

EFFECT OF TEMPERATURE ON THE BEHAVIOR OF OSMOTIC AND ACTIVITY COEFFICIENTS OF AMIDES IN AQUEOUS SOLUTIONS

Carmen M. Romero* and Maria E. González

Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia

The osmotic coefficients of acetamide, propionamide and butyramide in water were measured at 293.15, 298.15 and 308.15 K using the isopiestic method. The activity coefficients were calculated for the aliphatic amides and the pairwise free energy coefficients for solute-solute interactions were determined according to the McMillan–Mayer theory. The osmotic and activity coefficients of amides are discussed in terms of solute–solute interactions.

Keywords: activity coefficients, amides, isopiestic method, osmotic coefficients, pairwise interaction coefficients

Introduction

Thermodynamic properties of aqueous solutions of polar solutes are important as they provide elements to understand the interactions involved in aqueous solutions and in the elucidation of the nature of the interactions between polar and non-polar groups and water. In particular, activity coefficient data of binary non-electrolyte solutions are required to describe their thermodynamic behavior and are useful to predict thermodynamic properties.

The study of small model compounds such as amino acids, alcohols and amides are of special interest due to the information that can be obtained about the factors affecting protein stability in aqueous solutions.

Amides are important as model compounds because they have some of the elements of polypeptide chains as they contain amidic and apolar groups within the molecule. However, studies with amides in aqueous solution at temperatures different from 298.15 K are very scarce [1–13]. Other studies have been developed to obtain group additivity parameters from experimental data of pure amides [14] and information for interactions between amides and non aqueous solvents [15]. No activity coefficients from experimental data for aliphatic amides have been found in literature. Lilley reports osmotic coefficients for acetamide and propionamide obtained from freezing temperatures [12].

In this work we present a study of the effect of the increase in chain length in the osmotic and activity coefficients of acetamide, propionamide and butyramide in aqueous solutions at 293.15, 298.15 and 308.15 K.

The amides were chosen to examine the effect of increase in the number of CH₂ groups. The osmotic coefficients were measured using the isopiestic method [16–18]. Free energy interaction coefficients are evaluated and the results are discussed in terms of solute–solute interactions.

Experimental

The materials used in this work were acetamide Merck>99%, propionamide Aldrich>97% butyramide Fluka≥98%, NaCl and KCl RPE Carlo Erba. The amides were kept in desiccators before use; NaCl was dried at 383.15 K for 72 h and stored in dry atmosphere. Water was doubly distilled, degassed and treated according to literature [19]. All solutions were prepared by mass using a Precisa balance XR 205SM-DR with sensitivity of $\pm 5 \cdot 10^{-5}$ g.

The isopiestic method is based in the transference of solvent between solutions of different solutes until thermodynamic equilibrium is reached. The isopiestic apparatus used in this work has been described in previous works [16–18]. The cell was held in a constant temperature bath for the necessary time to achieve equilibrium with temperature control of ± 0.01 K. Most of the samples reached equilibrium between 8 and 16 days being longer the equilibrium times for the lowest molalities. NaCl aqueous solutions were used as reference standard solutions and the osmotic coefficients of aqueous KCl solutions were determined at each temperature to check the accuracy of the method used. Measurements were made at 293.15, 298.15 and 308.15 ± 0.01 K.

* Author for correspondence: cmromeroi@unal.edu.co

The osmotic coefficient ϕ is calculated from the equilibrium isopiestic molalities by means of the general equation:

$$\phi_i = \frac{v_r m_r \phi_r}{v_i m_i} \quad (1)$$

where m_i and m_r are the molalities of the solution and the reference solution, ϕ and ϕ_r , are the osmotic coefficients for the solution and the reference aqueous solution and v_i and v_r are the stoichiometric number of ions in solute and the reference electrolyte, respectively.

Activity of water by a_1 is calculated from the osmotic coefficient data using the expression:

$$\phi = -\frac{1000}{M_1 m_i} \ln a_1 \quad (2)$$

where M_1 is the solvent molecular mass.

The osmotic coefficient of NaCl was determined as a function of molality and temperature from the extended Bradley–Pitzer correlation [20–22] and the osmotic coefficient of KCl was determined using Eq. (1). Uncertainty in osmotic coefficient was calculated using Eq. (3):

$$\Delta\phi = \frac{\partial\phi}{\partial m_{\text{NaCl}}} \Delta m_{\text{NaCl}} + \frac{\partial\phi}{\partial m_{\text{KCl}}} \Delta m_{\text{KCl}} \quad (3)$$

Activity coefficients of solute denoted by subscript 2 in water were calculated using Eq. (4):

$$\ln \gamma_2^* = \phi - 1 + \int_0^m \frac{\phi - 1}{m} dm \quad (4)$$

where γ_2^* is the solute activity coefficient in the asymmetric reference system using the molality scale.

The excess partial molar Gibbs energy \bar{g}_i^E was calculated according to Eq. (5):

$$\bar{g}_i^E = RT \ln \gamma_i \quad (5)$$

where R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K).

Results and discussion

Osmotic and activity coefficients of aqueous KCl solutions were obtained using NaCl aqueous solutions as reference. The isopiestic molalities m are accurate to ± 0.0002 m. Calculated uncertainty in osmotic coefficient is between ± 0.0001 for lower concentrations and ± 0.0005 for higher concentrations. Average relative uncertainty was evaluated from the determined water activities of the checking KCl solutions and in all cases was less than 0.005% [18].

Tables 1–3 show the isopiestic molalities, the experimental osmotic coefficients and the calculated activity coefficients of acetamide, propionamide and butyramide in water measured at 293.15, 298.15 and 308.15 K in aqueous solutions using NaCl aqueous solutions as reference. For all the solutes the osmotic coefficients decrease with molality. A similar behavior is observed for activity coefficients.

Figure 1 shows the curves for the solute activity coefficients as a function of amide molality at the three temperatures considered. For all the amides, the activity coefficients decrease with molality, being the decrease higher as temperature increases. Figure 2 shows at each temperature the behavior of solute ac-

Table 1 Isopiestic molalities, osmotic and activity coefficients for aqueous solutions of aliphatic amides at 293.15 K

Acetamide			Propionamide			Butyramide		
$m/\text{mol kg}^{-1}$	ϕ	γ	$m/\text{mol kg}^{-1}$	ϕ	γ	$m/\text{mol kg}^{-1}$	ϕ	γ
0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000	1.0000	1.0000
0.1831	0.9824	0.9850	0.1826	0.9852	0.9691	0.1864	0.9652	0.9541
0.3994	0.9788	0.9646	0.4030	0.9678	0.9360	0.4116	0.9475	0.9007
0.5871	0.9751	0.9499	0.5989	0.9561	0.9098	0.6149	0.9312	0.8596
0.7242	0.9687	0.9406	0.7430	0.9442	0.8921	0.7712	0.9065	0.8314
0.9808	0.9641	0.9254	1.0173	0.9295	0.8619	1.0693	0.8842	0.7846
1.1809	0.9599	0.9153	1.2315	0.9205	0.8411	1.3081	0.8666	0.7521
1.3732	0.9573	0.9065	1.4402	0.9128	0.8226	1.5395	0.8539	0.7242
1.5284	0.9542	0.9000	1.6066	0.9077	0.8090	1.7261	0.8449	0.7036
1.7031	0.9494	0.8930	1.8070	0.8948	0.7938	1.9503	0.8291	0.6806
1.8992	0.9479	0.8855	2.0239	0.8895	0.7785	2.2273	0.8082	0.6543
2.1244	0.9437	0.8770	2.2226	0.8842	0.7653	2.5108	0.7985	0.6290
2.2759	0.9413	0.8711	2.4452	0.8759	0.7512	2.7342	0.7833	0.6097
2.3547	0.9410	0.8679	2.5376	0.8732	0.7456	2.8552	0.7760	0.5993
2.5665	0.9354	0.8591	2.7675	0.8666	0.7318			

Table 2 Isopiestic molalities, osmotic and activity coefficients for aqueous solutions of aliphatic amides at 298.15 K

Acetamide			Propionamide			Butyramide		
$m/\text{mol kg}^{-1}$	ϕ	γ	$m/\text{mol kg}^{-1}$	ϕ	γ	$m/\text{mol kg}^{-1}$	ϕ	γ
0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000	1.0000	1.0000
0.2015	0.9776	0.9766	0.2038	0.9667	0.9582	0.2064	0.9547	0.9432
0.4014	0.9731	0.9529	0.4073	0.9543	0.9177	0.4139	0.9390	0.8877
0.5998	0.9664	0.9340	0.6167	0.9399	0.8831	0.6363	0.9119	0.8375
0.7741	0.9609	0.9202	0.7980	0.9269	0.8576	0.8329	0.8942	0.7993
0.9907	0.9568	0.9060	1.0373	0.9138	0.8289	1.0943	0.8662	0.7553
1.1436	0.9525	0.8975	1.2028	0.9056	0.8118	1.2854	0.8475	0.7272
1.3560	0.9502	0.8873	1.4341	0.8972	0.7909	1.5372	0.8371	0.6945
1.5203	0.9461	0.8803	1.6087	0.8942	0.7770	1.7476	0.8231	0.6701
2.0423	0.9408	0.8610	1.8523	0.8876	0.7596	2.0432	0.8047	0.6394
2.1653	0.9382	0.8564	1.9761	0.8759	0.7515	2.3776	0.7817	0.6082
2.3585	0.9370	0.8490	2.1178	0.8776	0.7426	2.4762	0.7759	0.5995
2.5593	0.9318	0.8404	2.1968	0.8746	0.7377	2.9766	0.7513	0.5576
			2.5793	0.8670	0.7150			
			2.7777	0.8585	0.7031			

Table 3 Isopiestic molalities, osmotic and activity coefficients for aqueous solutions of aliphatic amides at 308.15 K

Acetamide			Propionamide			Butyramide		
$m/\text{mol kg}^{-1}$	ϕ	γ	$m/\text{mol kg}^{-1}$	ϕ	γ	$m/\text{mol kg}^{-1}$	ϕ	γ
0.0000	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000	1.0000	1.0000
0.2247	0.9719	0.9685	0.2301	0.9493	0.9489	0.2296	0.9436	0.9371
0.4528	0.9640	0.9379	0.3845	0.9440	0.9126	0.3886	0.9341	0.8915
0.8231	0.9547	0.9021	0.6114	0.9246	0.8696	0.6136	0.9053	0.8362
0.9839	0.9468	0.8903	0.8622	0.9114	0.8317	0.8947	0.8783	0.7779
1.1788	0.9449	0.8783	0.9877	0.9111	0.8157	1.0490	0.8579	0.7498
1.3644	0.9432	0.8686	1.2510	0.8904	0.7870	1.0479	0.8588	0.7500
1.5117	0.9379	0.8618	1.4485	0.8885	0.7687	1.3300	0.8375	0.7043
1.7035	0.9390	0.8538	1.6592	0.8821	0.7514	1.5847	0.8146	0.6681
1.9495	0.9323	0.8441	1.8352	0.8718	0.7382	1.8463	0.7924	0.6349
2.1075	0.9308	0.8380	2.1134	0.8618	0.7186	2.0635	0.7754	0.6098
2.3010	0.9279	0.8300	2.2981	0.8554	0.7059	2.4488	0.7422	0.5690
2.5762	0.9237	0.8172	2.5252	0.8455	0.6898	2.6900	0.7224	0.5454
			2.8469	0.8359	0.6652	2.9994	0.7105	0.5164

tivity coefficients. Comparing the data at low solute concentration, it can be observed that the largest decrease is for butyramide, followed by propionamide and acetamide. In all cases, the lowering of activity coefficients is higher as amide chain length increases.

Excess partial molar Gibbs energy was calculated using Eq. (5). Figure 3 shows the excess partial molar Gibbs energy as a function of molality and temperature. As expected, the trend of the curves resembles the behaviour of the activity coefficients.

Osmotic coefficients can be expressed as a virial expansion of solute molalities using Eq. (6):

$$(\phi-1)RT = g_{xx}m + g_{xxx}m^2 + \dots \quad (6)$$

Interaction coefficients g_{xx} , g_{xxx} of higher order represent the contribution of solute–solute interactions between pairs, triplets and higher order interactions of solvated molecules in a binary solution to excess Gibbs energy [23–26].

These coefficients were obtained fitting the experimental data by least squares to the polynomial ex-

pression [16–18, 23–27]. Three parameters were used to obtain the best fitting of the experimental data. The interaction coefficients obtained in this work, the concentration range and literature data are presented in Table 4. Due to the large uncertainty in the higher order coefficients the analysis is restricted to the pairwise coefficients g_{xx} .

The pairwise coefficients describe solute–solute interactions between solvated molecules and their values reflect the effect of apolar side-chains and the number of CH₂ groups. Free energy pairwise coefficients are negative for acetamide, propionamide and butyramide in water at all temperatures. Their magnitude becomes more negative as temperature increases

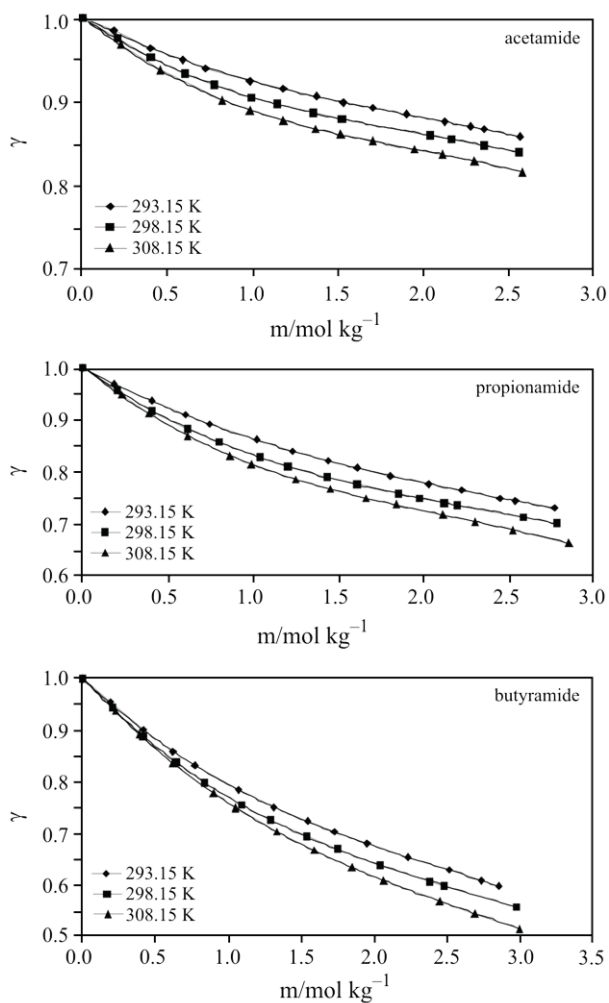


Fig. 1 Activity coefficients of acetamide, propionamide and butyramide in aqueous solutions at 293.15, 298.15 and 308.15 K

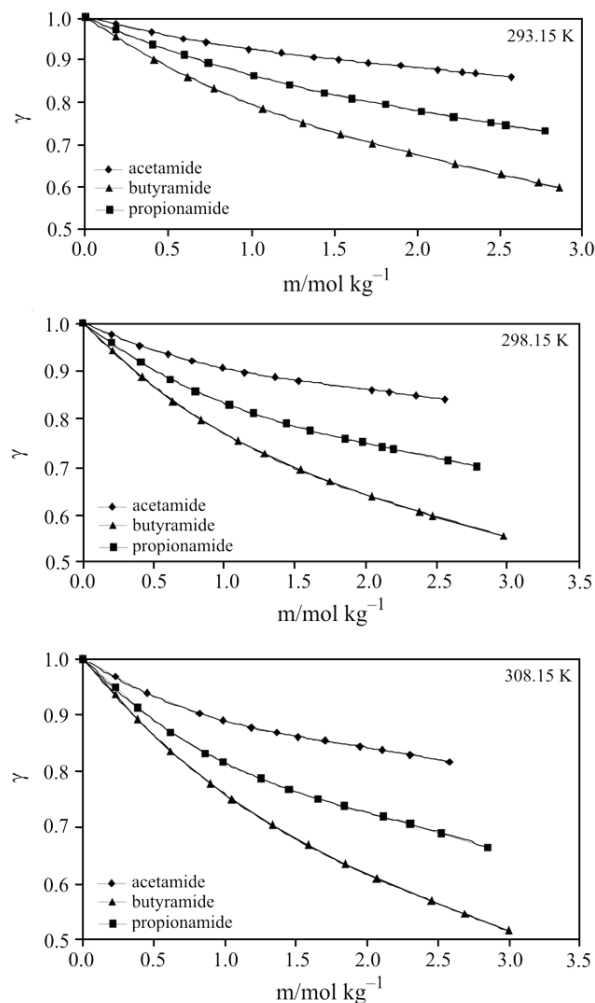


Fig. 2 Effect of chain length in the activity coefficients of acetamide, propionamide and butyramide in aqueous solutions

Table 4 Free energy interaction coefficients for aliphatic amides in water

Temperature/K	Amide	$g_{xx}/\text{J kg mol}^{-2}$	$g_{xxx}/\text{J kg}^2 \text{mol}^{-3}$	$g_{xxxx}/\text{J kg}^3 \text{mol}^{-4}$	Molality range/mol kg ⁻¹
293.15	acetamide	-132±12	54±14	-10±4	0.1831–2.5665
	propionamide	-211±6	51±7	-6±2	0.1826–2.7675
	butyramide	-362±16	112±17	-18±4	0.1864–2.8552
298.15	acetamide	-182±14	91±17	-17±5	0.2015–2.5593
	propionamide	-311±15	121±16	-20±4	0.2038–2.7777
	butyramide	-414±19	123±19	-18±5	0.2064–2.9766
308.15	acetamide	-214±21	98±24	-17±7	0.2247–2.5762
	propionamide	-389±30	174±32	-32±8	0.2301–2.8469
	butyramide	-460±32	132±33	-21±8	0.2296–2.9994

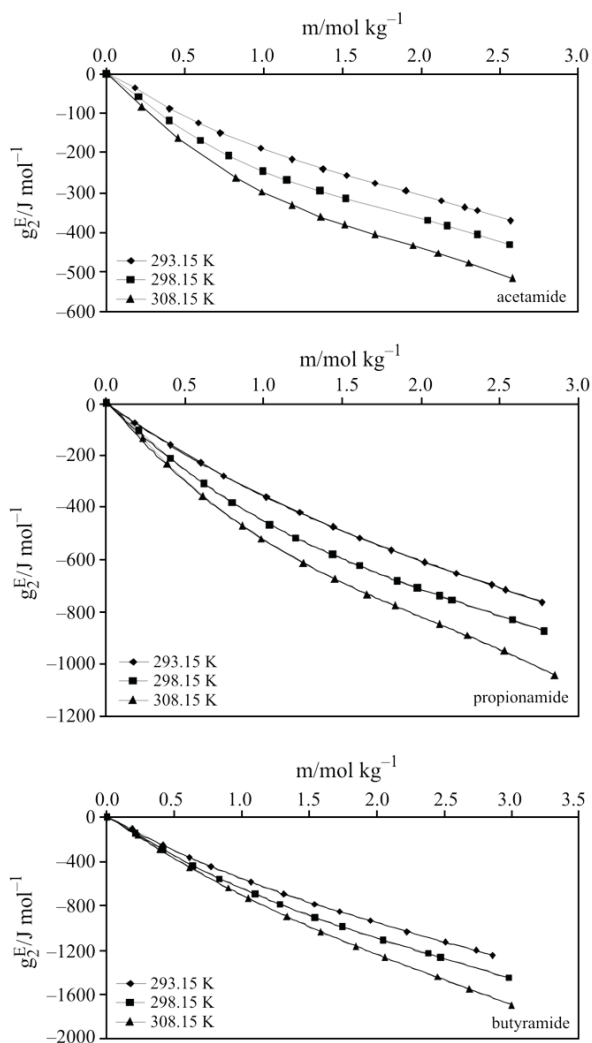


Fig. 3 Partial molar free energy of aliphatic amides in aqueous solution

and at constant temperature, the negative values become larger as chain length increases. Lilley reports pairwise coefficients for acetamide and propionamide at 298.15 K calculated from osmotic coefficients obtained from freezing temperature data [12]. The values are also negative and follow the same trend but the magnitudes do not agree with the results presented in this work. The difference can be attributed to the uncertainty in the calculation of the osmotic coefficients at 298.15 K in Lilley's work.

The pairwise coefficients between amide molecules can be described in terms of group-group contributions according to the Savage-Wood analysis [11–13, 27]. When similar group interactions are favored, such as interactions between polar groups hydrated with water or hydrophobic interactions involving apolar chains, the free energy pairwise coefficient has a negative value. A positive value results from interactions between groups having different effects on water structure [13, 27].

The negative values of free energy coefficients obtained for acetamide, propionamide and butyramide can be attributed to dominant apolar group interactions mediated by water. The increase of the negative value of the coefficients as chain length increases shows clearly the negative contribution of CH_2 groups to the free energy pairwise coefficients. According to the preferential configuration model interactions between apolar groups are favourable and hydrophobic interactions are enhanced. The hydrophobic behavior shown by aliphatic amides follows the same trend shown by aliphatic alcohols [13, 26, 27].

Acknowledgements

This work was supported by the Universidad Nacional de Colombia and the Instituto Colombiano para el Desarrollo de la Ciencia y la Tecnología, Francisco José de Caldas – Colciencias.

References

- 1 T. H. Lilley, *Pure Appl. Chem.*, 66 (1994) 429.
- 2 Y. Lu, X. Wang, G. Su and J. Lu, *Thermochim. Acta*, 406 (2005) 233.
- 3 S. Cabani, P. Gianni, V. Mollica and L. Lepori, *J. Solution Chem.*, 10 (1981) 563.
- 4 A. M. Zaichikov and M. V. Kulikov, *Russ. Chem. Bull.*, 46 (1997) 1710.
- 5 A. M. Zaichikov and N. G. Manin, *Russ. Chem. Bull.*, 50 (2001) 780.
- 6 A. M. Zaichikov and N. G. Manin, *Russ. J. General Chem.*, 73 (2003) 1043.
- 7 W. Zielonkiewicz and J. Poznanski, *J. Solution Chem.*, 27 (1998) 245.
- 8 M. M. Lopez and G. I. Makhatadze, *Biophys. Chem.*, 74 (1998) 117.
- 9 G. Barone and C. Giancola, *Pure Appl. Chem.*, 62 (1990) 57.
- 10 Y. Lu, Q. Cheng, M. Liu, Y. Han, X. Lou and J. Lu, *Thermochim. Acta*, 386 (2002) 103.
- 11 C. M. Criss and R. H. Wood, *J. Chem. Thermodyn.*, 28 (1996) 723.
- 12 T. H. Lilley and R. Wood, *J. Chem. Soc. Faraday Trans.*, I, 76 (1980) 901.
- 13 J. J. Savage and R. H. Wood, *J. Solution Chem.*, 5 (1976) 733.
- 14 S. P. Verevkin, *J. Therm. Anal. Cal.*, 60 (2000) 437.
- 15 A. Zaichikov, *J. Therm. Anal. Cal.*, 54 (1998) 279.
- 16 C. M. Romero and M. E. González, *Fluid Phase Equilib.*, 250 (2006) 99.
- 17 C. M. Romero and M. S. Páez, *Fluid Phase Equilib.*, 240 (2006) 140.
- 18 C. M. Romero, M. T. Dávila, L. H. Blanco and M. E. González, *Rev. Col. Quím.*, 35 (2006) 205.
- 19 A. Weissberger (Ed.), *Physical Methods of Chemistry*, Vol. 1, Part 4, 4th Ed., Wiley Interscience, New York 1972.
- 20 J. A. Rard and R. F. Platford, *Activity Coefficients in Electrolyte Solutions*, K. S. Pitzer, Ed., 2nd Ed., CRC Press, Boca Raton, FL 1991.

- 21 E. Amado and L. H. Blanco, *Fluid Phase Equilib.*, 226 (2004) 261.
- 22 D. J. Archer, *Phys. Chem. Ref. Data*, 28 (1999) 1.
- 23 W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, 13 (1945) 276.
- 24 T. H. Lilley and R. P. Scott, *J. Chem. Soc. Faraday Trans. I*, 72 (1976) 184.
- 25 G. M. Blackburn, T. H. Lilley and E. Walmsley, *J. Chem. Soc. Faraday Trans. I*, 78 (1982) 1641.
- 26 G. Borghesani, R. Pedriali and F. Pulidori, *J. Solution Chem.*, 18 (1989) 289.
- 27 G. Castronuovo, V. Elia, M. Niccoli and F. Velleca, *Phys. Chem. Chem. Phys.*, 3 (2001) 2488.

DOI: 10.1007/s10973-008-9022-2