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Excess Molar Volumes and Excess Gibbs Energies in *N*-Methylformamide + Water, or + Methanol, or + Ethanol at the Temperature 303.15 K

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Excess volumes V^E measured in a dilution dilatometer and total vapor pressures at the temperature 303.15 K are reported for (*N*-methylformamide + water), (*N*-methylformamide + methanol), and (*N*-methylformamide + ethanol) over the entire composition range. The total vapor pressure measurements were made by a modified static method. The excess molar volumes are negative for all the mixtures over the entire composition range; the vapor pressure measurements show only small negative deviations from ideality for these systems.

Introduction

This work continues the description of the thermodynamic properties of (amide + water) and (amide + alcohol) mixtures. In the previous set of articles (see Zielkiewicz (1997) and references given therein), the G^E and V^E values for the binary and ternary mixtures containing formamide derivatives (*N*-methylformamide and *N*,*N*-dimethylformamide), water, and aliphatic alcohols at the temperature 313.15 K were reported. In this work the excess molar volumes and the total vapor pressure measurements at the temperature 303.15 K are given.

Experimental Section

Reagents. *N*-Methylformamide (E. Merck, product "zur synthese") was dried twice over freshly ignited 0.4 nm molecular sieves, filtered, and stored under vacuum. Measured conductivity of this solvent was below 2.4×10^{-6}. Methanol, ethanol (both Polish Chemical Reagents, POCH, analytical reagent grade), and water were purified as described previously (Zielkiewicz, 1995, 1997). All the solvents were degassed prior to use by storing under vacuum. The mass fraction of water in all the organic solvents was below 0.0001, determined by titration using Karl Fischer reagent. No other estimation of purity was made. Characteristics of the pure substances are given in Table 1.

The volumes of mixing were determined using the Kumaran and McGlashan dilatometer (Kumaran and McGlashan, 1977); the experimental procedure has been described previously (Zielkiewicz 1994). The error of the V^E measurements was estimated as ±0.000 05 $\text{cm}^3\cdot\text{mol}^{-1}$. The vapor pressure measurements were carried out by the quasi-static method using the apparatus described previously (Zielkiewicz et al., 1990). Densities of pure liquids were measured using a pycnometer of volume ≈28 cm^3, calibrated on water. The error of this measurement was estimated as ±0.0001 $\text{g}\cdot\text{cm}^{-3}$.

The bath temperature was adjusted to 303.15 K by the measurements of the vapor pressure of pure standard substances. The standards used were acetone, hexane, methanol, ethanol, propan-1-ol, propan-2-ol, and water. During the measurements the temperature was controlled to 0.001 K using the Beckman thermometer and was constant within 0.002 K.

The mercury levels in the dilatometer and in the manometer were determined using a cathetometer with an accuracy of 0.01 mm. The refractive indices were measured using the Carl Zeiss refractometer equipped with the exchangeable thermostated prismas. The accuracy of determination of refractive indices was 0.000 01; the temperature during these measurements was constant within 0.1 K.

Results

Results of the V^E measurements are given in Table 2. Correlation of the binary results was carried out using a

Table 1. Densities ρ, Refractive Indices n_D, and Vapor Pressures *P*, of Pure Liquids Used in This Work, Measured at Temperatures *T*

		$\rho/(\text{g}\cdot\text{cm}^{-3})$		n_D		*P* (kPa)	
component	*T*/K	this work	lit.	this work	lit.	this work	lit
N-methylformamide	298.15	0.9993	0.996 1[a] 0.997 6[b]	1.430 09	1.430 0[a] 1.431 0[b]		
	303.15	0.9950	0.995 1[d]			0.060	0.056[f]
methanol	298.15	0.7864	0.786 635[c]	1.326 45	1.326 45[c]		
	303.15	0.7817	0.781 666[c]			21.849	21.870[e]
ethanol	298.15	0.7849	0.7849 62[c]	1.359 20	1.359 25[c]		
	303.15	0.7805	0.780 667[c]			10.459	10.458[e]

[a] *Beilstein's Handbuch der Organische Chemie 4*, 58, III 121, 1962. [b] *Beilstein's Handbuch der Organische Chemie 4*, 58, IV 170, 1977. [c] Benson and Kiyohara, 1980. [d] Pal and Singh, 1995. [e] Boublik et al., 1984. [f] Stephenson and Malanowski, 1987.

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Table 2. Experimental Mole Fractions x and Excess Molar Volumes V^E

x	V^E/ ($cm^3 \cdot mol^{-1}$)	x	V^E/ ($cm^3 \cdot mol^{-1}$)	x	V^E/ ($cm^3 \cdot mol^{-1}$)
xHCONHCH$_3$ + (1 − x)H$_2$O at T = 303.15 K					
0.8703	−0.1533	0.0968	−0.2359	0.8221	−0.2049
0.7565	−0.2758	0.1243	−0.2964	0.7953	−0.2353
0.6633	−0.3794	0.1482	−0.3436	0.7737	−0.2597
0.5779	−0.4620	0.1745	−0.3904	0.7526	−0.2830
0.5028	−0.5168	0.1952	−0.4229	0.7316	−0.3063
0.4489	−0.5410	0.2081	−0.4413	0.9926	−0.0093
0.3818	−0.5525	0.2216	−0.4588	0.9847	−0.0192
0.3395	−0.5465	0.2401	−0.4802	0.9786	−0.0249
0.3126	−0.5363	0.2543	−0.4945	0.9691	−0.0356
0.2850	−0.5198	0.9933	−0.0082	0.9628	−0.0428
0.2666	−0.5056	0.9793	−0.0239	0.9559	−0.0508
0.2474	−0.4878	0.9665	−0.0388	0.9486	−0.0590
0.2338	−0.4732	0.9546	−0.0525	0.9415	−0.0672
0.2200	−0.4569	0.9320	−0.0784	0.9364	−0.0730
0.0146	−0.0346	0.9117	−0.1019	0.9312	−0.0788
0.0457	−0.1106	0.8802	−0.1382		
0.0730	−0.1794	0.8479	−0.1753		
xHCONHCH$_3$ + (1 − x)CH$_3$OH at T = 303.15 K					
0.9706	−0.0305	0.4662	−0.3321	0.2406	−0.2849
0.9218	−0.0705	0.4489	−0.3343	0.2638	−0.2980
0.8638	−0.1124	0.4259	−0.3349	0.2867	−0.3090
0.7959	−0.1689	0.4039	−0.3346	0.3082	−0.3171
0.7356	−0.2149	0.0201	−0.0376	0.3282	−0.3232
0.6794	−0.2512	0.0455	−0.0757	0.3561	−0.3301
0.6295	−0.2786	0.0742	−0.1202	0.3805	−0.3338
0.5973	−0.2937	0.1043	−0.1601	0.3966	−0.3354
0.5516	−0.3122	0.1386	−0.1997	0.4170	−0.3362
0.5199	−0.3211	0.1769	−0.2374		
0.4913	−0.3276	0.2112	−0.2652		
xHCONHCH$_3$ + (1 − x)C$_2$H$_5$OH at T = 303.15 K					
0.9478	−0.0252	0.5624	−0.0902	0.2834	−0.0510
0.8706	−0.0547	0.5395	−0.0893	0.3247	−0.0600
0.8226	−0.0675	0.5174	−0.0873	0.3677	−0.0670
0.7658	−0.0805	0.4875	−0.0845	0.4016	−0.0729
0.7242	−0.0874	0.0544	−0.0052	0.4285	−0.0771
0.6673	−0.0922	0.1172	−0.0150	0.4624	−0.0816
0.6271	−0.0918	0.1747	−0.0270	0.4904	−0.0847
0.5933	−0.0918	0.2302	−0.0396	0.5133	−0.0868

Table 3. Parameters K_i of Eq 1 Along with Their Standard Deviations

xHCONHCH$_3$ + (1 − x)H$_2$O at T = 303.15 K

$K_1 = -2.072\,01 \pm 0.001\,97$ $\quad K_2 = 1.160\,76 \pm 0.011\,37$
$K_3 = 0.024\,08 \pm 0.026\,21$ $\quad K_4 = -0.164\,18 \pm 0.091\,60$
$K_5 = -0.174\,99 \pm 0.093\,43$ $\quad K_6 = -0.460\,48 \pm 0.227\,10$
$K_7 = 0.515\,03 \pm 0.086\,31$ $\quad K_8 = 0.049\,96 \pm 0.169\,31$
$s(\delta V^E) = 0.0008\ cm^3 \cdot mol^{-1}$

xHCONHCH$_3$ + (1 − x)CH$_3$OH at T = 303.15 K

$K_1 = -1.307\,29 \pm 0.001\,85$ $\quad K_2 = 0.426\,64 \pm 0.009\,88$
$K_3 = -0.016\,66 \pm 0.021\,90$ $\quad K_4 = 0.235\,89 \pm 0.061\,17$
$K_5 = -0.063\,36 \pm 0.037\,90$ $\quad K_6 = -0.268\,68 \pm 0.077\,33$
$s(\delta V^E) = 0.0013\ cm^3 \cdot mol^{-1}$

xHCONHCH$_3$ + (1 − x)C$_2$H$_5$OH at T = 303.15 K

$K_1 = -0.343\,10 \pm 0.000\,66$ $\quad K_2 = -0.200\,67 \pm 0.004\,27$
$K_3 = -0.003\,75 \pm 0.008\,94$ $\quad K_4 = -0.035\,54 \pm 0.026\,82$
$K_5 = 0.080\,86 \pm 0.016\,83$ $\quad K_6 = -0.000\,82 \pm 0.035\,32$
$s(\delta V^E) = 0.0005\ cm^3 \cdot mol^{-1}$

Redlich−Kister equation:

$$V^E/(cm^3 \cdot mol^{-1}) = x(1 - x)\sum_{i=1}^{k} K_i(2x - 1)^{i-1} \qquad (1)$$

The values of K_i parameters are given in Table 3, along with their standard deviations.

The V^E results for (N-methylformamide + water) at 303.15 K were published by Pal and Singh (Pal and Singh, 1995). Comparison between Pal and Singh's data and the results obtained in this work is given in Figure 1. The two data sets differ; the present data are approximately 4% lower than reported previously in the cited work (the maximum difference is about 0.020 cm^3·mol^{-1}, x = 0.41). Because there are no other V^E data in the literature for this system, no further comparison is possible. The reason for the discrepancy is not clear.

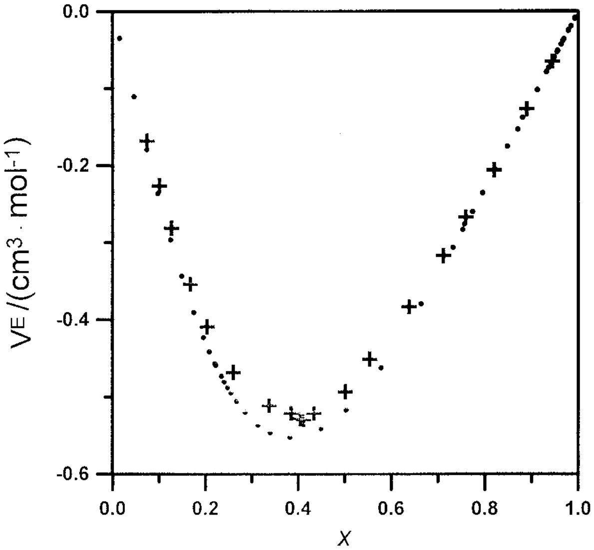

Figure 1. Comparisom of the present V^E (●) results at 303.15 K for (x N-methylformamide + (1 − x)water) with the data from Pal and Singh (1995) (+).

Table 4. Total Vapor Pressure P, Liquid-Phase Compositions x, and Calculated Vapor-Phase Compositions y

x	y	P/kPa	x	y	P/kPa
xHCONHCH$_3$ + (1 − x)H$_2$O at T = 303.15 K					
0.9773	0.4290	0.133	0.3045	0.0056	2.954
0.9204	0.1564	0.354	0.2764	0.0048	3.084
0.8709	0.0958	0.541	0.2309	0.0037	3.288
0.7471	0.0443	1.005	0.1877	0.0028	3.480
0.6283	0.0249	1.484	0.1672	0.0024	3.572
0.5438	0.0169	1.858	0.1379	0.0019	3.692
0.4815	0.0128	2.139	0.1166	0.0016	3.798
0.3977	0.0087	2.515	0.0751	0.0010	3.952
0.3613	0.0074	2.690	0.0310	0.0004	4.126
xHCONHCH$_3$ + (1 − x)CH$_3$OH at T = 303.15 K					
0.0310	0.0001	21.202	0.4571	0.0023	12.162
0.0814	0.0003	20.157	0.5037	0.0028	11.135
0.1049	0.0003	19.675	0.5699	0.0036	9.689
0.1479	0.0005	18.753	0.6312	0.0046	8.336
0.1982	0.0007	17.725	0.6696	0.0054	7.492
0.2233	0.0008	17.191	0.7267	0.0071	6.231
0.2652	0.0010	16.309	0.7948	0.0102	4.730
0.3040	0.0012	15.479	0.8575	0.0155	3.344
0.3881	0.0017	13.671	0.9395	0.0376	1.500
0.4058	0.0019	13.316			
xHCONHCH$_3$ + (1 − x)C$_2$H$_5$OH at T = 303.15 K					
0.9504	0.0809	0.716	0.4933	0.0054	5.812
0.8997	0.0398	1.355	0.4585	0.0048	6.126
0.8471	0.0253	2.005	0.4438	0.0046	6.259
0.7880	0.0175	2.714	0.3050	0.0028	7.551
0.7475	0.0143	3.177	0.2628	0.0023	7.956
0.6899	0.0111	3.820	0.2016	0.0017	8.523
0.6477	0.0094	4.274	0.1590	0.0013	8.930
0.5777	0.0073	4.983	0.0954	0.0008	9.534
0.5398	0.0064	5.353	0.0471	0.0004	10.009

The results of the vapor pressure measurements are given in Table 4. The binary data were correlated using the following Redlich−Kister equation:

$$G^E/RT = x(1 - x)\sum_{i=1}^{k} C_i(2x - 1)^{i-1} \qquad (2)$$

Table 5. Parameters C_i of Eq 2 Along with Their Standard Deviations

xHCONHCH$_3$ + (1 − x)H$_2$O at T = 303.15 K

$C_1 = -0.193\ 30 \pm 0.006\ 43$ $C_2 = -0.003\ 81 \pm 0.008\ 36$
$C_3 = 0.086\ 38 \pm 0.012\ 70$ $C_4 = -0.031\ 40 \pm 0.028\ 6$
$C_5 = -0.008\ 26 \pm 0.032\ 67$ $C_6 = -0.188\ 98 \pm 0.046\ 91$
$s(\delta P) = 0.005$ kPa

xHCONHCH$_3$ + (1 − x)CH$_3$OH at T = 303.15 K

$C_1 = 0.082\ 61 \pm 0.002\ 79$ $C_2 = -0.016\ 58 \pm 0.002\ 97$
$C_3 = 0.047\ 13 \pm 0.005\ 43$ $C_4 = -0.005\ 48 \pm 0.007\ 78$
$C_5 = 0.028\ 29 \pm 0.011\ 78$ $s(\delta P) = 0.013$ kPa

xHCONHCH$_3$ + (1 − x)C$_2$H$_5$OH at T = 303.15 K

$C_1 = 0.304\ 93 \pm 0.002\ 24$ $C_2 = -0.041\ 90 \pm 0.002\ 65$
$C_3\ -0.029\ 06 \pm 0.005\ 86$ $C_4 = -0.022\ 18 \pm 0.006\ 58$
$C_5 = 0.066\ 35 \pm 0.012\ 44$ $s(\delta P) = 0.007$ kPa

Because of the lack of data for the second virial coefficient of N-methylformamide, the vapor-phase behavior was assumed to be ideal. The vapor-phase compositions, y, were calculated according to the Barker's method; this involves iterative approximating of the total vapor pressure function $P = \mathrm{P}(x)$ by $P_{\mathrm{calc}} = P(x, y, C_1, ..., C_N)$, that is, by minimizing the difference $P_{\mathrm{calc}} - P_{\mathrm{exp}}$ for the same matrix of liquid-phase compositions, **X**. The following general relations were used

$$P = P{\cdot}(\sum_{i=1}^{k} y_i) = (\sum_{i=1}^{k} P{\cdot}y_i) \qquad (3)$$

and

$$P = \sum_{i=1}^{k} x_i{\cdot}\gamma_i{\cdot}P_i^0 \qquad (4)$$

where x_i and y_i are the liquid and vapor mole fraction of ith compound, respectively, and P_i^0 is the vapor pressure of the pure i compound. The coefficients C_i are given in Table 5, along with their standard deviations. The coefficients K_i and C_i were obtained by the least-squares method, using the optimization algorithm based on the Marquardt method.

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