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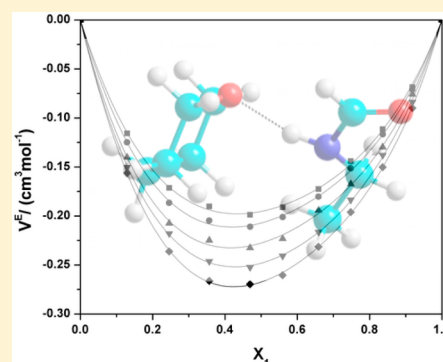
Volumetric Properties of Binary Mixtures of *N*-Ethylformamide with Tetrahydropyran, 2-Pentanone, and Propylacetate from (293.15 to 313.15) K

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Supporting Information

ABSTRACT: Densities of binary liquid mixtures of *N*-ethylformamide (NEF) with tetrahydropyran (THP), 2-pentanone (P), and propylacetate (PA) were measured at temperatures from (293.15 to 313.15) K and at atmospheric pressure over the whole composition range. Excess molar volumes, V^E , have been calculated from the experimental densities and were fitted to the Redlich–Kister polynomial equation. Investigated binary systems show negative excess molar volumes over the entire composition and temperature ranges. For all studied binary mixtures V^E values become more negative as the temperature increases. Other volumetric properties, such as thermal expansion coefficients, partial molar volumes, apparent molar volumes, and partial molar excess volumes, have been calculated, too.



INTRODUCTION

N-Substituted amides are the simplest model molecules having a peptide group, and consequently, many studies have been devoted to the intermolecular interactions of *N*-substituted amides. This paper is a part of our continuing and systematic investigation of the secondary amides in solutions from spectroscopic,^{1–3} thermodynamic,^{4,5} and densitometric^{6,7} aspects. In our previous papers⁸ on excess molar volumes, we have studied the *N*-methylformamide (NMF) with 2-pentanone, propylacetate, and tetrahydropyran. In the present work we have investigated the effect of an additional methylene group (in the alkyl substituent on *N*-atom of the amide) on the volumetric properties of the mixtures. Also, obtained results were compared with those obtained by the spectroscopic methods (NMR, IR). Namely, hydrogen bonding and intermolecular forces of NH group play very important roles in biological systems, and *N*-substituted amides serve as proper model systems. Thus, it is important to compare published spectroscopic data with those from nonspectroscopic methods, such as densitometry.

EXPERIMENTAL SECTION

N-Ethylformamide (NEF; Fluka, $\omega > 0.99$), 2-pentanone (P; Fluka, $\omega > 0.995$), propylacetate (PA; J. T. Baker, $\omega > 0.995$), and tetrahydropyran (THP; Merck, $\omega > 0.995$) were used without further purification (Table 1). The purity of the substances was controlled by gas–liquid chromatography/mass spectrometry (GLC-MS) and agrees well with the values reported by the manufacturers. The chemicals, as well as the mixtures, were not degassed.

Table 1. Chemical Information

chemical name	source	mole fraction purity	purification method	analysis method
<i>n</i> -ethylformamide	Fluka	>0.99	none	GLC-MS
2-pentanone	Fluka	>0.995	none	GLC-MS
propylacetate	J. T. Baker	>0.995	none	GLC-MS
tetrahydropyran	Merck	>0.995	none	GLC-MS

The vibrating tube densimeter, Rudolph Research Analytical DDM 2911, was used for density measurements. The precision of the densimeter were $\pm 0.00001 \text{ g}\cdot\text{cm}^{-3}$. The error of measured density was less than $6\cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. The instrument was automatically thermostatted (Peltier-type) within $\pm 0.02 \text{ K}$ and was calibrated at the atmospheric pressure before each series of measurements. The calibration was performed using ambient air and bidistilled ultra pure water. The mixtures were prepared by weighing the pure liquids. Denver instruments analytical balance weighing up to an accuracy of $\pm 0.00001 \text{ g}$ was used. The possible error in the mole fractions is estimated to be less than $3\cdot 10^{-4}$. The uncertainty in excess molar volume was estimated to be less than $\pm 0.02 \text{ cm}^3\cdot\text{mol}^{-1}$. The molar masses were based on the relative atomic mass table issued by the International Union of Pure and Applied Chemistry (IUPAC).⁹ Table 2 shows experimental and literature values of densities of the pure liquids at the specified temperatures.

Received: March 25, 2012

Accepted: March 13, 2013

Table 2. Experimental and Literature Data^a of Densities ($d/\text{g}\cdot\text{cm}^{-3}$) of the Pure Liquids at Specified Temperatures (T) and Atmospheric Pressure (0.1 MPa)

T/K	present work	literature
N-Ethylformamide		
293.15	0.95159	
298.15	0.94748	0.9447 ¹⁰
303.15	0.94329	
308.15	0.93904	0.9364 ¹⁰
313.15	0.93478	
Tetrahydropyran		
293.15	0.88408	
298.15	0.87895	0.87886; ¹¹ 0.8792; ⁸ 0.87723 ¹²
303.15	0.87379	0.8742 ⁸
308.15	0.86867	0.86880; ¹¹ 0.8692 ⁸
313.15	0.86343	0.8640; ⁸ 0.86460 ¹³
2-Pentanone		
293.15	0.80747	
298.15	0.80246	0.8021; ⁸ 0.80135; ¹⁴ 0.80145 ¹⁵
303.15	0.79753	0.7972; ⁸ 0.79657 ¹⁶
308.15	0.79252	0.7922; ⁸ 0.79161 ¹⁴
313.15	0.78744	0.7873 ⁸
Propyl Acetate		
293.15	0.88797	
298.15	0.88221	0.8823; ⁸ 0.8834; ¹⁷ 0.88333; ¹⁸ 0.8837 ¹⁹
303.15	0.87654	0.8767; ⁸ 0.87635 ²⁰
308.15	0.87081	0.8710 ⁸
313.15	0.86495	0.8653 ⁸

^aStandard uncertainties u : $u(d) = 6 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$; $u(T) = 0.02 \text{ K}$.**RESULTS AND DISCUSSION**

Excess molar volumes, V^E , were calculated from the density of the mixture, d , densities of the pure components, d_i , the corresponding mole fractions, x_i , and molar masses, M_i , using the equation:

$$V^E = x_1 M_1 \left(\frac{1}{d} - \frac{1}{d_1} \right) + x_2 M_2 \left(\frac{1}{d} - \frac{1}{d_2} \right) \quad (1)$$

where x_1 , M_1 , and d_1 relate to NEF and x_2 , M_2 , and d_2 relate to the second component (THP, P, or PA). The excess molar volumes are given in Table 3 and graphically represented in Figure 1. Using a Redlich–Kister-type²¹ equation:

$$V^E = x_1 x_2 \sum_{i=0}^n A_i (2x_1 - 1)^i \quad (2)$$

excess molar volumes were fitted by a method of the least-squares. Here, A_i are adjustable parameters, and n is the number of the coefficients in the equation. The standard deviation of the fit is given as:

$$\sigma V^E = \left[\sum_{i=1}^m (V_{\text{exp}}^E - V_{\text{calc}}^E)^2 / (m - n) \right]^{1/2} \quad (3)$$

where m denotes the number of experimental points. The coefficients in the Redlich–Kister equation,²¹ as well as the standard deviations of the fit and the square of the correlation coefficient, are given in Table 4.

Table 3. Density (d), Excess Molar Volumes (V^E), Apparent Molar Volumes ($V_{\phi i}$), and Partial Molar Volumes (V_i) at Different Temperatures (T), Compositions (x) of the Studied Mixtures, and Atmospheric Pressure (0.1 MPa)^a

x_1	NEF (1) + THP (2)							
	d $\text{g}\cdot\text{cm}^{-3}$	V^E $\text{cm}^3\cdot\text{mol}^{-1}$	V_1 $\text{cm}^3\cdot\text{mol}^{-1}$	V_1^E $\text{cm}^3\cdot\text{mol}^{-1}$	V_2 $\text{cm}^3\cdot\text{mol}^{-1}$	V_2^E $\text{cm}^3\cdot\text{mol}^{-1}$	$V_{\phi 1}$ $\text{cm}^3\cdot\text{mol}^{-1}$	$V_{\phi 2}$ $\text{cm}^3\cdot\text{mol}^{-1}$
$T/\text{K} = 293.15$								
0.12939	0.89225	−0.116	76.138	−0.681	97.394	−0.031	85.661	95.781
0.24564	0.89954	−0.171	76.405	−0.415	97.334	−0.091	84.509	94.312
0.35652	0.90652	−0.190	76.550	−0.264	97.273	−0.155	83.432	92.898
0.46942	0.91389	−0.199	76.634	−0.175	97.214	−0.216	82.327	91.452
0.55957	0.91991	−0.191	76.678	−0.132	97.168	−0.263	81.431	90.269
0.65866	0.92672	−0.172	76.717	−0.095	97.107	−0.320	80.428	88.971
0.74777	0.93300	−0.144	76.750	−0.064	97.029	−0.393	79.518	87.782
0.83634	0.93947	−0.111	76.780	−0.035	96.910	−0.509	78.583	86.617
0.91817	0.94556	−0.069	76.803	−0.011	96.745	−0.682	77.702	85.603
$T/\text{K} = 298.15$								
0.12939	0.88729	−0.125	76.417	−0.739	97.959	0.535	86.161	96.301
0.24564	0.89473	−0.187	76.715	−0.443	97.892	0.468	84.982	94.792
0.35652	0.90180	−0.205	76.875	−0.273	97.824	0.396	83.869	93.352
0.46942	0.90926	−0.211	76.965	−0.176	97.762	0.329	82.748	91.857
0.55957	0.91535	−0.201	77.009	−0.131	97.714	0.282	81.843	90.658
0.65866	0.92225	−0.180	77.047	−0.096	97.654	0.227	80.817	89.322
0.74777	0.92863	−0.151	77.081	−0.067	97.576	0.157	79.892	88.109
0.83634	0.93519	−0.117	77.112	−0.037	97.455	0.041	78.941	86.922
0.91817	0.94136	−0.071	77.136	−0.012	97.285	−0.143	78.041	85.868
$T/\text{K} = 303.15$								
0.12939	0.88235	−0.140	76.680	−0.816	98.532	−0.040	86.672	96.822
0.24564	0.88993	−0.207	77.018	−0.480	98.456	−0.116	85.454	95.272
0.35652	0.89709	−0.225	77.196	−0.294	98.381	−0.194	84.323	93.798
0.46942	0.90467	−0.232	77.294	−0.191	98.313	−0.265	83.168	92.279
0.55957	0.91086	−0.223	77.341	−0.144	98.263	−0.316	82.249	91.062

Table 3. continued

x_1	NEF (1) + THP (2)							
	d g·cm ⁻³	V^E cm ³ ·mol ⁻¹	V_1 cm ³ ·mol ⁻¹	V_1^E cm ³ ·mol ⁻¹	V_2 cm ³ ·mol ⁻¹	V_2^E cm ³ ·mol ⁻¹	$V_{\phi 1}$ cm ³ ·mol ⁻¹	$V_{\phi 2}$ cm ³ ·mol ⁻¹
$T/K = 303.15$								
0.65866	0.91778	-0.194	77.382	-0.105	98.199	-0.375	81.221	89.693
0.74777	0.92429	-0.167	77.417	-0.073	98.115	-0.453	80.272	88.474
0.83634	0.93093	-0.130	77.451	-0.040	97.984	-0.582	79.299	87.273
0.91817	0.93711	-0.076	77.477	-0.013	97.794	-0.780	78.402	86.182
$T/K = 308.15$								
0.12939	0.87739	-0.150	76.972	-0.872	99.112	-0.041	87.162	97.362
0.24564	0.88505	-0.218	77.320	-0.525	99.0342	-0.120	85.923	95.773
0.35652	0.89240	-0.246	77.510	-0.330	98.954	-0.202	84.774	94.263
0.46942	0.90006	-0.252	77.619	-0.218	98.878	-0.280	83.601	92.708
0.55957	0.90631	-0.241	77.675	-0.162	98.819	-0.339	82.659	91.472
0.65866	0.91338	-0.216	77.723	-0.116	98.744	-0.411	81.607	90.079
0.74777	0.91992	-0.183	77.763	-0.078	98.649	-0.503	80.648	88.842
0.83634	0.92657	-0.138	77.800	-0.041	98.505	-0.645	79.674	87.613
0.91817	0.93285	-0.084	77.828	-0.013	98.305	-0.851	78.762	96.544
$T/K = 313.15$								
0.12939	0.87228	-0.156	77.264	-0.948	99.712	-0.039	87.662	97.912
0.24564	0.88014	-0.236	77.632	-0.583	99.629	-0.122	86.408	96.284
0.35652	0.88760	-0.266	77.836	-0.361	99.543	-0.216	85.233	94.744
0.46942	0.89534	-0.270	77.955	-0.229	99.460	-0.307	84.041	93.148
0.55957	0.90171	-0.260	78.017	-0.168	99.395	-0.372	83.079	91.878
0.65866	0.90884	-0.231	78.070	-0.122	99.312	-0.444	82.018	90.472
0.74777	0.91546	-0.196	78.113	-0.085	99.209	-0.532	81.044	89.203
0.83634	0.92222	-0.150	78.153	-0.047	99.056	-0.678	80.053	87.961
0.91817	0.92854	-0.090	78.182	-0.015	98.845	-0.912	79.122	96.873
x_1	NEF (1) + P (2)							
	d g·cm ⁻³	V^E cm ³ ·mol ⁻¹	V_1 cm ³ ·mol ⁻¹	V_1^E cm ³ ·mol ⁻¹	V_2 cm ³ ·mol ⁻¹	V_2^E cm ³ ·mol ⁻¹	$V_{\phi 1}$ cm ³ ·mol ⁻¹	$V_{\phi 2}$ cm ³ ·mol ⁻¹
$T/K = 293.15$								
0.14201	0.82457	-0.218	75.583	-1.222	106.629	-0.044	94.572	102.48
0.26095	0.83940	-0.320	75.915	-0.890	106.546	-0.127	92.363	98.991
0.37729	0.85471	-0.386	76.159	-0.653	106.432	-0.237	90.155	95.503
0.48596	0.86994	-0.434	76.341	-0.475	106.294	-0.373	88.022	92.198
0.58273	0.88391	-0.422	76.478	-0.338	106.137	-0.531	86.064	89.234
0.67682	0.89809	-0.381	76.593	-0.220	105.940	-0.732	84.089	86.319
0.76276	0.91159	-0.320	76.683	-0.128	105.708	-0.969	82.244	83.648
0.84644	0.92535	-0.243	76.753	-0.058	105.419	-1.260	80.369	81.078
0.92212	0.93819	-0.146	76.796	-0.016	105.088	-1.582	78.633	78.817
$T/K = 298.15$								
0.14201	0.81984	-0.247	75.840	-1.288	107.280	-0.062	95.115	103.069
0.26095	0.83464	-0.337	76.246	-0.883	107.180	-0.161	92.832	99.518
0.37729	0.85005	-0.406	76.507	-0.639	107.059	-0.275	90.602	95.974
0.48596	0.86533	-0.450	76.682	-0.472	106.926	-0.401	88.447	92.615
0.58273	0.87938	-0.436	76.808	-0.345	106.782	-0.548	86.469	89.603
0.67682	0.89359	-0.389	76.916	-0.231	106.597	-0.742	84.491	86.653
0.76276	0.90719	-0.326	77.005	-0.138	106.368	-0.984	82.613	83.931
0.84644	0.92115	-0.257	77.078	-0.063	106.062	-1.293	80.722	81.348
0.92212	0.93402	-0.152	77.126	-0.018	105.690	-1.645	78.982	79.054
$T/K = 303.15$								
0.14201	0.81499	-0.253	76.137	-1.333	107.945	-0.061	95.590	103.671
0.26095	0.82986	-0.346	76.542	-0.929	107.845	-0.160	93.303	100.048
0.37729	0.84542	-0.425	76.812	-0.676	107.719	-0.278	91.054	96.452
0.48596	0.86076	-0.468	76.999	-0.499	107.578	-0.413	88.867	93.044
0.58273	0.87488	-0.454	77.135	-0.361	107.422	-0.571	86.884	89.989
0.67682	0.88919	-0.407	77.251	-0.239	107.224	-0.780	84.879	86.994
0.76276	0.90285	-0.341	77.344	-0.141	106.982	-1.034	82.991	84.244
0.84644	0.91686	-0.268	77.420	-0.064	106.666	-1.353	81.088	81.633
0.92212	0.92975	-0.156	77.469	-0.017	106.290	-1.709	79.333	79.285

Table 3. continued

x_1	NEF (1) + P (2)							
	d g·cm ⁻³	V^E cm ³ ·mol ⁻¹	V_1 cm ³ ·mol ⁻¹	V_1^E cm ³ ·mol ⁻¹	V_2 cm ³ ·mol ⁻¹	V_2^E cm ³ ·mol ⁻¹	$V_{\phi 1}$ cm ³ ·mol ⁻¹	$V_{\phi 2}$ cm ³ ·mol ⁻¹
$T/K = 308.15$								
0.14201	0.81011	-0.266	76.418	-1.388	108.626	-0.067	96.101	104.268
0.26095	0.82509	-0.365	76.836	-0.971	108.522	-0.170	93.778	100.605
0.37729	0.84071	-0.444	77.117	-0.722	108.392	-0.285	91.515	96.944
0.48596	0.85622	-0.498	77.312	-0.543	108.244	-0.422	89.313	93.482
0.58273	0.87035	-0.476	77.457	-0.396	108.078	-0.591	87.288	90.384
0.67682	0.88490	-0.443	77.581	-0.260	107.865	-0.823	85.274	87.365
0.76276	0.89851	-0.363	77.682	-0.150	107.604	-1.107	83.372	84.571
0.84644	0.91254	-0.282	77.765	-0.066	107.261	-1.456	81.464	81.927
0.92212	0.92553	-0.169	77.818	-0.017	106.851	-1.829	79.692	79.613
$T/K = 313.15$								
0.14201	0.80514	-0.275	76.706	-1.463	109.324	-0.069	96.618	104.901
0.26095	0.82027	-0.387	77.151	-1.019	109.213	-0.178	94.279	101.152
0.37729	0.83596	-0.466	77.446	-0.748	109.076	-0.304	91.981	97.433
0.48596	0.85152	-0.516	77.649	-0.558	108.922	-0.448	89.754	93.922
0.58273	0.86576	-0.496	77.797	-0.407	108.751	-0.622	87.723	90.778
0.67682	0.88034	-0.458	77.926	-0.270	108.532	-0.856	85.677	87.709
0.76276	0.89409	-0.381	78.030	-0.159	108.262	-1.144	83.762	84.885
0.84644	0.90821	-0.297	78.116	-0.072	107.905	-1.505	81.833	82.232
0.92212	0.92117	-0.171	78.171	-0.020	107.476	-1.906	80.059	79.822
x_1	NEF (1) + PA (2)							
	d g·cm ⁻³	V^E cm ³ ·mol ⁻¹	V_1 cm ³ ·mol ⁻¹	V_1^E cm ³ ·mol ⁻¹	V_2 cm ³ ·mol ⁻¹	V_2^E cm ³ ·mol ⁻¹	$V_{\phi 1}$ cm ³ ·mol ⁻¹	$V_{\phi 2}$ cm ³ ·mol ⁻¹
$T/K = 293.15$								
0.15195	0.89654	-0.216	75.858	-0.864	114.947	-0.100	85.422	113.069
0.28033	0.90350	-0.277	76.282	-0.461	114.834	-0.205	84.175	111.454
0.39692	0.91007	-0.293	76.489	-0.332	114.729	-0.269	83.088	109.924
0.50336	0.91650	-0.298	76.595	-0.258	114.644	-0.330	82.086	108.465
0.60207	0.92266	-0.271	76.658	-0.183	114.566	-0.424	81.145	107.048
0.68970	0.92861	-0.251	76.703	-0.112	114.484	-0.555	80.249	105.762
0.77680	0.93472	-0.207	76.744	-0.050	114.370	-0.724	79.338	104.444
0.85444	0.94020	-0.135	76.778	-0.014	114.220	-0.880	78.498	103.168
0.92840	0.94586	-0.072	76.803	-0.001	114.012	-0.987	77.661	101.953
$T/K = 298.15$								
0.15195	0.89104	-0.230	76.120	-0.935	115.694	0.647	85.992	113.755
0.28033	0.89820	-0.297	76.574	-0.502	115.572	0.534	84.688	112.064
0.39692	0.90495	-0.315	76.799	-0.356	115.459	0.461	83.594	110.469
0.50336	0.91154	-0.319	76.915	-0.271	115.365	0.392	82.563	108.964
0.60207	0.91788	-0.292	76.987	-0.190	115.280	0.290	81.577	107.512
0.68970	0.92391	-0.264	77.033	-0.115	115.191	0.153	80.684	106.174
0.77680	0.93021	-0.221	77.076	-0.052	115.072	-0.022	79.733	104.807
0.85444	0.93579	-0.141	77.111	-0.015	114.917	-0.183	78.884	103.480
0.92840	0.94163	-0.078	77.136	-0.001	114.706	-0.293	78.008	102.254
$T/K = 303.15$								
0.15195	0.88563	-0.248	76.385	-1.020	116.437	-0.108	86.564	114.424
0.28033	0.89295	-0.316	76.872	-0.552	116.307	-0.230	85.233	112.684
0.39692	0.89993	-0.344	77.113	-0.384	116.186	-0.314	84.087	111.032
0.50336	0.90664	-0.344	77.237	-0.289	116.085	-0.392	83.032	109.478
0.60207	0.91309	-0.313	77.311	-0.203	115.993	-0.498	82.028	107.982
0.68970	0.91927	-0.284	77.364	-0.127	115.898	-0.639	81.007	106.588
0.77680	0.92574	-0.241	77.411	-0.061	115.766	-0.821	80.131	105.211
0.85444	0.93141	-0.155	77.449	-0.021	115.595	-0.997	79.264	103.847
0.92840	0.93736	-0.086	77.477	-0.003	115.361	-1.140	78.371	102.587
$T/K = 308.15$								
0.15195	0.88007	-0.254	76.677	-1.075	117.208	-0.899	87.101	115.121
0.28033	0.88759	-0.331	77.156	-0.617	117.079	-1.020	85.748	113.313

Table 3. continued

x_1	NEF (1) + PA (2)							
	d g·cm ⁻³	V^E cm ³ ·mol ⁻¹	V_1 cm ³ ·mol ⁻¹	V_1^E cm ³ ·mol ⁻¹	V_2 cm ³ ·mol ⁻¹	V_2^E cm ³ ·mol ⁻¹	$V_{\phi 1}$ cm ³ ·mol ⁻¹	$V_{\phi 2}$ cm ³ ·mol ⁻¹
$T/K = 308.15$								
0.39692	0.89476	-0.364	77.406	-0.441	116.953	-1.108	84.587	111.615
0.50336	0.90171	-0.374	77.546	-0.332	116.839	-1.197	83.512	110.002
0.60207	0.90831	-0.341	77.636	-0.231	116.729	-1.323	82.477	108.459
0.68970	0.91464	-0.312	77.700	-0.142	116.612	-1.486	81.518	107.049
0.77680	0.92117	-0.258	77.755	-0.067	116.458	-1.693	80.540	105.625
0.85444	0.92704	-0.175	77.798	-0.022	116.268	-1.889	79.644	104.258
0.92840	0.93301	-0.093	77.828	-0.003	116.018	-2.042	78.738	102.938
$T/K = 313.15$								
0.15195	0.87446	-0.269	76.943	-1.167	118.001	-0.105	87.688	115.834
0.28033	0.88219	-0.354	77.445	-0.684	117.866	-0.232	86.301	113.959
0.39692	0.88956	-0.392	77.719	-0.483	117.728	-0.334	85.110	112.202
0.50336	0.89671	-0.406	77.877	-0.355	117.599	-0.439	84.001	110.533
0.60207	0.90344	-0.369	77.979	-0.241	117.472	-0.580	82.944	108.938
0.68970	0.90986	-0.331	78.050	-0.146	117.343	-0.755	81.965	107.487
0.77680	0.91656	-0.277	78.110	-0.068	117.179	-0.970	80.953	106.022
0.85444	0.92251	-0.184	78.153	-0.022	116.985	-1.170	80.033	104.615
0.92840	0.92864	-0.099	78.183	-0.003	116.738	-1.323	79.114	103.279

^aStandard uncertainties u : $u(d) = 6 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$; $u(T) = 0.02 \text{ K}$; $u(x) = 3 \cdot 10^{-4}$; $u(V^E) = 0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $u(V_{\phi}) = 0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$.

The excess molar volume has a negative value for all studied systems over whole composition range and at all temperatures. Similar results have been obtained for NMF with tetrahydrofuran (THF), 2-butanone (B), ethylacetate (EA), and NMF + THP, NMF + P, and NMF + PA mixtures.^{7,8} The negative excess molar volumes can be attributed to the dominance of the following effects: formation of heteromolecular complexes due to strong specific interactions such as hydrogen bonding, nonspecific van der Waals interactions between molecules of the components, and sterically favored fitting of one component molecules with other molecules.

The components THP, P, and PA are polar substances, with dipole moments:²² 1.87 D, 2.5 D, and 1.78 D, respectively. These compounds are not capable to self-associate through hydrogen bonding. On the other hand, *N*-substituted amides are highly polar molecules²³ ($\mu \approx 3.8 \text{ D}$). NEF has a dielectric constant:²⁴ $\epsilon \approx 100$. Spectroscopic^{25–27} and dielectric studies²⁸ clearly confirm the self-association of the secondary amides through $\text{N}-\text{H} \cdots \text{C}=\text{O}$ hydrogen bonds. It is very important to know that self-associated forms of the secondary amides may persist even in dilute solutions.^{29,30} Thus, this fact should be taken into account for the whole composition range of the mixtures.

$\text{N}-\text{H} \cdots \text{O}$ hydrogen bonded complex formation of *N*-substituted amides with ethers and ketones and consequently esters was clearly confirmed by spectroscopic techniques.^{31,32} Accordingly, the negative values obtained in this study can be mainly attributed to complex formation between the components of the investigated mixtures. Also, Keesom dipole–dipole van der Waals forces contribute to negative V^E due to the values of the dipole moments of the components.

The data in Table 3 and Figure 1 show that the THP system deviates less from ideality than P and PA ones. Lady and Whetsel³³ using IR spectroscopy have obtained equilibrium constants for $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonding between amines and

ethers, ketones and esters. They have found that ethers form less stable complexes with NH proton than ketones and esters. This fact is in accordance with values of V^E for the mixtures studied in this paper.

Since the equilibrium constants for hydrogen-bonded complex formation for ketones and esters are the similar values, *y*r more negative values for P mixture probably can be explained on the basis of the significantly higher values for its dipole moment.

For the investigated mixtures, a decrease in V^E over the whole composition range is noticeable with increasing temperature from (293.15 to 313.15) K. The same temperature dependence of the excess molar volumes has been detected for other mixtures.^{7,8} The increase of temperature leads to the increase in kinetic energy of the self-associated species of NEF; that is, it promotes their dissociation. Of course, the temperature has the same influence on the complex between the components of the mixture. The observed results indicate that the increase of the temperature has a greater effect on NEF self-association than it has on complex formation between the components. This assumption is confirmed by the hydrogen bonding enthalpies. Namely, dimerization enthalpies for *N*-substituted amides³⁴ are in the range from (−18 to −20) $\text{kJ} \cdot \text{mol}^{-1}$, while the corresponding enthalpy for $\text{N}-\text{H} \cdots \text{O}$ complexes of NH group with ethers, ketones, and esters³³ is about −14 $\text{kJ} \cdot \text{mol}^{-1}$.

Since the self-association is more exothermic than $\text{N}-\text{H} \cdots \text{O}$ complex formation between components in the mixture, the increase of the temperature has greater effect on the NEF self-association. As the result, the complex formation equilibrium is more shifted toward the complex, and V^E becomes more negative at higher temperatures.

A comparison of the data from this study with the data for NMF mixtures with THP, P, and PA⁷ reveals the fact that V^E values for NEF mixtures are less negative than V^E for NMF ones. In the other words, the ethyl group attached to *N*-atom of NEF is responsible for less volume contraction (more positive V^E)

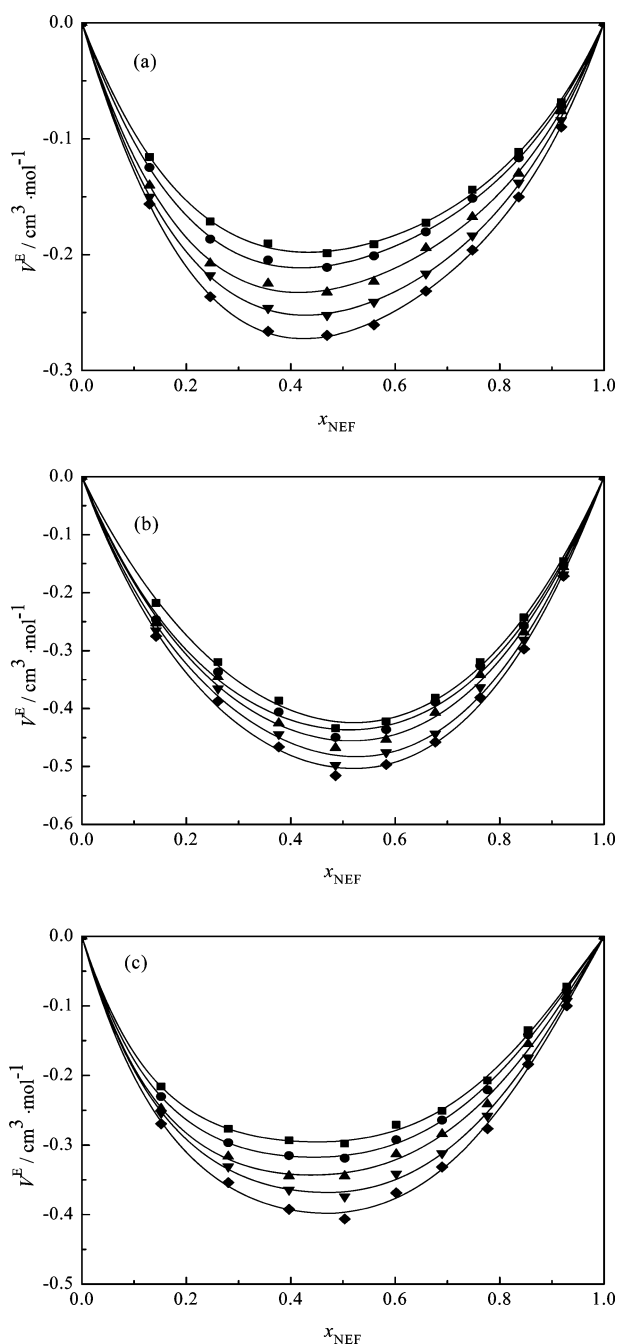


Figure 1. Variation of the excess molar volumes (V^E) of studied mixtures NEF + THP (a), NEF + P (b), and NEF + PA (c) at different temperatures: ■, 293.15; ●, 298.15; ▲, 303.15; ▼, 308.15; ◆, 313.15 K.

than in the systems with NMF. It can be explained on the basis of the difference in steric hindrance of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ N -substituents in NMF and NEF. Namely, van der Waals volumes³⁵ of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ groups are 13.67 and 23.90 $\text{cm}^3 \cdot \text{mol}^{-1}$, respectively.

From Figure 2 it is evident that mixtures of N -ethylformamide with THF (Figure 2a)³⁶ and EA (Figure 2c) have more negative V_m^E values comparing to those of THF and PA. These results are in a good agreement with the results of analogous studies of binary mixtures of N -methylformamide^{7,8} and N -methylacetamide.⁶ These differences in the additional molar volumes can be explained by the differences in the

Table 4. Coefficients (A_i) of the Redlich–Kister eq 2 and the Standard Deviations (σ) of the Fit at Various Temperatures (T)

T/K	A_0 $\text{cm}^3 \cdot \text{mol}^{-1}$	A_1 $\text{cm}^3 \cdot \text{mol}^{-1}$	A_2 $\text{cm}^3 \cdot \text{mol}^{-1}$	A_3 $\text{cm}^3 \cdot \text{mol}^{-1}$	σ $\text{cm}^3 \cdot \text{mol}^{-1}$
NEF (1) + THP (2)					
293.15	−0.7815	0.1467	−0.2715	−0.0442	0.0023
298.15	−0.8289	0.1956	−0.3015	−0.0741	0.0021
303.15	−0.9107	0.2199	−0.3516	−0.0538	0.0030
308.15	−0.9930	0.2061	−0.3446	−0.0326	0.0017
313.15	−1.0703	0.2488	−0.3445	−0.1329	0.0015
NEF (1) + P (2)					
293.15	−1.6943	−0.1225	−0.2123	0.0504	0.0078
298.15	−1.7455	−0.0663	−0.3843	0.1107	0.0111
303.15	−1.8215	−0.0906	−0.3517	0.1185	0.0108
308.15	−1.9279	−0.1569	−0.3841	0.2131	0.0115
313.15	−2.0109	−0.1289	−0.4108	0.1605	0.0093
NEF (1) + PA (2)					
293.15	−1.1753	0.1339	−0.4747	0.5318	0.0048
298.15	−1.2611	0.1662	−0.4810	0.5291	0.0049
303.15	−1.3612	0.1952	−0.5165	0.4852	0.0065
308.15	−1.4689	0.1287	−0.4698	0.5068	0.0051
313.15	−1.5872	0.1530	−0.4322	0.4910	0.0064

stability of the heteromolecular $\text{NH} \cdots \text{O}$ bonds. Components that have the additional methylene group (PA and THP) form less stable complexes with N -ethylformamide due to more pronounced steric hindrance. This trend is already observed in analogous systems of N -methylformamide with THF and THP.⁸

An unexpected difference in the additional molar volumes of the 2-butanone³⁶ and 2-pentanone can be observed in Figure 2b. Because of the additional methylene group, more negative V_m^E values are expected for the mixtures with 2-butanone. Oppositely, the additional molar volumes in the mole fraction range from (0.4 to 1.0) of N -ethylformamide are more negative for the system with 2-pentanone. This anomaly has been also observed in the binary mixtures of N -methylformamide with 2-butanone and 2-pentanone.^{7,8} A possible explanation for the unexpected results requires consideration of atypical hydrogen bonding and conformation of these amides and ketones. These differences in the volumetric properties of binary mixtures with ethers, esters, and ketones deserve further research.

In addition to V^E , other volumetric properties have been calculated, too. The apparent molar volumes, $V_{\phi 1}$ and $V_{\phi 2}$, reported in Table 3 are the apparent molar volumes of NEF and the second component.

Since Redlich–Kister polynomial equation very well describes the investigated systems, the coefficients A_i can be used to obtain the volumetric characteristics of the mixture.

The partial molar volumes of the components, V_1 and V_2 can be also calculated knowing the molar volumes of the pure components, V_1^0 (NEF) and V_2^0 (THP, P, or PA). The values for the partial molar volume are given in Table 3.

Partial molar properties at infinite dilution, V_1^∞ and V_2^∞ , provide useful information about solute–solvent interactions. Namely, at the infinite dilution solute–solute interaction can be neglected. Thus, we calculated these values together with partial excess molar values at infinite dilution of the components and thermal expansivities. Obtained results are given in the Supporting Information of this manuscript.

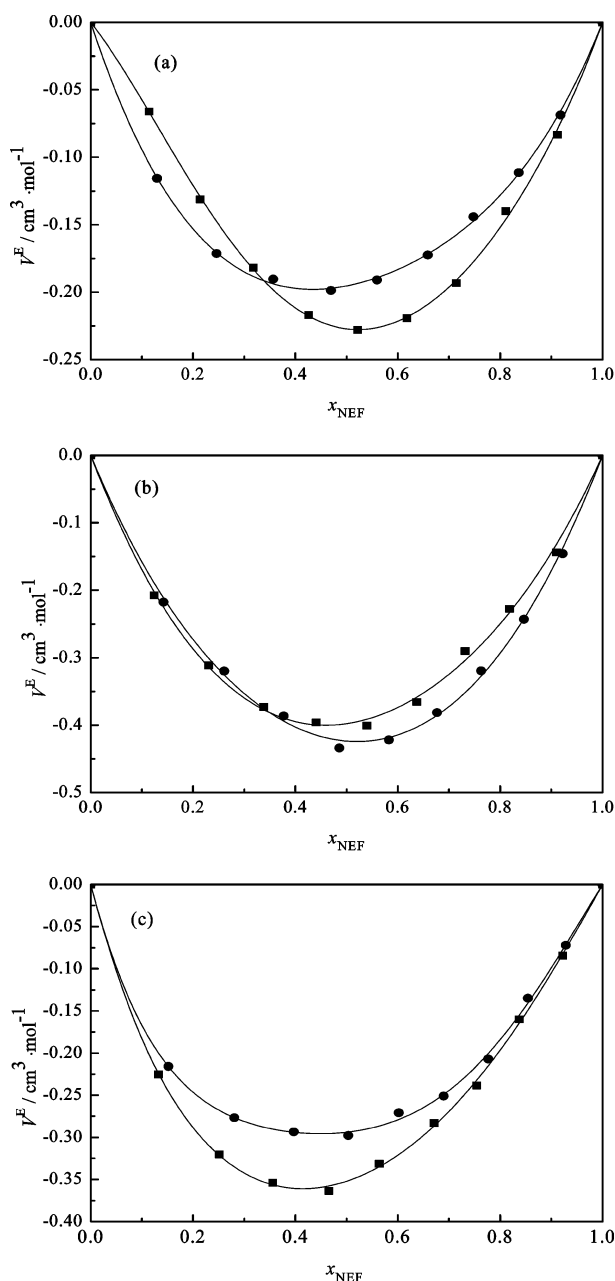


Figure 2. Comparison of the excess molar volumes (V^E) at 293.15 K for the binary mixtures of NEF with: (a) ■, THF; ●, THP; (b) ■, B; ●, P; (c) ■, EA; ●, PA.

CONCLUSION

Volumetric properties of *N*-ethylformamide binary liquid mixtures with tetrahydropyran, 2-pentanone, and propylacetate were studied at various temperatures at atmospheric pressure in the whole composition range. The deduced excess molar volumes for all of the investigated mixtures are negative in the whole mole fraction range and at all temperatures, but a decrease in V^E over the whole composition range is noticeable with increasing temperature from (293.15 to 313.15) K. The observed results indicate that the increase of the temperature has a greater effect on *N*-ethylformamide self-association than it has on complex formation between the components.

ASSOCIATED CONTENT

Supporting Information

Partial molar volumes and partial excess volumes at infinite dilution for the components of the studied mixtures at different temperatures and thermal expansion coefficients as a function of temperature for investigated mixtures (pdf) as well as experimental density results (xls). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

This work was financially supported by the Ministry of Education and Science of Serbia under contract number ON172012 and ON172013 and The Provincial Secretariat for Science and Technological Development of APV.

Notes

The authors declare no competing financial interest.

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