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Thermodynamic study of (heptane + amine) mixtures. II. Excess and partial molar volumes at 298.15 K

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ABSTRACT

Excess molar volumes V^E at 298.15 K were determined by means of a vibrating tube densimeter for binary mixtures of heptane + primary *n*-alkyl (C_3 to C_{10}) and branched amines (*iso*-propyl-, *iso*-, *sec*-, and *tert*-butyl-, *iso*-, *tert*-pentyl-, and pentan-3-amine) in the whole composition range. The apparent molar volumes of solid dodecyl- and tetradecylamine in heptane dilute solution were also determined. The V^E values were found positive for mixtures involving C_3 to C_8 linear amines, with V^E decreasing with chain lengthening. Heptane + nonyl and decylamine showed s-shaped, markedly asymmetric, curves. Mixtures with branched C_3 to C_5 amines displayed positive V^E's larger than those observed in the mixtures of the corresponding linear isomers. Partial molar volumes V° at infinite dilution in heptane were evaluated for the examined amines and compared with those of alkanes and alkanols taken from the literature. An additivity scheme, based on the intrinsic volume approach, was applied to estimate group (CH_3, CH_2, CH, C, NH_2, and OH) contributions to V°. The effect of branching on V° and the limiting slope of the apparent excess molar volumes were evaluated and discussed in terms of solute–solvent and solute–solute interactions.

1. Introduction

In the framework of a research project which aims to study the thermodynamic properties of non-electrolytes in different solvents, we have started a systematic determination of the excess quantities of (hydrocarbon + amine) mixtures. In a previous work (Part I of this series) we reported excess molar enthalpies H^E for binary mixtures of heptane with primary alkylamines with the aim of characterising the interaction between hydrocarbon and the NH_2 group [1]. As a prosecution of this investigation, we report here excess molar volumes V^E for heptane(1) with primary linear (C_3 to C_{10}, C_{12}, and C_{14}) or branched (*iso*propyl, *iso*-, *sec*-, and *tert*-butyl, *iso*-, *tert*-pentyl, and pentan-3-amine) alkylamines(2). From partial molar excess volumes at infinite dilution, $V_i^{E,\circ}$, and from molar volumes of pure liquids, V^*, the limiting partial molar volumes, V°, are calculated for each amine in heptane. Other work is in progress dealing with G^E, V^E, and H^E, of (secondary, tertiary, and cyclic amines + heptane), and G^E of (primary amines + heptane).

Volume changes on mixing for the above heptane containing mixtures have been reported in the literature [2–4] for six linear amines (propyl to octyl). In this work we carried out V^E measurements also for such systems in order to obtain a homogeneous set of results and accurate V° values by investigating the dilute regions.

An additivity scheme based on the intrinsic volume approach [5] is also applied: (i) to reproduce the partial molar volumes of amines and alcohols in heptane; (ii) to compare the V° contributions of different groups (CH_3, CH_2, CH, C, NH_2, and OH) in heptane; (iii) to investigate the effect of branching, *i.e.* of the molecular shape, on volumetric properties.

2. Experimental

2.1. Materials

All chemicals were high purity products and were used without further purification. Heptane, Fluka ⩾0.995, water ⩽0.0005; propanamine (common name: propylamine), Fluka ⩾0.99; propan-2-amine (*iso*-propylamine), Fluka ⩾0.995 water ⩽0.0005; butanamine (butylamine), Janssen 0.99 and Aldrich 0.995; 2-methylpropanamine (*iso*-butylamine), Aldrich 0.99 and Fluka 0.995; (+/−) butan-2-amine (*sec*-butylamine), Aldrich 0.99; 2-methylpropan-2-amine (*tert*-butylamine), Fluka ⩾0.995; pentanamine (pentylamine), Aldrich 0.99; 3-methylbutanamine (*iso*-pentylamine), Aldrich 0.99; pentan-3-amine, Aldrich 0.97,

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2-methylbutan-2-amine (*tert*-pentylamine), Aldrich 0.98; hexanamine (hexylamine), Aldrich 0.99; heptanamine (heptylamine), Aldrich 0.99; octanamine (octylamine), Aldrich 0.99; nonanamine (nonylamine), Aldrich 0.98; decanamine (decylamine), Fluka ⩾0.98; dodecanamine (dodecylamine) solid, melting temperature (27 to 29) °C, Fluka ⩾0.98; tetradecanamine (tetradecylamine), solid, melting temperature (38 to 40) °C, Fluka ⩾0.99.

Their purity, in mass fractions, was checked by gas-chromatography, and their water content by Karl-Fischer analysis. No significant difference was found with respect to the impurity content declared by the factories. The density of the pure substances by us measured is reported as molar volume in table 1.

As shown in a previous investigation [6], purity of substances is not a crucial factor in V^E measurements. Usually, the relative systematic error on V^E is less than the impurity content of the components. We have estimated that an impurity of 1% leads to an uncertainty on V^E lower than that coming from errors in density and weighing. This is confirmed by the close similarity of V^E and V° obtained using two different samples of the same amine (butyl and *iso*-butyl) coming from different factories and characterised by a different purity degree.

2.2. Apparatus and procedure

Density measurements were carried out by means of an A. Paar vibrating-tube densimeter (DMA 60/602) operating in the static mode and capable of a precision of better than $3 \cdot 10^{-6}\ \mathrm{g \cdot cm^{-3}}$. Temperature control inside the oscillation chamber (±0.001 K), calibration and test of the apparatus were described in detail elsewhere [7,8]. The accuracy, as calculated by comparing molar volumes with literature values (see table 1), is estimated better than 0.1%.

The liquid mixtures were prepared by weighing. Weights were corrected for buoyancy and for evaporation of the constituents in the space above the liquid. To this purpose, vapour pressure of pure substances and activity coefficients of constituents were taken from [1], where an analogous correction was applied. The liquid mole fractions x, after the above corrections (which never exceed 0.001) were evaluated to better than 0.0003. The overall uncertainty in V^E and V^E/x_1x_2, due to density and mole fraction errors, was usually (<0.005 and 0.05) $\mathrm{cm^3 \cdot mol^{-1}}$, respectively.

We neglected the effect of dissolved air on the density of mixtures. The uncertainty in V^E brought about by changes in dissolved air during mixing was estimated to be well within experimental error from different sources.

3. Results

The excess molar volumes of the mixtures were obtained from the measured values of the density by the usual equation

$$V^{\mathrm{E}} = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2, \tag{1}$$

where ρ is the density of the mixture and x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of the two liquid components, respectively. The results are collected in table 2.

Excess molar volumes, V^E, were fitted through a least square treatment to the Redlich–Kister polynomial:

$$V^{\mathrm{E}}/x_1x_2 = \sum_{j=0}^{n} a_j(x_1 - x_2)^j \tag{2}$$

using as the objective function the ratio V^E/x_1x_2 instead of V^E as is commonly done. This ratio tends to emphasize the dilute regions, whilst fitting V^E may result in large relative errors on the V^E of the dilute solutions and consequently lead to quite erroneous values of the limiting partial molar excess volumes $V_i^{\mathrm{E},\circ}$. On the other hand, for the examined systems the standard deviation of V^E resulted almost the same either by fitting V^E/x_1x_2 or V^E. The values of a_j parameters, together with the standard deviations σ for V^E/x_1x_2 and V^E, are given in table 3.

TABLE 1
Van der Waals volumes, V_w, molar volumes of the pure liquids, V^*, excess partial molar volumes at infinite dilution, $V_i^{\mathrm{E}\circ}$, partial molar volume at infinite dilution of the amines, V°, and limiting slope h of V^E/x_2, for {heptane(1) + amine(2)} mixtures at 298.15 K.

Compound	$V_w/(\mathrm{cm^3 \cdot mol^{-1}})$	$V^*/(\mathrm{cm^3 \cdot mol^{-1}})$	$V_1^{\mathrm{E},\circ}/(\mathrm{cm^3 \cdot mol^{-1}})$	$V_2^{\mathrm{E},\circ}/(\mathrm{cm^3 \cdot mol^{-1}})$	$V_2^\circ/(\mathrm{cm^3 \cdot mol^{-1}})$	$h^a/(\mathrm{cm^3 \cdot mol^{-1}})$
Heptane	77.61	147.46[b]	0			
Propylamine	44.37	83.15[c]	3.50	4.61	87.76	−6.4
iso-Propylamine	44.31	86.72	4.56	5.09	91.81	−7.7
Butylamine	54.46	99.87[d]	2.39	3.77	103.64	−5.5
iso-Butylamine	54.40	100.95	3.00	4.23	105.18	−7.0
sec-Butylamine	54.40	101.91	3.17	4.07	105.98	−5.8
tert-Butylamine	54.28	106.52	4.03	4.32	110.84	−5.5
Pentylamine	64.55	116.29[e]	1.37	3.29	119.58	−7.3
iso-Pentylamine	64.49	117.01	1.73	3.69	120.70	−7.9
Pentan-3-amine	64.49	117.22	1.90	3.37	120.59	−6.9
tert-Pentylamine	64.37	119.25	2.61	4.03	123.28	−7.7
Hexylamine	74.64	133.06[f]	0.82	2.49	135.55	−5.4
Heptylamine	84.73	149.62[g]	0.27	1.94	151.56	−5.4
Octylamine	94.82	166.16[h]	−0.01	1.25	167.41	−4.0
Nonylamine	104.91	182.87	−0.39	0.67	183.54	−2.8
Decylamine	115.00	199.00	−0.64	0.58	199.58	−4.3
Dodecylamine	135.18	232.3[i]		−1.02[j]	231.3[k]	−0.8
Tetradecylamine	144.36	265.5[i]		−1.90[j]	263.6[k]	−0.5

[a] $h = [\partial(V^E/x_2)/\partial x_2]_{x_2=0}$.
[b] 147.46 reference [3],[4].
[c] 83.13 reference [3].
[d] 99.77 reference [3].
[e] 116.44 reference [2].
[f] 133.10 reference [2], 132.95 reference [4].
[g] 149.52 reference [2].
[h] 166.10 reference [2].
[i] Molar volume of the undercooled liquid estimated by extrapolation of V^* of liquid *n*-alkylamines in the homologous series.
[j] Extrapolated from V^E/x_1x_2 using V^E calculated from estimated V^*.
[k] Obtained by extrapolation of $V^{\mathrm{E}}_{2,\varphi}$.