were in good agreement with the experimental data. The vapor pressure data of this system are available for the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. The vapor pressure data measured at low temperatures are particularly useful for the design of the absorber.

Glossary

A_n,B_n	constants in eqs 2 and 3
b	allowable pressure elevation in experimental apparatus 2, %
n	integer exponent in eqs 2 and 3
p	vapor pressure, Pa
T	absolute temperature, K
V	volume of experimental apparatus 2, cm^3
v	volumetric air-flow rate leaked on the vacuum side in experimental apparatus 2, cm^3 Pa s^{-1}
X	absorbent concentration, wt %

Greek Letters

ϵ	deviation, %
θ	time of measurement in experimental apparatus 2, s

Subscripts

cal	calculated value from eqs 2 and 3
exp	experimental data
min	minimum pressure of measurement in experimental apparatus 2

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Liquid-Liquid Equilibria for the Ternary System Water-Acetone-Isooctane

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Liquid-liquid equilibrium data for the ternary system water-acetone-isooctane were measured at 283, 293, 303, and 313 K. The experimental data were correlated by the UNIQUAC model. The reliability of the experimental data was ascertained by the Ishida correlation.

Introduction

Liquid-liquid equilibrium (LLE) data are an essential element in the design of equipment for liquid extraction. Although a large volume of LLE data exists in the literature, it did not receive much attention in terms of theoretical interpretation until the mid-seventies. Much interest has been generated in this area since Sorensen (*1*, *2*) made a systematic study of the published LLE data and correlated these data using the UNIQUAC and NRTL models. The purpose of this study was to generate additional data for the water-acetone-alkane series to aid in the correlation and prediction of liquid-liquid equilibria. LLE data for the ternary system water-acetone-isooctane (2,2,4-trimethylpentane) were measured at 283, 293, 303, and 313 K, at atmospheric pressure, and were correlated by using the UNIQUAC model.

Experimental Section

Materials. All materials used in this study were obtained from Fisher Scientific. Acetone and water were HPLC grades, and isooctane was Fisher's Optima grade. Although all materials had a stated minimum purity of 99.5 wt %, the purities of water and isooctane were determined by chromatographic analysis to be greater than 99.9 wt %, and these chemicals were used directly without any further purification. The major impurity in the acetone was water (0.5 wt %), which was removed by freshly activated Union Carbide Type 4A molecular sieve.

Procedure. The experimental work was carried out by using Supelco sample bottles sealed with Teflon-lined septum caps. Sampling of the lower phase was accomplished through the use of a glass capillary tube, inserted through the cap and extending to near the bottom of the bottle. A Forma Scientific constant-temperature bath, with a range of 253-343 K, maintained the samples at a constant temperature ±0.02 K. The samples were mixed with an air-driven magnetic stirrer and a Teflon-coated stirring bar. After equilibrium was attained, the two phases were allowed to separate and settle for a minumum of 22 h. Samples of both phases were taken using Hamilton Gastight 1701 syringes. The sample analysis was performed using a Hewlett-Packard 5890A gas chromatograph equipped with a single-channel thermal conductivity detector and a Spectra-Physics SP4270 electronic integrator. The sample size was 2 μL. In all cases, an 8 ft × $^1/_8$ in. Hayesep Q column was used. The injector and detector temperatures were maintained at 423 and 540 K, respectively. The column temperature was programmed for an initial temperature of 448 K and a final temperature of 535 K. The heating rate was 35 K/min, and the flow rate of helium carrier gas was 60 mL/min. Calibration analyses were performed to convert the peak area ratio to the weight composition of the sample. The gas chro-

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Table I. Experimental LLE Data for the System Water (1)–Acetone (2)–Isooctane (3), Weight Percent (x_{iL}) and Mole Percent (X_{iL}) Concentrations and Distribution Coefficient (K) as a Function of Temperature (T)

T/K	$x_{1,I}$	$x_{2,I}$	$x_{1,II}$	$x_{2,II}$	$X_{1,I}$	$X_{2,I}$	$X_{1,II}$	$X_{2,II}$	K
283	99.77	0.00	0.00	0.00	99.96	0.00	0.00	0.00	
	86.09	13.62	0.006	1.03	95.28	4.67	0.038	2.00	(2.33)
	73.42	26.18	0.019	3.69	89.97	9.95	0.12	6.99	1.42
	63.16	36.26	0.10	7.05	84.78	15.10	0.61	12.91	1.17
	33.65	64.44	0.20	18.11	62.38	37.06	1.07	30.02	1.24
	18.04	75.05	0.50	27.67	42.53	54.89	2.43	42.05	1.31
293	99.77	0.00	0.001	0.00	99.96	0.00	0.003	0.00	
	85.89	13.85	0.009	1.49	95.19	4.76	0.06	2.89	1.65
	74.11	25.50	0.04	4.52	90.21	9.64	0.22	8.50	1.13
	66.03	33.49	0.08	8.33	86.32	13.58	0.44	15.10	0.90
	34.56	63.45	0.41	21.78	63.26	36.13	2.08	34.76	1.04
	18.56	73.96	0.97	34.04	43.49	53.75	4.43	48.49	1.11
303	99.75	0.00	0.009	0.00	99.96	0.00	0.06	0.00	
	84.14	15.56	0.05	2.79	94.53	5.42	0.31	5.33	1.02
	72.72	26.82	0.11	6.86	89.65	10.26	0.65	12.58	0.82
	63.56	35.88	0.13	10.03	85.00	14.88	0.75	17.87	0.83
	38.72	59.42	0.60	22.87	67.41	32.08	3.04	35.89	0.89
	19.18	72.04	2.03	41.66	44.70	52.07	8.52	54.22	0.96
313	83.06	16.63	0.04	3.91	94.10	5.84	0.24	7.39	0.79
	77.11	22.52	0.08	6.86	91.63	8.30	0.47	12.60	0.66
	66.30	33.18	0.16	11.02	86.47	13.42	0.91	19.44	0.69
	45.93	52.69	0.76	25.83	73.50	26.15	3.71	39.37	0.66
	20.92	70.05	3.57	47.23	47.47	49.30	13.74	56.39	0.87

Table II. UNIQUAC Parameters (A_{ij}) and Root Mean Square Deviation (rmsd) Values, Equation 3, for the System Water (1)–Acetone (2)-Isooctane (3) as a Function of Temperature (T)

T/K	A_{12}/K	A_{21}/K	A_{13}/K	A_{31}/K	A_{23}/K	A_{32}/K	rmsd
283	-205.21	178.04	332.82	754.32	71.401	16.987	1.15
293	-224.79	194.32	343.16	772.15	49.744	1.1395	1.13
303	-238.98	143.13	362.49	780.75	23.051	-29.706	0.90
313	-121.48	322.35	346.03	799.26	-89.957	275.55	1.18

matograph was calibrated periodically to ensure the accuracy of the analyses. For each sample, three analyses were performed to obtain the mean value. Concentration measurements were generally accurate to within a relative error of 1%.

Results and Discussion

Experimental Results. The experimental LLE data for the water (1)–acetone (2)–isooctane (3) system at 283, 293, 303, and 313 K are presented in Table I. Concentrations of component i (i = 1, 2, 3) in phase L (L = I, aqueous phase; L = II, organic phase) are given in both weight percent, x_{iL}, and mole percent, X_{iL}. In addition, the distribution coefficient, defined as the ratio of mole percent of acetone in the organic phase to mole percent of acetone in the aqueous phase, $K = X_{2,II}/X_{2,I}$, is also listed. The effect of temperature on LLE for the system is shown in Figure 1. As expected, the size of the two-phase region decreases with an increase in temperature.

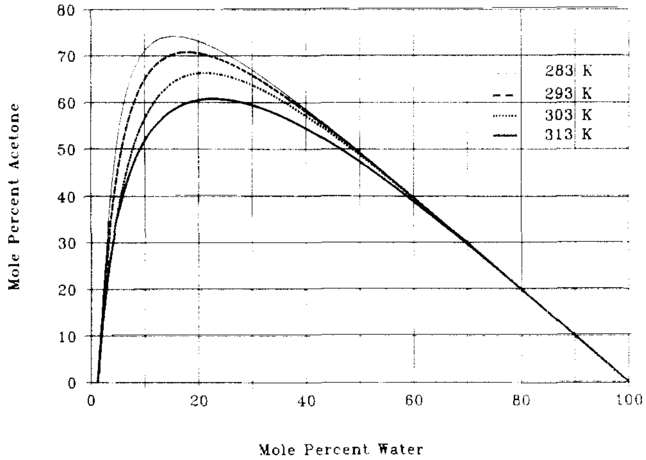

Figure 1. Effect of temperature on the LLE for the system water (1)–acetone (2)–isooctane (3): Curves, LLE results calculated by UNIQUAC.

Data Correlation. The experimental data were correlated by using the UNIQUAC model. This model was first proposed by Abrams and Prausnitz (*3*) and has been used extensively by Sorensen (*1*, *2*) and others in the correlation of LLE data. UNIQUAC is an excess Gibbs energy model, from which activities, a_{iL}, of component i in phase L can be evaluated. The UNIQUAC model has two adjustable interaction parameters, A_{ij}, for each binary. Several methods have appeared in the literature for estimating the interaction parameters and have been reviewed by Novak et al. (*4*). The methods generally employ an iterative computer program to minimize the value of an objective function. The computer program used in this work is a modified version of the program developed by Sorensen (*1*), in order to adapt it to an IBM AT computer. The solution is performed in two parts by using two objective functions. The first objective function, F_a, is based on activity

$$F_a = \sum_k \sum_i (a_{iIk} - a_{iIIk})^2 \tag{1}$$

where the sum is extended to all the tie lines k. The second objective function, F_X, minimizes the difference between the experimental and calculated concentrations.

$$F_X = \sum_k \sum_i \sum_L (X_{iLk,\mathrm{exp}} - X_{iLk,\mathrm{calc}})^2 \tag{2}$$

Computational details for the interaction parameters can be found elsewhere (*1*). The UNIQUAC model utilizes a relative volume, R_i, and a relative molecular surface area, Q_i, for the pure species in the computational procedures; these values come from tabulations in the literature (*2*).

The estimated interaction parameters for the ternary system at 283, 293, 303, and 313 K are presented in Table II. Also

Table III. Plait-Point Mole Percent Compositions X_i for the System Water (1)-Acetone (2)-Isooctane (3) Estimated from UNIQUAC Model, as a Function of Temperature (T)

T/K	X_1	X_2	X_3
283	13.35	73.48	14.17
293	16.54	70.72	12.74
303	22.03	66.36	11.61
313	28.57	59.97	11.46

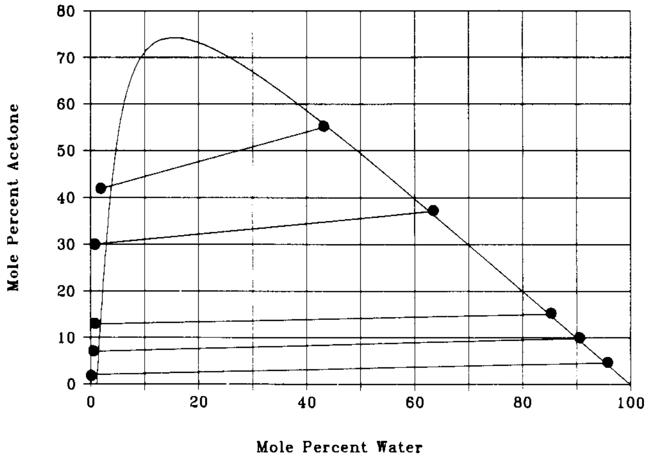

Figure 2. LLE data for the system water (1)-acetone (2)-isooctane (3) at 283 K: curves and tie lines, LLE results calculated by UNIQUAC; points, experimental values (this study).

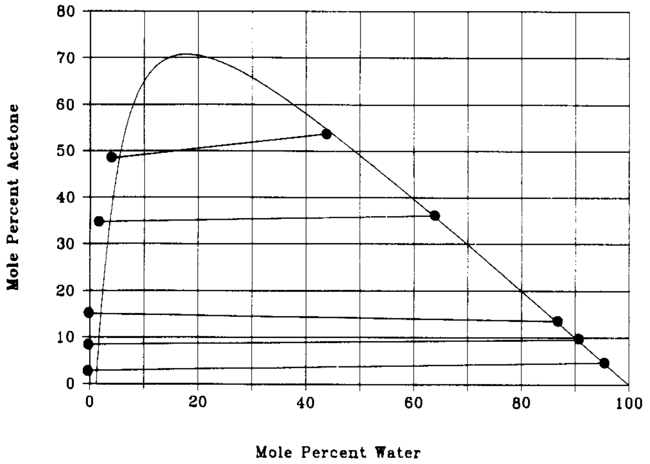

Figure 3. LLE data for the system water (1)-acetone (2)-isooctane (3) at 293 K: curves and tie lines, LLE results calculated by UNIQUAC; points, experimental values (this study).

included in the table is the root mean square deviations (rmsd) defined as

$$\text{rmsd} = \Big[\sum_k \sum_i \sum_L (X_{iLk,\text{exp}} - X_{iLk,\text{calc}})^2/6M\Big]^{1/2} \qquad (3)$$

where M is the number of experimental tie lines. The rmsd is a measure of the agreement between experimental and calculated data. The values reported here compare favorably with those reported in several recently published articles (*5*, *6*) on LLE studies. The plait-point concentrations estimated from the UNIQUAC model are presented in Table III.

The calculated LLE data and the experimental tie-lines for the temperatures studied are plotted in Figures 2-5. Inspection of the figures reveals that there is an inversion of the slopes of the tie-lines between temperatures of 293 and 303 K. At 283 K, the slopes of the tie-lines near the plait point are highly positive. As the system temperature increases, the lines begin to level out until slope inversion occurs between 293 and 303 K. Further increase in temperature results in the tie-line slopes becoming progressively negative. DeFre and Verhoeye (*7*) suggested that the slopes of tie-lines are dictated by the different nonideality of the homogeneous binary subsystems and the tie-lines are sloped toward the less ideal homogeneous subsystems. The inversion of the slopes of the tie-lines observed in this study is apparently a result of the temperature effect on the relative nonideality of the homogeneous binary subsystems.

Finally, the Ishida correlation (*8*) was used to ascertain the reliability of the experimental results. The correlation calls for

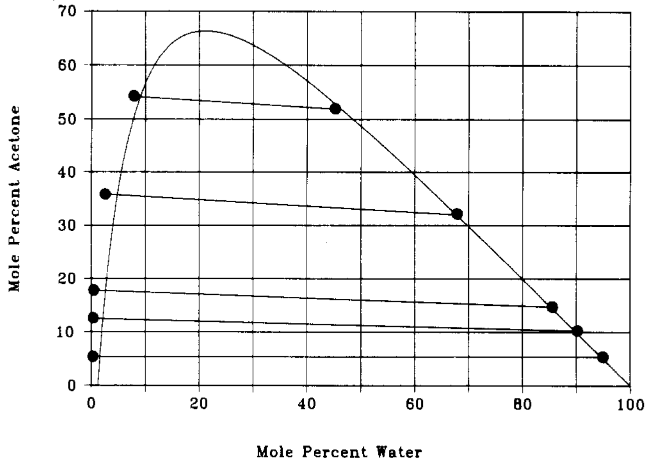

Figure 4. LLE data for the system water (1)-acetone (2)-isooctane (3) at 303 K: curves and tie lines, LLE results calculated by UNIQUAC; points, experimental values (this study).

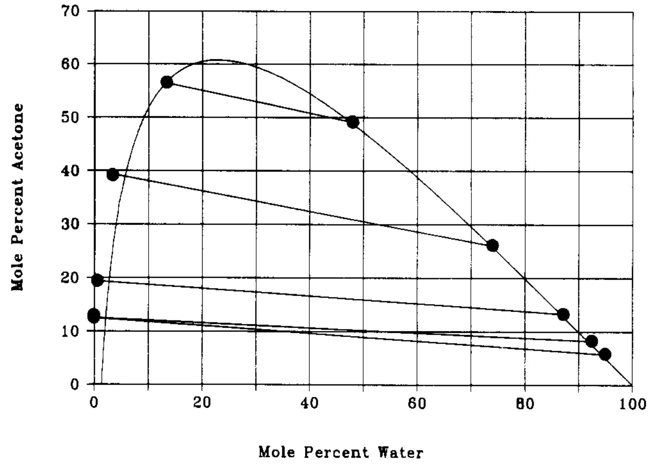

Figure 5. LLE data for the system water (1)-acetone (2)-isooctane (3) at 313 K: curves and tie lines, LLE results calculated by UNIQUAC; points, experimental values (this study).

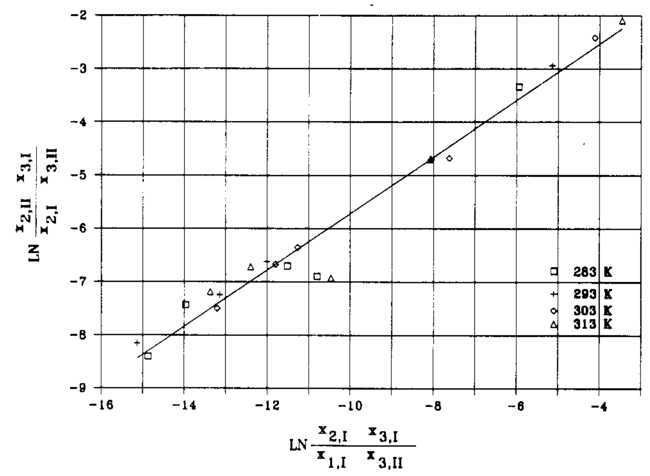

Figure 6. Ishida's correlation for the system water (1)-acetone (2)-isooctane (3).

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the tie-line data to have the following functional relationship:

$$(X_{2,\mathrm{II}}X_{3,\mathrm{I}}/X_{2,\mathrm{I}}X_{3,\mathrm{II}}) = b(X_{2,\mathrm{I}}X_{3,\mathrm{I}}/X_{1,\mathrm{I}}X_{3,\mathrm{II}})^m \qquad (4)$$

The results of the regression analysis are presented in Figure 6. The probability that the data do not form a straight line is less than 0.01%. The slope m of the regressed line is 0.57. The goodness of the fit confirms the reliability of the experimental LLE data.

Glossary

$a_{i\mathrm{L}}$	activity of component i in phase L
A_{ij}	UNIQUAC binary interaction parameter, k^{-1}
K	distribution coefficient, $K = X_{2,\mathrm{II}}/X_{2,\mathrm{I}}$
T	temperature, K
$x_{i\mathrm{L}}$	experimental weight percent concentration of component i in phase L
$X_{i\mathrm{L}}$	experimental mole percent concentration of component i in phase L
rmsd	mole percent root mean square deviation, eq 3

Subscripts

i,j	components (i,j = 1, 2, 3)
L	phases (I, aqueous; II, organic)
k	tie lines (1, 2, 3, ..., M)

Registry No. Acetone, 67-64-1; isooctane, 540-84-1.

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Vapor–Liquid Equilibria below 0 °C of Hydrogen Chloride Solutions Saturated with Calcium Chloride

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The vapor–liquid equilibria of HCl–H_2O solutions saturated with $CaCl_2$ were determined for HCl molalities of 5.031–15.691 g-mol of HCl/kg of H_2O for the nominal temperature range of 0 to −40 °C. Total pressures were measured by means of capacitance gauges, vapor compositions by direct vapor-phase sampling with a quadrupole mass filter, and liquid-phase compositions by electric conductivity measurements. Solubilities of $CaCl_2$ in the hydrochloric acid at these temperatures are also reported.

Introduction

The thermodynamic properties of hydrochloric acid and acid solutions containing salts, specifically the vapor–liquid equilibria, have been investigated more thoroughly than for any other strong electrolyte. However, relatively few studies have been reported for hydrochloric acid solutions below 0 °C, possibly because of the experimental difficulties involved. Kao (*1*) reported data for HCl–H_2O down to −10 °C. For the temperature range of 0 to −40 °C, Miller (*2*, *3*) measured the vapor–liquid equilibria of pure HCl–H_2O solutions and of acid solutions containing unsaturated to near-saturated NaCl concentrations.

The present experimental study is a continuation of the effort to fill the gap in data for hydrochloric acid solutions containing dissolved salts, in this case $CaCl_2$, in the temperature range of 0 to −40 °C. Vapor–liquid equilibria are reported for solutions with HCl molalities of 5.013–15.691 g-mol of HCl/kg of H_2O saturated with $CaCl_2$. $CaCl_2$ is an important industrial additive used in the recovery of waste hydrochloric acids by extractive distillation (*4*). The design analysis in ref 4 was based on the vapor–liquid equilibria data of Synowiec and Bobrownicki (*5*) for HCl–$CaCl_2$–H_2O solutions with 0–39 wt % HCl and unsaturated concentrations of $CaCl_2$ of 0–50 wt %. These data were for higher boiling temperatures at a constant pressure of 750 mmHg.

Experimental Section

As shown schematically in Figure 1, a 2-L Pyrex flask containing the test solution was immersed in an insulated methylene chloride bath cooled by a two-stage mechanical refrigeration system. The temperature of the bath was maintained to within ±0.1 °C of the desired temperature, monitored by a calibration platinum resistance thermometer.

All valves, tubing, and fittings were made of AISI 304 or 316 stainless steel. Viton O-rings and copper gaskets were used in the valves and flanges, respectively. All metal parts in continuous contact with the vapor were coated with silicone vacuum grease. No significant corrosion of any of the metals was observed so long as care was taken to avoid contact with the liquid acid.

Removal of air from the system was effected by a mechanical vacuum pump in series with a liquid nitrogen trap. Equilibrium pressures were measured with two MKS Baratron Type 220 capacitance gauges (10^{-4}–1 and 10^{-2}–10^{2} Torr) calibrated by the manufacturer using a transfer standard to ±0.02% of full-scale accuracy. Samples of the liquid solution were analyzed for acid and $CaCl_2$ content, after their separation as described below, by electroconductivity measurements made by using a Barnstead Model PM-70CB bridge and a Yellowstone Springs YSI 3400 Pyrex cell with a maximum deviation of ±1% at 25 ± 0.1 °C. Vapor samples were drawn directly from the vapor chamber into a Varian VGA-100 quadrupole mass filter, and the composition was derived from the recorded mass spectral areas in the mass number ranges 34–39 and 15–20 for HCl and water, respectively. The spectra were obtained at a nominal pressure of 3.0×10^{-6} Torr, sampling continually from the vapor chamber into the quadrupole mass

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