent (3)} Ternary Systems at 298.15 K and 101.3 kPa

w_1	w_2	w_3
Water (1) + Morpholine (2) + Ethyl Nonanoate (3)		
0.999	0	0.001
0.878	0.121	0.001
0.749	0.250	0.001
0.600	0.399	0.001
0.544	0.451	0.005
0.400	0.589	0.011
0.243	0.711	0.046
0.169	0.728	0.103
0.119	0.701	0.180
0.088	0.639	0.273
0.064	0.561	0.375
0.038	0.481	0.481
0.024	0.390	0.586
0.015	0.296	0.689
0.011	0.199	0.790
0.005	0.090	0.905
0.009	0	0.991
Water (1) + Morpholine (2) + Dimethyl Phthalate (3)		
0.990	0	0.010
0.791	0.199	0.010
0.685	0.298	0.017
0.583	0.388	0.029
0.475	0.445	0.080
0.356	0.453	0.191
0.298	0.419	0.283
0.242	0.379	0.379
0.192	0.329	0.479
0.129	0.264	0.607
0.068	0.186	0.746
0.027	0	0.973
Water (1) + Morpholine (2) + Isoamyl Alcohol (3)		
0.974	0	0.026
0.864	0.105	0.031
0.768	0.194	0.038
0.664	0.285	0.051
0.536	0.358	0.106
0.416	0.375	0.209
0.360	0.350	0.290
0.306	0.286	0.408
0.254	0.221	0.525
0.208	0.158	0.634
0.162	0.080	0.758
0.103	0	0.897

Table 2. Experimental Tie-Line Data of {Water (1) + Morpholine (2) + Solvent (3)} Ternary Systems at 298.15 K and 101.3 kPa

water-rich (1) phase			solvent-rich (3) phase				
w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}	d_2	S
Water (1) + Morpholine (2) + Ethyl Nonanoate (3)							
0.8540	0.1448	0.0012	0.0064	0.0067	0.9869	0.0463	6.1733
0.7019	0.2967	0.0014	0.0074	0.0118	0.9808	0.0398	3.7905
0.5492	0.4484	0.0024	0.0089	0.0196	0.9715	0.0437	2.6975
0.4470	0.5441	0.0089	0.0092	0.0316	0.9592	0.0581	2.8204
0.2912	0.6901	0.0187	0.0104	0.0699	0.9197	0.1013	2.8375
Water (1) + Morpholine (2) + Dimethyl Phthalate (3)							
0.4026	0.4688	0.1286	0.0298	0.0512	0.9190	0.1092	1.4757
0.5711	0.3971	0.0318	0.0326	0.0437	0.9237	0.1100	1.9264
0.7333	0.2472	0.0195	0.0331	0.0325	0.9344	0.1315	2.9157
0.8542	0.1354	0.0104	0.0356	0.0217	0.9427	0.1603	3.8441
Water (1) + Morpholine (2) + Isoamyl Alcohol (3)							
0.8579	0.1092	0.0329	0.1172	0.0214	0.8614	0.1960	1.4348
0.7290	0.2290	0.0420	0.1483	0.0641	0.7876	0.2799	1.3761
0.6085	0.3209	0.0706	0.1797	0.1200	0.7003	0.3739	1.2662
0.5322	0.3599	0.1079	0.2058	0.1624	0.6318	0.4512	1.1668

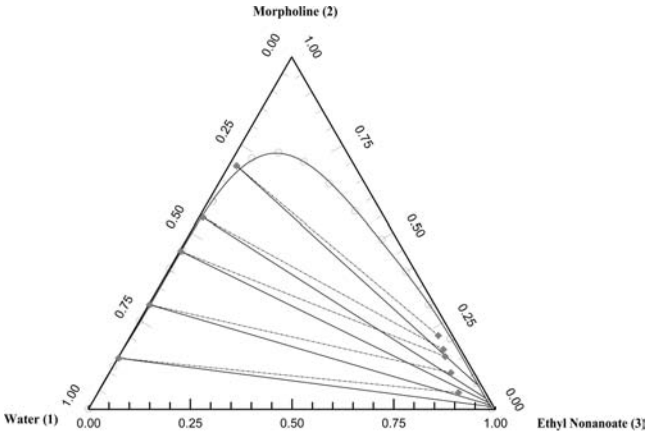

Figure 1. Ternary diagram of {water (1) + morpholine (2) + ethyl nonanoate (3)} at 298.15 K; ○, experimental solubility curve; △, experimental tie-lines; ◆, calculated UNIQUAC tie-lines.

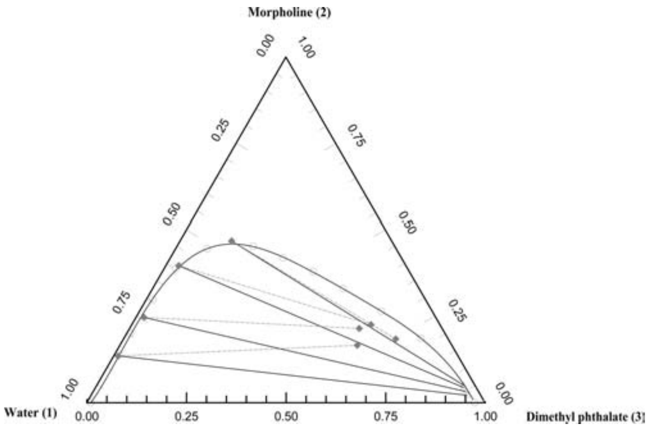

Figure 2. Ternary diagram of {water (1) + morpholine (2) + dimethyl pthalate (3)} at 298.15 K; ○, experimental solubility curve; △, experimental tie-lines; ◆, calculated UNIQUAC tie-lines.

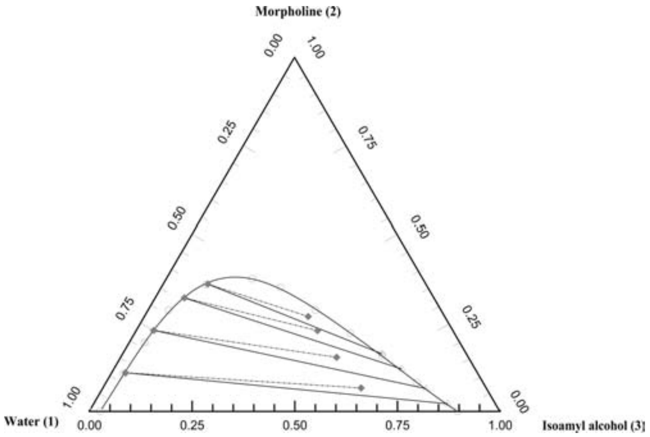

Figure 3. Ternary diagram of {water (1) + morpholine (2) + isoamyl alcohol (3)} at 298.15 K; ○, experimental solubility curve; △, experimental tie-lines; ◆, calculated UNIQUAC tie-lines.

distribution coefficients allow the use of lower solvent-to-water flow ratios. As seen in Table 2, the distribution coefficients obtained in this work show that morpholine is more soluble in water than in the solvents.

The effectiveness of a solvent can be expressed by the separation factor. The separation factor, which is a measure of the ability to separate morpholine from water, is given by

$$S = d_2/d_1 \tag{3}$$

The extracting power of the solvents was given by means of the distribution coefficient (d_2) of morpholine between water and solvent phases and separation factors (S) in Figures 5 and 6, respectively. Distribution coefficients and separation factors increased with the increasing concentration of morpholine. Since the separation factors in all cases are greater than 1, the extraction is possible.

UNIQUAC Correlation. Since the results of the universal functional activity coefficient (UNIFAC) prediction model were unsuccessful, the experimental data were correlated by the universal quasi-chemical activity coefficient (UNIQUAC) model. The UNIQUAC interaction parameters were estimated using the Newton−Raphson numerical technique for simultaneous nonlinear equations. The objective function (OF)[16] given below

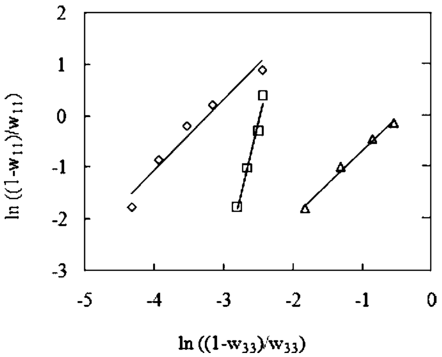

Figure 4. Othmer−Tobias plots of the {water (1) + morpholine (2) + solvent (3)} ternary systems at T = 298.15 K; ◇, ethyl nonanoate; □, dimethyl phthalate; △, isoamyl alcohol.

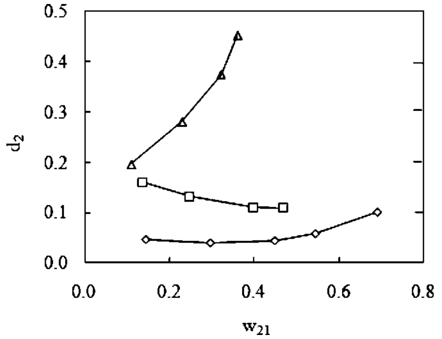

Figure 5. Distribution coefficient of morpholine, d_2, plotted against the mass fraction of morpholine in raffinate phase, w_{21}; ◇, ethyl nonanoate; □, dimethyl phthalate; △, isoamyl alcohol.

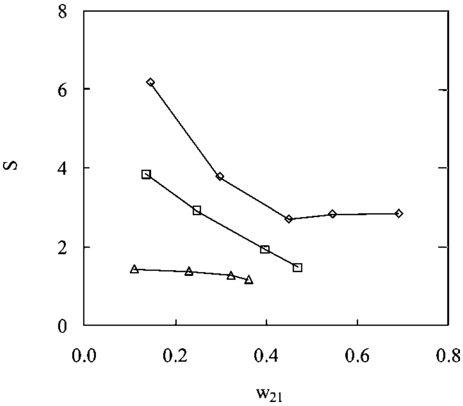

Figure 6. Separation factor, S, plotted against the mass fraction of morpholine in raffinate phase, w_{21}; ◇, ethyl nonanoate; □, dimethyl phthalate; △, isoamyl alcohol.

Table 3. UNIQUAC Interaction Parameters and Objective Function and rmsd Values for Ternary Systems

i	j	τ_{ij}	τ_{ji}	OF	rmsd
Water (1) + Morpholine (2) + Ethyl Nonanoate (3)					
1	2	0.2040	1.9715		
1	3	3.2882	0.8752	0.6101	0.1378
2	3	2.0111	0.8071		
Water (1) + Morpholine (2) + Dimethyl Phthalate (3)					
1	2	1.9128	0.3590		
1	3	2.2216	0.9588	0.4155	0.2507
2	3	1.2804	1.6051		
Water (1) + Morpholine (2) + Isoamyl Alcohol (3)					
1	2	2.4279	0.4838		
1	3	2.6462	0.3389	0.0735	0.2185
2	3	2.4606	1.5473		

is employed for the evaluation of the best estimates of these interaction parameters from LLE data, because of the property weighing small and large activities equally, that is, it operates on the ratio of rather than the difference between activities;

$$\mathrm{OF} = \sum_k \sum_i [\ln(x_{ik}^{\mathrm{I}}\gamma_{ik}^{\mathrm{I}}) - \ln(x_{ik}^{\mathrm{II}}\gamma_{ik}^{\mathrm{II}})]^2 \qquad (4)$$

where $x_{ik}{}^{\mathrm{I}}$ and $x_{ik}{}^{\mathrm{II}}$ refer to the mole fractions of component i in phase I and II, respectively, at tie-line k.

The experimental tie-line data were correlated using these estimated UNIQUAC parameters, and the optimization results were judged by calculating the corresponding root-mean-square deviation (rmsd) values using the following equation;

$$\mathrm{rmsd} = \left[\frac{\sum_k \sum_j \sum_i (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2}{6n}\right]^{0.5} \qquad (5)$$

where n is the number of tie-lines. The indices i, j, and k refer to the component, phase, and tie-line, respectively.

The values of UNIQUAC interaction parameters with the objective function (OF) calculated from eq 4 and the correlation results of the experimental tie-line data are given in Table 3. The rmsd values of the following ternary systems for the UNIQUAC model were calculated as follows: 0.1378 for (water + morpholine + ethyl nonanoate), 0.2507 for (water + morpholine + dimethyl phthalate), and 0.2185 for (water + morpholine + isoamyl alcohol). Visual comparisons of experimental tie-line data with calculated UNIQUAC values are plotted in Figures 1 to 3, where it can be seen that the model does not agree well, especially for the system with dimethyl phthalate.

Conclusions

LLE data for three ternary systems comprising of (water + morpholine + ethyl nonanoate, dimethyl phthalate, or isoamyl alcohol) were measured at 298.2 K and 101.3 kPa. The reliability of experimentally measured tie-line data of each ternary system were confirmed by the Othmer−Tobias correlation. The Othmer−Tobias correlation being linear (regression coefficients for ethyl nonanoate: 0.9564; dimethyl phthalate: 0.9426; isoamyl alcohol: 0.9912) indicates the reliability of the experimental data.

Separation factors, which are indications of the ability of the solvents chosen to separate morpholine from water, were found varying between 1.1668 and 6.1733. This result means that the extraction of morpholine from water by means of selected solvents reported here is possible, since the separation factors are greater than unity. The heterogeneous gaps, the regions under each solubility curve, and changes in the order of ethyl nonanoate > dimethyl phthalate > isoamyl alcohol are due to the polarities of these compounds. Being the least polar of all of these solvents, the system with ethyl nonanoate has the biggest heterogeneous gap. With respect to the distribution coefficient, the order changes to be isoamyl alcohol > dimethyl phthalate > ethyl nonanoate. Morpholine, which is a heterocyclic compound with amine and ether functional groups, prefers the most electronegative one, isoamyl alcohol.

The UNIQUAC model parameters were calculated for (water + morpholine + ethyl nonanoate, dimethyl phthalate, or isoamyl alcohol) systems with OF values given in Table 3. The correlation results gave rmsd values of 0.1387, 0.2587, and 0.2185 for the systems with ethyl nonanoate, dimethyl phthalate, and isoamyl alcohol, respectively. These comparative data show that the calculated UNIQUAC parameters can be cautiously used to correlate experimental tie-line data. This model especially exhibits relatively less satisfactory data for the (water + morpholine + dimethyl phthalate) ternary system than the others.

Literature Cited

(1) Lee, M. J.; Su, C. C.; Lin, H. Isothermal vapor-liquid equilibria for binary mixtures composed of the closely boiling compounds 1,2-dimethoxybenzene and 2-methoxyphenol with an adducted agent: *tert*-butanol or morpholine. *J. Chem. Eng. Data* **2004**, *49*, 588–593.

(2) Noyori, R.; Yokoyama, K.; Hayakawa, Y. Cyclopentenones from α,α′-dibromoketones and enamines: 2,5-dimethyl-3-phenyl-2-cyclopenten-1-one. *Org. Synth.* **1988**, *6*, 520.

(3) McGuire, R. G.; Dimitroglou, D. A. Evaluation of shellac and sucrose ester fruit coating formulations that support biological control of post-harvest grapefruit decay. *Biocontrol Sci. Technol.* **1999**, *9*, 53–65.

(4) Henni, A.; Naami, A.; Tontiwachwuthikul, P. Densities, viscosities, and derived functions of binary mixtures: (triethylene glycol dimethyl ether + water) and (*N*-acetylmorpholine + water) from 298.15 to 343.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1038–1042.

(5) Ko, M.; Na, S.; Kwon, S.; Lee, S.; Kim, H. Liquid-liquid equilibria for the binary systems of *N*-formylmorpholine with branched cycloalkanes. *J. Chem. Eng. Data* **2003**, *48*, 699–702.

(6) Jou, F. Y.; Schmidt, K. A. G.; Mather, A. E. Solubility of ethane in *N*-formyl morpholine. *J. Chem. Eng. Data* **2003**, *48*, 224–225.

(7) Al-Dujaili, A. H.; Yassen, A. A.; Awwad, A. M. Refractive indices, densities, and excess properties of 4-(2-hydroxyethyl)morpholine + water at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2000**, *45*, 647–649.

(8) Ridley, M. K.; Xiao, C.; Palmer, D. A.; Wesolowski, D. J. Thermodynamic properties of the ionization of morpholine as a function of temperature and ionic strength. *J. Chem. Eng. Data* **2000**, *45*, 502–507.

(9) Lee, M. J.; Su, C. C.; Lin, H. Vapor pressures of morpholine, diethyl methylmalonate, and five glycol ethers at temperatures up to 473.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1535–1538.

(10) Minevich, A.; Marcus, Y. Densities and excess and partial molar volumes of aqueous pyrrolidine at 25 and 50 °C and aqueous morpholine at 25 and 60 °C. *J. Chem. Eng. Data* **2003**, *48*, 208–210.

(11) Maham, Y.; Chevillard, A.; Mather, A. E. Surface thermodynamics of aqueous solutions of morpholine and methylmorpholine. *J. Chem. Eng. Data* **2004**, *49*, 411–415.

(12) Park, S. J.; Fischer, K.; Gmehling, J. Excess volumes for alkanol + morpholine systems at 298.15 and 308.15 K. *J. Chem. Eng. Data* **1994**, *39*, 859–862.

(13) Kırbaşlar, Ş. İ.; Şahin, S.; Bilgin, M. (Liquid + liquid) equilibria of (water + acetic acid + diethyl succinate or diethyl glutarate or diethyl adipate) ternary systems. *J. Chem. Eng. Data* **2007**, *52*, 1108–1112.

(14) Sevgili, L. M.; Şahin, S.; Kırbaşlar, Ş. İ. (Liquid−liquid) equilibria of (limonene + linalool + ethylene glycol or diethylene glycol or triethylene glycol or 1,2-propylene glycol) ternary systems. *J. Chem. Eng. Data* **2008**, *53*, 737–741.

(15) Othmer, T. F.; Tobias, P. E. Tie-line correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

(16) Sorensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. Liquid-liquid equilibrium data: their retrieval, correlation and prediction. Part II: Correlation. *Fluid Phase Equilib.* **1979**, *3*, 47–82.

Received for review January 4, 2010. Accepted April 28, 2010. The authors are grateful to the Research Fund of Istanbul University, Project No. UDP-3300/23022009.

JE1000022