different cell loadings on the propane–*n*-dodecane systems, and the standard deviation of the smoothed compositions of Table IV and the raw data was 1.85%.

The raw data corresponding to the two ethane–solvent systems are shown in Figure 1, and the raw data for the two propane–solvent systems are shown in Figure 2. These figures also present the smoothed composition lines and "ideal" solubility lines. From this representation, it appears that there is a high degree of linearity of the composition lines at values of $1/T^*$ larger than 1.40 for the systems with ethane as a solvent and larger than 1.35 for the systems with propane as a solvent. This, in fact, is the region in which Henry's law might be expected to hold. Thus extrapolation of the data into even more dilute regions would be likely to be reasonably accurate.

The discontinuities in both ethane solvent binary systems in Figure 1 were not exhibited by any of the previously studied ethane systems. These discontinuities are caused by the fact that the triple point of both solutes exceeds that of the critical point of the solvent. For the 2-methylnaphthalene–solute system, there is a four-phase solid-liquid 1-liquid 2-vapor point (Q point). The compositional difference between the liquid-1 and liquid-2 phases causes a discontinuity with respect to composition along the three-phase solid–liquid–vapor locus. For the naphthalene-solute system, an even higher solute triple-point temperature causes a temperature range in which no liquid phase exists. Noteworthy in the composition behavior of this naphthalene–solute system is the maximum in the composition which occurs at the high-temperature end of the low-composition branch of the S-L-V locus. At this point the system, already extremely dilute in hydrocarbon solute, is approaching the vicinity of the critical point of pure ethane. Apparently the increase in molar volume of the liquid phase effects a decrease in composition, in contrast to what one experiences at lower temperatures. This phenomenon has been observed before in the binary systems methane–*n*-octane and methane–cyclohexane (*3*).

Glossary

L_1	ethane-lean liquid phase
L_2	ethane-rich liquid phase
T	temperature in K
T_T	triple point temperature in K: 307.73 K for 2-methylnaphthalene, 353.2 K for naphthalene, 243.51 K for *n*-decane, 263.61 K for *n*-dodecane
T^*	T/T_T
x	solute mole fraction

Literature Cited

(1) Din, F., "Thermodynamic Functions of Gases", Vol 2, Butterworths London, 1961, p 112.
(2) Kohn, J. P., Luks, K. D., Liu, P. H., *J. Chem. Eng. Data*, **21**, 360 (1976).
(3) Kohn, J. P., Luks, K. D., Liu P. H., Tiffin, D. L., *J. Chem. Eng. Data*, **22**, 419 (1977).
(4) Lee, K. H., Kohn, J. P., *J. Chem. Eng. Data*, **14**, 292 (1969).
(5) Liu, P. H., Luks, K. D., Kohn, J. P., *J. Chem. Eng. Data*, **22**, 220 (1977).
(6) Tiffin, D. L., Kohn, J. P., Luks, K. D., *J. Chem. Eng. Data*, **23**, 207 (1978).
(7) Tiffin, D. L., Kohn, J. P., Luks, K. D., *J. Chem. Eng. Data*, preceding paper in this issue.

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Supplementary Material Available: Four tables of raw data corresponding to Tables I–IV (4 pages). Ordering information is given on any current masthead page.

Activity Coefficients from Solid–Liquid and Vapor–Liquid Equilibria of Some Associated Solutions

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Solid–liquid and low-pressure vapor–liquid equilibria were experimentally determined for binary solutions of acetic acid and carbon tetrachloride, benzene, or chloroform. Activity coefficients from vapor–liquid data reduction, taking into account vapor-phase dimerization of acetic acid, were compared with those derived from the solubility of solid acetic acid in the liquid solvent.

Introduction

Information on the activity coefficients in liquid solutions can be obtained from data reduction of vapor–liquid equilibria and of solubilities of solids in liquids. Therefore, in principle, the activity coefficients obtained from either of the two-phase equilibria could be used for the prediction of the other equilibrium and vice versa. However, for isobaric equilibria it is necessary to know the heat of mixing, mainly in the case of large temperature ranges or in the case of high thermal effects.

In this note vapor–liquid and solid–liquid equilibrium data are reported for solutions of an associated component, namely, acetic acid, and a common solvent such as carbon tetrachloride, benzene, or chloroform.

The scope of the work is the comparison of the sets of activity coefficients obtained from both types of data. This comparison also allows an indirect check of consistency of the procedure which evaluates vapor-phase nonidealities of associated systems.

The choice of acetic acid is due to its melting temperature (16.6 °C), which allows measurements of solubilities at temperatures close to ambient.

Measurements of vapor–liquid equilibrium data are carried out at pressures of the order of 100 mmHg, to approach the temperature ranges pertaining to both equilibria.

Experimental Section

Solubilities of solid acetic acid in the liquids were determined by analyzing samples of the liquid phase in equilibrium with the solid.

To this purpose, liquid–solid systems were agitated in a thermostatic bath (±0.1 °C). After equilibrium was reached,

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Table I. Solubility of Acetic Acid in Chloroform, Carbon Tetrachloride, and Benzene

chloroform		carbon tetrachloride		benzene	
T, °C	x_2	T, °C	x_2	T, °C	x_2
−3.9	0.685	−4.3	0.440	−3.3	0.535
−3.0	0.700	−2.8	0.495	−1.1	0.595
2.2	0.780	−1.3	0.547	2.2	0.690
4.3	0.805	0.7	0.595	4.2	0.735
7.9	0.860	2.3	0.650	5.3	0.770
10.0	0.900	5.2	0.727	6.2	0.780
12.5	0.930	7.5	0.795	7.3	0.815
		10.0	0.870	10.0	0.880
		12.0	0.925	11.9	0.915

Table II. Vapor-Liquid Equilibrium Data of the System Carbon Tetrachloride-Acetic Acid at 100 mmHg

T, °C	x_2	y_2
23.5	0.065	0.033
23.7	0.110	0.050
24.0	0.162	0.062
24.4	0.217	0.080
25.4	0.344	0.106
26.0	0.407	0.128
27.1	0.528	0.158
27.7	0.656	0.157
30.2	0.708	0.215
37.1	0.872	0.345
43.7	0.932	0.454

the solid was allowed to settle in the flasks and supernatant sample was removed for the analysis of concentration. Each determination was repeated five times with good reproducibility; calculated standard deviations are of the order of 0.005.

Vapor-liquid equilibrium data at 100 mmHg for the system carbon tetrachloride-acetic acid, at 80 mmHg for the system benzene-acetic acid, were determined with a Gillespie still modified by the method of Fowler and Norris (*1*).

To reduce the influence of pressure oscillations on the equilibrium temperature, pure acetic acid and the solution were boiled in two separated stills, connected through condensers to a mercury manometer. The difference between boiling temperatures was determined by differential measurement of the signals of the thermocouples from the stills. The emf was indicated by a Leeds and Northrup recorder.

Saturation pressures of acetic acid were determined in the same way in comparison to distilled water.

Accuracy of the temperature measurements was ±0.05 °C. Analyses of mixture samples from both equilibria were carried out by means of a precision refractometer; at 25 °C calibration curves of the three systems do not deviate much from straight lines. The accuracy of mole fraction data was estimated to ±0.005.

Purity of the components (Carlo Erba) was 99.9 wt % for acetic acid, 99.9% for carbon tetrachloride, 99.0% for chloroform, and 99.5% for benzene.

Solubilities of solid acetic acid in the liquid solvents are reported in Table I; vapor-liquid equilibrium data are reported in Tables II and III.

Data Reduction

Activity coefficients of acetic acid were obtained from the experimental solubilities of the solid acid in the liquid solvents through the equilibrium relationship (*2*)

$$\ln \gamma_2 = -\ln x_2 + \frac{\Delta H_t}{RT_t}\left(1 - \frac{T_t}{T}\right) + \frac{\Delta C_p}{R}\left(\frac{T_t}{T} - 1 - \ln \frac{T_t}{T}\right) \tag{1}$$

Table III. Vapor-Liquid Equilibrium Data of the System Benzene (1)-Acetic Acid (2) at 80 mmHg

T, °C	x_2	y_2
23.2	0.050	0.032
23.8	0.118	0.057
24.0	0.170	0.073
24.1	0.180	0.077
25.2	0.318	0.120
26.1	0.430	0.165
27.8	0.560	0.232
29.8	0.677	0.319
31.6	0.752	0.309
36.1	0.848	0.437
38.6	0.885	0.501
38.8	0.890	0.494
49.2	0.963	0.744

Table IV. Values of the Constants of Equation 5[a]

	A	B	C	D
CH_3COOH	−1196.072	2.331	0.005	−2.112
CCl_4	−1934.417	4.404	−0.008	0.113
C_6H_6	−1672.571	3.318	−0.002	0.027

[a] Temperatures are in K, saturation pressures in mmHg.

In data reduction, normal melting temperature and heat of fusion were substituted in eq 1 to the correspondent values pertaining to the triple point (*2*).

The last term of eq 1 has a negligible effect on the values of activity coefficients.

Literature values (*3*) of the heat of fusion (2756.9 cal/mol) and of the melting temperature (289.8 K) were used.

Activity coefficients of both components were obtained from the vapor-liquid equilibrium data, treating the vapor phase as an ideal ternary system containing monomer (acetic acid), dimer, and solvent. Mole fractions in the vapor phase and saturation pressures of the monomer can be obtained from the temperature dependence of the dimerization equilibrium costant, as usual (see for example ref 4-6). Without detailing the procedure, the equilibrium relationships which allow the evaluation of activity coefficients are

$$\gamma_2 = \frac{1}{x_2}\,\frac{([1 + 4Ky_2(2 - y_2)p]^{1/2} - 1)/2(2 - y_2)K}{[(1 + 4Kp_{s2})^{1/2} - 1]/2K} \tag{2}$$

$$\gamma_1 = \frac{p - p_m(1 + Kp_m)}{x_1 p_{s1}} \tag{3}$$

In eq 2 the numerator represents the partial pressure p_m of the monomer and the denominator the saturation pressure of the monomer.

The dimerization constant is normally derived correlating volumetric data of pure associated vapor (acetic acid). In this work the dimerization constant was calculated by the following equation used by other authors (*7*).

$$\log K = -10.4205 + 3166/T \tag{4}$$

Accuracy of the saturation pressure of pure components in the reduction of vapor-liquid equilibrium data was emphasized by Van Ness et al. (*8*). Therefore saturation pressures were calculated with the following equation:

$$\log p_s = A/T + B \log T + CT + D \tag{5}$$

The values of the four constants were obtained by fitting experimental data (*3*, *9*, *10*) in the relevant temperature range and are reported in Table IV.

Discussion

Figure 1 shows the activity coefficients of the system carbon tetrachloride-acetic acid obtained from both phase equilibria. Activity coefficients from isothermal and isobaric vapor-liquid

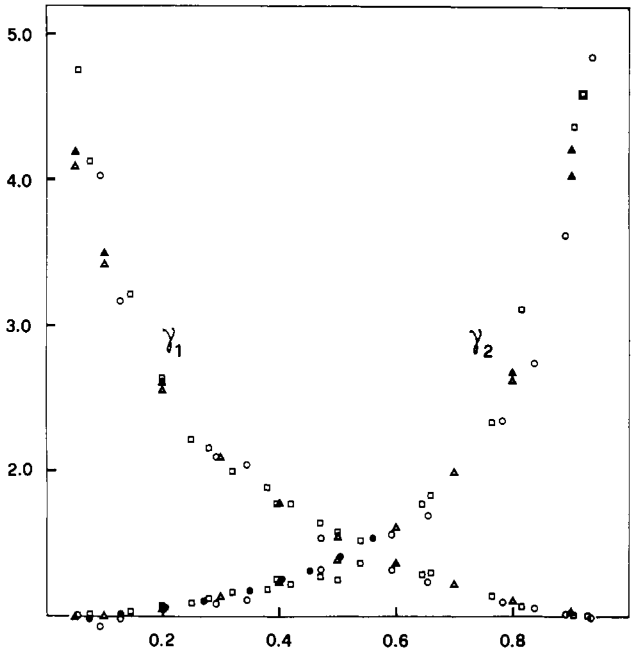

Figure 1. Experimental activity coefficients for the system carbon tetrachloride (1)-acetic acid (2) (○, from vapor-liquid data; ●, from solid-liquid data; □, from vapor-liquid data at 417 mmHg (*7*); ▲▲, from vapor-liquid data at 40 and 20 °C (*10*)).

equilibrium data of other authors (*7*, *10*) are also shown.

It can be observed that the various sets of activity coefficients agree practically within the limits of experimental uncertainties.

The temperature dependence of activity coefficients appears to be low; on the other hand this could be predicted from the following thermodynamic relationship:

$$\ln \gamma_2 = \ln \gamma_2^{(0)} + \frac{\bar{H}_2 - H_2}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{6}$$

where $\gamma_2^{(0)}$ is the activity coefficient at the temperature T_0. Equation 6 is valid for negligible temperature dependence of the heat of mixing in the considered temperature region.

The second term of eq 6, calculated from the experimental heat of mixing data of Liszi (*11*), is 1 order of magnitude less than the first term.

Important, however, is the remarkable agreement between the activity coefficients of acetic acid obtained from solid-liquid and vapor-liquid equilibrium data.

This result indicates not only the reliability of the measurements but also the essential correctness of the procedure of treating vapor-phase nonidealities neglecting the influence of the other component on the dimerization of the associated substance.

Therefore, one equilibrium could be quantitatively predicted from activity coefficient data obtained from the other equilibrium and vice versa (the values of activity coefficients of the solvent from solid-liquid data could be obtained by integrating the Gibbs-Duhem equation).

A similar conclusion holds for the system benzene-acetic acid: positive deviations from ideality of the liquid phase are comparable when obtained from both equilibria.

Good results were obtained when calculating solubilities of acetic acid in carbon tetrachloride and in benzene by the Wilson equation (see Appendix) with binary parameters obtained from vapor-liquid data. Small deviations are due to partial inadequacy of the Wilson equation in correlating experimental activity coefficients.

Isothermal (*12*) and isobaric (*13*, *14*) vapor-liquid equilibrium data clearly show that chloroform-acetic acid liquid solution is ideal if dimerization of the acid in the vapor phase is taken into account. In this case, the enthalpic (*15*) and entropic contributions to the excess Gibbs free energy cancel out.

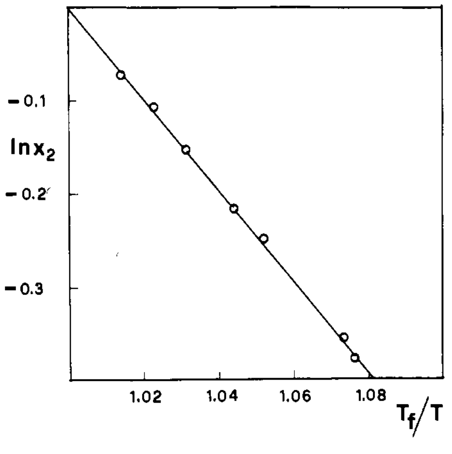

Figure 2. Experimental and calculated solubilities of solid acetic acid in chloroform.

Therefore solubilities of solid acetic acid in chloroform were calculated by eq 1 assuming $\gamma_2 = 1$. The excellent results in the comparison between experimental and calculated solubilities shown in Figure 2 confirm the ideality of this liquid solution.

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We are grateful to Mr. A. Prantera for his suggestions on the experimental part of the work.

Appendix

The Wilson equations are

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{7}$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{8}$$

with

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\frac{-(\lambda_{12} - \lambda_{11})}{RT} \tag{9}$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\frac{-(\lambda_{12} - \lambda_{22})}{RT} \tag{10}$$

Parameters of these equations were obtained by fitting experimental activity coefficients from vapor-liquid data reduction. For the minimization procedure the following objective function (*16*) was used:

$$F = \frac{\sum_i(\gamma_{1\text{exptl}} - \gamma_{1\text{calcd}})_i^2}{\sum_i(\gamma_{1\text{exptl}} - 1)_i^2} + \frac{\sum_i(\gamma_{2\text{exptl}} - \gamma_{2\text{calcd}})_i^2}{\sum_i(\gamma_{2\text{exptl}} - 1)_i^2} \tag{11}$$

Values of the binary parameters λ and standard deviations σ of activity coefficients are as follows: carbon tetrachloride-acetic acid $\lambda_{12} - \lambda_{11} = 13.56$ cal/mol, $\lambda_{12} - \lambda_{22} = 39.73$ cal/mol, $\sigma_1 = 0.117$, $\sigma_2 = 0.121$; benzene-acetic acid, $\lambda_{12} - \lambda_{11} = -2.76$ cal/mol, $\lambda_{12} - \lambda_{22} = 58.57$ cal/mol, $\sigma_1 = 0.075$, $\sigma_2 = 0.207$.

Glossary

A, B, C, D	constants in eq 5

ΔC_p	difference between specific heat of the liquid and the solid, cal/(mol K)
H	molar enthalpy, cal/mol
$\bar{H}$	partial molar enthalpy, cal/mol
ΔH	heat of fusion, cal/mol
K	dimerization equilibrium constant, mmHg^{-1}
p	pressure, mmHg
R	gas constant, cal/(mol K)
T	temperature, K
v	molar volume, cm^3/mol
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
γ	activity coefficient
λ	parameters of the Wilson equation, cal/mol

Subscripts

1	relative to the solvent
2	relative to acetic acid
f	at normal melting conditions
m	relative to the monomer
s	at saturation conditions
t	at the triple point

Literature Cited

(1) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor-Liquid Equilibrium", Pergamon, Oxford, 1967, Chapter 5.
(2) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1969, Chapter 9.
(3) R. C. Weast, "Handbook of Chemistry and Physics", The Chemical Rubber Co., 52nd ed., Cleveland, Ohio, 1971, Section C.
(4) Marek, J., Standart, G., *Collect. Czech. Chem. Commun.*, **19**, 1074 (1954).
(5) Sebastiani, E., Lacquaniti, L., *Chem. Eng. Sci.*, **22**, 1155 (1967).
(6) Chueh, C. F., *AIChE Symp. Ser.*, **70**, 110 (1974).
(7) Wisniak, J., Tamir, A., *J. Chem. Eng. Data*, **20**, 168 (1975).
(8) Van Ness, H. C., Byer, S. M., Gibbs, R. E., *AIChE J.*, **19**, 238 (1973).
(9) Unpublished data of saturation pressures, University of Rome, 1977.
(10) Miksch, G., Ratkovics, F., Kohler, F., *J. Chem. Thermodyn.*, **1**, 257 (1969).
(11) Liszi, J., *Acta Chim. Acad. Sci. Hung.*, **63**, 371 (1970).
(12) Campbell, A. N., Kartzmark, E. M., Gieskes, J. M. T. M., *Can. J. Chem.*, **41**, 407 (1963).
(13) Campbell, A. N., Gieskes, J. M. T. M., *Can. J. Chem.*, **42**, 186 (1964).
(14) Conti, J. J., Othmer, D. F., Gilmont, R., *J. Chem. Eng. Data*, **5**, 301 (1960).
(15) Campbell, A. N., Gieskes, J. M. T. M., *Can. J. Chem.*, **43**, 1004 (1965).
(16) Holmes, M. J., Van Winkle, M., *Ind. Eng. Chem.*, **62**, 21 (1970).

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Effect of Morpholine on Vapor–Liquid Equilibrium of the System Methylcyclohexane–Toluene

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The effect of morpholine on the vapor–liquid equilibrium of the methylcyclohexane–toluene system is reported at 760 mmHg and molar compositions of morpholine of 0.15, 0.30, and 0.45. An increase in the relative volatility and also a small increase in the boiling temperature with respect to the binary mixture are found. Vapor–liquid equilibrium data are also reported for the benzene–methanol and methylcyclohexane–toluene binary systems. Data for the latter systems have been correlated by the Wilson equation.

Vapor–liquid equilibrium data for the methylcyclohexane–toluene system have been determined at atmospheric (*1*) and at lower pressures (*2*). Activity coefficients, at constant composition, tend to increase as pressure is reduced (*2*), and therefore separation by distillation should be easier at low pressures.

The addition of a solvent to the binary mixture modifies the vapor–liquid equilibrium and therefore the relative volatilities, making possible the separation by extractive distillation. Morpholine and its derivatives have been used as extractive solvents for the separation of aromatic and aliphatic hydrocarbons (*3*). It is the purpose of this work to study the behavior of this solvent on a mixture of an aromatic and a cyclic aliphatic hydrocarbon.

Selectivities at infinite dilution for the mixture methylcyclohexane–toluene were determined by a chromatographic technique (*4*) and results were promising enough (*5*) to carry out a study of the vapor–liquid equilibrium in the presence of morpholine as a low volatile component.

Experimental Section

Vapor–liquid equilibrium data were determined in an Othmer still (*6*), similar to an apparatus previously described (*7*). Teflon stemmed valves were used to avoid greased stopcocks. The boiling point temperature was measured within an accuracy of ±0.05 °C by using a mercury-in-glass thermometer (0.1 °C divisions) calibrated against a standard thermometer.

To avoid concentration and temperature gradients in the liquid phase, magnetic stirring was provided at the bottom of the still. A pressure of 760 mmHg was maintained by using a water column and pumping through it a small amount of dried air. The difference with atmospheric local pressure was measured with a butyl phthalate manometer.

The local pressure in the laboratory was measured by a mercury manometer and a cathetometer with an accuracy of ±0.05 mmHg. All pressures were corrected to the equivalent height of a mercury column at 0 °C and standard gravity.

The operation of the equilibrium still was checked with the binary system benzene–methanol. Analysis of vapor and liquid samples was made by measuring densities and refractive indices (PAY refractometer of the Abbe type) and by gas–liquid chromatography (Hewlett-Packard 5710, flame ionization detector). Calibration curves had been previously determined for mixtures of known composition.

Densities were measured with an Ostwald type picnometer with an accuracy estimated of ±0.0002 g/cm^3.

Refractive indices were determined with an accuracy of ±0.0001 at 25.00 ± 0.10 °C. A deviation of ±0.0001 in refractive index is equivalent to a variation of 0.002 in mole fraction.

For the ternary system studied in this work, gas chromatography was used as the analytical method, obtaining compositions by the internal standard technique. This method is insensitive to changes in sample size and makes it possible to check the composition of the extractive solvent in the liquid phase. A previous calibration of the chromatograph with benzene–methylcyclohexane–morpholine mixtures of known composition showed an accuracy in the analysis of liquid and

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