

ISOTHERMAL LIQUID-VAPOR EQUILIBRIUM IN ACETONITRILE-WATER SYSTEM

Rodica Vilcu*, Zoica Cenuse

abstract: The study of this system started from the importance that acetonitrile has as the component of some mixtures appearing in plastics synthesis or as a consequence of the extractive distillation in some industrial processes. The paper presents a systematic and critical study of the isothermal equilibrium acetonitrile-water system at 20, 30 and 40°C. The systems present a maximum in the total vapour pressure diagram which is moving with temperature. The processing of the experimental data existing in the literature [1-3] on acetonitrile-water system as well as the authors experimental data obtained under isothermal conditions at 40°C in an installation based on the static principle, $p=f(x)$, were presented. The activity coefficients were correlated and generalized on the basis of several models of the liquid state, i.e. by Margules, Wilson, NRTL and UNIFAC equations. The analysis of the correlation shows that the best generalized equation for this system is UNIFAC with a deviation in G^E/RT of the order of 10^{-2} and $k_{ij}=0.01$.

Introduction

Although separation of multicomponent system is largely investigated, deeper theoretical and experimental researches are still possible and necessary.

The speciality literature dealing with separation processes reveals that the challenge of the experimental technique is to obtain, by separation, of several high purity components out of the multicomponent mixture with numerous azeotropes or partial miscible components, sometimes under extreme pressure and temperature conditions.

The most important informational value at present seems to be using of the estimation methods with respect the structural parameters. This assertion is supported by the frequent use and perfection of the equation resulted from different models of the liquid state as Margules, Wilson, NRTL, UNIFAC, ASOG and so on, equations

For a better picture of acetonitrile behaviour in water, the data in the literature [1-3] referring to the liquid – vapour equilibrium of acetonitrile and water were completed by the isothermal study of this system at 40°C and a critical analysis on the basis of several models of the liquid state was performed.

* Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta 4-12, 030018, Bucharest, Romania

Results and Discussion

The measurements of the isothermal liquid-vapour equilibrium were carried out in an installation based on the principle of the isotensioscopic method. The performance of the installation was already analysed [4].

The properties of the components of the system are presented in Table 1 (a, b).

Table 1a. Physical properties of the substances

Subst.	M (g/mol)	Purity (%)	T _m (°C)	T _b (°C)	ρ (g/cm ³)	η	T _C (K)	P _C (atm)	V _C (cm ³ /mole)	ω
Acetonitrile	41.05	99.8	-43.8	81.6	0.7857*	1.3441	547.9	47.9	173.1	0.321
Water	18.01	99.8	0	100	0.9970	1.3336*	647.14	217.8	56	0.344

* at 20°C

Table 1b. Physical properties of the substances

Subst.	Antoinnes's parameters		
	A	B	C
Acetonitrile	7.39104	1495.858	250.00
	7.24299	1397.929	238.89
	[3]	[3]	[3]
Water	7.966681	1668.21	228

A determination of the saturation pressure of acetonitrile was carried out initially and the A, B, C parameters of the Antoine equations were calculated (see Table 1b).

The acetonitrile was spectroscopic R.C.B-Bruxelles reagent and was used as received, with indicated purity of at least 99.8%. The water was triple deionized.

Vapour pressure of the pure acetonitrile was measured and an Antoine equation was fitted to the experimental data. The A, B, C parameters calculated from own experimental data together with the relative deviation $\delta(P)=0.0627$ for acetonitrile and 0.0056 for water. The experimental saturation pressure for acetonitrile are listed in Table 2.

The experimental saturation pressure for acetonitrile – water system are listed in Table 3. In Figure 1 are illustrated the experimental liquid –vapour equilibrium in binary acetonitrile-water system at 20, 30, 40 and 50°C. With experimental or calculated values of the equilibrium vapour phase.

Table 2. Saturation pressures of acetonitrile

t (°C)	21.9	22.95	30.60	32.2	43.0	43.75	50.9	59.5
P _{exp} (mm Hg)	77.61	81.45	114.8	123.08	193.07	198.77	262.89	361.32
P _{calc} (mm Hg)	77.54	81.41	114.85	123.12	193.07	198.88	262.88	361.32
$\delta(P) = \left[\frac{(P_{\text{exp}} - P_{\text{calc}})^2}{N-f} \right]^{1/2}$	0.0627							

Table 3 Saturation pressure (mm Hg) in acetonitrile-water system

20°C [1]			30°C [1]			40°C			50°C [3]	
x _{ACN}	P (mm Hg)	y _{ACN}	x _{ACN}	P (mm Hg)	y _{ACN}	x _{ACN}	P (mm Hg)	y _{ACN}	x _{ACN}	P (mm Hg)
0.00	17.18	0.000	0.00	31.38	0.000	0.00	55.22	0.000	0.000	92.10
0.07	63.00	0.794	0.03	80.00	0.630	0.06	184.00	0.600	0.0328	92.61
0.15	71.50	0.829	0.07	101.00	0.720	0.09	190.20	0.635	0.0974	171.21
0.19	73.20	0.847	0.17	114.90	0.770	0.15	195.00	0.654	0.1699	243.22
0.35	74.20	0.858	0.41	119.00	0.797	0.28	197.30	0.670	0.2261	265.18
0.65	74.70	0.879	0.65	120.00	0.800	0.41	198.50	0.685	0.2846	276.35
0.76	74.30	0.885	0.87	119.40	0.830	0.52	199.50	0.755	0.3556	278.04
0.92	74.78	0.889	0.92	119.00	0.870	0.55	200.00	0.786	0.4215	277.56
1.00	70.92	1.00	1.00	111.86	1.00	0.60	207.00	0.835	0.5041	271.46
						0.68	208.00	0.850	0.5748	281.45
						0.80	200.00	0.893	0.6687	283.32
						0.85	196.00	0.880	0.7418	285.15
						0.92	185.00	0.942	0.8330	286.04
						0.95	178.00	0.985	0.9026	278.69
						1.00	170.97	1.00	0.9472	283.95
									1.00	254

The activity coefficients were calculated by equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - v_i^l)(P - P_i^0) + P y_j^2 \delta_{ij}}{RT}$$

The integration of the general coexistence equation allowed the calculation of the vapour phase composition in equilibrium with liquid phase for the binary system.

$$\frac{v^{\text{ev}} + x_1 \bar{v}_1^{\text{v}} + x_2 \bar{v}_2^{\text{v}} - v^{\text{l}}}{KT} dP = (y_1 - x_1) d \ln \frac{\gamma_1^{\text{v}}}{\gamma_2^{\text{v}}} \cdot \frac{y_2 - x_1}{y_1(1 - y_1)} dy_1$$

where vapour excess volume, v^{ev} , can be calculated by the equation:

$$v^{\text{ev}} = v^{\text{v}} - y_1 \bar{v}_1^{\text{v}} - y_2 \bar{v}_2^{\text{v}}$$

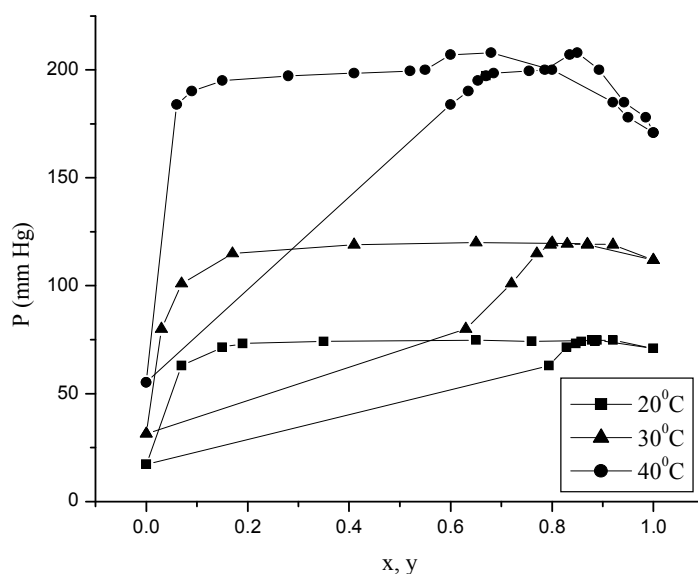


Fig. 1 Liquid-vapor equilibrium data in binary system acetonitrile-water

The data from the Table 3 allowed the appreciation of the activity coefficients, the non-dimensional Gibbs excess free enthalpy and the Q function for the thermodynamic consistency checking up using the Redlich-Kister criteria. The Rackett's parameters, Tsonopolous' constants and UNIFAC parameters are listed in Table 4.

Table 4. Constants for activity coefficients correlation's

Rackett's parameters		Tsonopolous' constants		UNIFAC		Ionisation potential
V_{ref}	X	a	b	R	Q	(eV)
1418.83	0.318	-0.1198	0	1.8701	1.724	12.39
36.23	2.285	0	0	0.9200 [5]	1.400 [5]	14.163

The experimental data were correlated by Margules, Wilson, NRTL and UNIFAC equations and the standard deviations by applying these equations to the experimental data are given in Table 5.

Table 5. Correlating parameters for acetonitrile – water system

t (°C)	K _{ij}	Model	Redlich- Kister deviation	Parameters of the correlation equation			Standard deviation in:						
				A ₁₂	A ₂₁	a ₁₂	G ^E /RT	γ ₁	γ ₂				
20	0.00	Margules	0.1690	0.1185	1.1399	0.2	0.0695	3.2440	0.5014				
	0.01			0.1232	0.1130								
	0.00	Wilson	0.1691	-541.53	5627.35		0.075	3.3353	0.2427				
	0.01			0.0589	-539.70		3518.90	0.0509	3.3303	0.4892			
	0.00		NRTL	0.1593	2272.72		-283.74	0.0192	11.9420	0.5457			
0.00	UNIFAC	0.1685	2899.39	-490.51	0.06873	3.2131	0.6054						
30	0.00	Margules	0.1620	0.7447	0.9157	0.2	0.0064	2.3805	0.2719				
	0.01			0.1624	0.7496					0.9153			
	0.00	Wilson	0.0101	21.74	1575.17					0.0101	3.9510	0.2196	
	0.01			0.0103	13.88					1678.00	0.0103	3.9764	0.2200
	0.00		NRTL	0.0716	931.14					481.75	0.0064	2.3805	0.2719
	0.01	UNIFAC	0.0699	925.44	490.04					0.0062	2.3695	0.2055	
	0.00			0.0090	903.55					-141.80	0.0091	3.9768	0.2127
0.01			0.0057	895.71	-137.14	0.0087	3.9572	0.2136					
40	0.00	Margules	0.1929	0.9569	0.6701	0.2	0.0670	0.5056	2.3447				
	0.01			0.1936	0.9625					0.6714			
	0.00	Wilson	0.0602	2946.65	1116.32					0.0602	3.0590	1.2556	
	0.01			0.0608	2996.71					1122.59	0.0600	3.910	1.2565
	0.00		NRTL		282.95					1483.21	0.0674	0.5450	2.4203
	0.01	UNIFAC		282.51	1496.25					0.0674	0.5450	2.4203	
	0.00			0.0032	144.08					466.31	0.0680	0.3303	1.1573
0.01			0.00318	129.82	491.78	0.06814	0.3977	1.1744					

The best equation which correlates the 20°C equilibrium data is Wilson equation with a $k_{ij}=0.01$. The Redlich-Kister deviation is the smallest one, equals 0.0589.

On the other hand the best equation which correlates the 30°C and 40°C equilibrium data is UNIFAC equation. The Redlich-Kister deviation is of the third order $(3.18-9) \cdot 10^{-3}$, the deviation in G^E/RT are of the order 10^{-2} . The best results were obtained for UNIFAC equation with $k_{ij}=0.01$.

Using UNIFAC correlation equation values of the activity coefficients are in a good agreement with the experimental data within the range of molar fraction: $x_{ACN}=0.1 \dots 0.9$.

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