(10) Katayama, H.; Harada, Y. *J. Chem. Eng. Data* **1985**, *29*, 373–375.
(11) Simnick, J. J.; Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469–476.
(12) Nasir, P.; Hwang, S. C.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 298–301.
(13) Wilson, G. M.; Johnston, R. H.; Hwang, S. C.; Tsonopoulos, C. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 94–104.
(14) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238–244.
(15) Van Ness, H. C.; Mrazek, R. V. *AIChE J.* **1959**, *5*, 209.
(16) Van Ness, H. C. *Chem. Eng. Sci.* **1959**, *11*, 118.
(17) Daubert, T. E.; Danner, R. P. *Data Compilation Tables of Properties of Pure Compounds*; Design Institute for Physical Property Data, AIChE, Aug. 1983.

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Liquid–Liquid Equilibria for the System Water–*tert*-Butyl Alcohol–Diisobutylene at 25, 45, and 75 °C

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Liquid–liquid equilibria for the system water–*tert*-butyl alcohol–diisobutylene have been measured at 25, 45, and 75 °C. The experimental data presented in this paper are correlated in terms of the NRTL and UNIQUAC models, and the relevant parameters are presented.

Table I. Experimental Equilibrium Data for the System Water (1)–*tert*-Butyl Alcohol (2)–Diisobutylene (3)

temp, °C	aqueous phase		organic phase	
	x_1	x_2	x_1	x_2
25	0.9807	0.0192	0.0012	0.0387
	0.9731	0.0267	0.0030	0.1208
	0.9638	0.0359	0.0625	0.2003
	0.9581	0.0416	0.0780	0.2953
	0.9535	0.0462	0.1483	0.3817
	0.9490	0.0507	0.2228	0.4155
	0.9447	0.0550	0.3209	0.4313
	0.9406	0.0590	0.4518	0.4108
	0.9275	0.0718	0.5824	0.3474
45	0.9845	0.0154	0.0263	0.0525
	0.9769	0.0230	0.0267	0.1412
	0.9720	0.0279	0.0581	0.2361
	0.9678	0.0321	0.1127	0.3318
	0.9644	0.0354	0.1608	0.3888
	0.9603	0.0396	0.2377	0.4309
	0.9571	0.0427	0.3390	0.4367
	0.9528	0.0470	0.4471	0.4164
	0.9446	0.0550	0.5756	0.3587
75	0.9897	0.0099	0.0114	0.0856
	0.9832	0.0167	0.0489	0.1705
	0.9794	0.0205	0.0676	0.2641
	0.9746	0.0252	0.1187	0.3438
	0.9726	0.0272	0.1606	0.4112
	0.9703	0.0295	0.2462	0.4433
	0.9672	0.0326	0.3267	0.4578
	0.9630	0.0368	0.4251	0.4407
	0.9583	0.0415	0.5504	0.3834

Introduction

tert-Butyl alcohol containing some water is dehydrated to isobutylene in the presence of sulfuric acid or other acid-acting catalyst such as sulfonic acid type cation-exchange resins. When an acid catalyst is applied to *tert*-butyl alcohol, two reactions are catalyzed, dehydration and polymerization. However, a small amount of diisobutylene (2,4,4-trimethyl-1-pentene) is produced in most dehydration processes. It is therefore necessary to separate an aqueous phase containing *tert*-butyl alcohol from an organic phase containing diisobutylene. In the present study, the liquid–liquid equilibria for the ternary system water–*tert*-butyl alcohol–diisobutylene were measured at three different temperatures, 25, 45, and 75 °C, and correlated with the NRTL and UNIQUAC models.

Experimental Section

Chemicals. Diisobutylene (Wako Pure Chemical Industries, Ltd.) and *tert*-butyl alcohol (Junsei Chemical Co., Ltd.) were of guaranteed reagent grade and were used directly without any further purification. The certified minimum purities of these chemicals were 99.5 mol %. A chromatographic analysis on them showed major peak areas of more than 99.9%. Water was deionized and distilled in an all-glass distillation unit prior to use.

Procedure. The experimental work was carried out using screw-capped Pyrex glass tubes similar to that described by Alonso and Recasens (*1*). Each sample tube was 1.5 cm i.d. and 16 cm long. It contained about 20 cm^3 liquid and 8 cm^3 gas-phase (air and solution vapor). The equilibrium cells containing different mixtures of the three components were placed in a thermostated shaking bath operated at 130 rpm (Taiyo incubator M-1). Temperature was controlled within an accuracy of 0.2 °C by using a temperature regulator. After 2 h, the shaker was stopped and the samples were allowed to settle for a period of 5 h. Once equilibrium had been reached, samples of both phases were then taken with long-needled syringes and rapidly injected into a gas chromatograph (Shimadzu GC-9A) equipped with a thermal conductivity detector (100 mA) and connected to an integration unit (Shimadzu C-R3A). Samples of known composition were injected to determine the chromatographic factors for calibration. Chromatographic analyses were performed by injecting 1-μL samples. Special care was

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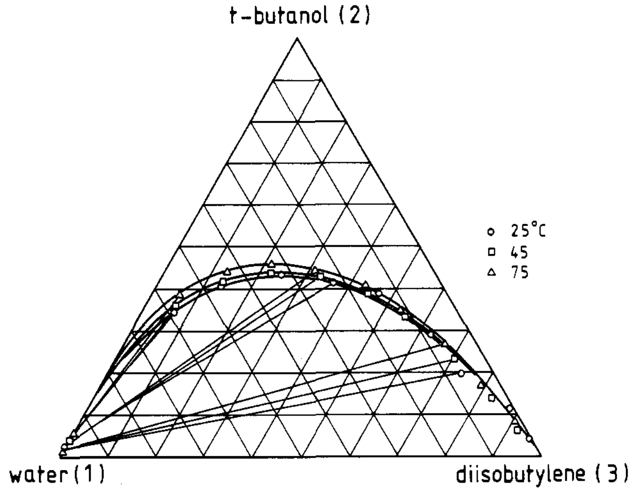

Figure 1. Liquid-liquid equilibria for the system water (1)-*tert*-butyl alcohol (2)-diisobutylene (3) at 25, 45, and 75 °C.

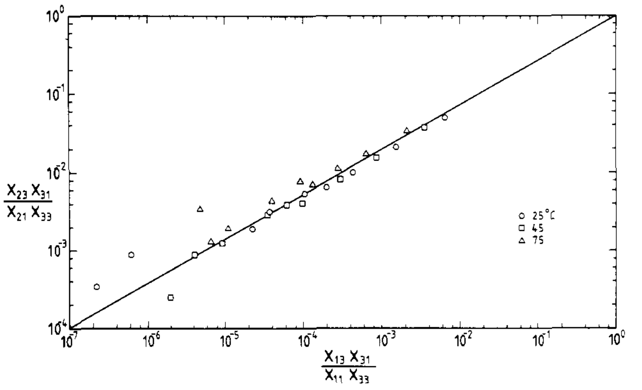

Figure 2. Ishida's correlation for the system water (1)-*tert*-butyl alcohol (2)-diisobutylene (3) at 25, 45, and 75 °C.

Table II. Estimated Values of Compositions at the Plait Points

temp, °C	x_1	x_2	x_3
25	0.8840	0.1132	0.0028
45	0.9000	0.0984	0.0016
75	0.9229	0.0762	0.0009

taken in tie-line determinations above ambient temperatures to prevent phase splitting due to cooling. In such case the syringe was heated to the sample temperature prior to sampling. In all cases a 10 ft × $^1/_8$ in. Porapak-Q column was used at the operating temperature of 250 °C. GC-grade helium carrier gas was used at 50 mL/min at room temperature. For each sample, four analyses were performed to obtain a mean value. The average absolute deviation from the mean value was estimated to be 0.0005 mole fraction.

Results and Discussion

The LLE data for the ternary system water-*tert*-butyl alcohol-diisobutylene at three different temperatures, 25, 45, and 75 °C, are summarized in Table I and plotted in Figure 1. No experimental data for this system were found in the data compilations of DECHEMA series (*2*) and other literature. As shown in Figure 1, the solubility as well as the area of heterogeneity increases with increasing temperatures with a minimal variation. The plait points estimated from the Treybal's method (*3*) are presented in Table II. Reliability of the LLE data has been ascertained by the fact that linear relationship of $X_{13}X_{31}/X_{11}X_{33}$ versus $X_{23}X_{31}/X_{21}X_{33}$ on log-log coordinates is given with a slope of 0.57 in the case where Ishida's correlation (*4*) is applied, as shown in Figure 2.

Table III. NRTL Parameters and Rmsd Values for the Ternary System Water (1)-*tert*-Butyl Alcohol (2)-Diisobutylene (3)

temp, °C	a_{12}, K	a_{21}, K	a_{23}, K	a_{32}, K	a_{13}, K	a_{31}, K	rmsd
25	1164.8	-321.9	-304.5	758.9	1437.6	1014.3	0.91199
45	1273.1	-333.1	-380.8	801.4	1395.2	971.2	0.93258
75	1451.0	-380.2	-437.7	693.2	1847.2	1146.9	0.82797

Table IV. UNIQUAC Parameters and Rmsd Values for the Ternary System Water (1)-*tert*-Butyl Alcohol (2)-Diisobutylene (3)

temp, °C	b_{12}, K	b_{21}, K	b_{23}, K	b_{32}, K	b_{13}, K	b_{31}, K	rmsd
25	623.6	155.9	-169.6	708.6	2053.1	2463.6	2.36506
45	1145.0	-253.4	-449.4	957.5	2665.8	2674.4	1.65892
75	1315.6	-286.2	-752.3	1513.4	2781.7	3445.6	1.13689

The NRTL and UNIQUAC models proposed respectively by Renon and Prausnitz (*5*) and Abrams and Prausnitz (*6*) were used to correlate the experimental LLE data. The interaction parameters $(g_{ij} - g_{jj})$ and $(g_{ji} - g_{ii})$ for the NRTL equation and the parameters $(u_{ij} - u_{jj})$ and $(u_{ji} - u_{ii})$ corresponding to the residual excess Gibbs energy contribution of the UNIQUAC equation were estimated by using the method previously described by Sorensen et al. (*7*). For the NRTL model, the nonrandomness parameter α_{ij} was set to a value of 0.2. An objective function defined in terms of concentrations has been adopted to obtain the best fit of the experimental tie lines.

$$F = \sum_{i}^{M} \min \sum_{j}^{3} \sum_{k}^{2} \{x_{jk}(i) - \hat{x}_{jk}(i)\}^2 \qquad (1)$$

where $x_{jk}(i)$ is the experimental mole fraction of component j in phase k and $\hat{x}_{jk}(i)$ the mole fraction predicted from the NRTL and UNIQUAC models; i denotes tie line (i = 1, 2, ..., M). The NRTL and UNIQUAC parameters obtained for the ternary system water-*tert*-butyl-alcohol-diisobutylene at three different temperatures are presented in Tables III and IV, respectively. The results of the fitting are compared on the basis of the root mean square deviation defined as

$$\text{rmsd} = 100\{\sum_{i}^{M} \min \sum_{j}^{3} \sum_{k}^{2} [x_{jk}(i) - \hat{x}_{jk}(i)]^2/6M\}^{1/2} \qquad (2)$$

The correlation of the experimental data by means of the NRTL equation with α = 0.3 gave results very much like the ones obtained with α = 0.2. The numerical values of the rmsd are also reported in Tables III and IV.

Glossary

a_{ij}	NRTL binary interaction parameter, $(g_{ij} - g_{jj})/R$, K
b_{ij}	UNIQUAC binary interaction parameter, $(u_{ij} - u_{jj})/R$, K
F	objective function defined by eq 1
g_{ij}	NRTL binary interaction parameter, cal mol^{-1}
M	number of experimental tie lines
R	gas constant, cal mol^{-1} K^{-1}
u_{ij}	UNIQUAC binary interaction parameter, cal mol^{-1}
x_{jk}	mole fraction of component j in phase k
X_{jk}	mass fraction of component j in phase k
$x_{jk}(i)$	mole fraction of component j in phase k for the i-th tie line
$\hat{x}_{jk}(i)$	mole fraction of component j in phase k calculated from the NRTL and UNIQUAC models

Greek Letter

α_{ij}	NRTL nonrandomness parameter

Registry No. *tert*-Butyl alcohol, 75-65-0; diisobutylene, 25167-70-8.

Literature Cited

(1) Alonso, M.; Recasens, F. *J. Chem. Eng. Data* **1986**, *31*, 164.
(2) Sorensen, J. M.; Arlt, E. *DECHEMA Chemistry Data Series Liquid-Liquid Equilibrium Data Collection*; VCH: Weinheim, FRG, 1980; Vol. 5.
(3) Treybal, R. E.; Weber, L. D.; Daley, J. F. *Ind. Eng. Chem.* **1946**, *38*, 817.
(4) Ishida, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 693.
(5) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(6) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(7) Sorensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. *Fluid Phase Equilib.* **1979**, *3*, 47.

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V_m^E of Mixtures Containing Ethyl Propanoate or Ethyl Butanoate with 1-Chloroalkanes

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The excess molar volumes, V_m^E, of the binary mixtures ethyl propanoate + 1-chloroalkanes and ethyl butanoate + 1-chloroalkanes are indirectly determined from densities at 298.15 K. All the systems studied exhibit positive excess molar volumes along the range of concentrations, increasing, for a specific ester, with the 1-chloroalkane chain. On the contrary, the V_m^Es decrease with the increase in R_1 in R_1–CO–O–C_2H_5, upon mixing with a specific 1-chloroalkane.

Introduction

As a continuation of our study of the excess thermodynamic properties of binary systems formed by aliphatic esters with alkyl chlorides the V_m^Es of the mixtures $\{xC_mH_{2m+1}CO_2C_2H_5$ (m = 2, 3) + $(1 - x)ClC_nH_{2n+1}$ (n = 5, 6, 7, 8)$\}$ are presented here. In a previous article (*1*) we reported the excess molar volumes of the systems formed by the same 1-chloroalkanes with other ethyl esters (formate and acetate). In order to perform a more through analysis of the volumetric behavior of these systems, the data presented in (*1*) will be used, aiding confirmation of the considerations carried out in the interpretation of the results.

Taking into account other works reported in the same field of research we found analogies between our results and the plots of V_m^Es versus composition of mixtures of aliphatic esters and ketones with other compounds such as *n*-alkanes (*2*, *3*) and *n*-alkanols (*4*, *5*) having a similar molecular structure. These analogies are mainly manifested by two effects: The first is the increase in the V_m^Es for any one ester or ketones with the length of the chain of the second compound (*n*-alkane, *n*-alkanol, or 1-chloroalkane). The second, and more difficult to define, is the decrease in the V_m^Es of the mixture with an R_1–CO–O–R_2 ester or a R_1–CO–R_2 ketone, as the length of the aliphatic radicals, R_1 or R_2, increases if the second compound is the same one.

Dusart et al. found some anomalies in the behavior of mixtures containing certain esters and ketones by means of volumetric (*3*), spectroscopic (*6*), and enthalpic (*7*) studies, attributing them to the existence of pseudocycles brought about by turns around the bonds joined on either side to the carbonyl group, =C=O. The existence of these rotational isomers have also been observed by Mido et al. (*8*) in esters and by Hirota et al. (*9*), Shimanouchi et al. (*10*), and Redondo et al. (*11*) in ketones, among others. These and other considerations will be taken into account when justifying the behavior of some of the systems studied in this work.

Experimental Section

The characteristics of the 1-chloroalkanes used in this work were reported in a previous paper (*1*). The purity specifications indicated by the manufacturer, Fluka, were the following: for ethyl propanoate, puriss >99 mol %, and for ethyl butanoate, purum >98 mol %. However, all products were degassed in vacuo and later dried with a molecular sieve (Union Carbide, Type 4A, from Fluka). After this treatment the physical properties experimentally determined by us and those taken from data found in the literature (in parentheses) at 298.15 K are as follows: for ethyl propanoate, ρ = 883.98 kg·cm^{-3} (884.0 (*12*)) and n_D = 1.3817 (1.3814 (*12*)); for ethyl butanoate, ρ = 872.73 kg·m^{-3} (873.94 (*12*)) and n_D = 1.3896 (1.3904 (value estimated from ref *12*)).

Preparation of samples, the technique of density measurements, and determination of the excess molar volumes were as described in previous papers (*13*, *14*). The mean errors in V_m^E were smaller than ±0.0003 cm^3·mol^{-1} as indicated in (*1*).

Results and Discussion

V_m^Es of the $\{xC_mH_{2m+1}CO_2C_2H_5$ (m = 2, 3) + $(1 - x)ClC_nH_{2n+1}$ (n = 5, 6, 7, 8)$\}$ systems determined from the densities and over the entire range of concentrations are given in Table I. V_m^Es were correlated as a function of the composition of the ester by using a polynomial expression which has afforded excellent results in the treatment of excess thermodynamic magnitudes. The equation has the form

$$V_m^E\ (\mathrm{cm^3 \cdot mol^{-1}}) = x(1 - x)\sum A_i\{x/[x + k(1 - x)]\}^i \qquad i = 0, 1, 2, \ldots \quad (1)$$

The coefficients A_i for each system were determined by using a least-squares linear regression procedure (employing an F-test). Each of the correlations was optimized for the best

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