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## THERMODYNAMIC PROPERTIES OF SOLUTIONS OF ETHACRYLIC ACID IN ACETONITRILE AND ACETIC ACID

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**Abstract.** The saturated vapor pressure of ethacrylic acid solutions in acetonitrile and acetic acid was measured by a static tensimetric method in the temperature range of 295–355 K. The composition of the equilibrium phases as well as the activity coefficients were received from the experimental measurements of the temperature-dependent saturated vapor pressure. We then used the temperature and concentration dependent activity coefficients to calculate the excess thermodynamic functions of the solutions mixing ( $H^E$ ,  $G^E$ ,  $S^E$ ).

**Keywords:** ethacrylic acid, saturated vapor pressure, activity coefficients, vapor-liquid equilibrium, excess thermodynamic functions.

### 1. Introduction

Acrylic-based acids and their esters are attractive classes of raw materials for the production of polymers with wide range of properties. The thermodynamic properties of the individual neat components are extensively studied [1-3]. There have also been a number of studies of the liquid-vapor equilibrium of the acrylic acid and their ethers solutions. Most works [4-12] are focused on the liquid-vapor equilibrium for solutions of acrylic and methacrylic acids and their ethers under isobaric conditions and atmospheric pressure. Based on the experimental values, parameters of the Local Composition Models (Wilson equation [13], NRTL equation [14], UNIQUAC equation [15]) were evaluated. These equations may be used to calculate the parameters of liquid-vapor equilibrium at different pressures. In this work the excess thermodynamic functions of solutions mixing based on the experimental data of the temperature dependent vapor pressure on ethacrylic acid solutions in acetonitrile and acetic acid were calculated. A particular utility of our data is that they can be used for direct calculation of the equilibrium phases composition for studying systems within the investigated temperature and pressure ranges.

Such studies of liquid-vapor equilibrium are useful, as they can provide the necessary information about the individual components behavior in these complex systems. In this work, to estimate the thermodynamic functions of mixing based on the vapor-liquid equilibrium, we adopted the commonly used methodology developed by V. Belousov and A. Morachevsky [16, 17].

### 2. Experimental

The ethacrylic acid was synthesized by the known methods [18]. The acetonitrile and acetic acids were of the commercial grade and were supplied by MERCK (Germany). The chemicals received were further purified by repeated evaporation, ethacrylic and acetic acids were additionally purified by recrystallization. The chemicals were then selected based on their unique boiling temperature as well as the refractive index and density. The contamination was kept below 0.2 wt %, verified by chromatography.

Experimental measurements of the vapor pressure over the solutions at various temperatures were at the basis of our static methodology approach [19]. Standard measurement error for pressure was  $\pm 65$  Pa and for temperature  $\pm 0.1$  K.

First, we verified our measurement methodology, as well as the correctness of our approach, by conducting series of experiments with well-known substances, such as heptane and hexane. The obtained results are in agreement with the reported literature data [20].

### 3. Results and Discussion

To test our experimental systems we prepared several solutions with the concentration ranged from 17 to 81 mol %. Notably, to prevent the undesired polymerization of the ethacrylic acid, we inhibited the systems by adding the inhibitor – hydrochinon – in amount of about 0.2 wt %. We further verified that such minuscule amount

of hydrochinon did not influence the measurements. The solutions concentration was measured using chromatography in the end of the experiment, after the system reached room temperature. These data, as well as the temperature dependent saturated vapor pressure, are reported in Table 1. The concentration data point to a more volatile component of the solution (*i.e.* acetonitrile or acetic acid).

We used the Antuan equation (1) to describe the temperature (K) dependence of the saturated vapor pressure (Pa) over the solutions and individual components [1, 20]:

$$\lg P = A - \frac{B}{T + C} \quad (1)$$

The fitting coefficients, along with the standard deviation of the experimental data evaluated in a given temperature range are listed in Table 2.

Received temperature dependences of the saturated vapor pressure enabled us to create the isothermal sections for obtaining concentration dependence of vapor pressure. The obtained values were approximated by the order polynomials. The polynomial order was chosen based on the value of standard deviation between polynomial and experimental values. If the standard deviation was comparable with experimental error the polynomial order was considered acceptable.

Table 1

The dependence of the vapor pressure on temperature

<i>T</i> , K	<i>P</i> , kPa	<i>T</i> , K	<i>P</i> , kPa	<i>T</i> , K	<i>P</i> , kPa	<i>T</i> , K	<i>P</i> , kPa
Acetonitrile–Ethacrylic acid							
18.0 mol %		28.1 mol %		49.4 mol %		79.5 mol %	
295.3	6.36	290.3	5.96	287.6	5.75	291.3	7.93
304.6	8.93	304.7	11.04	305.2	13.08	304.2	14.59
315.4	12.88	314.3	15.81	314.6	19.16	314.8	22.84
324.4	16.82	324.3	22.12	323.9	27.08	326.6	35.92
339.5	26.01	334.0	29.54	334.0	38.44	334.3	47.42
352.2	35.50	343.1	38.06	343.8	52.42	343.1	63.67
		352.3	48.06	343.9	52.56	346.7	71.62
				352.4	68.03		
Acetic acid–Ethacrylic acid							
17.0 mol %		36.5 mol %		62.7 mol %		81.2 mol %	
293.0	0.43	296.3	0.91	298.9	1.60	289.0	1.07
299.1	0.59	304.7	1.48	304.1	2.20	304.2	2.63
310.3	1.11	316.2	2.68	314.5	3.73	314.0	4.29
319.7	1.76	325.5	4.02	324.7	6.00	323.9	6.81
331.0	2.97	334.4	6.01	335.5	9.71	335.3	11.59
341.7	4.75	343.0	8.75	343.9	14.09	343.3	16.25
350.4	6.51	352.6	12.81	352.7	19.84	352.9	23.80

Table 2

Fitting coefficients for the Antuan equation

<i>x</i> , mol %	<i>A</i>	<i>B</i>	<i>C</i>	<i>T</i> , K	<i>S<sub>n</sub></i> , kPa
Acetonitrile–Ethacrylic acid					
0.0	10.79936	2546.98	-13.36	350–410	–
18.0	7.37311	766.35	-80.60	295–352	0.09
28.1	7.00504	513.60	-131.24	290–352	0.03
49.4	8.08076	849.65	-90.90	287–352	0.13
79.5	8.57144	1007.11	-75.71	291–346	0.07
100.0	9.28443	1355.37	-37.85	288–362	–
Acetic acid–Ethacrylic acid					
0.0	10.79936	2546.98	-13.36	350–410	–
17.0	8.26024	1202.65	-79.69	293–350	0.04
36.5	8.99930	1456.26	-55.08	296–352	0.07
62.7	9.29562	1507.42	-51.19	298–352	0.09
81.2	9.46717	1558.07	-46.89	289–352	0.07
100.0	9.68767	1642.54	-39.76	290–391	–

Table 3a

**Equilibrium composition, partial vapor pressure  
and the activity coefficients of acetonitrile in ethacrylic acid**

$x$	$y$	$p_1$	$p_2$	$\gamma_1$	$\gamma_2$
mol %		kPa			
300 K					
0.0	0.00	0.00	0.09	–	1.0000
10.0	98.47	5.07	0.08	3.9066	1.0000
20.0	99.08	7.91	0.07	3.0425	1.0019
30.0	99.26	9.32	0.07	2.3905	1.0706
40.0	99.33	9.97	0.07	1.9180	1.2057
50.0	99.38	10.34	0.07	1.5912	1.4034
60.0	99.43	10.75	0.06	1.3775	1.6733
70.0	99.51	11.32	0.06	1.2444	2.0193
80.0	99.62	12.05	0.05	1.1587	2.5023
90.0	99.73	12.73	0.03	1.0877	3.6526
100.0	100.00	13.00	0.00	1.0000	–
340 K					
0.0	0.00	0.00	1.00	–	1.0000
10.0	94.61	15.96	0.91	2.5402	1.0185
20.0	97.06	27.39	0.83	2.1792	1.0233
30.0	97.91	35.61	0.76	1.8877	1.0685
40.0	98.35	41.66	0.70	1.6564	1.1465
50.0	98.63	46.39	0.64	1.4754	1.2606
60.0	98.86	50.38	0.58	1.3352	1.4245
70.0	99.07	53.99	0.51	1.2268	1.6672
80.0	99.27	57.37	0.42	1.1405	2.0777
90.0	99.48	60.39	0.31	1.0671	3.0774
100.0	100.00	62.88	0.00	1.0000	–

Table 3b

**Equilibrium composition, partial vapor pressure  
and the activity coefficients of acetic acid in ethacrylic acid**

$x$	$y$	$p_1$	$p_2$	$\gamma_1$	$\gamma_2$
mol %		kPa			
300 K					
0.0	0.00	0.00	0.08	–	1.0000
10.0	80.59	0.33	0.08	1.4103	1.0000
20.0	89.85	0.64	0.07	1.3460	1.0070
30.0	93.46	0.92	0.06	1.2868	1.0223
40.0	95.41	1.17	0.06	1.2324	1.0464
50.0	96.66	1.40	0.05	1.1824	1.0826
60.0	97.55	1.62	0.04	1.1368	1.1361
70.0	98.23	1.82	0.03	1.0957	1.2172
80.0	98.81	2.01	0.02	1.0589	1.3504
90.0	99.34	2.19	0.01	1.0266	1.6195
100.0	100.00	2.38	0.00	1.0000	–
340 K					
0.0	0.00	0.00	1.00	–	1.0000
10.0	82.98	2.05	0.93	1.2459	1.0000
20.0	89.08	4.05	0.83	1.2295	1.0008
30.0	92.45	5.96	0.73	1.2067	1.0071
40.0	94.59	7.76	0.63	1.1789	1.0199
50.0	96.09	9.45	0.54	1.1477	1.0428
60.0	97.22	11.01	0.45	1.1146	1.0811
70.0	98.15	12.46	0.36	1.0813	1.1442
80.0	99.00	13.82	0.26	1.0496	1.2527
90.0	68.75	15.13	0.15	1.0214	1.4696
100.0	100.00	16.48	0.00	1.0000	–

Further, we calculated the partial vapor pressure of the components ( $p_1$  and  $p_2$ ) using the Duhem-Margules equation [19, 23], assuming the gas phase was close to an ideal gas phase. The Duhem-Margules equation was solved by the Runge method, integrating in the direction of the increased pressure.

The calculation of the partial vapor pressure of each component,  $p_1$  and  $p_2$ , allowed us to arrive at the composition of the gas phase as well as the activity coefficients of the components ( $\gamma_1$  and  $\gamma_2$ ), in the temperature range from 300 to 340 K. Table 3 lists the composition of the liquid phase ( $x$ ), gas phase ( $y$ ), vapor pressure of components  $p_1$  and  $p_2$ , as well as the activity coefficients  $\gamma_1$  and  $\gamma_2$ , at the minimum and maximum temperature range.

To describe the properties of the non-ideal solutions we used the excess thermodynamic functions of mixing and calculated the differential between the functions of mixing of the experimental and the ideal solutions. For instance, the Gibbs energy of mixing is calculated based on  $\gamma_1$  and  $\gamma_2$ :

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (2)$$

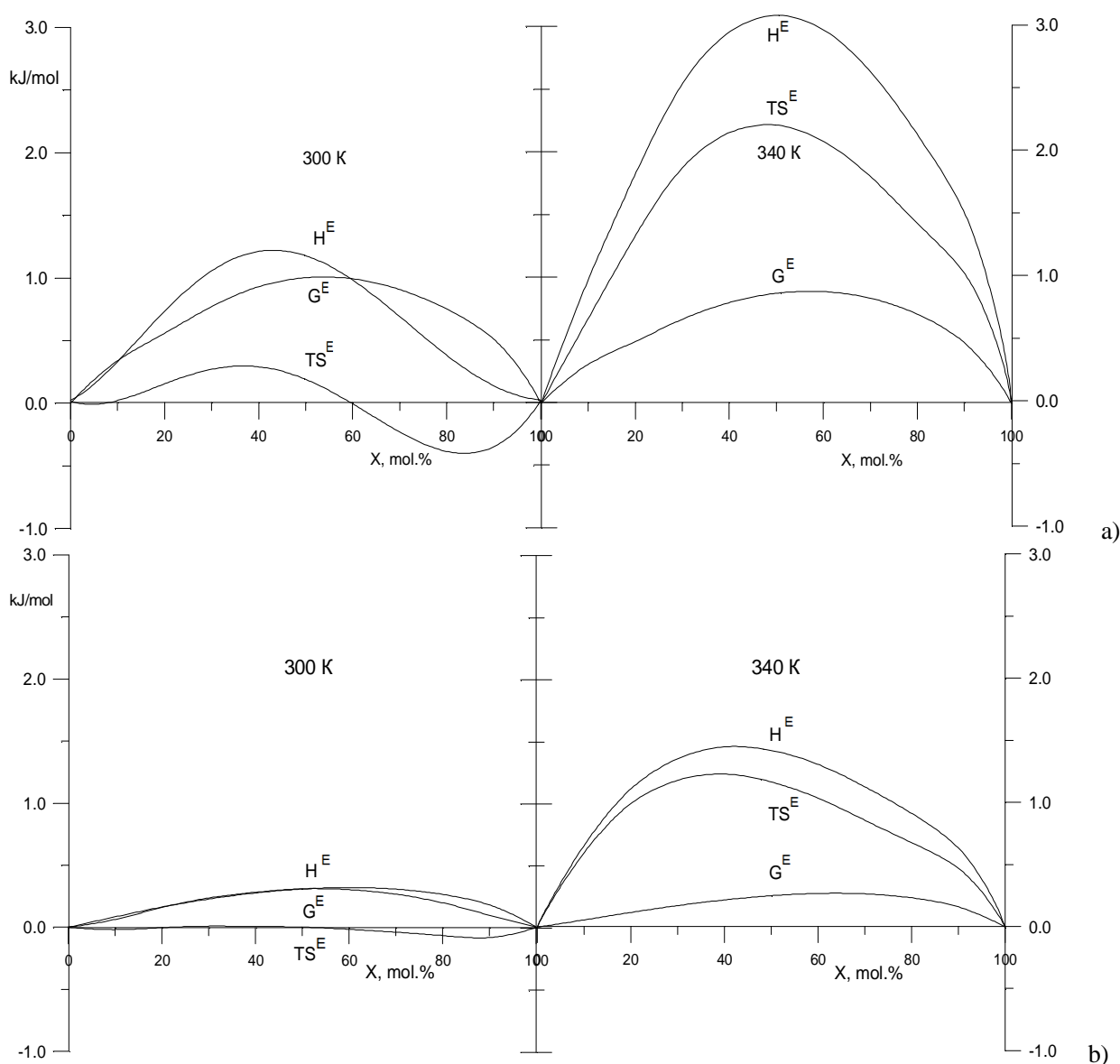
The enthalpy of systems mixing is then calculated based on  $\gamma_1$  and  $\gamma_2$  at different temperatures:

$$\Delta H^E = -RT^2 \cdot [x_1 \cdot \left(\frac{\partial \ln \gamma_1}{\partial T}\right)_x + x_2 \cdot \left(\frac{\partial \ln \gamma_2}{\partial T}\right)_x] \quad (3)$$

Finally, one may evaluate the entropy of mixing:

$$T\Delta S^E = \Delta H^E - \Delta G^E \quad (4)$$

The results of these calculations are shown in Fig. 1.



**Fig. 1.** The thermodynamic functions of mixing of the acetonitrile in ethacrylic acid (a) and acetic acid in ethacrylic acid (b)

Table 4

Properties of solvents and solutions

Solvent	$E_T^N$	AN	RM	$H_{300}^E$ , kJ/mol	$G_{300}^E$ , kJ/mol
Acetonitrile	0.460	18.9	11.13	1.23	1.00
Acetic acid	0.648	52.9	12.99	0.31	0.31

In order to determine the role of the solvents on the ensuing properties of the corresponding solutions, we considered the dependences of the Dimroth-Reichardt parameter  $E_T^N$  [21], the acceptor number AN [22], and the molecular refraction RM, on the thermodynamic functions of formation of the equimolecular solutions of eth acrylic acid at 300 K. These parameters and enthalpies of mixing and Gibbs energy of mixing are shown in Table 4.

As follows from the data in Table 4, the magnitudes of all these three parameters for acetonitrile were lower than those for the acetic acid. However, the magnitude of the enthalpy of mixing, the excess Gibbs energy, as well as the magnitude of the deviation from the ideal solutions were greater in case of the acetonitrile.

#### 4. Conclusions

All investigated systems (within the whole range of the concentrations and temperatures) exhibit positive magnitudes of their excess Gibbs energy, confirming the positive deviation from the Raoult's law. The same positive change was observed for the enthalpy of mixing, indicating the endothermic effect of the solutions formation. The increase in temperature increases the enthalpy of mixing, *i.e.* the heat capacity change is also positive.

It appears that in the studied systems the deviation from the behavior of the ideal solution decreases with the increase in the solvent molecular refraction, the Dimroth-Reichardt parameter, as well as the AN number, accompanied by the lower enthalpy of mixing.

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#### ТЕРМОДИНАМІЧНІ ВЛАСТИВОСТІ РОЗЧИНІВ ЕТАКРИЛОВОЇ КИСЛОТИ В АЦЕТОНІТРИЛІ ТА ОЦТОВІЙ КИСЛОТІ

**Анотація.** Статичним тензиметричним методом виміряно тиск насиченої пари над розчинами етакрилової кислоти в ацетонітрилі та оцтовій кислоті в температурному інтервалі 295–355 K. За даними температурної залежності тиску насиченої пари розраховано склад рівноважних фаз та коефіцієнти активності компонентів. За температурною та концентраційною залежністю коефіцієнтів активності розраховані надлишкові термодинамічні функції змішування досліджених розчинів ( $H^E$ ,  $G^E$ ,  $S^E$ ).

**Ключові слова:** етакрилова кислота, тиск насиченої пари, коефіцієнти активності, рівновага рідина-пара, надлишкові термодинамічні функції.

