

VAPOUR-LIQUID EQUILIBRIUM IN THE METHANOL-ACETONITRILE SYSTEM

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The vapour-liquid equilibrium in the binary methanol-acetonitrile system was determined. The measurements were performed in isobaric conditions at pressures of 281.6, 423.4, 645.5 Torr and in isothermal conditions at 52.89 and 60.31°C in a recirculation apparatus of the Gillespie type. Measured data were correlated individually by the three-suffix Margules, three-suffix van Laar, Wilson, Renon, HMW, and Orye equations. The last four equations were also used for a simultaneous correlation of all the equilibrium data sets. Results of this simultaneous correlation showed that these equations describe well the investigated system in the whole experimental range with two temperature-independent constants.

As a part of the systematic study of binary mixtures in homologic series, we had investigated two series of the nonpolar hydrocarbon - n-alcohol type^{1,2} and started to study the third parallel series, in which the nonpolar component was replaced by a strongly polar one. As for the polar component, we selected acetonitrile whose dipole moment of 3.94 D ($13.1 \cdot 10^{-30}$ Cm) is considerable. Its binary systems with n-alcohols display large positive deviations from Raoult's law and, moreover, scarce literature data offer a wide area for experimental work. So, already for the first term of the series which is investigated in our work - the methanol-acetonitrile system - practically no literature information is available. The most relevant reason for this is probably, besides the toxicity, the difficult analysis of equilibrium mixtures.

EXPERIMENTAL

Preparation of Pure Substances

Methanol. Methanol, A.R. grade, was mixed with the Grignard reagent and the mixture was refluxed. The main portion of methanol was added to the boiling mixture and all was further boiled for about five hours. The dried product was rectified on a 40-plate bubble cap column and its final density and refractive index (d_D^{25} 0.7866, n_D^{20} 1.3285) agreed well with literature data³. The Fischer analysis showed that the water content was lower than 0.008 wt.%.

Acetonitrile. Acetonitrile, A.R. grade, was refluxed for several hours with a small amount of 1% KOH (1 ml of 1% KOH to 1 l of acetonitrile) to remove remnants of acrylonitrile. This was followed by rectification on a 150 cm-long column packed with stainless helices. The final drying of the product was performed on Linde 3A molecular sieves. The measured values of physicochemical constants (d_D^{25} 0.7766, n_D^{25} 1.3415) corresponded with those in the literature⁴.

Analysis of Equilibrium Mixtures

Popular physicochemical analytic methods such as measurements of refractive index, density, dielectric constant, and others fail for this system, since values of the corresponding physicochemical constants of pure components are extremely close to each other. This fact is not surprising as sizes and shapes of both molecules are also similar. In the same manner, spectroscopic methods do not give required accuracy or their evaluation is made difficult by the presence of associated molecules. Gas chromatography is also unsuitable since in a half of the concentration range its error would amount to at least 0.5 mol.%, which is too much for the given purpose. A purely chemical method would take too much time and its accuracy would be unacceptable, too. On the basis of our analysis of possibilities of the analytic methods outlined, finally we decided to employ interferometry.

The approximate composition of the analyzed mixture (within a 1 mol.% error) was found refractometrically by a Pulfrich refractometer using a preliminarily prepared calibration graph. For each analyzed mixture, two standard solutions of a concentration close to that of the analyzed mixture were prepared by weighing. Optical shifts of both standard solutions with respect to the analyzed solution were determined interferometrically. On the assumption of a linear relation between the refractive index and composition in a narrow concentration range (this assumption is well satisfied in our case), these data are sufficient for determining the composition of the analyzed mixture. The interferometric measurements were performed at room temperature and equilibrium cells for collecting the liquid and vapour phases were also thermostated to this temperature. The analysis of several solutions prepared by weighing showed that the maximum error of the analysis was not higher than 0.04 mol.%.

Apparatus

The vapour-liquid equilibrium was measured on a Gillespie still as modified by Otsuki and Williams. The experimental arrangement has been described in detail in one of our earlier communications⁵. In the usual arrangement of the measuring system at isobaric conditions the vacuum pump was controlled by a mercury manostat and the temperature was measured by a platinum resistance thermometer. At isothermal conditions — in contrast to our earlier measurements — we employed a new a.c. regulating relay. The sensing element was again a platinum resistance thermometer connected to an a.c. bridge. The a.c. signal from the unbalanced bridge is amplified and through the relay it controls an electromagnetic valve which transfers the vacuum from the first reservoir to the measuring system. The unfavourable effect of the large time constant of the regulating system was eliminated by blocking the input signal of the relay. The pressure drop between the first and second reservoir is maintained by the oil vacuum pump controlled by a liquid column manostat. In this manner, the temperature control in the adjusted system is guaranteed within 0.02°C, *i.e.* within experimental accuracy of the resistance thermometer. The pressure was measured indirectly by an ebulliometer filled with redistilled water and connected parallelly to the equilibrium still. The error of the pressure measurement was approximately 0.3 Torr.

TABLE I

Experimental Data from the Vapour-Liquid Equilibrium in the Methanol(1)-Acetonitrile(2) System

x_1	y_1	$t, ^\circ\text{C}$	x_1	y_1	$t, ^\circ\text{C}$
$P = 281.6 \text{ Torr}$					
0.0284	0.1095	50.64	0.5265	0.6230	39.98
0.0563	0.1816	48.99	0.5450	0.6315	39.96
0.1106	0.3024	46.18	0.6058	0.6568	39.74
0.1447	0.3497	45.16	0.6541	0.6829	39.62
0.2310	0.4449	42.98	0.6881	0.7035	39.60
0.2683	0.4774	42.26	0.7654	0.7479	39.60
0.3240	0.5111	41.63	0.7998	0.7734	39.65
0.3754	0.5419	41.04	0.8790	0.8393	40.01
0.4032	0.5566	40.69	0.9125	0.8711	40.24
0.4736	0.5970	40.30	0.9719	0.9536	40.98
$P = 423.4 \text{ Torr}$					
0.0361	0.1298	61.25	0.5074	0.6253	49.89
0.1110	0.2892	57.22	0.5712	0.6578	49.49
0.1355	0.3295	56.12	0.6383	0.6882	49.29
0.1791	0.3926	54.62	0.6870	0.7157	49.12
0.2595	0.4622	52.76	0.7542	0.7544	49.07
0.2902	0.4944	52.14	0.8161	0.7970	49.12
0.3315	0.5238	51.52	0.8471	0.8244	49.18
0.3738	0.5470	51.00	0.8935	0.8623	49.40
0.3960	0.5551	50.76	0.9254	0.9005	49.65
0.4726	0.6048	50.07	0.9653	0.9481	50.05
$P = 645.45 \text{ Torr}$					
0.0468	0.1518	72.86	0.5345	0.6369	60.47
0.1161	0.2983	69.01	0.5982	0.6805	60.13
0.1407	0.3419	67.78	0.6281	0.6993	59.93
0.1850	0.4019	66.08	0.6794	0.7253	59.77
0.2534	0.4613	64.36	0.7296	0.7528	59.63
0.3065	0.5030	63.26	0.7798	0.7838	59.55
0.3564	0.5393	62.41	0.8241	0.8181	59.56
0.4049	0.5717	61.79	0.8715	0.8530	59.64
0.4398	0.5863	61.35	0.9193	0.8992	59.83
0.4826	0.6124	60.96	0.9714	0.9590	60.31

TABLE I
(Continued)

x_1	y_1	P , Torr	x_1	y_1	P , Torr
$t = 52.89^\circ\text{C}$					
0.0375	0.1399	314.4	0.4105	0.5769	467.7
0.0712	0.2203	339.1	0.5207	0.6304	481.2
0.0833	0.2345	347.2	0.6125	0.6771	490.3
0.1121	0.3001	363.2	0.7029	0.7288	494.2
0.1503	0.3572	383.6	0.7307	0.7441	494.4
0.2146	0.4326	415.4	0.7831	0.7799	495.7
0.2524	0.4655	426.3	0.8267	0.8105	494.2
0.2653	0.4806	431.7	0.8820	0.8551	490.8
0.3046	0.5127	442.0	0.8975	0.8745	488.9
0.3343	0.5302	450.7	0.9654	0.9495	476.2
$t = 60.31^\circ\text{C}$					
0.0361	0.1241	420.2	0.5844	0.6739	652.0
0.0905	0.2583	477.7	0.6417	0.7043	665.7
0.1635	0.3734	518.4	0.6791	0.7265	669.4
0.1875	0.4055	537.2	0.7271	0.7541	671.8
0.2096	0.4366	545.8	0.8028	0.8073	672.7
0.2934	0.4964	579.2	0.8311	0.8254	672.8
0.3260	0.5257	596.5	0.8869	0.8702	664.0
0.3968	0.5714	614.9	0.9403	0.9255	652.0
0.4242	0.5884	621.8	0.9721	0.9593	644.8
0.4682	0.6126	628.0			

RESULTS

Our isobaric measurements were performed at pressures of 281.6, 423.4, 645.5 Torr whereas isothermal ones at 52.89°C and 60.31°C. The isobaric and isothermal data satisfied well the Herrington test and the integral consistence criterion, respectively. The experimental data are summarized in Table I.

The measured data were correlated separately by the van Laar and Margules three-suffix equations, by the Wilson, NRTL, and Orye equations, and by the Wilson enthalpic equation (in the following denoted as HMW). The last two equations, which are not commonly employed in the literature, were tested by Bruin⁶. His results indicate that both equations would deserve more attention.

In our correlation calculations, the following expression was minimized

$$\sum w_i |\ln (\gamma_1/\gamma_2)_i^{\text{exp}} - \ln (\gamma_1/\gamma_2)_i^{\text{calc}}|, \quad (1)$$

where w_i is the weight of point i which enables to minimize the distance from the slope of the functional dependence at this point

$$w_i = 1/[1 + (\partial F/\partial x_1)_i^2]. \quad (2)$$

The activity coefficients were calculated from experimental data by the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - v_i^L)(P - P_i^0)}{RT} + \frac{P D_{ij} y_j^2}{RT}, \quad (3)$$

where

$$D_{ij} = 2B_{ij} - B_{ii} - B_{jj}.$$

Second virial coefficients of pure substances and the cross virial coefficient were estimated according to the relation proposed by O'Connell and Prausnitz⁷. Vapour pressures of both pure substances were expressed by the Antoine equation. The temperature dependence of molar volumes was assumed to be linear, $v^L = O_A + O_B T$. All the data employed are collected in Table II.

TABLE II
Constants for the Calculation of Activity Coefficients

Substances	Constants in the Antoine equation				Constants of the temperature dependence of the molar volume		
	<i>A</i>	<i>B</i>	<i>C</i>	Ref.	<i>O_A</i>	<i>O_B</i>	Ref.
Methanol	7.87863	1 473.11	230	8	24.16	0.05734	3
Acetonitrile	7.33986	1 482.29	250.523	9	31.31	0.07227	3
	<i>T_c</i>	<i>P_c</i>	<i>v_c</i>	ω_H	μ	η	Ref.
Methanol	513.2	78.5	118.0	0.105	1.66	1.21	10
Acetonitrile	547.9	47.7	173.1	0.152	3.94	0	10

Results of separate correlations are given in Table III. Constants of the corresponding equation are always in the first two rows of the table, the third row contains the mean deviation between experimental and calculated compositions of the vapour phase. It is obvious from this table that all the equations investigated yield practically equivalent results. A comparison of values of constants for the separate data sets indicates that the lowest temperature variability is apparently exhibited by constants in the HMW and also Orye equations. This finding has led us to the assumption that these equations could be successful in simultaneous correlations of equilibrium data.

TABLE III
Separate Correlations of the Methanol(1)-Acetonitrile(2) System^a

Equation	<i>P</i> 281.6	<i>P</i> 423.4	<i>P</i> 645.5	<i>T</i> 52.89	<i>T</i> 60.31
van Laar	0.9805	0.8935	0.8300	0.9496	0.8671
	1.0288	0.9519	0.8962	0.9421	0.9151
	0.0047	0.0034	0.0040	0.0048	0.0043
Margules	0.9805	0.8937	0.8301	0.9492	0.8674
	1.0287	0.9503	0.8940	0.9419	0.9138
	0.0047	0.0034	0.0040	0.0048	0.0044
Wilson	494.4	468.6	453.9	510.6	456.9
	241.6	218.6	204.5	195.5	217.3
	0.0044	0.0029	0.0034	0.0058	0.0043
Renon (0.47)	337.8	306.8	286.3	350.2	292.9
	391.0	374.2	366.4	349.7	376.0
	0.0048	0.0034	0.0035	0.0048	0.0047
HMW	372.5	366.8	365.9	381.3	362.3
	80.8	71.0	64.0	64.4	72.5
	0.0048	0.0032	0.0033	0.0048	0.0043
Orye	288.8	281.4	276.4	302.6	276.5
	0.3	-5.8	-8.2	-21.2	-3.6
	0.0047	0.0032	0.0037	0.0047	0.0044

^a *P* resp. *T* denotes an isobar resp. isotherm; the attached figure expresses the pressure in Torr resp. temperature in °C. First two rows in each equation section contain constants of the corresponding equation, i.e. constants *A* resp. *B* for the van Laar and Margules equations and constants $\lambda_{12} - \lambda_{11}$ resp. $\lambda_{12} - \lambda_{22}$ for the equations based on the local composition concept. The mean deviation in the vapour phase composition is always in the third row.

TABLE IV

The Simultaneous Correlation of the Equilibria Vapour-Liquid

The mean absolute deviation δ_{red} reduced to the maximal value in the given data set and expressed percentually^a.

Equation	Wilson	Renon ($\alpha = 0.47$)	Orye	HMW
Constants ^b	452	291	265	362
cal/mol	226	382	6.80	70.2
<i>P</i> 281.6	1.8	1.7	1.7	1.4
<i>P</i> 423.4	1.1	1.1	1.1	1.0
<i>P</i> 645.5	1.7	1.8	1.1	1.3
<i>T</i> 52.89	1.4	1.4	1.5	1.4
<i>T</i> 60.31	2.9	2.9	3.5	3.3

^a $\delta_{red,j} \equiv (100/\sum_i w_i) \sum_i |w_i [(g^E/RT)_{ij}^{exp} - (g^E/RT)_{ij}^{calc}] / (g^E/RT)_{ij}^{max}$, where w_i is the weight of point i which enables to minimize the perpendicular distance from the slope of the functional dependence at this point. Indices i resp. j denote a point of a set resp. a set. ^b *P* resp. *T* denotes an isobar resp. an isotherm.

In the minimization criterion of simultaneous correlations, the weighted deviation $[(g^E/RT)^{exp} - (g^E/RT)^{calc}]$ was employed. Results of the simultaneous correlations are shown in the table; it contains values of constants of the correlation equations together with the so called mean absolute deviation reduced to the maximal value in the given set and expressed percentually. It is obvious that all the equations yield practically identically good description of the given system. This, together with other experiences obtained from correlations of other systems by the HMW and Orye equations, shows that these relatively young and up to now not too frequently used relations deserve further attention.

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