Thermochimica Acta, 162 (1990) 203-212
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

EXCESS VOLUMES OF BINARY MIXTURES CONTAINING MORPHOLINE *

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(Received in final form 9 September 1989)

ABSTRACT

The results of an experimental investigation of five binary mixtures of morpholine with water and alcohols are reported. Data from volumetric measurements (T and x) are used to compute excess volumes (V^E) and partial molar volumes at infinite dilution. The V^E data are correlated with Redlich-Kister polynomials.

INTRODUCTION

Precise measurements of excess volumes (V^E) over the whole composition range are necessary to understand the nature of the interactions between the components of a liquid mixture. In addition, experimental data are of great importance for the thermodynamic design of industrial processes. Such data are required for the custody transfer of morpholine, which is of particular interest in the petrochemical industry because of its high efficiency in the extraction of monocyclic aromatic hydrocarbons from petroleum products. Experimental V^E data for the system morpholine-methanol have been reported by Awward et al. [1], but no measurements are available for mixtures containing water and other alcohols.

EXPERIMENTAL

Materials

All the alcohols used in the present study were HPLC grade supplied by Fluka. Ethanol and propanol were used as received with a stated purity of > 99.9 mol.%. Morpholine was dried over fresh sodium after one hour of refluxing and fractionated through a 40TP column to collect the main fraction boiling over a 0.005 K range. Methanol was distilled twice over

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* Presented at the 10th AICAT, Pisa, Italy, 11-14 December 1988.

0040-6031/90/$03.50

TABLE 1

Comparison between measured and literature data for the density (δ) of the pure components at 298.15 K

Component	δ (g cm^{-3})	
	This work	Literature [4]
Morpholine	0.99523	0.99547
Methanol	0.78640	0.78637
Ethanol	0.78500	0.78493
1-Propanol	0.79957	0.79960
2-Propanol	0.78082	0.78126

CaH_2 in a 2 m column packed with glass helixes (estimated number of stages, 150), using a different reflux ratio. The purity of morpholine and methanol after purification was, according to density measurements, > 99.7 mol%. Care was taken to prevent contamination by water and oxidation of the chemicals after their purification. Alcohols were stored in bottles over 3A molecular sieves and the morpholine was kept in a nitrogen atmosphere. Nitrogen and doubly distilled water were used for the densimeter calibration. The purity of the doubly distilled water was assumed to be 100 mol% and that of nitrogen was higher than 99.9999 mol%. The densities of the pure components at 298.15 K and atmospheric pressure were measured before preparing the mixtures and compared with literature values to check their purity (see Table 1).

Mixture preparation

All the solutions were prepared by using a Mettler balance (precision, 1×10^{-5} g) and air-tight stoppered bottles. The more volatile component was poured directly into the bottle. The charged bottle was then closed and weighed. The second component was injected into the bottle through the stopper using a syringe. This procedure prevented vapour loss, contamination and oxidation. The possible error in the mole fraction can be regarded as lower than 5×10^{-5}.

Density measurements

A digital densimeter (Anton Paar DMA 602H - DMA 60) was employed to determine the densities of the pure components and the binary mixtures. The density determination is based on measuring the period of oscillation of the vibrating U-shaped borosilicate glass (Duran 50) sample tube filled with the sample (liquid or gas). The following relationship between the density (δ) and the period of oscillation (Ω) was used

$$\delta = (\Omega^2 - B)/A \qquad (1)$$

where A and B were determined by instrument calibration at 298.15 K with doubly distilled water ($\delta = 0.997\,047$ g cm^{-3}) and nitrogen ($\delta = 0.001\,145\,6$ g cm^{-3}). Water and nitrogen gas were chosen as calibrating fluids because they span a wide density range, can be obtained with a high purity and their densities are known at a high precision level. Calibration was performed before each measurement under the same conditions of temperature and pressure. All the measurements were carried out at atmospheric pressure. Pressure was measured by means of a mercury barometer. Density data for water and nitrogen were taken from refs. 2 and 3. A time interval of 15 min was chosen to attain a satisfactory temperature constancy and oscillation-period stability (fluctuations restricted to the sixth decimal digit). All the measurements were performed at 10 k period-select switch. A Hetofrig constant-temperature bath circulator was used with a temperature control interval of ± 0.01 K. Temperature was detected with a digital precision thermometer (Anton Paar DT 100-20), calibrated against a platinum resistance thermometer (Rosemount mod. 162 CE) and checked at the water triple point.

The precision of the densities measured is estimated to be better than 1×10^{-5} g cm^{-3}.

RESULTS AND CORRELATION

Table 1 compares the pure component densities measured in this work with the literature data taken from ref. 4 at 298.15 K and atmospheric pressure: the agreement is satisfactory.

Table 2 gives the measurements for the systems investigated in mole fractions. It includes density data (δ) and excess volumes (V^E). V^E values were calculated by means of the following equation [5]

$$V^E = [(x_1M_1 + x_2M_2)/\delta] - x_1M_1/\delta_1 - x_2M_2/\delta_2 \qquad (2)$$

where x_i are mole fractions, M_i are molecular weights and δ_i are densities of the pure components. The precision of the V^E data is estimated to be better than 0.000 5 cm^3 mol^{-1}.

Partial molar excess volumes of the components are defined as the volume variation on addition of a small amount of component i [6]. Partial molar excess volumes at infinite dilution are then calculated by extrapolation to zero concentration. A different way of determining the values at infinite dilution is that of Cordray and Eckert [7], which is based on an extrapolation method similar to that used in the determination of the infinite dilution activity coefficients by ebulliometry [8]. The partial molar excess volume of a component in a binary mixture is given by

$$\bar{V}_i^E = V^E + (1 - x_i)(\partial V^E/\partial x_i) \qquad (3)$$

At the limit of infinite dilution, V^E and x_i become zero

$$\bar{V}_i^{E,\infty} = \left(\partial V^E / \partial x_i\right)_{x_i=0} \qquad (4)$$

i.e. the slope of the excess volume versus mole fraction curve at infinite

TABLE 2

Experimental results for binary systems containing morpholine (1) at 298.15 K

x_1	V^E (cm^3 mol^{-1})	δ (g cm^{-3})
Morpholine–water		
0.9215	−0.3489	0.99951
0.8879	−0.4905	1.00144
0.8256	−0.7320	1.00506
0.7965	−0.8461	1.00693
0.7422	−1.0225	1.01019
0.7039	−1.1583	1.01289
0.6587	−1.2822	1.01581
0.5904	−1.4569	1.02063
0.5712	−1.5038	1.02209
0.5233	−1.5810	1.02530
0.4723	−1.6556	1.02906
0.4018	−1.6705	1.03319
0.3511	−1.6339	1.03558
0.3079	−1.5330	1.03606
0.2366	−1.3489	1.03648
0.1994	−1.2371	1.03622
0.1544	−0.9785	1.03124
0.1000	−0.6566	1.02328
0.0568	−0.3983	1.01501
Morpholine–methanol		
0.9440	−0.1831	0.99176
0.9170	−0.2644	0.98992
0.8512	−0.4748	0.98532
0.7977	−0.6344	0.98115
0.7403	−0.7930	0.97619
0.6990	−0.8967	0.97223
0.6511	−1.0053	0.96720
0.6020	−1.0939	0.96135
0.5479	−1.1849	0.95432
0.5010	−1.2435	0.94744
0.4613	−1.2677	0.94083
0.3990	−1.2944	0.92941
0.3212	−1.2363	0.91189
0.2820	−1.1818	0.90173
0.2461	−1.1156	0.89152
0.2000	−0.9868	0.87664
0.1396	−0.7875	0.85461
0.1010	−0.6183	0.83841
0.0505	−0.3391	0.81422

dilution. $\overline{V}_i^{E,\infty}$ is thus obtained by fitting V^E data versus composition, and calculating the slope of the curve at zero concentration. Typically, ten data points at mole fractions from 0.005 up to 0.09 were used to determine $\overline{V}_i^{E,\infty}$.

TABLE 2 (continued)

x_1	V^E (cm^3 mol^{-1})	δ (g cm^{-3})
Morpholine–ethanol		
0.9377	−0.1627	0.98814
0.8978	−0.2628	0.98338
0.8380	−0.4131	0.97597
0.8014	−0.4958	0.97116
0.7614	−0.5840	0.96572
0.6964	−0.7154	0.95637
0.6331	−0.8218	0.94651
0.6025	−0.8659	0.94147
0.5609	−0.9163	0.93430
0.5014	−0.9627	0.92329
0.4511	−0.9892	0.91338
0.3947	−0.9857	0.90133
0.3406	−0.9576	0.88891
0.3054	−0.9259	0.88034
0.2636	−0.8625	0.86949
0.1980	−0.7299	0.85123
0.1498	−0.5980	0.83669
0.1009	−0.4345	0.82093
0.0623	−0.2847	0.80775
Morpholine–1-propanol		
0.9377	−0.1627	0.98814
0.9317	−0.1562	0.98542
0.8987	−0.2316	0.98060
0.8634	−0.3101	0.97535
0.8007	−0.4293	0.96565
0.7504	−0.5363	0.95785
0.7209	−0.5712	0.95289
0.6750	−0.6609	0.94548
0.6114	−0.7295	0.93439
0.5823	−0.7628	0.92926
0.5504	−0.8162	0.92377
0.4993	−0.8301	0.91403
0.4271	−0.8607	0.90013
0.3871	−0.8450	0.89192
0.3437	−0.8353	0.88298
0.2906	−0.7720	0.87131
0.2120	−0.6461	0.85334
0.1613	−0.5305	0.84116
0.0885	−0.3212	0.82291
0.0311	−0.1209	0.80791

TABLE 2 (continued)

x_1	V^E ($cm^3\ mol^{-1}$)	δ ($g\ cm^{-3}$)
Morpholine–2-propanol		
0.9511	−0.1058	0.98716
0.9020	−0.2090	0.97890
0.8641	−0.2834	0.97238
0.8145	−0.3698	0.96362
0.7498	−0.4847	0.95203
0.7073	−0.5562	0.94425
0.6608	−0.6064	0.93531
0.6114	−0.6556	0.92564
0.5778	−0.6934	0.91903
0.5413	−0.7084	0.91150
0.4904	−0.7179	0.90073
0.4412	−0.7306	0.89023
0.3712	−0.7028	0.87455
0.3112	−0.6615	0.86069
0.2577	−0.5988	0.84788
0.1860	−0.4892	0.83019
0.1400	−0.3869	0.81835

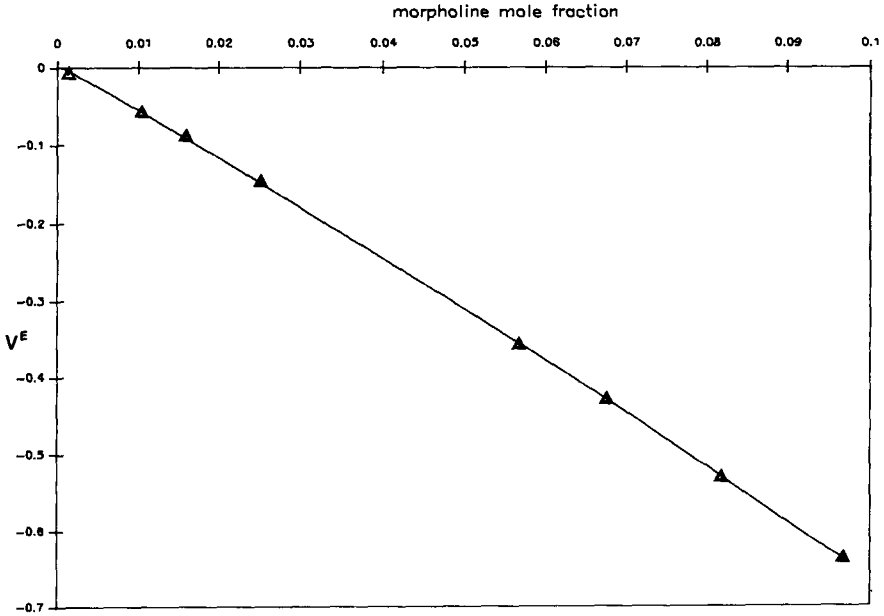

Fig. 1. Excess volume data for morpholine in water at 298.15 K; the line is the quadratic fit of the data.

TABLE 3

Values of the coefficients of the correlation equation for excess volumes and standard deviations: component 1 is morpholine

Component 2	Coefficients (a_i) of eqn. (5)				σ_{VE}
Water	−6.5027	2.4378	0.4930	−1.2983	0.0134
Methanol	−4.9568	1.8399	−0.3459	0.2494	0.0051
Ethanol	−3.8733	1.2501	0.0577	−0.0743	0.0018
1-Propanol	−3.3531	1.0589	0.1524	−0.2433	0.0073
2-Propanol	−2.9001	0.5551	0.1609	−0.0080	0.0049

Of the different extrapolation methods, the best results were given by the quadratic polynomial form used in this work. Figure 1 shows the graph of this extrapolation for the morpholine–water system. The line is the quadratic fit of the data.

The following equation was used to describe the composition dependence of the excess volumes [9]

$$V^{E}_{calc} = x_1 x_2 \sum_{j=0}^{3} a_j (x_1 - x_2)^j \tag{5}$$

Data reduction was performed with a least-squares method that minimised an objective function made up of the sum of the squares of the absolute differences between experimental and calculated values.

The coefficients obtained, a_i (eqn. (5)), are listed in Table 3, along with the standard deviations, σ_{VE}, for each system calculated by means of the following equation [10]

$$\sigma_{VE} = \left[\sum_i \left(V^{E}_{cal} - V^{E}_{exp} \right)_i^2 / (N - n) \right]^{1/2} \tag{6}$$

TABLE 4

Partial molar excess volume at infinite dilution for morpholine containing systems at 298.15 K showing results with eqns. (5) and (4)

Component 1	Component 2	$\bar{V}_1^{E,\infty}$ eqn. (5)	$\bar{V}_1^{E,\infty}$ eqn. (4)
Water	Morpholine	−4.9	−4.78
Morpholine	Water	−8.1	−5.88
Methanol	Morpholine	−3.2	−3.19
Morpholine	Methanol	−6.7	−6.69
Ethanol	Morpholine	−2.6	−2.10
Morpholine	Ethanol	−5.1	−5.08
1-Propanol	Morpholine	−2.4	−2.25
Morpholine	1-Propanol	−4.3	−4.11
2-Propanol	Morpholine	−2.2	−2.15
Morpholine	2-Propanol	−3.6	−3.22

where N is the number of data points for each system and n is the number of coefficients.

The $\overline{V}_i^{\mathrm{E},\infty}$ data (Table 4) are compared with the values obtained by extrapolating the V^{E} data for the whole composition range.

DISCUSSION

The experimental data are reported in Fig. 2 with the values calculated by means of eqn. (5).

Comparison with the only literature data for the morpholine–methanol system [1] (Fig. 3) shows good agreement for the dilute morpholine region, but substantial deviation in the morpholine-rich region. The morpholine used by Awward et al. [1] may have been impure as they report a density value for pure morpholine of 0.905 71 g cm^{-3}, compared with 0.995 47 g cm^{-3} [4] and 0.995 23 g cm^{-3} of this work.

All the systems investigated display a negative deviation from the linear volumetric behaviour, suggesting the formation of strong hydrogen bonds. Morpholine acts as a proton donor, and water, or alcohols, as a proton acceptor. The V^{E} value is highest for the morpholine–water system (-1.67 cm^3 mol^{-1}) and decreases smoothly as the aliphatic chain length increases.

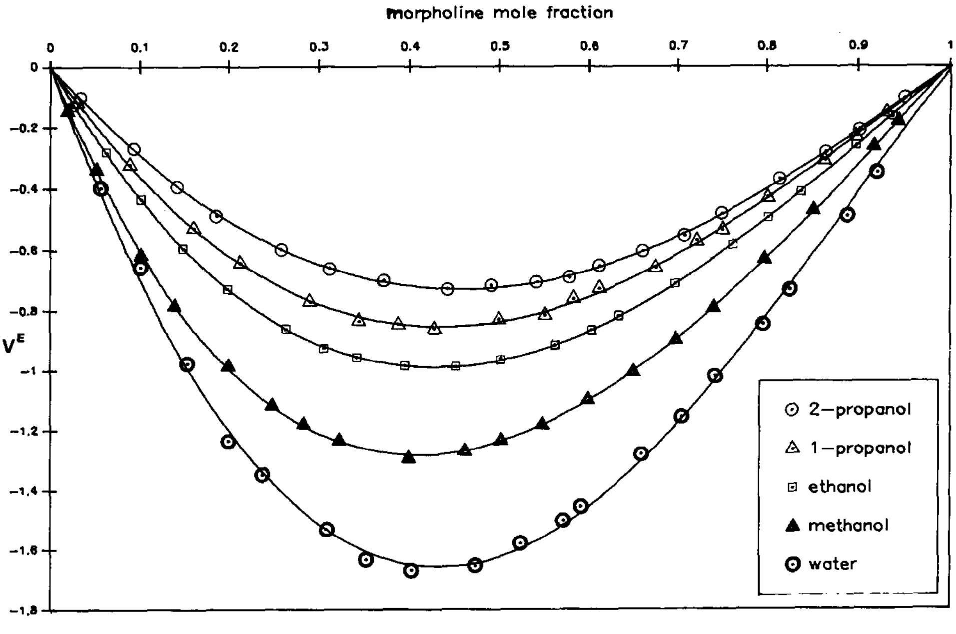

Fig. 2. Excess volume data for morpholine binary systems at 298.15 K: comparison between calculated (line) and experimental data.

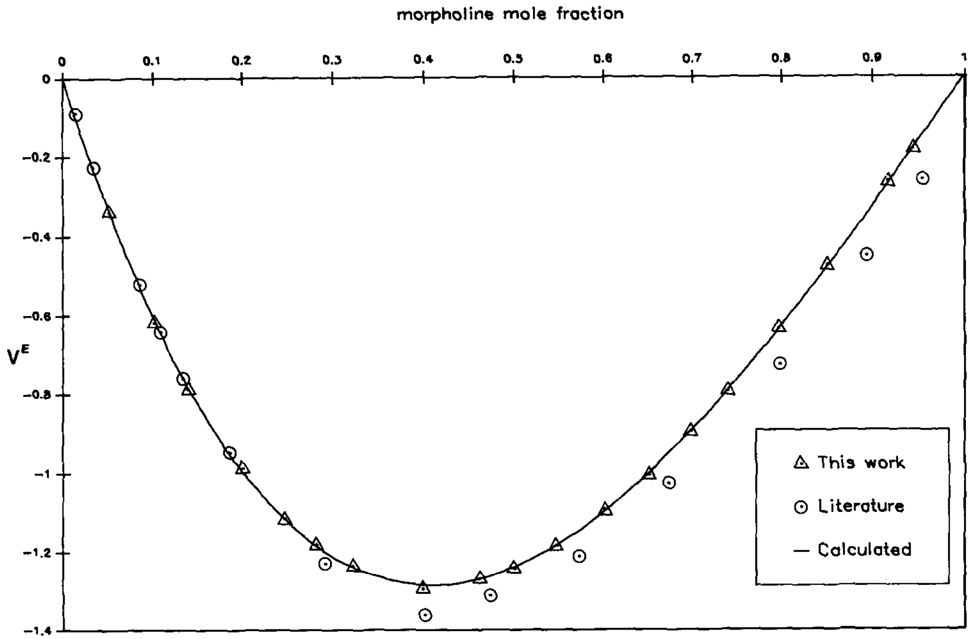

Fig. 3. Comparison between calculated (line), experimental and literature excess volume data for the morpholine–methanol system at 298.15 K.

The smallest effect is found in the morpholine–2-propanol system, which shows smaller V^E values than the morpholine–1-propanol system.

The $\bar{V}_i^{E,\infty}$ values given by eqn. (4) are listed in Table 4 (column 4). The error estimation for $\bar{V}_i^{E,\infty}$ depends on the scatter of the V^E data and the curvature of the V^E versus mole fraction curve. An error analysis [7] indicated that V^E data are less accurate for systems in which the solvent has a large molar volume, or when the two pure component densities differ greatly. In general, the results are accurate to ±0.1 cm^3 mol^{-1} or 5% of $\bar{V}_i^{E,\infty}$, whichever is greater.

Table 4 also includes the $\bar{V}_i^{E,\infty}$ values obtained by extrapolating the data of Table 2 with eqn. (5) (column 3). The error here is greater and there are considerable differences between the values obtained from the two equations, e.g. see the morpholine–water system.

LIST OF SYMBOLS

A, B	instrument constants, eqn. (1)
a	coefficients, eqn. (5)
M	molecular weight
N	number of experimental data points
n	number of parameters
V^E	excess volume (cm^3 mol^{-1})
$\bar{V}_i^{E,\infty}$	partial molar excess volume of component i at infinite dilution

Greek letters

x	mole fraction
δ	density (g cm^{-3})
Ω	period of oscillation
σ_{VE}	standard deviation of excess volumes

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