Liquid−Liquid Equilibria for Acetic Anhydride + Selected Alkanes

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Liquid−liquid equilibria (LLE) temperatures for systems of acetic anhydride with hexane, heptane, octane, decane, cyclohexane, and methylcyclohexane have been measured between 314 K and the upper critical solution temperature (UCST). The coexistence curves were determined visually. They have a rather horizontal top, and their symmetry depends on the size of the alkane. Interaction parameters in the framework of the DISQUAC model for anhydride (CO−O−CO)/cyclohexane contacts are reported. The same set of interaction parameters can be used to represent, LLE, vapor−liquid equilibria, and molar excess enthalpies.

1. Introduction

We are engaged in a systematic study of mixtures containing the carbonyl (CO) and/or the oxygen (O) groups. Our final purpose is to characterize, experimentally and theoretically, intra- and intermolecular effects related to the presence of the CO and O groups in the same or in different molecules. So, we have reported data on molar excess enthalpies, H_m^E,[1,2] molar excess volumes, V_m^E,[3] vapor−liquid equilibria, VLE,[4] or liquid−liquid equilibria, LLE,[5] of linear organic carbonate (OCOO group) + organic solvent mixtures. Similarly, we have provided H_m^E and V_m^E measurements for systems formed by organic anhydrides (CO−O−CO group) and alkanes,[6−8] or for *n*-alkanone + oxaalkane mixtures.[9,10] On the other hand, the interactions present in the mentioned solutions have been characterized in terms of DISQUAC,[11−13] an extended group contribution model.[14]

As a continuation of this work, we report here LLE for mixtures containing acetic anhydride and hexane, heptane, octane, decane, methylcyclohexane, or cyclohexane. LLE data for the systems with heptane or cyclohexane are available in the literature.[15,16] We derive DISQUAC interaction parameters for organic anhydride + cyclohexane mixtures.

2. Experimental Section

2.1. Materials. Acetic anhydride, hexane, heptane (puriss p.a. ≥99.5 mol %), octane (purum >99 mol %), decane (purum ≥98 mol %), cyclohexane (puriss p.a. >99.5 mol %), and methylcyclohexane (purum >98 mol %) were from Fluka. Prior to the measurements, the chemicals were stored over molecular sieves (Union Carbide Type 4D from Fluka). All these chemicals were used without other further treatment. The densities, ρ, and the refractive indexes, n_D, at 298.15 K and atmospheric pressure were in good agreement with literature values (Table 1). The water contents, determined by the Karl Fischer method, were as follows (in mole %): 0.014, 0.018, 0.026, 0.013, 0.061, 0.049, and 0.013 for acetic anhydride, hexane, heptane, octane, decane, cyclohexane, and methylcyclohexane, respectively.

Table 1. Refractive Index, n_D, and Density, ρ, of Pure Compounds at 298.15 K

	n_D		ρ/kg·m^{-3}	
compound	this work	lit.	this work	lit.
acetic anhydride	1.3875	1.3879[39]	1075.02	1074.74[39]
hexane	1.3729	1.3723[40]	654.94	654.84[40]
heptane	1.3846	1.3851[40]	679.52	679.46[40]
octane	1.3954	1.3951[40]	698.56	698.62[40]
decane	1.4097	1.4097[40]	726.43	726.35[40]
cyclohexane	1.4240	1.4235[40]	773.83	773.89[40]
methylcyclohexane	1.4203	1.4206[40]	765.01	765.06[40]

2.2. Apparatus and Procedure. Mixtures were prepared by mass, with weighing accurate to ±0.0001 g, in Pyrex tubes of 0.9 cm i.d. and about 4 cm length, which then were immediately sealed by capping at atmospheric pressure and room temperature. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986.[17]

The coexistence curves of the binary mixtures were determined visually.[18−20] The samples in the sealed Pyrex tubes were placed in a thermostat bath a few hundredths of degree above the expected temperature, and the appearance of a second phase upon slow cooling (4 K h^{-1}) was noted. The separation temperatures were reproducible to ±0.02 K for temperatures near the upper critical solution temperature. The precision of the equilibrium composition is expected to be better than 0.0005 in mole fraction. The weighing technique gives a precision better than 0.0001 in mole fraction, but this is reduced slightly because of partial evaporation of the more volatile component to the free volume of the ampule ($\simeq$1.17 cm^3).

The temperature was measured with a precision of ±0.01 K and an estimated uncertainty of ±0.1 K with a Hewlett-Packard model 2804A quartz thermometer calibrated on the basis of the ITS-90 scale of temperature using the triple point of water.

2.3. Results. Table 2 lists the direct experimental results of the liquid−liquid equilibrium temperatures, *T*, versus the mole fraction of acetic anhydride, x_1, for the investigated mixtures (see also Figure 1).

All the systems show an upper critical solution temperature (UCST). LLE coexistence curves have a rather

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Table 2. Experimental Liquid−Liquid Equilibrium Temperatures for Acetic Anhydride (1) + Alkane (2) Mixtures

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
			Hexane				
0.1945	325.30	0.3571	334.21	0.4832	335.05	0.5666	334.64
0.2373	329.19	0.3652	334.32	0.4878	335.00	0.5963	334.40
0.2438	329.61	0.3829	334.57	0.5022	334.93	0.6498	332.49
0.2548	330.41	0.4112	334.92	0.5086	334.94	0.6590	332.10
0.2590	330.91	0.4173	334.97	0.5183	334.93	0.6606	331.90
0.2707	331.64	0.4194	334.96	0.5198	334.93	0.6627	332.05
0.2948	332.84	0.4356	334.99	0.5235	334.93	0.6748	331.40
0.3147	333.49	0.4477	334.99	0.5351	334.90	0.7522	326.11
0.3282	333.73	0.4634	335.00	0.5430	334.86	0.7846	323.20
0.3360	333.84	0.4658	334.99				
			Heptane				
0.1477	323.95	0.4354	342.22	0.5204	342.47	0.6646	341.48
0.1567	325.46	0.4454	342.24	0.5319	342.57	0.6662	341.34
0.1959	329.97	0.4475	342.51	0.5402	342.52	0.6980	340.02
0.2300	333.56	0.4512	342.43	0.5536	342.43	0.6947	340.40
0.2638	336.40	0.4756	342.58	0.5618	342.40	0.7162	339.07
0.2737	337.04	0.4815	342.63	0.5683	342.64	0.7377	338.26
0.3313	340.01	0.4850	342.57	0.5828	342.42	0.8063	331.87
0.3401	340.40	0.4928	342.47	0.5991	342.17	0.8423	326.95
0.3779	341.37	0.5196	342.53	0.6098	342.13	0.9056	314.69
			Octane				
0.2710	341.44	0.4506	349.47	0.5650	349.89	0.6948	348.84
0.3141	344.64	0.4709	349.62	0.5655	349.90	0.7164	348.02
0.3319	346.09	0.4847	349.71	0.5933	349.87	0.7475	346.69
0.3727	347.57	0.5017	349.78	0.6002	349.86	0.7844	344.41
0.4103	348.66	0.5203	349.84	0.6276	349.74	0.8195	340.91
0.4233	348.98	0.5447	349.88	0.6593	349.46	0.8423	337.07
0.4302	349.18						
			Decane				
0.4930	362.98	0.5604	363.71	0.6457	363.83	0.7321	363.18
0.5146	363.31	0.5924	363.82	0.6865	363.72	0.7503	362.74
0.5416	363.59	0.6233	363.85	0.7114	363.53		
			Cyclohexane				
0.1726	319.72	0.2799	324.70	0.4276	325.47	0.5156	325.12
0.1872	320.82	0.3164	325.14	0.4387	325.46	0.5479	324.64
0.1964	321.70	0.3440	325.31	0.4460	325.45	0.5766	324.02
0.2134	322.37	0.3858	325.45	0.4649	325.41	0.6114	322.76
0.2307	323.16	0.4076	325.47	0.4872	325.31	0.6587	320.53
0.2650	324.25	0.4181	325.48	0.4960	325.28	0.7064	317.27
			Methylcyclohexane				
0.1922	322.09	0.3643	328.97	0.4873	329.28	0.6588	326.85
0.2214	324.14	0.3899	329.21	0.5131	329.25	0.6844	325.53
0.2505	325.80	0.4005	329.25	0.5324	329.20	0.7071	324.26
0.2679	326.64	0.4254	329.27	0.5687	328.93	0.7129	323.63
0.2884	327.33	0.4404	329.31	0.5922	328.60	0.7247	322.89
0.3236	328.36	0.4630	329.30	0.6339	327.73	0.7305	321.69
0.3639	328.94						

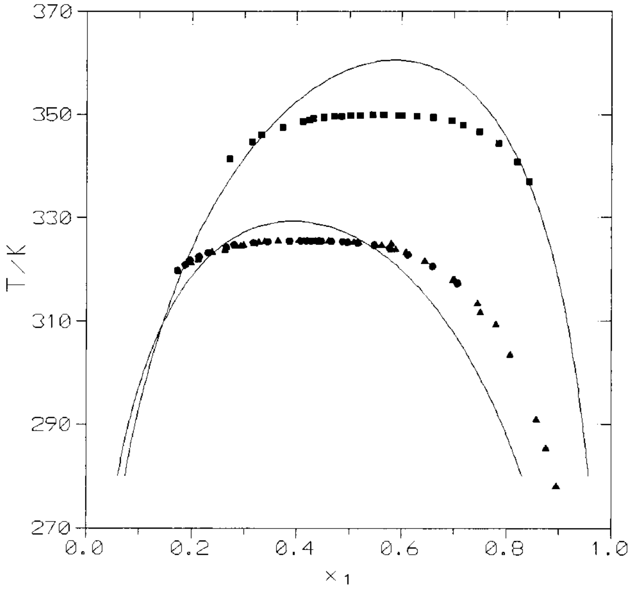

Figure 1. LLE of acetic anhydride (1) + alkanes (2) mixtures. Points, experimental results: cyclohexane (▲, ref 16; ●, this work); octane (■, this work). Solid lines, DISQUAC calculations.

Table 3. Coefficients in Eq 1 for the Fitting of the (x_1, T) Pairs Given in Table 2 for Acetic Anhydride (1) + Alkane (2) Mixtures[a]

N[b]	m	K	α	T_c/K	x_{1c}	σ/K
			Acetic Anhydride (1) + Hexane (2)			
38	2.95	−397	1.17	335.00	0.466	0.116
			Acetic Anhydride (1) + Heptane (2)			
36	3.06	−439	0.87	342.52	0.521	0.116
			Acetic Anhydride (1) + Octane (2)			
25	3.30	−608	0.78	349.83	0.560	0.145
			Acetic Anhydride (1) + Decane (2)			
11	2.98	−365	0.51	363.84	0.628	0.010
			Acetic Anhydride (1) + Cyclohexane (2)			
24	3.11	−394	1.23	323.46	0.409	0.071
			Acetic Anhydride (1) + Methylcyclohexane (2)			
25	3.26	−549	0.87	329.28	0.472	0.126

[a] σ is the standard deviation defined by eq 5. T_c and x_{1c} are the coordinates for the critical points. [b] Number of experimental data points.

horizontal top, and their symmetry depends on the size of the alkane.[5,21,22] In acetic anhydride + alkanes mixtures, the UCST increases with the length of the second component (Table 3). The same trends are encountered in solutions of alkoxyethanols[21,22] or n-alkanones[23] with alkanes or in sulfolane + 1-alkanol mixtures.[24]

The coordinates of the critical points, x_{1c} and T_c (Table 3), were obtained by reducing the experimental data with the equation[25,26]

$$T/\mathrm{K} = T_c/\mathrm{K} + k|y - y_c|^m \tag{1}$$

where

$$y = \frac{\alpha x_1}{1 + x_1(\alpha - 1)} \tag{2}$$

$$y_c = \frac{\alpha x_{1c}}{1 + x_{1c}(\alpha - 1)} \tag{3}$$

In eqs 1−3, m, k, α, T_c, and x_{1c} are the coefficients to be fitted to the experimental results. When α = 1, eq 1 is similar to the well-known equation[27−29]

$$\Delta\lambda_1 = B\tau^{\beta} \tag{4}$$

where $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ is the so-called order parameter, which can be any density variable in the conjugate phase (in our case $\lambda_1 = x_1$), τ is the reduced temperature $(T_c - T)/T_c$, and β is a critical exponent corresponding to this order parameter. The β value depends on the theory applied to its determination.[27,29] More detail is given elsewhere.[30]

The fitting was developed using the Marquardt algorithm[31] with all the points weighted equally. Results are collected in Table 3. Also listed is the standard deviation defined by

$$(\sigma(T)/\mathrm{K}) = [\textstyle\sum(T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}})^2/(N - n)]^{1/2} \tag{5}$$

where N and n stand for the number of data points and the number of fitted parameters, respectively. We note that eq 1 fits well the experimental data.

Table 4. Coordinates of Critical Points (x_{1c}, T_c) of Acetic Anhydride (1) + Alkanes (2) and Comparison with DISQUAC Results Using the Interaction Parameters from Table 5

	T_c/K		x_{1c}		
alkane	exp	DQ	exp	DQ	ref
hexane	335.00	341.3	0.466	0.486	this work
heptane	342.52	351.6	0.521	0.540	this work
	341.67		0.529		15
octane	349.83	360.4	0.560	0.588	this work
decane	363.84	374.6	0.628	0.664	this work
cyclohexane	325.46	329.3	0.409	0.391	this work
	325.7				16
	325.86		0.415		41
methylcyclohexane[a]	329.28	332.0	0.472	0.450	this work

[a] Assumed as an alkane in DISQUAC calculations.[12]

For mixtures including heptane or cyclohexane, our critical points are in good agreement with literature values (Table 4, see also Figure 1)

3. DISQUAC Model

In the framework of DISQUAC, solutions of organic anhydrides and cyclohexane are regarded as possessing three types of surface: type a, aliphatic, CH_3, or CH_2 in anhydrides; type n, CO−O−CO in anhydrides; and type c, cyclic c-CH_2 in cyclohexane. The total relative molecular volumes, the surfaces, and the molecular surface fractions of the mixture components are calculated additively on the basis of the group volumes and surfaces recommended by Bondi.[32] The geometrical parameters are given elsewhere.[11,33,34]

The equations used to calculate the excess functions are well-known.[34] The interactional terms in the excess functions contain a dispersive (DIS) and a quasichemical (QUAC) contribution which are obtained independently by the classical formulas and then simply added. The degree of nonrandomness is thus expressed by the relative amounts of the DIS and QUAC terms:

$$G_m^E = G_m^{E,COMB} + G_m^{E,DIS} + G_m^{E,QUAC} \tag{6}$$

$$H_m^E = H_m^{E,DIS} + H_m^{E;QUAC} \tag{7}$$

where $G_m^{E,COMB}$ is the Flory−Huggins combinatorial term.[33] For the QUAC part, as coordination number the reference value is used, that is $z = 4$.

The temperature dependence of the interaction parameters is expressed in terms of the DIS and/or QUAC interchange coefficients, $C_{st,1}^{DIS/QUAC}$, where st = a, c, or n and $l = 1$ for Gibbs energy, $l = 2$ for enthalpy, or $l = 3$ for heat capacity.

The three type of surface generate three pairs of contacts: (a, c), (a, n), and (c, n).

The (a, c) contacts are characterized by DIS parameters only, which are determined from the thermodynamic properties of cyclohexane + *n*-alkane mixtures.[33]

The (a, n) contacts are characterized by DIS and QUAC parameters calculated from the thermodynamic properties of organic anhydride + *n*-alkane systems.[11]

So, only the (c, n) contacts must be fitted. In the present case, the fitting of the interaction parameters is somewhat difficult because of the lack of experimental data, as well as the fact that the acetic anhydride + cyclohexane mixture shows a miscibility gap. The general procedure applied is explained in detail elsewhere.[24] Nevertheless, it is important to remark that calculations were developed assuming that $C_{an,l}^{QUAC} = C_{cn,l}^{QUAC}$ as in many other applications.[12,35] On the other hand, we used $C_{cn,3}^{DIS/QUAC} = 0$. The final parameters are listed in Table 5.

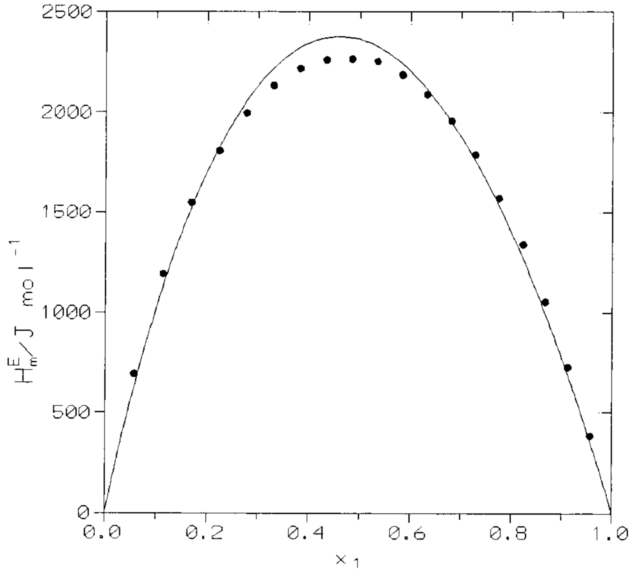

Figure 2. H_m^Eat 363.15 K of the acetic anhydride (1) + cyclohexane (2) mixture: points, experimental results;[42] solid line, DISQUAC calculations.

Table 5. Interchange Coefficients, Dispersive, $C_{cn,l}^{DIS}$, and Quasichemical, $C_{cn,l}^{QUAC}$ (l = 1, Gibbs Energy; l = 2, Enthalpy), for (c, n) Contacts (Type c, c-CH_2 in Cyclohexane; Type n, CO−O−CO in $CH_3(CH_2)_{u-1}CO{-}O{-}CO(CH_2)_{v-1}CH_3$) in Organic Anhydride + Cyclohexane Mixtures

u	v	$C_{cn,1}^{DIS}$	$C_{cn,2}^{DIS}$	$C_{cn,1}^{QUAC}$	$C_{cn,2}^{QUAC}$
1	1	1.06	2.65	3.00	3.75
1	>1	1.06	2.65	2.95[a]	3.60[a]
>1	>1	1.06	2.65	2.90	3.55

[a] Estimated.

4. Discussion

Table 4 and Figures 1 and 2 show comparisons between the experimental data and the DISQUAC calculations. It is remarkable that the same set of interaction parameters can be used to represent quite accurately different thermodynamic properties, such as VLE, H_m^E, or LLE. DISQUAC predicts an azeotrope for the acetic anhydride (1) + cyclohexane (2) mixture at 353.27 K, $x_1 = 0.016$, and 99.6 kPa. At the same temperature, the experimental values are $x_1 = 0.065$ at 101 kPa.[36]

It should be noted that the theoretical calculations on the LLE are developed under the basic and wrong assumption that G_m^E is an analytical function close to the critical point. This is an important shortcoming of any mean field theory, such as DISQUAC. In accord with the mentioned assumption, the model provides LLE curves which are too high at the UCST and too low at the LCST (lower critical solution temperature).[28,37] So, the calculated UCSTs are higher than the experimental values (Table 4).[24,38]

5. Conclusions

LLE have be measured for mixtures formed by acetic anhydride and hexane, heptane, octane, decane, cyclohexane, or methylcyclohexane. DISQUAC interaction parameters for the CO−O−CO/c-CH_2 contacts have been determined.

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