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(Vapour + liquid) equilibrium in (*N*,*N*-dimethylacetamide + ethanol + water) at the temperature 313.15 K

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Abstract

Total vapour pressures, measured at the temperature 313.15 K, are reported for the ternary mixture (*N*,*N*-dimethylacetamide + ethanol + water), and for binary constituent (*N*,*N*-dimethylacetamide + ethanol). The present results are also compared with previously obtained data for (amide + ethanol) binary mixtures, where amide = *N*-methylformamide, *N*,*N*-dimethylformamide, *N*-methylacetamide, 2-pyrrolidinone, and *N*-methylpyrrolidinone. We found that excess Gibbs free energy of mixing for binary (amide + ethanol) mixtures varies roughly linearly with the molar volume of amide.

Keywords: *N*,*N*-Dimethylacetamide; Water; Ethanol; Amides; Binary mixtures; Ternary mixtures; (Vapour + liquid) equilibrium; Excess Gibbs free energy; Correlation

1. Introduction

This work continues the systematic studies for determination of the thermodynamic properties (the excess Gibbs free energy, and the molar volumes of mixing) of the binary and ternary mixtures containing amide, water and an aliphatic alcohol (methanol and ethanol). References to the previous results, describing the thermodynamic properties of other amides are given in our previous paper [1].

Based on the results obtained, it is possible to estimate the preferential solvation of the amide molecule by water or alcohol by the estimation of the local mole fraction of components of the solution. It is important for understanding the interactions between the amide and hydroxyl group in the solution. A valuable tool for this investigation is the Kirkwood and Buff's theory of solutions [2]. This theory describes thermodynamic properties of solutions in an exact manner and over the whole concentration range, using the so-called Kirkwood–Buff integrals, G_{ij}. The theory gives the relation between G_{ij} parameters and thermodynamic quantities such as the chemical potential, the partial molar volumes and isothermal compressibility and links macroscopic (thermodynamic) properties with the microscopic structure of solution. The above considerations explain why this series of papers has been initiated.

2. Experimental

2.1. Purification of solvents

Dimethylacetamide, DMA (Lancaster, >0.99 mass fraction purity) was dried over anhydrous $CaSO_4$, then passed through a column filled with the freshly ignited molecular sieves 0.4 nm and finally distilled in a vacuum. The refined solvent was stored in a steel dessicator in a vacuum. Ethanol, analytical reagent grade, produced by Polish Chemical Reagents (POCh) was dried

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using freshly ignited molecular sieves 0.3 nm, distilled over this sieves and under nitrogen, and finally stored over molecular sieves. The water content was determined in both solvents using Karl-Fischer reagent, and it was below 0.0001 mass fraction. Water was distilled twice in a glass apparatus.

2.2. Physical measurements

Total vapour pressures were determined by a modified static method. The apparatus and experimental procedure have been described in detail elsewhere [3]. During the measurements the temperature was constant within 0.002 K. The absolute error in temperature was estimated to be equal to ±0.02 K. The absolute error in pressure measurements is less than 0.004 kPa, due to the cathetometer reading. The binary and ternary samples of volume about 0.005 to 0.010 dm^3 were prepared by weight. The errors in the mole fraction of samples were less than 0.0005. The refractive indices for pure solvents were measured using the Carl Zeiss refractometer equipped with the exchangeable thermostated prisms. The uncertainties in determination of refractive indices was 0.00001, and the temperature during measurements was constant within 0.1 K. Densities of pure liquids were determined using a pycnometer with a volume of 28 cm^3 approximately, with two capillaries of i.d. 1 mm. Errors in density measurements are estimated to be equal to $\pm 0.0001\ \mathrm{g \cdot cm^{-3}}$.

Characteristics of pure substances, and comparison with the literature data are given in table 1. It should be noted here, as it can be seen in table 1, a large discrepancy between the vapour pressure of pure *N*,*N*-dimethylacetamide reported from various sources is observed, which is unexpected. This discrepancy has been discussed in details in the previous work [1].

Because the lack of data for the second virial coefficient for DMA, the vapour phase behaviour was assumed to be ideal. The vapour phase compositions, y, were calculated according to the Barker's method; this procedure involves iterative approximation of the total vapour pressure function $p_{\mathrm{exp}} = p(x)$ by $p_{\mathrm{calc}} = p(x, y, C_1, \ldots, C_N)$ that is, by minimising the difference $p_{\mathrm{exp}} - p_{\mathrm{calc}}$. The coefficients C_i have been determined by the least squares method, using an optimisation algorithm based on the Marquardt method [4], and the standard deviations of parameters were determined using covariance matrix.

3. Results and discussion

The (DMA + water) and (ethanol + water) binary systems at $T = 313.15$ K were described previously, in references [1,5], *n*, and therefore these data are not reported here. Binary results for (DMA + ethanol) at $T = 313.15$ K (table 2) were correlated using the familiar Redlich–Kister equation [13]

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

where N is the number of adjustable parameters, and x is the mole fraction of DMA in the mixture. To avoid over-fitting, it is recommended to use no less than 3 to 4 data points per parameter [14]. We used therefore four adjustable parameters in equation (1) for data description.

TABLE 2

Experimental liquid mole fractions of *N*,*N*-dimethylacetamide, x_1, calculated (from equation (1)) vapour phase composition, y_1, experimental total vapour pressure, p_{exp}, and difference between experimental and calculated values of total vapour pressure, $\Delta p = p_{\mathrm{exp}} - p_{\mathrm{calc}}$, for the investigated {*N*,*N*-dimetyloacetamide (1) + ethanol (2)} binary mixture at $T = 313.15$ K

x_1	y_1	p_{exp}/kPa	Δp/kPa
0.9299	0.4623	1.314	−0.008
0.8441	0.2468	2.224	−0.006
0.7550	0.1455	3.336	0.014
0.7037	0.1099	4.036	0.006
0.6210	0.0711	5.303	0.000
0.5631	0.0526	6.272	−0.018
0.4952	0.0368	7.541	−0.002
0.4221	0.0247	9.000	0.004
0.3807	0.0195	9.858	0.000
0.3359	0.0149	10.820	0.003
0.2993	0.0118	11.625	0.010
0.2478	0.0083	12.750	−0.001
0.1973	0.0057	13.874	0.008
0.1435	0.0035	15.021	−0.015
0.1158	0.0026	15.617	−0.007
0.0733	0.0014	16.489	−0.009
0.0382	0.0007	17.173	−0.012

TABLE 1

Density, d, and total vapour pressure, p, measured at $T = 313.15$ K, and refractive indices, n_{D}, measured at $T = 298.15$ K, of pure substances used in this work, and comparison with the literature data

Substance	$d/(\mathrm{kg \cdot m^{-3}})$		p/kPa		n_{D}	
	This work	Literature	This work	Literature	This work	Literature
N,*N*-Dimethylacetamide	922.4	923.1 [6]	0.658	0.453 [8] to 1.255 [9]	1.43556	1.4345 [10] to 1.4356 [11]
Ethanol	772.2	772.2 to 772.4 [7]	17.886	17.908 [9]	1.35920	1.35925 [12]
Water			7.375	7.372 [9]		