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Thermodynamic study of heptane + amine mixtures. V. Excess and solvation Gibbs energies



FLUID PHASE

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ABSTRACT

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Keywords: Vapour–liquid equilibrium Excess Gibbs energy Activity coefficient Gibbs energy of solvation Amines Heptane Group contribution Vapor–liquid equilibria of binary mixtures of *n*-heptane with 15 amines, primary *n*-alkyl (C3–C8), secondary (diethyl to dibutyl), branched (*iso*-propyl and *sec*-butyl) and cyclic amines (piperidine, hexamethyleneimine, heptamethyleneimine and cyclopentylamine) have been determined by head-space gas chromatographic analysis of the vapor phase directly withdrawn from an equilibration apparatus. Excess molar Gibbs energies and activity coefficients for the systems investigated have been obtained by a least-square treatment of the equilibrium results. All mixtures exhibit positive deviations from ideality, decreasing with the amine size. The Gibbs energy of solvation for amines in heptane has been evaluated and its dependence on polar groups, chain lengthening, branching and cyclization has been discussed.

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1. Introduction

In the frame of a research project which aims to study the main thermodynamic properties of non-electrolytes in different solvents, we have carried out a systematic determination of the excess quantities and the corresponding solvation properties of hydrocarbon + amine mixtures.

In previous works, we reported excess molar enthalpies, H^{E} [1,2] and volumes, V^{E} [3,4] for binary mixtures of heptane with different kinds of amines (primary, secondary, tertiary, both open chain and cyclic) with the aim of characterizing the interaction between the hydrocarbon chain and the amine groups (NH₂, NH, N). As a prosecution, we here report the vapor–liquid equilibria (VLE) and excess Gibbs energies, G^{E} , for mixtures of heptane with primary linear (C3–C8) and branched (*iso*-propyl and *sec*-butyl) alkylamines, secondary dialkylamines (diethyl, dipropyl and dibutyl), cyclic imines (piperidine, hexa- and heptamethyleneimine) and cyclopentylamine.

VLE data have been collected by means of an equilibration cell coupled with a gas-chromatographic apparatus. Excess Gibbs energies and related quantities such as activity coefficients, γ , have been calculated by a treatment similar to that of Barker for *x*-*P* data [5]. VLE and G^{E} for the above mixtures were reported in the literature only for butylamine, diethylamine [6] and piperidine [7]. Velasco et al. [8] reviewed G^{E} and H^{E} , and applied the DISQUAC model to *n*-alkylamine + *n*-alkane mixtures.

The molar Gibbs energies of solvation, $\Delta_{solv}G^{\circ}$, have been obtained from activity coefficients at infinite dilution, γ^{∞} , and discussed in terms of solute–solvent interactions. Activity coefficients here obtained and volumetric properties previous studied will also be used in a subsequent paper for computing the Kirkwood–Buff integrals [9] over the whole composition domain. Analysis of such data should allow gaining information on the local structure of the examined mixtures.

2. Experimental

2.1. Materials

All chemicals were commercial products of the best grade quality and were used without further purification. Their purity, in mass fraction x, was checked by gas-chromatography (GC) and their water content by Karl-Fischer-titration. No significant difference was found with respect to the impurity content declared by the factories. The list of the amines here investigated with indication of the factory and purity is given in Table 1. Thanks to the GC technique employed in determining the vapor composition, impurities as large as those here indicated (<3%) do not affect



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Nomenclature

Latin symbols

- а Third parameter of Wilson equation
- Constant term Α
- Area of chromatographic peak A_i
- B_{ii} Virial coefficient
- Bi Group contribution
- C_{cy} G^E Cyclization term
- Molar excess Gibbs energy
- $H^{\rm E}$ Molar excess enthalpy
- k Running index for experimental points and components
- Р Total pressure
- p^* Vapor pressure of pure liquid
- Thermodynamic property 0
- Gas constant R
- Chromatographic response factor r_f
- S_w van der Waals surface area
- SE Molar excess entropy
- Т Absolute temperature
- V^* Molar volume of pure liquid
- $V^{\rm E}$ Molar excess volume
- w Correction term for vapor non-ideality
- Liquid mole fraction х
- Vapor mole fraction v

Greek symbols

γ	Activity coefficient
$\Delta_{ m solv}G^\circ$	Gibbs energy of solvation
$\Delta_{ m solv} H^\circ$	Enthalpy of solvation
$\Delta_{ m solv}S^\circ$	Entropy of solvation
Λ_{ij}	Wilson parameter
σ	Standard deviation

appreciably the reliability of the results. In fact, differently to the conventional techniques based on P-x-y measurements, the separation of impurities that occurs in the vapor phase is taken advantage of.

2.2. VLE apparatus

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The head-space GC analysis for measuring the vapor phase mole fraction, y, as a function of the liquid phase mole fraction, x, was employed. The apparatus, composed of an equilibration cell and a gas chromatograph (C. Erba 5300 Mega), was described in detail elsewhere [17,18]. A SE52 fused silica capillary column and a flame ionization detector were used in all analyses. All mixtures were prepared by weight. The mole fractions, x, after correction for buoyancy and for evaporation of the constituents in the vapor space of the container, were evaluated to better than 0.0005. At least three vapor samples were analyzed for each given composition. The values of vapor mole fractions of heptane, y_1 , were obtained by Eq. (1):

$$y_1 = \frac{1}{[1 + r_f / (A_1 / A_2)]} \tag{1}$$

where A_1/A_2 is the measured peak area ratio of the two components in the vapor phase and r_f is the response factor of the chromatograph for the mixture under consideration. This latter is given by:

$$r_f = \frac{A_1^2 / A_2^2}{p_1^* / p_2^*} \tag{2}$$

 A_i^* being the peak area of the vapor equilibrated with the pure liquid *i* with vapor pressure p_i^* . As explained in Section 3, the calculation procedure makes unnecessary carrying out calibration measurements to determine r_{f} . The overall uncertainty in v_{i} , resulting mostly from the uncertainty on the quantity A_1/A_2 , was generally less than 0.005 and, in the dilute regions, lower than 2% of *y* of the less concentrated component.

3. Data treatment

The experimental peak area ratio A_1/A_2 of the components in the vapor phase is related to the ratio of the experimental activity coefficients, $(\gamma_1/\gamma_2)_{exp}$ according to:

$$\left(\frac{\gamma_1}{\gamma_2}\right)_{\exp} = \left(\frac{x_2}{x_1}\right) \left(\frac{A_1}{A_2}\right) \left(\frac{A_2^*}{A_1^*}\right) \left(\frac{w_1}{w_2}\right) \tag{3}$$

where w_i is the factor relevant to vapor phase non-ideality of component *i*, calculated accounting for the presence of air, assuming the latter as a third component equal to nitrogen. The expression of w_i is given elsewhere [19]. Table 1 gives the values of the vapor pressures and molar volumes of the pure compounds, as well as the molar virial coefficients B_{ii} used for the evaluation of w_i . Although some *B_{ii}*'s are estimated values probably affected by large uncertainties, the w_i terms usually differ from 1 by less than 5%.

As the function representing the ratio of calculated activity coefficients we found convenient the modified Wilson equation with three parameters:

$$\ln\left(\frac{\gamma_{1}}{\gamma_{2}}\right)_{\text{calc}} = \ln\frac{x_{2} + \Lambda_{21}x_{1}}{x_{1} + \Lambda_{12}x_{2}} + \left(\frac{\Lambda_{12}}{x_{1} + \Lambda_{12}x_{2}} - \frac{\Lambda_{21}}{x_{2} + \Lambda_{21}x_{1}}\right) + a(x_{2}^{2} - x_{1}^{2})$$
(4)

The third term in the right-hand side was added following Novák et al. [20] This modified form usually fits better than the simple Wilson equation for binary mixtures. For describing ln (γ_1/γ_2) (and G^E) we also tried the Redlich–Kister equation with three parameters; this substantially gave the same fitting as Eq. (4). The coefficients Λ_{12} , Λ_{21} and *a* of Eq. (4) were obtained by a non-linear least-squares procedure, similar to that of Barker [5] for the treatment of P-x data, using the following objective function OF:

$$OF = \sum_{k=1}^{n} \left[ln \left(\frac{\gamma_1}{\gamma_2} \right)_{exp} - ln \left(\frac{\gamma_1}{\gamma_2} \right)_{calc} \right]_k^2$$
(5)

the sum of the residuals being extended over all *n* experimental points. In Eq. (3), the ratio $A_2^*/A_1^* = p_2^*/p_1^*/r_f$ was used as an additional adjustable parameter in the least-square calculation. As a consequence, neither the direct determination of the relative response factor r_f via calibration experiments nor the measurement of the vapor pressures p^* were necessary for obtaining the activity coefficients. Excess molar Gibbs energies $G^{\rm E}$ and vapor mole fractions y_i were calculated through

$$\left(\frac{G^{\rm E}}{RT}\right)_{\rm calc} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) + ax_1x_2 \tag{6}$$

$$y_i^{\text{calc}} = \frac{\gamma_i^{\text{calc}} x_i p_i^* / w_i}{\sum_k (\gamma_k^{\text{calc}} x_k p_k^* / w_k)}$$
(7)

with γ ^{calc} obtained using parameters of Eq. (6) [20].

Besides the actual experimental quantities y_i and γ_1/γ_2 , we can also obtain the following mixed quantity, γ_i^{exp} :

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