Partial Molar Excess Volumes at Infinite Dilution of Binary Liquid Mixtures of Nonelectrolytes

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A vibrating-tube density meter was used to obtain excess volumes (v^E) of binary liquid mixtures of nonelectrolytes in the dilute region. The excess volume data were extrapolated to obtain partial molar excess volumes at infinite dilution ($\bar{v}_i^{E\infty}$) for 17 systems at 25 °C.

Introduction

Most of the attempts to model solution behavior have focused on the excess Gibbs energy (g^E) of mixing, which is the property generally considered to be of most interest for phase equilibria. The resulting expressions (e.g., Wilson, NRTL, UNIQUAC) are sufficiently accurate to correlate VLE data well, but they have been less successful in representing some aspects of LLE data, and they provide little information about the other excess properties which comprise the temperature and pressure derivatives of g^E. These derivative relationships may be summarized as follows

$$(\partial g^E/\partial T)_{P,x} = -s^E$$

$$[(\partial g^E/T)/\partial T]_{P,x} = -h^E/T^2$$

$$(\partial g^E/\partial P)_{T,x} = v^E$$

where s^E, h^E, and v^E are the excess entropy, excess enthalpy, and excess volume of mixing.

From a theoretical standpoint, examination of the partial molar derivative excess properties at infinite dilution ($\bar{s}_i^{E\infty}$, $\bar{h}_i^{E\infty}$, $\bar{v}_i^{E\infty}$) appears to be of particular interest. At the limit of infinite dilution, solute–solute interactions disappear; thus, the values of the infinite dilution partial molar excess properties provide insight into the relationships between the solute–solvent interactions and the respective thermodynamic properties, independent of composition effects.

As part of a continuing investigation into the properties of the derivatives of g^E, we have used a vibrating-tube density meter to measure the densities of binary liquid mixtures in the dilute region. From these data we obtained values of the partial molar excess volume at infinite dilution ($\bar{v}_i^{E\infty}$) for 33 compounds in 17 binary systems.

Experimental Section

Densities of dilute liquid mixtures at 25 °C were determined with a Mettler-Parr vibrating-tube density meter, the principle of operation of which has been presented previously (*1*, *2*). The density meter was calibrated daily with distilled water and air. The liquid mixtures were prepared by weight in 30-mL flasks. In performing the weighings, a flask was first weighed with a septum cap and magnetic stirring bar. Then approximately 25 cm^3 of solvent was added to the flask, the flask was capped, and the flask and solvent were weighed. Then a small amount of solute was injected through the septum into the flask, and the weighing was repeated. The vapor space in the flask was approximately 2-3 cm^3.

Table I. Analysis of v^E Data and Determination of $\bar{v}_1^{E\infty}$ for the Chloroform (1)–Methyl Acetate (2) System[a]

x_1	v^E(exptl), cm^3/mol	v^E(calcd), cm^3/mol	
		linear fit	quadratic fit[b]
0.0101	0.0137	0.0117	0.0122
0.0203	0.0242	0.0237	0.0242
0.0309	0.0349	0.0360	0.0363
0.0364	0.0426	0.0424	0.0424
0.0448	0.0520	0.0521	0.0515
		$A = 1.16$	$A = 1.23$
			$B = -1.70$
		$\sigma = 0.0013$	$\sigma = 0.0012$
		$E = 0.0020$	$E = 0.0015$

[a] $\sigma = (\sum(v^E_{calcd} - v^e_{exptl})^2/(\mathrm{NDAT} - \mathrm{NPAR}))^{1/2}$ where NDAT is the number of data points and NPAR is the number of adjustable parameters in the fit. E = maximum error of the fit. A and B are the parameters obtained from the least-squares fit of the data. [b] $\bar{v}_1^{E\infty} = 1.23$ cm^3/mol.

Weighings were performed on a Mettler Type H16 balance accurate to ±0.1 mg, and buoyancy corrections were applied to account for air displacement by the liquid. After the third and final weighing, the dilute solution was mixed thoroughly and a sample was injected into the cell of the density meter, where its density was recorded. Constant temperature water flowed through a water jacket surrounding the cell, reducing temperature fluctuations in the cell to ±0.003 °C during the course of a run. The absolute temperature of the cell was measured with a thermistor calibrated with a Hewlett-Packard 2804A quartz thermometer; the absolute cell temperature was always 25.00 ± 0.02 °C.

The densities of the pure components were also determined experimentally during each run. Measuring the pure component densities negates the possible error in v^E due to small amounts (less than 1%) of impurities in the pure components. This is true since any impurities would affect the mixture densities and pure component densities similarly, and v^E is determined from the density differences between the mixture and the pure components.

Materials. Acetone, 2-butanone, carbon disulfide, carbon tetrachloride, chloroform, and ethyl acetate were Aldrich's HPLC grade, 99.9+%, and were used as purchased. Butylamine, furfural, heptane, hexane, methyl acetate, methylcyclohexane, 1-propanol, and vinyl acetate were Aldrich's, at least 99%, and were used as purchased. Ethanol was from U. S. Industrial Chemicals Co., 200 proof, and toluene was Baker Analyzed Reagent, stated assay 100%. Both were used as purchased. Nitroethane and nitromethane were Aldrich's, 96%, and were fractionally distilled, the middle 60% being collected. In all cases, nondegassed liquids were used.

Data Reduction

The molar excess volumes were calculated from the density data by the equation

$$v^E = x_1 M_1\left(\frac{1}{\rho_m} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho_m} - \frac{1}{\rho_2}\right) \qquad (1)$$

where x_i, M_i, ρ_i are the mole fraction, molecular weight, and

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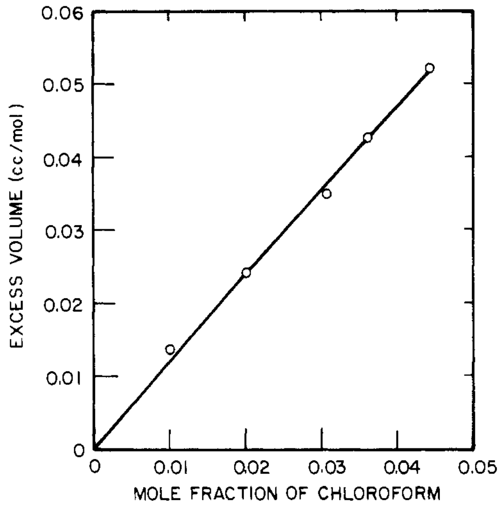

Figure 1. v^E data for chloroform dilute in methyl acetate at 25 °C. The curve is the quadratic fit of the data.

density of component i, and ρ_m is the density of the mixture.

The partial molar excess volume of a component in a binary mixture can be determined from excess volume data

$$\bar{v}_i^E = v^E + (1 - x_i)(\partial v^E/\partial x_i) \qquad (2)$$

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

$$\bar{v}_i^{E\infty} = (\partial v^E/\partial x_i)_{x_i=0} \qquad (3)$$

or the infinite dilution partial molar excess volume is the slope of the excess volume vs. mole fraction curve at infinite dilution. Thus, $\bar{v}_i^{E\infty}$ can be obtained by fitting dilute v^E vs. composition data to a curve, and obtaining the slope of the curve at x_i = 0.

Typically, five to ten data points at mole fractions ranging from approximately 0.005 to 0.05 were used to determine $\bar{v}_i^{E\infty}$. Various equations were used to fit the data by the least-squares method. The equations employed depended on the amount of curvature of the v^E data and on the number of data points taken. Since no theoretically correct equation exists, the uncertainties cited in the results reflect the minor differences in fitting with the various forms. The following fitting equations, where component 1 is the solute, were used:

$$v^E = Ax_1 \qquad (4)$$

$$v^E = Ax_1 + Bx_1^2 \qquad (5)$$

$$x_1x_2/v^E = Ax_1 + B \qquad (6)$$

$$v^E/x_1 = A + Bx_1 \qquad (7)$$

Equations 4 and 5 simply represent linear and quadratic fits. Equation 6 is a van Laar type fit, which was used when the data displayed substantial curvature, as usually occurred in dilute alcohol solutions. Equation 7 is a fit of v^E/x_1, which is similar to the quadratic fit but has the effect of placing greater emphasis on the more dilute points. More complex fitting equations could be used, but since the curvature of the data is usually not great and since some scatter usually exists in the data, more complex expressions would not substantially improve the analysis.

When suitable fitting equations had been applied to the data, the accuracy and relative merits of the correlations were examined and a $\bar{v}_i^{E\infty}$ value was determined. An example of such an analysis is shown in Table I for chloroform (1) dilute in methyl acetate (2). Since the data exhibit slight curvature, the linear and quadratic fitting equations were used. The quadratic equation gives a slightly better fit of the data, indicated by the smaller standard deviation (σ). Thus the $\bar{v}_i^{E\infty}$ value for chloroform in methyl acetate is taken to be the A value for the quadratic equation, which is 1.23 cm^3/mol. A graph of the v^E data for this system is presented in Figure 1.

Table II. Infinite Dilution Partial Molar Excess Volumes at 25 °C

component 1	component 2	$\bar{v}_1^{E\infty}$, cm^3/mol	$\bar{v}_2^{E\infty}$, cm^3/mol
acetone	hexane	5.0 ± 0.3	3.8 ± 0.2
2-butanone	hexane	3.3 ± 0.2	2.0 ± 0.15
$CHCl_3$	hexane	2.2 ± 0.2	1.34 ± 0.1
acetone	ethanol	−0.47 ± 0.1	−0.20 ± 0.1
hexane	ethanol	2.03 ± 0.1	8.0 ± 0.5
heptane	ethanol	2.85 ± 0.15	
CS_2	acetone	5.0 ± 0.25	4.7 ± 0.25
hexane	vinyl acetate	3.7 ± 0.3	6.6 ± 0.35
CCl_4	1-propanol	−0.75 ± 0.1	5.1 ± 0.4
heptane	butylamine	1.9 ± 0.15	4.2 ± 0.3
acetone	$CHCl_3$	−1.0 ± 0.1	0.60 ± 0.1
ethanol	toluene	1.6 ± 0.15	−1.4 ± 0.1
methyl acetate	$CHCl_3$	0.0 ± 0.1	1.23 ± 0.1
ethyl acetate	$CHCl_3$	−0.42 ± 0.1	0.70 ± 0.1
heptane	furfural	−2.32 ± 0.15	4.9 ± 0.2
nitroethane	hexane	4.1 ± 0.3	0.28 ± 0.1
nitromethane	methylcyclohexane	6.5 ± 0.3	4.45 ± 0.3

Table III. Comparison of $\bar{v}_1^{E\infty}$ Values at 25 °C Determined in This Study to Literature Values

	$\bar{v}_1^{E\infty}$		
system	this study	lit.	ref
ethanol (1) in toluene (2)	1.6 ± 0.15	1.495	*4*
toluene (1) in ethanol (2)	−1.4 ± 0.1	−1.400	*4*
heptane (1) in ethanol (2)	2.85 ± 0.15	2.90	*3*
hexane (1) in ethanol (2)	2.03 ± 0.1	2.01	*5*
ethanol (1) in hexane (2)	8.0 ± 0.5	8.4	*5*

Presentation of Results

The 33 $\bar{v}_i^{E\infty}$ values obtained in this study are listed in Table II. The last three systems, heptane–furfural, nitroethane–hexane, and nitromethane–methylcyclohexane, exhibit partial miscibility at 25 °C at higher concentrations than those studied here. The $\bar{v}_i^{E\infty}$ value of ethanol in heptane was found in the literature (*3*) and was not determined experimentally. The error estimates in Table II take into account the scatter of the v^E data and uncertainty in $\bar{v}_i^{E\infty}$ due to substantial curvature of the data. Generally the results are accurate to ±0.1 cm^3/mol or 5–8% of $\bar{v}_i^{E\infty}$, whichever is greater. An error analysis indicated that the v^E values tend to be slightly less accurate for systems in which the solvent has a large molar volume (such as hexane or heptane), or in which the densities of the two components differ greatly. Conversely, greater accuracy in v^E is obtained when the solvent has a small molar volume and when the two components have similar densities. In five cases, literature data were found that correspond to data obtained in this study. A comparison of these values is shown in Table III. The agreement is quite satisfactory.

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Registry No. $CHCl_3$, 67-66-3; CS_2, 75-15-0; CCl_4, 56-23-5; methyl acetate, 79-20-9; acetone, 67-64-1; hexane, 110-54-3; 2-butanone, 78-93-3; ethanol, 64-17-5; heptane, 142-82-5; vinyl acetate, 108-05-4; 1-propanol, 71-23-8; butylamine, 109-73-9; toluene, 108-88-3; furfural, 98-01-1; nitroethane, 79-24-3; nitromethane, 75-52-5; methylcyclohexane, 108-87-2.

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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of NaCl and $MgCl_2$ at 25 °C

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The osmotic and activity coefficients of aqueous mixtures of NaCl and $MgCl_2$ have been determined at 25 °C by using the isopiestic method. These measurements extend from low concentrations to the crystallization limits of the mixtures. They are critically compared to published isopiestic, direct vapor pressure, and emf data for this system. Our data agree well with previous isopiestic data and two sets of emf values, but direct vapor pressure data are significantly discrepant. Osmotic and activity coefficients for NaCl–$MgCl_2$ mixtures are fairly reliably represented by both Pitzer's equations and Scatchard's neutral electrolyte equations.

Introduction

A wide variety of chemical, geochemical, biochemical, and industrial systems and processes involve aqueous electrolyte mixtures. Osmotic and activity coefficient data are essential for these systems in order to quantitatively characterize and to model their reaction thermodynamics, their chemical speciation, and their solubilities. Activity data and their derivatives are also needed to calculate thermodynamic diffusion coefficients, which are based on chemical potential gradient rather than concentration gradient driving forces (*1*–*3*).

Several important ternary brine salt mixtures have been reinvestigated recently at 25 °C. Seidel et al. (*4*) and Kuschel and Seidel (*5*) have provided accurate data for aqueous KCl–$MgSO_4$, KCl–$MgCl_2$, and K_2SO_4–$MgSO_4$ mixtures by using the isopiestic method. Ananthaswamy and Atkinson (*6*) studied NaCl–$CaCl_2$ mixtures by using Na^+ and Ca^{2+} ion-sensitive electrodes, and Filippov and Cheremnykh (*7*) studied $MgCl_2$–$MgSO_4$ mixtures by using the isopiestic method.

Another important brine salt mixture is NaCl–$MgCl_2$. An extensive series of diffusion coefficient measurements is currently in progress in our laboratory. To analyze and interpret these data requires accurate activity coefficient derivatives. Since differentiation magnifies experimental errors, very precise experimental data are required.

Several workers have previously studied aqueous NaCl–$MgCl_2$ at 25 °C. Experimental water activity data were reported from isopiestic measurements in two studies (*8*, *9*) and from direct water vapor measurements by the static method (*10*), and NaCl activities were reported in three studies (*11*–*13*) using emf measurements. Freezing point depression data (*14*) seem to be consistent with the 25 °C isopiestic values, but published enthalpy and heat capacity data are not adequate to convert the freezing point data to 25 °C. Thus, freezing point data will not be considered further. Additional enthalpy and heat capacity data would be desirable.

The most extensive investigation of NaCl–$MgCl_2$ activities is Platford's isopiestic study (*9*) which covers the ionic strength range of $I = 0.11$–8.02 mol·kg^{-1}, where the kg refers to H_2O. An et al.'s vapor pressure measurements (*10*) cover the ionic strength range of 6.37–13.84 mol·kg^{-1}, but they are restricted to NaCl ionic strength fractions of 0.021–0.065. Osmotic coefficients from these two studies differ by 1–4% in the overlap region, and this exceeds the usual experimental errors for these methods by an order of magnitude. In addition, both studies are somewhat scattered. The main source of these discrepancies seems to be the solution preparation method. Both studies (*9*, *10*) used direct weighing of "$MgCl_2{\cdot}6H_2O$" that had been dried with a water aspirator at 50 °C. It has been our experience that attempts to dry hydrated chlorides to stoichiometric hydrates frequently results in samples that are overdried or underdried, so direct weighing of "$MgCl_2{\cdot}6H_2O$" generally gives unreliable concentrations. Wu et al.'s isopiestic investigation (*8*) is free of this objection, but only 15 points were reported.

Christenson (*13*) reported NaCl activities in NaCl–$MgCl_2$ at $I = 1$ mol·kg^{-1} and Lanier (*11*) at $I = 1$, 3, and 6 mol·kg^{-1}. Both used sodium-sensitive glass electrodes and Ag/AgCl electrodes. Butler and Huston (*12*) did a more detailed study, $I = 0.52$–5.99 mol·kg^{-1}, using Na(Hg)/Na^+ and Ag/AgCl electrodes, but it was necessary to add ≤ 0.004 mol·kg^{-1} NaOH to their solutions in order to use the amalgam electrode.

The data of Christenson (*13*) and Lanier (*11*) at $I = 1$ mol·kg^{-1} are in excellent agreement, with maximum differences of about 0.002 in the activity coefficients of NaCl. Butler and Huston (*12*) are in general agreement with the other two studies (*11*, *13*), but have about 5 times as much scatter. Unfortunately, at $I = 6$ mol·kg^{-1} the only two studies (*11*, *12*) give inconsistent results. Lanier's values are in general agreement with the isopiestic data. We, therefore, reject Butler and Huston's data as inaccurate, most probably due to problems with the amalgam electrodes which are notoriously difficult to work with.

As noted above, we need very accurate data for the calculation of activity derivatives. However, some of the available data for aqueous NaCl–$MgCl_2$ solutions are of doubtful quality, and the remaining data do not completely cover the accessible concentration regions. Consequently, we decided to reinvestigate this system by the isopiestic method. Our data extend from moderately low concentrations ($I = 0.295$ mol·kg^{-1}) to the