J. Chem. Eng. Data **1983**, *28*, 328–330

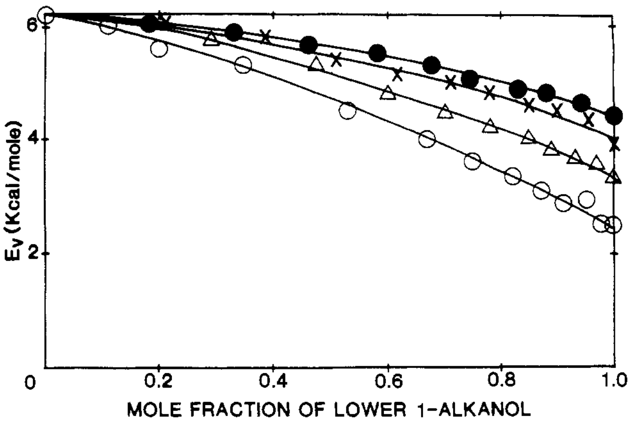

Figure 2. Viscous heat vs. mole fraction of lower 1-alkanol for binary mixtures of C_9 with C_1, C_2, C_3, and C_4: (○) C_1–C_9; (△) C_2–C_9; (×) C_3–C_9; (●) C_4–C_9.

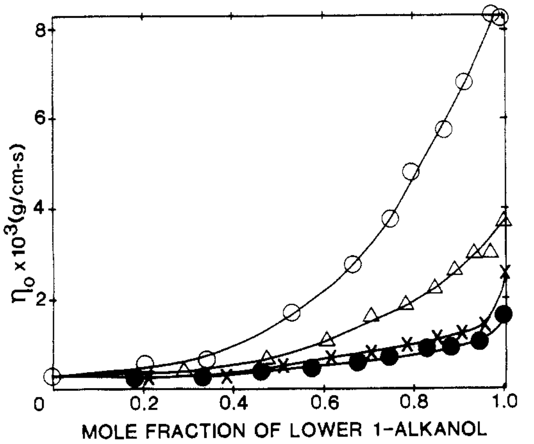

Figure 3. Preexponential factor vs. mole fraction of lower 1-alkanol for binary mixtures of C_9 with C_1, C_2, C_3, and C_4: (○) C_1–C_9; (△) C_2–C_9; (×) C_3–C_9; (●) C_4–C_9.

for all mixtures investigated are available as supplementary material.

Glossary

A, B, C, D, E	polynomial parameters
M_1	molecular weight of the lower component in a binary mixture
M_2	molecular weight of the higher component in a binary mixture
$\bar{V}$	molar volume of a sample
$\bar{V}_1$, $\bar{V}_2$	molar volumes of lower and higher components, respectively, in a binary mixture
X_1	mole fraction of the lower component in a binary mixture
X_2	mole fraction of the higher component in a binary mixture
α_{12}, α_{21}	interaction parameters
β_{12}, β_{21}	coefficients which need to be determined by eq 2
η	viscosity of a sample
η_1, η_2	viscosity of lower and higher components, respectively, in a binary mixture
ρ	density of a sample

Registry No. 1-Decanol, 112-30-1; 1-nonanol, 143-08-8; 1-octanol, 111-87-5; 1-heptanol, 111-70-6; 1-butanol, 71-36-3; 1-propanol, 71-23-8; ethanol, 64-17-5; methanol, 67-56-1.

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Supplementary Material Available: Table of rms errors for fits of viscosities of mixtures to various equations, and three figures for viscous heats and three figures for preexponential factors as functions of mole fractions of lower 1-alkanols in binary mixtures of 1-alkanols (9 pages). Ordering information is given on any current masthead page.

Solubility of Solid Acetic Acid in Liquid Organic Solvents

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The solubilities of acetic acid in some organic solvents (*n*-heptane, cyclopentane, carbon tetrachloride, toluene, chloroform, ethyl acetoacetate, methanol, ethanol, and acetone) have been measured for temperatures ranging from melting point to −30 °C. The results are compared with those predicted with UNIFAC and those calculated with the NRTL equation (vapor–liquid equilibrium (VLE) parameters).

Introduction

The experimental measurements of vapor–liquid (VLE), liquid–liquid (LLE), and liquid–solid equilibria available provide an abundance of information both theoretical and of interest in process design. While numerous experimental data are readily available for the first two types of equilibria (VLE and LLE), this is not so for liquid–solid equilibria (*1*, *2*).

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Table I. Solubilities of Acetic Acid in Some Common Organic Solvents

t, °C	X_2	γ_{exptl}[a]	γ_{calcd}[b]	t, °C	X_2	γ_{exptl}[a]	γ_{calcd}[b]	t, °C	X_2	γ_{exptl}[a]	γ_{calcd}[b]
Cyclopentane				Carbon Tetrachloride				*n*-Heptane			
12.5	0.905	1.0309	1.0189	12.0	0.925	0.9999	1.0074	14.8	0.935	1.0064	1.0179
11.9	0.870	1.0615	1.0352	10.0	0.870	1.0272	1.0235	13.7	0.885	1.0250	1.0521
11.3	0.845	1.0817	1.0499	7.5	0.795	1.0330	1.0626	12.4	0.680	1.2769	1.3497
10.1	0.780	1.1340	1.1009	5.2	0.727	1.1071	1.1532	11.9	0.550	1.7343	1.5809
8.7	0.775	1.1394	1.1056	3.8	0.689	1.1538	1.1752	9.5	0.305	2.5783	3.1149
6.5	0.430	1.9550	1.8767	2.3	0.650	1.1988	1.2079	7.5	0.240	3.0566	3.8679
5.6	0.345	2.3979	2.3436	0.7	0.595	1.2717	1.2949	5.4	0.205	3.3231	4.4221
4.3	0.275	2.9389	2.3436	−1.3	0.547	1.3327	1.3907	3.5	0.155	4.1062	5.4539
3.2	0.230	3.4447	3.4976	−2.8	0.495	1.4315	1.5209	1.7	0.145	3.9750	5.6190
−0.1	0.155	4.8106	5.0166	−4.3	0.440	1.5650	1.6981	−0.9	0.115	4.7113	6.7003
−2.4	0.115	6.2099	6.4046	−6.7	0.402	1.6317	1.8891	−2.6	0.080	6.3549	8.1240
−3.9	0.100	6.9404	7.1276	−9.0	0.365	1.7211	2.0395	−3.5	0.075	6.6018	8.3936
−9.0	0.095	7.7302	8.2013	−15.2	0.270	2.0507	2.7618	−4.9	0.075	6.2115	8.4873
−15.2	0.065	8.5183	9.9600	−21.1	0.170	2.8717	4.3463	−14.1	0.040	7.5520	12.8441
−21.0	0.055	8.8761	11.3653	−26.8	0.110	3.9073	6.4595	−29.2	0.020	8.3688	15.4985
Chloroform				Toluene				Ethanol			
12.5	0.930	1.0032	1.0217	10.0	0.870	1.0273	1.0241	11.2	0.922	1.0002	0.9944
10.0	0.900	0.9931	1.0247	7.2	0.805	1.0573	1.0564	7.2	0.861	0.9892	0.9868
6.9	0.855	0.9927	1.0485	4.6	0.735	1.1056	1.1092	1.9	0.816	0.9489	0.9777
4.3	0.805	0.9927	1.0712	2.4	0.678	1.1516	1.1683	−4.1	0.718	0.9628	0.9537
2.2	0.785	0.9965	1.0971	0.0	0.605	1.2348	1.2698	−6.7	0.700	0.9381	0.9481
0.7	0.740	0.9962	1.1347	−2.0	0.562	1.2804	1.3466	−8.0	0.657	0.9743	0.9364
−3.0	0.700	1.0087	1.1717	−4.0	0.485	1.4283	1.5240	−12.3	0.623	0.9435	0.9251
−3.9	0.675	1.0243	1.1964	−5.5	0.462	1.4567	1.5907	−14.9	0.595	0.9364	0.9159
−7.3	0.620	1.0448	1.2550	−9.0	0.400	1.5705	1.8099	−16.9	0.573	0.9324	0.9086
−9.0	0.615	1.0480	1.2443	−15.2	0.300	1.8456	2.3500	−20.3	0.548	0.9203	0.8973
−15.2	0.580	0.9543	1.3020	−21.1	0.260	1.8776	2.6892	−20.9	0.540	0.9154	0.8910
−21.1	0.520	0.9388	1.3769	−26.8	0.180	2.3878	3.5859	−24.9	0.503	0.8921	0.8834
−26.8	0.440	0.9551	1.4719					−29.4	0.457	0.8856	0.8669
−29.2	0.380	1.0701	1.5735								
Ethyl Acetoacetate				Methanol				Acetone			
10.4	0.915	0.9834	1.0366	10.4	0.934	0.9434	1.0230	10.5	0.918	0.9819	0.9968
7.1	0.855	0.9935	1.0384	7.1	0.880	0.9653	1.0444	3.7	0.821	0.9736	0.9844
2.7	0.782	0.9911	1.0128	2.7	0.820	0.9573	1.0568	−2.4	0.763	0.9358	0.9718
−2.0	0.730	0.9846	0.9659	−2.0	0.778	0.9238	1.0562	−7.9	0.681	0.9428	0.9478
−4.8	0.660	0.9942	0.8963	−7.7	0.712	0.9053	1.0420	−13.4	0.640	0.8980	0.9311
−9.0	0.610	1.0288	0.8420	−12.3	0.663	0.8866	1.0210	−18.6	0.575	0.8962	0.9012
−12.3	0.551	1.0668	0.7731	−17.1	0.602	0.8838	0.9866	−24.0	0.507	0.9021	0.8628
−14.9	0.510	1.0925	0.7230	−24.7	0.522	0.8635	0.9250	−29.0	0.460	0.8881	0.8297
−20.3	0.442	1.1239	0.6364	−30.3	0.464	0.8541	0.8725				
−24.5	0.420	1.0783	0.6003								
−29.0	0.365	1.1195	0.5312								

[a] exptl = experimental. [b] calcd = calculated from UNIFAC.

This article had the dual purpose of offering an additional contribution to existing experimental data and verifying the possibilities of predicting solubilities of solids in liquids by using the UNIFAC method. In fact, while it has been ascertained that the latter method represents with considerable accuracy VLE and LLE (*3–5*), much less attention has been given to the application to liquid–solid equilibria (*5–7*), i.e., at temperatures lower than the estimated one of the parameters.

Furthermore, the possibility was considered of extending the properties derived from the data reduction of the vapor–liquid equilibria to those of the liquid–solid (*8*), resorting in this case to one of the analytical tools which presents greater flexibility in the representation of VLE, namely, the NRTL equation (*9*). For this equation the parameters were estimated at temperatures relating to the VLE and, when these parameters were used, the liquid–solid equilibrium was predicted at much lower temperatures.

The paper aims, apart from making a contribution and addition to existing experimental data, at providing a reliable tool for the evaluation of the possibility that certain components can give rise to precipitates in the process liquids. The study was restricted, for the purpose of this paper, to systems in which acetic acid is the solid component, both owing to its particular solidification temperature (16.6 °C) and in view of its dipole moment (≈1.7 D), which ranks it halfway between nonpolar and strongly polar molecules.

Experimental Section

Solubilities of solid acetic acid in the liquid were determined by analyzing samples of the liquid phase in equilibrium with the solid. For this purpose liquid–solid systems were agitated in a thermostatic bath (±0.1 °C). 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.

Analyses of mixture samples were carried out by means of a precision refractometer as well as a Perkin-Elmer gas chromatograph (a 3-m column was packed with Carbowax 20M, +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; cyclopentane, 99.0; toluene, 99.5; chloroform, 99.4; *n*-heptane, 99.5; ethanol, 99.9; methanol, 99.9; carbon tetrachloride, 99.9; ethyl acetoacetate, 99.0; acetone, 99.7.

Experimental solubilities of acetic acid in *n*-heptane, cyclopentane, carbon tetrachloride, toluene, chloroform, ethyl acetoacetate, methanol, ethanol, and acetone are reported in Table I.

Data Reduction and Discussion

Activity coefficients of acetic acid have been obtained from

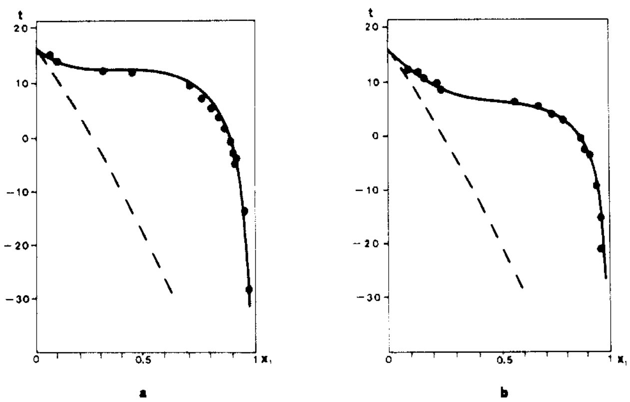

Figure 1. Solubilities of acetic acid in *n*-heptane (a) and in cyclopentane (b): (—) from UNIFAC; (- - -) ideal; (●) experimental.

the experimental solubilities of solid acetic acid in liquid solvents through the equilibrium relationship

$$\ln \gamma_2 = -\ln X_2 + \frac{\Delta H_t}{RT_t}\left(1 - \frac{T_t}{T}\right) + \frac{\Delta C_p}{R}\left(\frac{t_t}{T} - 1 - \ln \frac{T_t}{T}\right) \quad (1)$$

In data reduction, the normal melting temperature and the enthalpy of fusion have been substituted into eq 1 for the corresponding values pertaining to the triple point (*10*, *11*). The last term in eq 1 has little effect on the values of the activity coefficients and has therefore been neglected. Activity coefficients obtained from experimental solubilities have been compared with those predicted by using UNIFAC (Table I).

For nonpolar solvent systems rather pronounced positive deviations from Raoult's law ($\gamma_2 > 1$) are observed; these are correctly predicted with UNIFAC, which represents well the activity coefficients of these solutions, at least for temperatures down to 0 °C. At lower temperatures this representation deteriorates for some systems, even if always correct from a qualitative point of view.

As for the systems acetic acid–chloroform and acetic acid–ethyl acetoacetate, it should be observed that the solid–liquid equilibrium is predicted—within the limits of experimental error—also by assuming ideality ($\gamma_2 = 1$).

Negative deviations from Raoult's law ($\gamma_2 < 1$) are encountered in the systems acetic acid–methanol, acetic acid–ethanol, and acetic acid–acetone. Such deviations, which could be attributed to interaction of a chemical nature between the acid and the solvent, are likewise correctly predicted by using UNIFAC; in particular, for the latter two systems there is very good agreement over the entire range of temperatures examined.

Figures 1 and 2 give a comparison for some systems between solubilities predicted by using activity coefficients calculated with UNIFAC and experimental values. For the systems reported the agreement is excellent.

For those systems where negative deviations from ideality exist, the solubility of acetic acid was also calculated by means of the NRTL equation, employing the binary parameters obtained from the correlation of the respective vapor–liquid equilibria (*12*, *13*). Mean errors are 5.94% for the system acetic acid–methanol, 1.44% for acetic acid–ethanol, and 3.11% for acetic acid–acetone.

In conclusion, UNIFAC enables reliable estimates to be made for solubilities of solids in liquid solvents. Moreover, the possibility of predicting liquid–solid from vapor–liquid equilibria has been further corroborated.

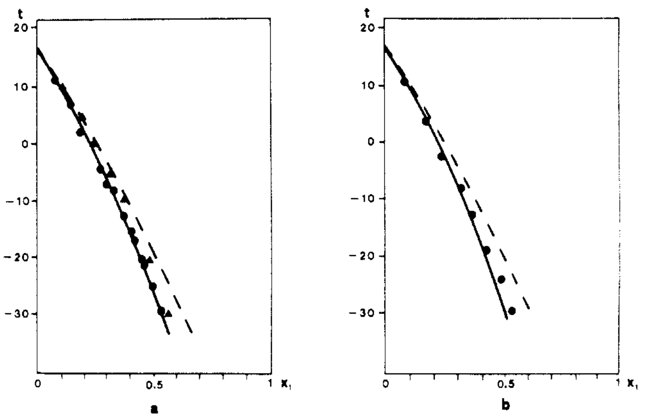

Figure 2. Solubilities of acetic acid in ethanol (a) and in acetone (b): (—) from UNIFAC, (- - -) ideal; (●) experimental, (▲) from ref *14*.

Glossary

ΔC_p	difference between specific heat of the liquid and that of the solid, cal/(mol K)
ΔH	enthalpy of fusion, cal/mol
R	gas constant, cal/(mol K)
t	temperature, °C
T	temperature, K
X	mole fraction in the liquid phase
γ	activity coefficient

Subscripts

1	relative to solvent
2	relative to acetic acid
t	at triple point

Registry No. Acetic acid, 64-19-7; heptane, 142-82-5; cyclopentane, 287-92-3; carbon tetrachloride, 56-23-5; toluene, 108-88-3; chloroform, 67-66-3; ethyl acetoacetate, 141-97-9; methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1.

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