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Solubility of Solid Acetic Acid in Acetone–Ethanol Mixtures

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The solubility of acetic acid in acetone–ethanol mixtures has been measured for temperatures ranging from melting point to 245.2 K. The experimental results are compared with values calculated by means of the Wilson, NRTL, and UNIQUAC equations, utilizing the parameters from vapor–liquid equilibria, and with values predicted by the UNIFAC method. The mean deviations between the measured and the calculated solubilities are always very low.

Introduction

Accurate knowledge of fluid-phase equilibrium data is of primary importance for the design and operation of chemical plants. While quite a lot of experimental data are readily available for vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE), there is much less abundance for liquid–solid equilibria.

Particularly poor attention has been given so far to solubilities of solid in mixed liquid solvents. The present study was undertaken to provide additional liquid–solid experimental data because our recent studies have dealt with the solubility of acetic acid in different solvents (*1*). Here the system acetic acid in acetone–ethanol mixtures was chosen, our aim being to verify the possibility of predicting solubilities of solids in liquid mixtures. To this end two different procedures have been applied: one uses the UNIFAC method (*2*) to estimate activity coefficients from group contributions (*1*, *3–5*) and the other extends the properties derived from the data reduction of vapor–liquid equilibria to those of the liquid–solid (*1*, *6*) employing the Wilson (*7*), NRTL (*8*), and UNIQUAC (*9*) equations.

Experimental Section

Solubilities of solid acetic acid in the liquid were determined by analyzing samples of the liquid phase in equilibrium with the solid. To this end liquid–solid systems were agitated in a thermostatic bath (±0.1 K). After equilibrium was reached, supernatant sample was removed for the analysis of concentration. Each determination was repeated 5 times with good reproducibility; the calculated standard deviation is of the order of 0.005.

Analysis of mixture samples were carried out by means of a Perkin Elmer gas chromatograph (a 3-m column was packed with Carbowax 20 M, +2% H_3PO_4, on Chromosorb W.Aw. 80–100 mesh).

Purities of the components (Carlo Erba) were as follows (wt %): acetic acid 99.9; ethanol 99.9; acetone 99.7. Experimental solubilities of acetic acid in acetone–ethanol mixtures and in pure solvents are reported in Table I for the five temperatures studied.

Data Reduction and Discussion. Activity coefficients of acetic acid reported in Table I have been obtained from the experimental solubilities of solid acetic acid in liquid solvents through the equilibrium relationship (*10*)

$$\ln \gamma_3 = -\ln x_3 + \frac{\Delta H_t}{RT_t}\left(1 - \frac{T_t}{T}\right) + \frac{\Delta C_p}{R}\left(\frac{T_t}{T} - 1 - \ln \frac{T_t}{T}\right) \tag{1}$$

Table I. Solubilities of Acetic Acid in Acetone–Ethanol Mixtures

T_3, K	x_3	x_2	x_1	$\gamma_{3,\mathrm{exptl}}$
245.2	0.468	0.532		0.893
	0.487	0.433	0.080	0.858
	0.486	0.389	0.125	0.861
	0.484	0.306	0.210	0.864
	0.492	0.241	0.267	0.849
	0.470	0.145	0.385	0.889
	0.457	0.041	0.502	0.915
	0.469		0.531	0.892
252.7	0.555	0.445		0.891
	0.542	0.390	0.068	0.913
	0.546	0.346	0.108	0.906
	0.543	0.272	0.185	0.911
	0.564	0.204	0.232	0.877
	0.550	0.121	0.329	0.900
	0.535	0.035	0.430	0.925
	0.538		0.462	0.919
263.1	0.650	0.350		0.946
	0.649	0.295	0.056	0.947
	0.649	0.267	0.084	0.947
	0.645	0.210	0.145	0.952
	0.650	0.164	0.186	0.946
	0.653	0.094	0.253	0.940
	0.632	0.029	0.339	0.972
	0.640		0.360	0.960
273.9	0.781	0.219		0.969
	0.784	0.183	0.033	0.965
	0.785	0.164	0.051	0.964
	0.784	0.126	0.090	0.965
	0.777	0.103	0.120	0.974
	0.770	0.062	0.168	0.983
	0.775	0.017	0.208	0.976
	0.782		0.218	0.968
283.2	0.911	0.089		0.981
	0.898	0.086	0.016	0.995
	0.907	0.069	0.024	0.986
	0.903	0.046	0.051	0.990
	0.901	0.036	0.063	0.992
	0.901	0.021	0.078	0.992
	0.905	0.007	0.088	0.987
	0.904		0.096	0.989

In data reduction, the normal melting temperature and the enthalpy of fusion have been substituted into eq 1 for the corresponding values of the triple point (*11*). The last term in eq 1 has little effect on the values of the activity coefficients and has therefore been neglected. From Table I negative deviations from Raoult's law ($\gamma < 1$) are observed; such deviations could be attributed to interaction of a chemical nature between acid and the solvents.

In order to predict solubility values in different temperature conditions, four models have been tested for the evaluation of activity coefficients. Three of these (Wilson, NRTL, UNIQUAC) are correlative models, the other (UNIFAC) is a predictive one based on a group contribution method.

As shown in Figure 1 the equations are in good agreement with the experimental data also at lowest temperature (245.2 K).

To calculate the solubilities by means of the Wilson, NRTL, and UNIQUAC equations, the parameters obtained from the correlation of VLE of the binary systems have been utilized.

Table II gives the values of the binary parameters and physical data utilized in the correlation models (*2*, *3*), where A_{ij}

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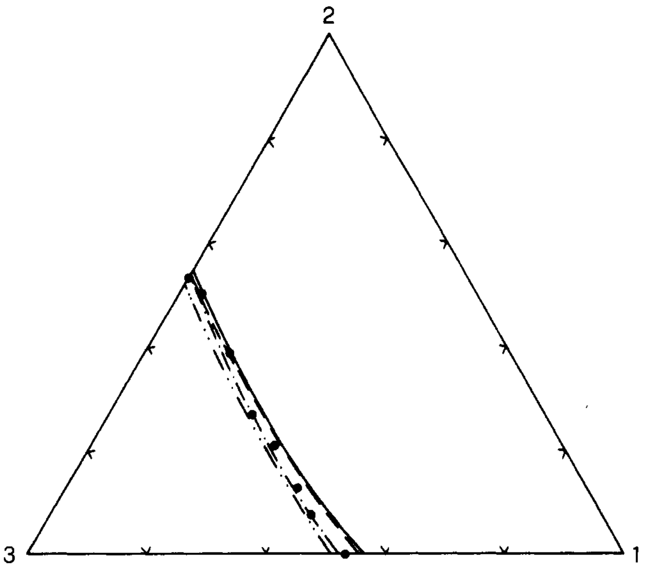

Figure 1. Solubilities of solid acetic in acetone (1)–ethanol (2) mixtures at 245.2 K: (●) experimental; (—) from NRTL; (- - -) from Wilson; (-·-) from UNIQUAC; (-···-) from UNIFAC.

Table II. Binary Parmeters of the Wilson, NRTL, and UNIQUAC Equations, and Pure Components' Physical Data[a]

		A_{12}	A_{21}
acetone (1)–acetic acid (2)	Wilson	-482.5624	482.5547
	NRTL	317.5711	-345.9460
	UNIQUAC	211.5711	-211.7709
acetone (1)–ethanol (2)	Wilson	236.9935	272.4254
	NRTL	48.4642	-445.9208
	UNIQUAC	97.2529	-125.5395
ethanol (1)–acetic acid (2)	Wilson	197.1403	-265.2895
	NRTL	-293.6825	209.2778
	UNIQUAC	-162.7242	122.3620

	V_i	R_i	Q_i
acetone	74.05	2.573	2.336
ethanol	58.68	2.105	1.972
acetic acid	57.54	2.202	2.072

has the following meaning: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})$ cal/mol; NRTL, $A_{ij} = (g_{ij} - g_{ii})$ cal/mol; UNIQUAC, $A_{ij} = (u_{ij} - u_{ii})$ cal/mol. The nonrandomness parameter α in the NRTL model is fixed at 0.3.

In Table III are listed the mean deviations $\bar{E}_{x_3}$ calculated with all of the equations tested. The very low deviations obtained indicate the possibility to predict liquid–solid equilibria, also from a quantitative point of view, utilizing VLE data. The UNIQUAC model gives the best results, and as indicated in Figure 2 a good representation of experimental data is obtained for all of the temperature studied.

In Figure 3 are reported the isotherms calculated with the UNIFAC method. The deviations listed in Table III and the comparison of Figures 2 and 3 point out that results obtained on the basis of the UNIQUAC and the UNIFAC models are very close.

In conclusion the UNIFAC method enables quantitative estimates to be made for solubilities of solids in mixed liquid solvents. Moreover, the possibility of predicting liquid–solid solubility from VLE has been further confirmed.

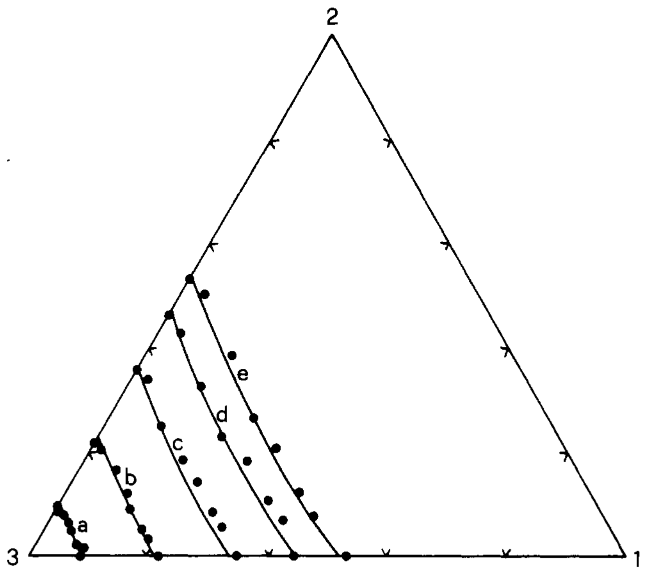

Figure 2. Solubilities of solid acetic acid in acetone (1)–ethanol (2) mixtures. (●) experimental; (—) from UNIQUAC: e at 245.2 K; d at 252.7 K; c at 263.1 K; b at 273.9 K; a at 283.2 K.

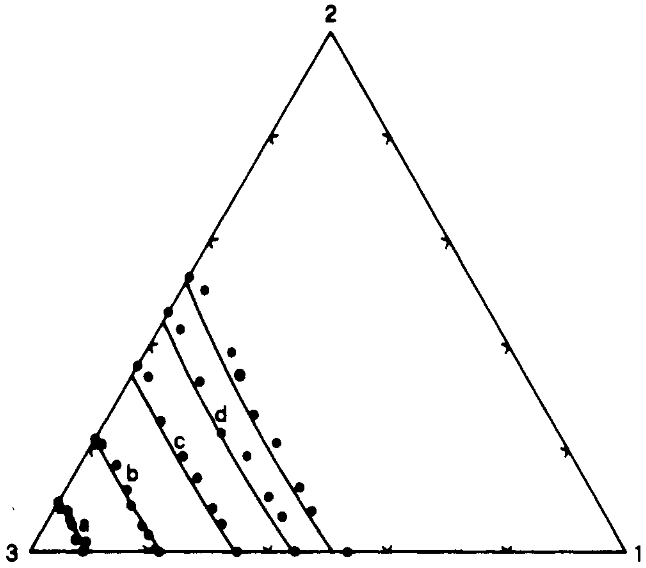

Figure 3. Solubilities of solid acetic acid in acetone (1)–ethanol (2) mixtures. (●) experimental; (—) from UNIFAC: e at 245.2 K; d at 252.7 K; c at 263.1 K; b at 273.9 K; a at 283.2 K.

Glossary

A_{ij}	parameters used in the Wilson, NRTL, and UNIQUAC equations
g_{ij}	interaction parameter in the NRTL equation
α_{ij}	nonrandomness parameter in the NRTL equation
λ_{ij}	interaction parameter in the Wilson equation
u_{ij}	interaction parameter in the UNIQUAC equation
q_i	relative van der Waals surface area of component i
r_i	relative van der Waals volume of component i

Table III. Mean Deviation between Experimental and Calculated Solubilities

	Wilson		NRTL		UNIQUAC		UNIFAC	
T, K	$\bar{E}_{x_3}$, %	$E_{x_3,\max}$, %	$\bar{E}_{x_3}$, %	$E_{x_3,\max}$, %	$\bar{E}_{x_3}$, %	$E_{x_3,\max}$, %	$\bar{E}_{x_3}$, %	$E_{x_3,\max}$, %
245.2	3.0	5.6	3.8	6.9	1.8	3.2	3.7	6.0
252.7	2.5	6.9	3.4	8.1	1.6	3.3	2.9	4.7
263.1	1.5	3.4	1.6	3.9	1.8	2.5	2.6	4.3
273.9	1.5	2.4	1.6	2.5	0.8	1.4	0.7	1.8
283.2	0.8	1.8	0.8	1.8	0.4	1.1	0.4	1.3

v_i	liquid molar volume of component *i*
x_i	mole fraction of component *i* in the liquid phase
n	number of data
E_{x_3}	local deviation between experimental and calculated values; $E_{x_3} = (x_{3,\mathrm{exptl}} - x_{3,\mathrm{calcd}})/x_{3,\mathrm{exptl}}$
$\bar{E}_{x_3}$	mean deviation; $\bar{E}_{x_3} = (1/n)\sum_1^n \lvert E_{x_3} \rvert$
$E_{x_3,\mathrm{max}}$	maximum absolute deviation for x_3
R	gas constant, cal/(mol K)
t	temperature, °C
T	temperature, K
Δc_p	difference between specific heat of the liquid and of the solid, cal/(mol K)
ΔH	enthalpy of fusion, cal/mol
γ	activity coefficient

Subscripts

1	relative to acetone
2	relative to ethanol
3	relative to acetic acid
t	at triple point
exptl	experimental
calcd	calculated

Registry No. Acetic acid, 64-19-7; ethanol, 64-17-5; acetone, 67-64-1.

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Quaternary Liquid–Liquid Equilibrium: Water–Ethanol–Chloroform–Toluene at 25 °C. Experimental Determination and Graphical and Analytical Correlation of Equilibrium Data

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Mutual solubility and tie line data at 25 °C and atmospheric pressure are presented for the quaternary system water–ethanol–chloroform–toluene. The obtained results have been correlated by the graphical method of Ruiz and Prats and by the UNIQUAC equation.

Introduction

In this work, liquid–liquid equilibrium (LLE) data for the quaternary system water (W)–ethanol (E)–chloroform (C)–toluene (T) are measured at 25 °C and atmospheric pressure. This system contains two pairs of partly miscible compounds: W–C and W–T. The experimental results have been obtained by applying a systematic method of selection of the points to be measured as reported in previous paper (*1*). This method permits the heterogeneous region to be fully characterized as well as allows graphical representation (method of Ruiz and Prats (*2*)) and analytical correlation (UNIQUAC (*3*)) of the equilibrium data in a form suitable for the interpolation of quaternary tie lines.

Experimental Section

All chemicals (analytical reagent grade) were supplied by Merck. The contents of volatile impurities were determined by gas chromatographic analysis. With the exception of chloroform, all the compounds contained negligible amounts of impurities (less than 0.1%). Chloroform was stabilized with ethanol in a percentage varying from 0.7% to 0.8%; the ethanol was removed by extraction with water.

Data for the binodal curves of the component ternary and quaternary systems were determined by using the cloud point method. The experimental device was that used by Ruiz and Prats (*4*).

Equilibrium data were obtained by preparing mixtures of known overall composition, intense stirring, and setting for at least 2 h at constant temperature (25 ± 0.1 °C). At the end of each experiment, samples were taken from both phases and analyzed by means of gas chromatography. Good separation of the four components was obtained on a 2 m × $^{1}/_{8}$ in. column packed with Chromosorb 101 100/120. The column temperature was 170 °C and detection was carried out by thermal conductivity. The detector current was 100 mA at a helium flow rate of 40 mL/min. To obtain quantitative results we applied the internal standard method, 1-propanol being the standard compound used for this purpose. The relative accuracy of the weight fraction measurements was 1%.

The methodology applied in selecting the points to be determined experimentally was as reported in a previous paper (*1*). The quaternary system water (W)–ethanol (E)–chloroform (C)–toluene (T) is represented schematically in Figure 1, using a regular tetrahedron. To characterize the solubility surface fully, ternary solubility curves for the systems W–E–T and W–E–C were determined experimentally, and also the four quaternary solubility curves which form the intersections of four

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