Volumetric properties of binary mixtures of *N*-ethylformamide with tetrahydrofuran, 2-butanone, and ethylacetate from *T* = (293.15 to 313.15) K

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ABSTRACT

Densities of binary liquid mixtures of *N*-ethylformamide (NEF) with tetrahydrofuran (THF), 2-butanone (B), and ethylacetate (EA) 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 obtained from values of the experimental density and were fitted to the Redlich–Kister polynomial equation. The V^E values for all three mixtures are negative over the entire composition and temperature ranges. The V^E values become more negative as the temperature increases for all binary mixtures studied. Other volumetric properties, such as isobaric thermal expansion coefficients, partial molar volumes, apparent molar volumes, partial molar excess volumes and excess thermal expansions have been calculated.

1. Introduction

The *N*-substituted amides have been attracting scientific attention for many years since this class of compounds can be regarded as a simple model of biological systems with the peptide groups. The paper is a part of a systematic investigation of the secondary amides in solutions and in the binary mixtures. These studies have been performed from spectroscopic [1–3], thermodynamic [4,5], and densitometric [6,7] aspects. The last two papers have included *N*-methylformamide (NMF) with THF, B, and EA. The intention of the present paper is to investigate the effect of an additional methylene group (in the alkyl substituent on *N*-atom of the amide) on the volumetric properties of the mixtures. Thus, this study includes the mixtures of *N*-ethylformamide with THF, B, and EA for the first time. Volumetric properties of selected organic solvents (THF, B, and EA) were studied earlier in mixtures with different liquids. Mixtures and properties of THF with water [8], n-alkynes [9], and chloro ethane [10], B with hydrofluoroethers [11] and EA with methanol and ethanol [12] were described earlier by other authors.

2. Experimental

The NEF (Fluka, mass fraction purity ⩾ 0.99), B (Fluka, mass fraction purity ⩾ 0.995), EA (J.T. Baker, mass fraction purity ⩾ 0.995),

and THF (Merck, mass fraction purity ⩾ 0.995) were used without further purification. The purity of the substances was controlled by the GLC–MS method and agrees well with the values reported by the manufacturers. The summary of the provenance and purity is given in table 1. The chemicals, as well as the mixtures, were not degassed.

The vibrating tube densimeter, Rudolph Research Analytical DDM 2911, was used for density measurements. The accuracy and precision of the densimeter were ±0.00001 g · cm^{-3}. The instrument was automatically thermostatted (Peltier-type) within ±0.02 K and was calibrated at the atmospheric pressure before each series of measurements. The calibration was performed using ambient air and bi-distilled ultra pure water. The mixtures were prepared by weighing the pure liquids. A Denver instruments analytical balance weighing up to an accuracy of ±0.00001 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 ±0.001 cm^3 · mol^{-1}. The molar masses were based on the relative atomic mass table issued by IUPAC [13]. Table 2 contains experimental and literature values of densities of the pure liquids at the specified temperatures.

3. Results and discussion

Values of the excess molar volume, V^E, were calculated from the density of the mixture, ρ, densities of the pure components, ρ_i, the

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TABLE 1
Provenance and purity of the samples.

Chemical name	Provenance	Mass fraction purity
N-ethylformamide	Fluka	$\geqslant 0.99$
2-Butanone	Fluka	$\geqslant 0.995$
Ethylacetate	J.T. Backer	$\geqslant 0.995$
Tetrahydrofuran	Merck	$\geqslant 0.995$

TABLE 2
Experimental and literature values of densities (ρ) of the pure liquids at the specified temperatures.

Component	$\rho/(\text{g} \cdot \text{cm}^{-3})$		
	T/K	This work	References
N-Ethylformamide	293.15	0.95159	0.9552^a
	298.15	0.94748	0.9447^b
	303.15	0.94329	
	308.15	0.93904	0.9364^b
	313.15	0.93478	
Tetrahydrofuran	293.15	0.88873	0.8897^c
	298.15	0.88324	0.8827^d; 0.8833^e
	303.15	0.87760	0.8770^c; 0.8773^d; 0.8779^e
	308.15	0.87202	0.8718^d; 0.8724^e
	313.15	0.86623	0.8612^c
2-Butanone	293.15	0.80864	0.80512^f; 0.80495^g;
	298.15	0.80324	0.79989^f; 0.79974^g; 0.79971^h; 0.79985^i
	303.15	0.79788	0.79467^f; 0.79448^g
	308.15	0.79245	0.78940^f
	313.15	0.78694	0.78412^f
Ethylacetate	293.15	0.90026	0.90062^j; 0.90053^k; 0.8935^l
	298.15	0.89414	0.89444^k; 0.8946^m
	303.15	0.88785	0.88839^j; 0.88831^k; 0.8828^l; 0.8885^m
	308.15	0.88152	0.88214^k; 0.8825^m
	313.15	0.87514	0.87603^j; 0.87275^k; 0.8735^l

[a] Reference [14].
[b] Reference [15].
[c] Reference [16].
[d] Reference [17].
[e] Reference [18].
[f] Reference [19].
[g] Reference [20].
[h] Reference [21].
[i] Reference [22].
[j] Reference [23].
[k] Reference [24].
[l] Reference [25].
[m] Reference [26].

corresponding mole fractions, x_i, and molar masses, M_i, using the equation:

$$V^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2}\right), \tag{1}$$

where x_1, M_1, ρ_1 relate to NEF and x_2, M_2, ρ_2 relate to the second component (THF, B, or EA). Values of the excess molar volumes are given in Table 3 and graphically represented in figure 1. Using a Redlich–Kister-type [27] equation:

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

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

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

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

The excess molar volume has a negative value for all systems studied over the whole composition range and at all temperatures. Similar results have been obtained for {N-methylformamide (NMF) + acetone [28]} and (NMF + THF), (NMF + B), and (NMF + EA) mixtures [7]. The negative excess molar volumes can be attributed to the dominance of the following effects:

– specific, relatively strong interactions between components, as hydrogen bonding,
– non-specific, van der Waals interactions between molecules of the components and
– size and structure of the molecule which favours fitting of the molecules with each other.

The components THF, B, and EA are polar substances, with dipole moments [28] of 1.63 D, 2.8 D, and 1.78 D, respectively. They are not capable to self-associate through hydrogen bonding. On the other hand, N-substituted amides are highly polar molecules [29] ($\mu \approx 3.8$ D). NEF has dielectric constant [15]: $\varepsilon \approx 100$. Spectroscopic [30,31], theoretical [32], and dielectric studies clearly confirm the self-association of the secondary amides through N–H$\cdots$C=O hydrogen bonds. It should be kept in mind that the secondary amides persist in self-associated forms even in dilute solution [32–35]. Thus, this fact should be taken into account for the whole composition range of the mixtures.

There is clear spectroscopic evidence for N–H$\cdots$O hydrogen bonded complex formation of N-substituted amides with ethers and ketones [36,37] and consequently esters. 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 the negative V^E due to the values of the dipole moments of the components.

The data in table 3 and figure 1 show that THF system deviate less from ideality than is the case for B and EA. Lady and Whetsel [38], using IR spectroscopy found that ethers form less stable complexes with NH proton than do 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 of the similar values, more negative values for B mixture probably can be explained on the basis of the significantly higher value for its dipole moment.

For the mixtures investigated, a decrease in V^E over the whole composition range is noticeable with increasing temperature from (293.15 to 313.15) K. The increase of temperature leads the increase in kinetic energy of the self-associated species of NEF, i.e. 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 amides [39] are in the range from (-18 to -20) kJ $\cdot$ mol^{-1}, while the corresponding enthalpy for N–H$\cdots$O complexes of NH group with ethers, ketones, and esters [38] is about -14 kJ $\cdot$ mol^{-1}.

Since the self-association is more exothermic than N–H$\cdots$O complex formation between components in the mixture, the increase of the temperature has greater effect on the NEF self-associ-