New tools for the analysis of refractive index measurements in liquid mixtures. Application to 2-diethylaminoethanol + water mixtures from 283.15 to 303.15 K†

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Drawing on methods currently used in chemical thermodynamics, apparent and partial molar refractions of mixing for the components of a liquid mixture are defined. These optical properties are calculated from the experimentally measured refractive index and density of aqueous 2-diethylaminoethanol mixtures at five different temperatures between 283.15 and 303.15 K and at least at 37 different mole fractions spanning the entire composition range at each temperature. The new optical properties, partial molar refractions of mixing, are discussed in terms of their composition dependence and the effect of temperature on the limiting apparent molar refraction of mixing of the organic component dispersed in water is examined. These profiles are compared with the corresponding profiles obtained for volumetric excess partial molar properties using literature data. This advanced analysis shows that optical properties are able to give new insights into the mixing process.

Introduction

Thermodynamic volumetric properties such as partial molar volumes, V_i, partial molar isobaric expansions, $E_{P,i}$, and partial molar isentropic compressions, $K_{S,i}$, have been used with great success to probe intermolecular interactions in a variety of solutions and in particular in aqueous solutions of oligopeptides and proteins.[1–4] These properties have yielded interesting information on the state of molecules in solution and on the role of solvation on protein stability.[5,6] Excess partial molar isobaric expansions and excess partial molar isentropic compressions are routinely used to analyse changes in aggregation and solvation patterns in different liquid mixtures brought about by changes in composition, temperature and pressure.[7,8] However, these macroscopic methods of analysis do not give much insight into changes in the conformation of molecules which accompany mixing processes.

In spite of many investigations on molecular structure, including bond lengths, bond angles, polarity of bonds and internal molecular motions, using optical, electric and spectroscopic methods, the changes occurring during the process of mixing are difficult to assess. Among the optical methods, measurements of the refractive index have been extensively made in the past[9] and in the present,[10–13] with the aim of exploring its dependence on structural details.

The index of refraction, n, is defined as the ratio of the speed of light in a vacuum to the speed of light in a material medium.[14] This dimensionless optical property is very sensitive to changes in the molecular organisation of pure liquid substances, solutions and mixtures. Although not themselves being thermodynamic properties, both the refractive index and the corresponding Lorentz–Lorenz function, $(n^2 - 1)/(n^2 + 2)$, are intensive properties of homogeneous mixtures. Since the molar refraction, R, is defined by

$$R = \left(\frac{n^2 - 1}{n^2 + 2}\right) V_\mathrm{m} \quad (1)$$

where V_m is the molar volume, then molar refractions are expressed in the same units as molar volumes. The molar refraction of pure chemical substances has been found to be an additive property of structural elements. Indeed, tables of atomic and bond molar refractions, evaluated at the mean sodium D-lines, are given in various handbooks. It is also well known that group-additivity calculations and observed molar refractions agree very closely, except for open-chain molecules with conjugated double bonds or for cyclic molecules, in which cases calculated values underestimated observed values (optical exaltation).

In the present state of the art only R values for solutions and empirical molar refraction deviation functions for liquid mixtures at different compositions, and apparent molar refractions, $R_{\varphi,i}$, for dilute solutions are reported and analysed for describing interactions in solution.[15–17] However, it should be mentioned that Fucaloro[18] has defined partial molar

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† Electronic supplementary information (ESI) available: Table S1: Refractive index and molar refractions of 2-diethylaminoethanol + water mixtures at 283.15, 288.15, 293.15, 298.15 and 303.15 K. Table S2: Least-squares fitting coefficients of eqn (10), respective standard uncertainties and the standard deviation of the fits for the system 2-diethylaminoethanol (2) + water (1) at 283.15, 288.15, 293.15, 298.15 and 303.15 K. See DOI: 10.1039/b516167c

refractions, R_i, only to demonstrate the inadequacy of using the deviation of molar refraction from a volume fraction average of the components for binary liquid mixtures, for assessing intermolecular electronic interactions.

In this context it should also be noted that the term 'partial molar refraction' was used by Paljk *et al.*[19] for a quantity which was in fact the apparent molar refraction. On the other hand Douhéret and Pal[20] have defined and used apparent molar susceptibilities and polarisabilities, which are electric properties akin to molar refractions, to probe patterns of molecular aggregation in mixtures of amphiphiles with water.

In the present work, apparent and partial molar refractions of mixing for the components of a liquid mixture are defined for the first time. The novel resources are shown to be helpful for depicting structural details occurring during the mixing process between 2-diethylaminoethanol (DEEA) and water.

Experimental

Chemicals

DEEA was a reagent-grade product supplied by Merck (99% quoted purity) and was used without further purification. Its purity was tested by density measurement, $\rho = 879.50$ kg m^{-3} at 298.15 K and $\rho = 884.14$ kg m^{-3} at 293.15 K. Literature values reported at the same temperatures are $\rho = 879.54$ kg m^{-3} and $\rho = 884.20$ kg m^{-3}, respectively.[21] Water was ion exchange (resistivity, 18 MΩ cm) high purity from Milli-Q reagent-grade system, supplied by Millipore.

Physical techniques

The refractive index at 283.15, 288.15, 293.15, 298.15 and 303.15 K, n_t^D, was measured, with a reproducibility of 0.007% and an accuracy of 0.015%, using an Abbe 60 refractometer made by Bellingam & Stanley and working at the mean sodium D wavelength (589.6 nm). Temperature in the refractometer was kept constant to within ±0.05 K by means of circulating water from a F6 Haake thermostat. The refractometer has been calibrated, at the five experimental temperatures, with a traceable standardisation plate (silica test plate RI 1.45839). The temperature at the entrance of the refractometer was measured with a standard uncertainty of 0.01 K with a platinum resistance thermometer, calibrated against a SPTR (standard platinum resistance thermometer) which in turn had been calibrated at NPL (National Physical Laboratory) with an uncertainty of ±0.005 K. All (water + DEEA) mixtures were prepared by weight in volumetric flasks specially designed to prevent evaporation, using a Mettler AX 205 Balance with a reproducibility of 0.01 mg. Buoyancy corrections were applied. The uncertainty in the mixture composition, expressed in mole fraction, was found to be less than ±0.000 05.

Results and discussion

Defining partial molar refractions and partial molar refractions of mixing

According to Fucaloro[18] and eqn (1), molar refractions can be formally treated as molar volumes and therefore the partial molar refraction of component i, R_i, at mole fraction x_i can be defined by

$$R_i = R + (1 - x_i)\left(\frac{\partial R}{\partial x_i}\right)_{T,P} \qquad (2)$$

The summation rule of partial molar properties[22,23] also holds for these new quantities, which for the case of a solution or mixture of components 1 and 2 gives

$$R = x_1R_1 + x_2R_2 \qquad (3)$$

As for common partial molar properties, R_1 and R_2 can be envisaged as the molar contribution of respectively components 1 and 2 to the molar refraction of the solution or mixture when the composition is changed at fixed T and P. The underlying chemical significance of R_1 and R_2 can be analysed by comparing their values in solution with respectively, R_1* and R_2*, *i.e.* with the corresponding values in the pure state at the same T and P; or else by comparing, for example, R_2 with R_2^{∞}, *i.e.* the limiting value of partial molar refraction of component 2 at infinite dilution in solvent 1. The latter method of analysis is potentially important to detect structural changes of the solute associated with modifications on solution conditions, with wide application in the field of polymer science and biophysics.

In spite of different opinions,[12,13,18] at the present stage of theoretical analysis it is not yet clear how to estimate molar refractions of thermodynamically ideal mixtures, a development which would allow an unambiguous definition of the excess molar refraction. In these terms, drawing again on the thermodynamic formalism for liquid mixtures a change in molar refraction of mixing, $\Delta_{\text{mix}}R$, can be introduced, which in the case of a binary mixture is given by

$$\Delta_{\text{mix}}R = R - (x_1R_1{}^* + x_2R_2{}^*) \qquad (4)$$

The optical property defined in eqn (4) has been known as a 'molar refraction deviation function'.[12] Recently, Fucaloro[18] and Brocos *et al.*[12] demonstrated that the proper deviation function should be related to the pure component molar refractions on a mole fraction basis, as in eqn (4). The last new tools are the associated partial molar refraction of mixing of components 1 and 2, $\Delta_{\text{mix}}R_1$ and $\Delta_{\text{mix}}R_2$, defined by the following equations:

$$\Delta_{\text{mix}}R_1 = \Delta_{\text{mix}}R - x_2\left(\frac{\partial \Delta_{\text{mix}}R}{\partial x_2}\right)_{T,P} \qquad (5)$$

$$\Delta_{\text{mix}}R_2 = \Delta_{\text{mix}}R + (1 - x_2)\left(\frac{\partial \Delta_{\text{mix}}R}{\partial x_2}\right)_{T,P} \qquad (6)$$

Eqn (5) and (6) are formal defining expressions. They can be considerably simplified using eqn (3) and (4) in conjunction with the Gibbs–Duhem equation for partial molar properties. Thus, from combining eqn (3)–(5):

$$\Delta_{\text{mix}}R_1 = x_1(R_1 - R_1^*) + x_2(R_2 - R_2^*) - x_2\left\{\frac{\partial[x_1(R_1 - R_1^*) + x_2(R_2 - R_2^*)]}{\partial x_2}\right\}_{T,P} \qquad (7)$$

Working out the latter expression and bearing in mind the Gibbs–Duhem constraint, $x_1(\partial R_1/\partial x_2)_{T,P} + x_2(\partial R_2/\partial x_2)_{T,P} = 0$, yields

$$\Delta_{\text{mix}}R_1 = R_1 - R_1^* \tag{8}$$

and similarly for the other component

$$\Delta_{\text{mix}}R_2 = R_2 - R_2^* \tag{9}$$

This expected result lends theoretical support to the method suggested above for discussing partial molar refractions.

Molar refractions and partial molar refractions of mixing of aqueous mixtures of 2-diethylaminoethanol

Refractive index measured in water + DEEA mixtures at 283.15, 288.15, 293.15, 298.15 and 303.15 K and over the entire composition range are reported in Table S1 (ESI†) jointly with the respective molar refraction, calculated using eqn (1). Molar volumes were evaluated from accurate density data, previously reported.[7,24]

Molar refractions of mixing DEEA with water at the different experimental temperatures were calculated using eqn (4). For the sake of clarity, Fig. 1 shows only the profiles of the composition dependence of $\Delta_{\text{mix}}R$ at 283.15, 293.15 and 303.15 K.

As evidenced in this figure, $\Delta_{\text{mix}}R$ values are negative for the most part of the composition range. Interestingly, in the amphiphile-rich region these values became significantly positive at every temperature examined. Fig. 1 also shows that at 283.15 K the optical behaviour of this mixture at x_2 between 0.2 and 0.6 seems to be considerably different from the behaviour at the other temperatures shown. Although the curve for 288.15 K is not shown in this figure, it neatly points out to a transition of behaviour. At this stage of analysis it is reasonable to relate this feature with the presence, at 283.15 K, of some water aggregates still possessing ice-like structures. This peculiar behaviour will be better examined later.

To probe the underlying meaning of these findings, it is necessary to separate the roles of the two components in terms of partial molar contributions, using eqn (5) and (6). To the best of our knowledge, this is the first time that these equations are applied to a particular system, probably due to the high sensibility of $\Delta_{\text{mix}}R$ to rounding errors in mole fraction which usually results in very scattered values.[12] In order to calculate the derivative $(\partial\Delta_{\text{mix}}R/\partial x_2)_{T,P}$, the R data in Table S1 (ESI†) as a function of the composition were least-squares fitted using eqn (10) with an appropriate degree. Eqn. (10) is commonly known as Redlich–Kister equation,[25] although recently it was argued that it should be renamed as Guggenheim–Scatchard equation.[26] The resulting curves are represented as full lines in Fig. 1. The number n of the A_k coefficients in eqn (10) was fixed by testing the statistical significance of including each further term using the F test at a 95% confidence level.

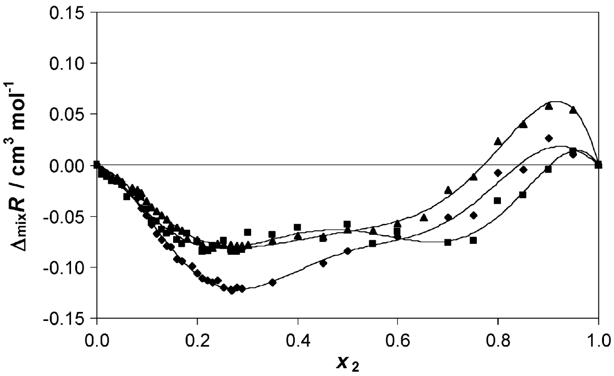

Fig. 1 Molar refraction of mixing for the binary system water (1) + DEEA (2) as a function of composition at: (◆), 283.15 K; (▲), 293.15 K; and (■), 303.15 K. Regression lines are described by eqn (10) with the parameters given in Table S2 (ESI†).

$$\Delta_{\text{mix}}R = x_1x_2\sum_{k=0}^{k=n} A_k(2x_2-1)^k \tag{10}$$

The optimised number of these coefficients was found to correspond to $n = 4$ at all temperatures. These parameters alongside their standard uncertainties and the standard deviation of the fits are reported in Table S2 (ESI†). Analysis of these deviations indicates that eqn (10) with $n = 4$ provides a very good fit of the experimental $\Delta_{\text{mix}}R$ data. In fact, at each of the five temperatures, the largest absolute value of $\Delta_{\text{mix}}R$ is at least one order of magnitude greater than the standard deviation of the fit. Fig. 2 shows the profile of the smoothed curves representing $\Delta_{\text{mix}}R_1$ and $\Delta_{\text{mix}}R_2$ as a function of x_2 at 293.15 K as an example. Similar profiles were found at the other temperatures, although the minimum in $\Delta_{\text{mix}}R_2$ becomes more pronounced at the lowest temperature investigated.

The striking feature in this type of representation is the apparent insensitivity of the $\Delta_{\text{mix}}R_i$ function for both components to changes in composition between $x_2 \approx 0.3$ and $x_2 \approx 0.5$. Moreover, in this composition range the negative $\Delta_{\text{mix}}R_i$ values are of small magnitude. According to eqn (8) and (9), this behaviour strongly suggests that the mixing process, in this composition range, does not significantly destroy the patterns of molecular aggregation existing in the pure liquids making up the mixture. Interestingly, this observation lends further support to our previous suggestion, made on the basis of volumetric data,[7] that in this region lamellar aggregates are probably formed in which sheets of DEEA molecules are intercalated with sheets of water molecules.

Fig. 3 shows, side by side, the composition dependence of both thermodynamic, V_i^{E}, and optical, $\Delta_{\text{mix}}R_i$, properties. In this figure we are able to distinguish, in both curve profiles regarding the DEEA molecule, two well-defined changes in the slope value, defining at least three composition segments. This probably reflects a sequence of different patterns of molecular

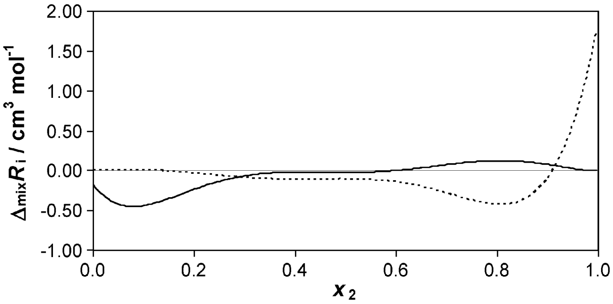

Fig. 2 Partial molar refractions of mixing of components 1 (···) and 2 (—), for the binary system water (1) + DEEA (2) at 293.15 K.

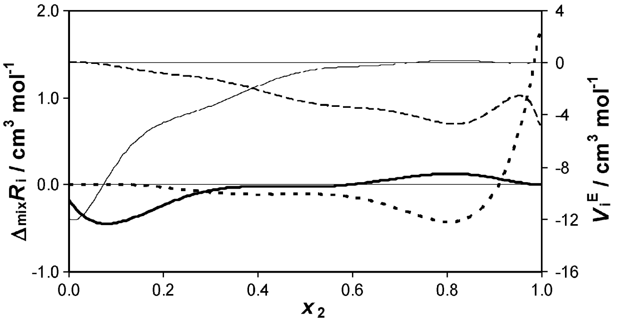

Fig. 3 Partial molar refractions of mixing of components 1 (···) and 2 (—), and excess partial molar volumes of components 1 (--) and 2 (—), for the binary system water (1) + DEEA (2) at 293.15 K.

aggregation, as has been previously anticipated on the basis of volumetric data only.[7,24]

Nevertheless, in the case of $\Delta_{mix}R_2$ the composition range of each segment, as well as the important singularity shown as a minimum, are somewhat displaced to higher DEEA concentrations. The foregoing differences may reflect different sensibility of those properties to different aspects of a particular geometry or molecular aggregation pattern. Aspects such as electronic distribution, polarizability, volume, bond angles and bond lengths, should be mentioned. To clarify this aspect the use of other physical methods of structure investigation, including X-ray, light scattering and other relaxation techniques, would be helpful.

Because changes in molar refractions are expected to arise exclusively from structural changes, the minimum in $\Delta_{mix}R_2$ observed in the water-rich region may reflect changes in the conformation of DEEA molecules. In the same way as differences between observed and calculated molar refractions, using group contribution approaches, have been interpreted as reflecting modifications of bond angles, bond lengths and polarizability of the molecules,[27] also in this case differences between R_i and R_i^* may be the reflection of similar features.

Limiting values of apparent molar refractions of mixing

The concept of a non-thermodynamic apparent molar physical property has already been used in the context of solutions[15–17] and binary liquid mixtures.[20] Thus the apparent molar refraction of, for example, component 1 is defined as:

$$R_{\varphi,1} = (R - x_2R_2^*)/x_1 \qquad (11)$$

In view of eqn (4), it follows from eqn (11) that

$$R_{\varphi,1} - R_1^* = \Delta_{mix}R/x_1 \qquad (12)$$

An analogous expression is obtained for component 2:

$$R_{\varphi,2} - R_2^* = \Delta_{mix}R/x_2 \qquad (13)$$

On the other hand, apparent molar and partial molar properties become equal at infinite dilution, *i.e.* $R_{\varphi,i}^{\infty} = R_i^{\infty}$. Then the limiting values of eqn (12) and (13) can be equated to the limiting values of, respectively, eqn (8) and (9), and therefore

$$\Delta_{mix}R_i^{\infty} = R_{\varphi,i}^{\infty} - R_i^* \qquad (14)$$

An interesting observation springs from the latter analysis. According to the concept of an apparent molar property,[28] the difference $R_{\varphi,i} - R_i^*$ (*cf.* eqn (12) and (13)) is formally the 'apparent molar refraction of mixing of component i', which is suggested to be denoted as $\Delta_{mix}R_{\varphi,i}$. In general terms, the apparent molar property of mixing just introduced corresponds effectively to an alternative definition of apparent molar property,[28] which has been used before[8,29–31] in the context of non-Gibbsian properties of liquid mixtures.[32]

In order to obtain $\Delta_{mix}R_i^{\infty}$ values, the right-hand side of eqn (14) can be evaluated as limiting values of either eqn (11) or (12), which in turn can be expressed in terms of the A_k coefficients of eqn (10). The resulting expressions, which are identical with those found for various thermodynamic properties,[7,24,33–35] are given in eqn (15) and (16) for, respectively, components 1 and 2.

$$\lim_{x_1\to0}\Delta_{mix}R_{\varphi,1} = \Delta_{mix}R_1^{\infty} = \sum_k A_k \qquad (15)$$

$$\lim_{x_2\to0}\Delta_{mix}R_{\varphi,2} = \Delta_{mix}R_2^{\infty} = \sum_{k=\mathrm{even}} A_k - \sum_{k=\mathrm{odd}} A_k \qquad (16)$$

The corresponding values are shown in Table 1, together with their standard uncertainties, which were estimated from the standard uncertainties of the A_k coefficients, reported in Table S2 (ESI†).

The effect of temperature on $\Delta_{mix}R_i^{\infty}$ values is depicted in Fig. 4. For water, these values are all positive with a maximum at 298.15 K. In analogy with the phenomenon of optical exaltation,[27] this behaviour suggests that water molecules dispersed in DEEA as a solvent bear a more open-chain structure than in pure water.

For DEEA, all of the corresponding values are negative and increase in magnitude with rising temperature. This behaviour is consistent with the assumption[7,24] of changes in the conformation of DEEA molecules which would be responsible for a more closed packed structure when infinitely diluted in water than in pure DEEA. This suggestion corresponds to the operation of a phenomenon which is effectively a "negative optical exaltation". For DEEA infinitely diluted in water, it is interesting to compare $\Delta_{mix}R_2^{\infty}$ with thermodynamic properties such as $K_{S,2}^{E,\infty}$ and $E_{P,2}^{E,\infty}$, which were previously reported.[7] This exercise is done in the form of the double plot of Fig. 5, where each point refers to values at a common temperature.

Fig. 5 shows that $K_{S,2}^{E,\infty}$ varies with temperature in the opposite way as $\Delta_{mix}R_2^{\infty}$ does. This observation probably signifies that, upon a temperature increase, DEEA molecules

Table 1 Limiting partial molar refractions of mixing, $\Delta_{mix}R_i^{\infty}$, for water (1) + DEEA (2) mixtures at different temperatures

T/K	$\Delta_{mix}R_1^{\infty}$/ cm^3 mol^{-1}	σ^a/cm^3 mol^{-1}	$\Delta_{mix}R_2^{\infty}$/ cm^3 mol^{-1}	σ^a/cm^3 mol^{-1}
283.15	0.9	0.1	−0.11	0.06
288.15	1.5	0.2	0.00	0.09
293.15	1.8	0.1	−0.15	0.04
298.15	2.3	0.1	−0.23	0.01
303.15	0.8	0.1	−0.29	0.01

[a] Standard uncertainty related to both $\Delta_{mix}R_i^{\infty}$ parameters, calculated from the standard uncertainties of the A_k coefficients of eqn (10).

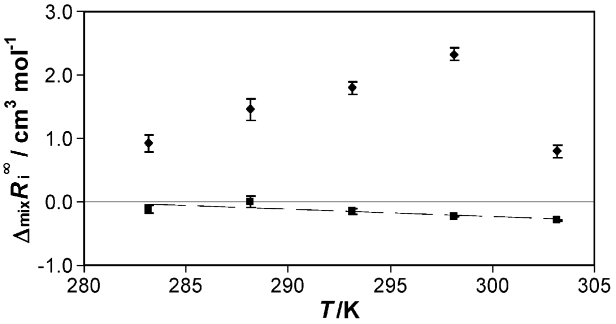

Fig. 4 Temperature dependence of limiting partial molar refractions of mixing, $\Delta_{mix}R_i^\infty$ for water (◆) + DEEA (■) mixtures. A regression straight line describes the effect of temperature on $\Delta_{mix}R_2^\infty$.

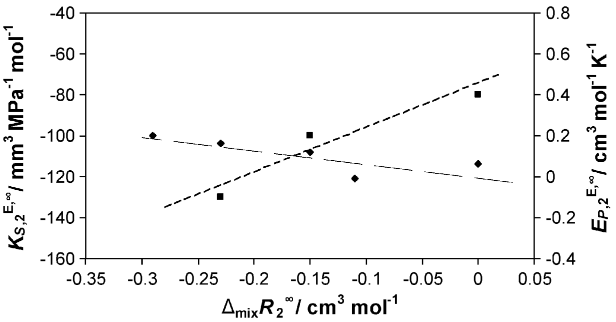

Fig. 5 Correlation between $\Delta_{mix}R_2^\infty$ and $K_{S,2}^{E,\infty}$ values (◆, left scale), and $E_{P,2}^{E,\infty}$ values (■, right scale) at various temperatures. The dashed lines are only eye guides.

dispersed in water change their conformation progressively to a less closed and thus more flexible structure which becomes more compressible at higher temperatures.

By contrast, the properties $E_{P,2}^{E,\infty}$ and $\Delta_{mix}R_2^\infty$ vary in the same fashion with changing temperature. This seems to reflect the disruption of the ice-like structure of water, with rising temperature, leading to an increase in the strength of solute–solvent interactions.

Conclusions

The optical properties apparent and partial molar refraction of mixing have been introduced for the components of liquid mixtures. The change in molar refraction of mixing is defined as the proper 'molar refraction deviation function'. A previous proposal for defining an apparent molar non-Gibbsian property is shown to yield effectively an apparent molar property of mixing. The aforementioned optical properties were calculated for the liquid binary mixture water + 2-diethylaminoethanol over the entire composition range at five different temperatures between 283.15 and 303.15 K. The profiles for their composition dependence are discussed and compared with results previously obtained for different volumetric excess partial molar properties of the organic component. From this comparison has emerged that optical properties, besides seeming to confirm the existence of a lamellar aggregation region of mixing in this binary system, disclosed additional peculiar singularities which may reflect particular sensibility of these properties to structural features of the DEEA molecule in the diluted region in water and of the water molecule in the DEEA-rich region. The former aspect is tentatively ascribed to conformational changes in the amphiphile molecule. Partial molar refractions of mixing have also been calculated at infinite dilution. In particular, from their values for the amphiphile it is inferred that the conformation of 2-diethylaminoethanol molecules at high dilution in water is sensitive to changes in temperature.

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