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Isobaric Vapor–Liquid Equilibrium Data for the Cyclohexanone + *N*-Methylacetamide System

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Isobaric vapor–liquid equilibrium data for the binary system cyclohexanone + *N*-methylacetamide were measured at 6.66, 13.33, and 26.66 kPa using a recirculating still. The experimental data obtained in this study are thermodynamically consistent according to the point-to-point consistency test and deviation from ideal behavior is small in all cases. The data were correlated with five liquid-phase activity coefficient models (Margules, Van Laar, Wilson, NRTL, and UNIQUAC).

Introduction

The experimental determination of vapor–liquid equilibrium (VLE) data is an important contribution to chemical engineering because the data are necessary for the correct design of distillation columns or any other equipment based on VLE processes.

On the other hand, group-contribution predictive methods such as UNIFAC (*1–3*) need a lot of experimental information to determine the interaction parameters of the functional groups. When this work began, the interaction parameters between the functional groups CONH and CH_2CO were not available. We decided therefore to study experimentally the VLE of cyclohexanone + *N*-methylacetamide.

Recently (*4*), interaction parameters have been proposed for the main group CON (with six subgroups) to represent amides. We hope that the present experimental data will contribute to improve this first estimate.

The equilibrium data at reduced pressures (6.66, 13.33, and 26.66 kPa) were obtained to avoid high boiling temperatures, which could damage both components. Previously, we determined the vapor pressures of pure *N*-methylacetamide and cyclohexanone.

Experimental Section

Chemicals. Cyclohexanone, from Proquimed Co., and *N*-methylacetamide from Merck were high-purity grade materials (>99.9% and >99.8%, respectively). They were not purified further. The purity of all chemicals was checked by gas chromatography (GC). The physical properties of these components are listed in Table I together with literature values (*5*).

Apparatus and Prodedure. The apparatus used in this work was an all-glass, dynamic recirculating still described by Walas (*6*), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures P from 0.25 up to 400 kPa, and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact with the temperature sensing element. The equilibrium temperature T was measured with a digital Fischer thermometer with an accuracy of 0.1 K and the pressure with a digital manometer with an accuracy of 0.01 kPa. VLE data were obtained at three pressures, 6.66, 13.33, and 26.66 kPa. The vapor pressures of pure components were measured with the same recirculating still.

Table I. Physical Properties of Chemicals: Densities *d*, Refractive Indexes *n*, and Boiling Temperatures T_b

compound	property	exptl	lit. (*5*)
cyclohexanone	d(293.15K)/(g cm^{-3})	0.948 51	0.9478
	n(293.15K)	1.4506	1.4507
	T_b(26.66kPa)/K	383.05	
N-methylacetamide	d(298.15K)/(g cm^{-3})	0.955 50	0.9571
	n(298.15K)	1.4301	1.4301
	T_b(26.66kPa)/K	436.95	

Table II. Vapor Pressure $P_i°$ Data as a Function of Temperature *T* and Fitted Antoine Constants *A*, *B*, and *C*

cyclohexanone		*N*-methylacetamide			
T/K	$P_i°$/kPa	T/K	$P_i°$/kPa	T/K	$P_i°$/kPa
318.15	1.69	353.15	0.60	404.25	8.15
330.25	3.11	359.75	0.94	407.15	9.18
341.95	5.35	360.15	0.97	409.75	10.31
349.95	7.61	362.85	1.10	411.95	11.07
355.85	9.69	367.85	1.48	414.05	11.99
370.35	16.92	374.35	2.10	416.05	13.14
382.25	25.90	379.35	2.76	416.55	13.21
392.35	36.02	384.75	3.48	418.15	14.00
402.25	48.95	390.75	4.57	419.95	15.01
410.55	62.41	393.05	5.11	422.05	16.15
419.85	81.01	395.85	5.70	423.65	17.27
424.05	90.43	397.65	6.21	425.95	18.73
425.35	94.04	399.95	7.00	426.85	19.26
428.25	101.37	401.45	7.28	427.75	19.86

	A	B	C
cyclohexanone	14.00725	3402.602	−65.8948
N-methylacetamide	12.49715	2658.377	−148.3473

In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was connected. It was kept at the boiling point for 15 min to ensure the stationary state. The latter was corroborated by the reproducibility of the results of GC analysis of successive samples. Once it was certain that the stationary state was reached, 3-μL samples of liquid and condensed vapor of the Cottrell pump were taken by means of special syringes under partial vacuum.

The composition was measured by GC with a Hewlett-Packard 5710 A GC with a thermal-conductivity detector. GC response peaks were integrated by using a Hewlett-Packard 3394 A integrator. The GC column was packed with Carbopack C (80/100) by Technokroma. Chromatographic analyses were carried out at the following conditions: temperature, 120 °C; gas carrier, helium (25 cm^3/min).

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Table III. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the Cyclohexanone (1) + *N*-Methylacetamide (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
6.66	0.000	0.000	399.15		
	0.028	0.294	391.65	2.007	1.005
	0.060	0.521	384.25	2.109	0.994
	0.111	0.697	377.15	1.927	0.943
	0.143	0.759	372.85	1.907	0.974
	0.192	0.835	367.85	1.877	0.926
	0.260	0.878	363.25	1.733	0.970
	0.298	0.895	361.05	1.675	0.997
	0.354	0.922	358.25	1.622	0.953
	0.433	0.937	355.25	1.521	1.053
	0.535	0.952	352.95	1.374	1.143
	0.598	0.960	351.75	1.303	1.172
	0.681	0.969	350.65	1.208	1.239
	0.752	0.976	349.65	1.150	1.316
	0.821	0.980	348.85	1.093	1.605
	0.917	0.990	347.75	1.037	1.812
	1.000	1.000	346.65		
13.33	0.000	0.000	416.75		
	0.026	0.232	410.15	1.948	1.008
	0.056	0.434	403.25	2.066	1.009
	0.105	0.618	395.55	1.966	0.994
	0.186	0.775	386.75	1.846	0.958
	0.287	0.858	380.25	1.652	0.941
	0.338	0.884	377.45	1.594	0.958
13.33	0.412	0.908	374.25	1.501	1.005
	0.526	0.929	371.05	1.352	1.137
	0.590	0.939	369.75	1.277	1.225
	0.661	0.948	368.75	1.196	1.312
	0.751	0.956	367.35	1.117	1.649
	0.828	0.970	366.15	1.076	1.731
	0.918	0.982	364.85	1.032	2.350
	1.000	1.000	363.75		
26.66	0.000	0.000	436.95		
	0.015	0.135	432.75	2.053	1.005
	0.053	0.348	425.45	1.851	1.008
	0.095	0.516	418.85	1.835	0.987
	0.114	0.572	416.25	1.815	0.982
	0.250	0.778	403.85	1.616	0.972
	0.283	0.805	402.05	1.560	0.960
	0.377	0.865	396.65	1.481	0.963
	0.491	0.900	392.65	1.341	1.046
	0.552	0.917	390.65	1.298	1.079
	0.670	0.934	388.35	1.174	1.280
	0.743	0.952	386.15	1.160	1.329
	0.830	0.967	385.25	1.086	1.446
	0.919	0.980	384.25	1.028	1.926
	1.000	1.000	383.05		

Table IV. Correlation Parameters for Activity Coefficients

P/kPa		A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD(y)	MAD(T)
6.66	Margules	0.6735[a]	1.5225[a]		1.9611	4.5837	0.0059	0.68
	Van Laar	0.7363[a]	1.6823[a]		2.0882	5.3779	0.0074	0.20
	Wilson	−277.34[b]	1512.91[b]		2.1217	5.9758	0.0083	0.19
	NRTL	1453.03[b]	−257.99[b]	0.3152[a]	2.0200	5.4040	0.0074	0.28
	UNIQUAC	901.27[b]	−362.47[b]		2.1404	5.4450	0.0073	0.20
13.33	Margules	0.7188	1.3725		2.0520	3.9452	0.0047	0.56
	Van Laar	0.7482	1.3929		2.1132	4.0265	0.0075	0.19
	Wilson	−182.29	1225.43		2.1695	4.2261	0.0078	0.18
	NRTL	1180.96	−159.52	0.3104	2.0615	4.0426	0.0079	0.21
	UNIQUAC	771.28	−319.28		2.1294	4.0964	0.0076	0.19
26.66	Margules	0.6212	1.2104		1.8612	3.3548	0.0072	0.60
	Van Laar	0.6401	1.3368		1.8967	3.8068	0.0090	0.34
	Wilson	−282.55	1330.17		1.9835	3.9490	0.0086	0.35
	NRTL	1310.47	−287.12	0.3013	1.8722	3.6642	0.0098	0.38
	UNIQUAC	885.00	−390.29		1.9212	3.8913	0.0086	0.32

[a] Dimensionless. [b] Calories per mole.

The GC was calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made of each liquid and each vapor composition.

Results and Discussion

The experimental vapor pressure data of the pure components $P_i°$ are shown in Table II, together with the fitted constants of the Antoine equation

$$\ln\,(P_i°/\mathrm{kPa}) = A - \frac{B}{(T/\mathrm{K}) + C} \qquad (1)$$

using a linear regression method with the following objective function F:

$$F = \sum [\ln P_{\mathrm{exptl}} - \ln P_{\mathrm{calcd}}]^2 \qquad (2)$$

The experimental VLE data for the binary system at 6.66, 13.33, and 26.66 kPa are presented in Table III and Figure 1.

The liquid-phase activity coefficients γ_i were calculated assuming vapor-phase ideality and neglecting the Poynting factor. The fugacity coefficients estimated from the Redlich–Kwong (*7*) equation of state modified by Soave (*8*) are nearly unity.

The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness et al. (*9*), modified by Fredenslund et al. (*1*), using a third-order Legendre polynomial. According to this test, the data are considered consistent if the mean absolute deviation in y, MAD(y), is less than 0.01. In that case, MAD(y) = 0.0076 for P = 6.66 kPa, 0.0075 for P = 13.33 kPa, and 0.0094 for P = 26.66 kPa, thereby showing them to be thermodynamically consistent.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*10*). The adjustable parameters A_{12}, A_{21}, and α_{12} for the correlation equations, mean absolute deviations, and activity coefficients at infinite dilution γ_i^∞ are listed in Table IV. Mean absolute deviations between experimental and calculated temperatures, MAD(T), and vapor compositions, MAD(y), are of the order of the estimated experimental uncertainties.

For fitting the binary parameters the Rosenbrok method (*11*) was used to minimize the following objective function, using the activity coefficients obtained from the consistency

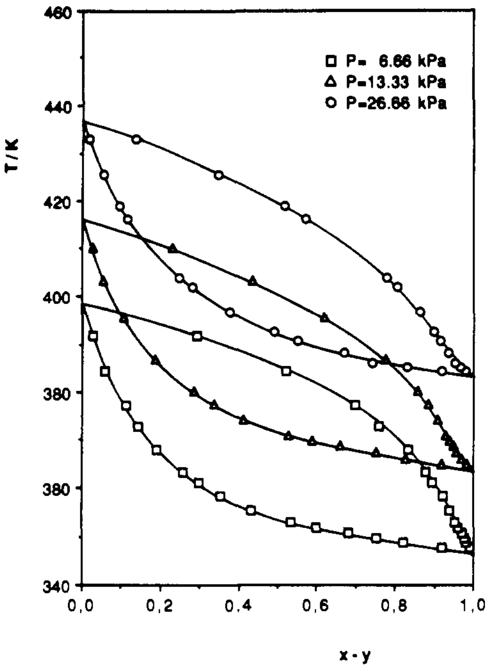

Figure 1. Temperature T vs composition (x_1, y_1) diagram for the system cyclohexanone (1) + N-methylacetamide (2) at constant pressure, P = 6.66, 13.33, and 26.66 kPa.

test as experimental values:

$$F = \sum_n \sum_i \left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}} \right)^2_{i,n} \tag{3}$$

where n is the number of data points.

According to the data reported in Table III, the cyclohexanone + N-methylacetamide system shows positive deviations from ideal behavior. In this system, the molecular interactions are quite complex. On the one hand, the dipole interactions in cyclohexanone and the self-association of N-methylacetamide contribute to positive deviations from ideality. On the other hand, the CO group of cyclohexanone interacts with the NH group of the amide, forming hydrogen bonds, and this results in negative deviations from ideal behavior. Therefore, the final deviation from ideality depends on the actual values of the different contributions. From the experimental results obtained in this work, we can conclude that the like interactions prevail between the CO and NH groups.

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