are consistent with the excess volumes obtained for Mg-Bi, Mg-Pb, and Mg-Sn alloys (*5-7*). Notice also that the minimum in the excess volume curve corresponds rather well with the stoichiometry of the Mg_3Sb_2 compound.

Though the In-Sb system also shows evidence of the formation of a weak 1:1 compound in the liquid phase (*8*), our excess volumes are positive. This could have two explanations: either the physical interactions are more important than the chemical interactions or the volume of the compound is larger than the sum of the volumes of its components. The former explanation seems to be more likely for this system since the maximum in the curve occurs far from the equimolar concentration. Also, our excess volume model (*1*) predicts an equimolar excess volume of about 0.22 cm^3/mol compared to the experimental result, 0.24 cm^3/mol. This model was developed for non-compound-forming alloys and seems to work reasonably well for systems that exhibit positive excess volumes.

The solid-liquid phase diagram for the Pb-Sb system is that of a simple eutectic (*9*). The physical interactions of these types of alloys generally lead to positive excess volumes as observed here. Our model (*1*) predicts an equimolar excess volume of 0.08 cm^3/mol, which agrees nearly exactly with experiment.

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Limiting Activity Coefficients from an Improved Differential Boiling Point Technique

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Infinite dilution activity coefficients were measured for 54 systems with an improved differential boiling point apparatus. Following the suggestions of Scott, a radical new boiler design is used that exhibits better temperature stability, allowing more precise and accurate data to be measured. The results are compared to available literature data. The temperature dependence of γ^∞ was also studied and found to be reasonable. Estimates of the partial molar excess enthalpy at infinite dilution are reported.

Introduction

The direct experimental determination of limiting activity coefficients was first proposed by Gatreaux and Coates (*2*). Through the years, advancements in boiler design and temperature measurement have increased the precision, accuracy, and range of applicability of the differential boiling point technique. The experimental apparatus first employed was that of the ebulliometer (*3-5*). The ebulliometers were of the Swietoslawski type, with use of the principle of the Cottrell pump. Recently, Scott (*1*) has introduced a radical change in the design of the apparatus, incorporating a round-bottom flask with high-speed stirring. These changes significantly reduced the temperature fluctuations. Also, with the use of a larger charge of solvent, composition errors are reduced and data can be obtained for systems of higher relative volatility. Further modifications to minimize leak problems and reduce maintenance have since been made and will be presented here. Data from use of the original Scott design as well as the modified apparatus will be presented and discussed.

To determine γ^∞ from dilute $T-x$ data, the following expression is used:

$$\gamma_1^\infty = \{\phi_1^{(P_2^s)}[P_2^s - (1 - P_2^s v_2/RT + (P_2^s/\phi_2^s)(\partial\phi_2/\partial P)_T) \times (\mathrm{d}P_2^s/\mathrm{d}T)(\partial T/\mathrm{d}x_1)_p^\infty]\}/\{P_1^s\phi_1^s \exp(v_1(P_2^s - P_1^s)/RT)\} \quad (1)$$

The rigorous derivation is given by Newman (*6*). Fugacity coefficients were determined from the volume explicit virial equation truncated after the second term. The second virial coefficients are obtained from experimental measurement (*7*) or estimated by the method of Hayden and O'Connell (*8*). Saturation pressures and liquid molar volumes are calculated from standard correlations as outlined by Trampe (*9*). The quantity that is determined experimentally is $(\partial T/\partial x_1)_p^\infty$, the limiting slope of the isobaric $T-x$ data.

Apparatus

The boiler design initially used was that of Scott (*1*) as shown in Figure 1. The boilers are 500-mL round-bottom flasks fitted with high-speed stirrers driven with Bodine 1800 rpm synchronous motors. A quartz thermometer probe (Hewlett-Packard, Model 2804A) is immersed in mineral oil in the thermowell attached to the top of the flask. The thermowell is completely vacuum-jacketed and silvered to reduce heat losses and is connected to a reflux condenser containing ethylene glycol at -20 °C. Condensate is returned to the boiling flask with a capillary tube. Heat is supplied to the boiling flask with a Glas-Col heating mantle. This design was found to give much improved temperature stability over the previous ebulliometer apparatus. Depending on experimental conditions, the temperature stability approached the precision of the quartz thermometer, 0.0001 °C. However, leak problems often occurred with the high-speed stirrers, and under heavy use, maintenance of the stirrer become troublesome. To rectify these problems, the Scott apparatus was modified by incorporating magnetic

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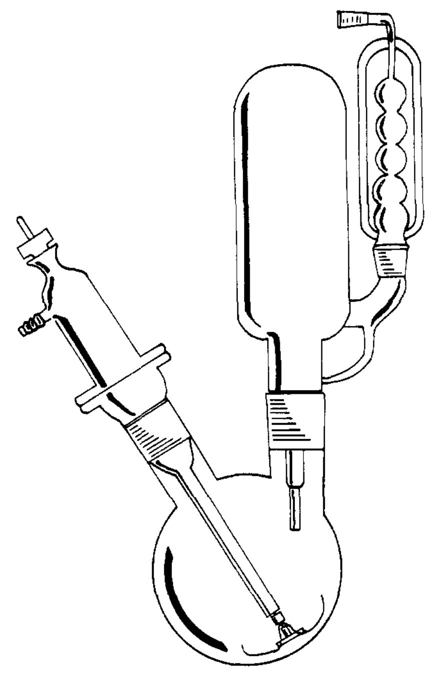

Figure 1. Scott design of boiler.

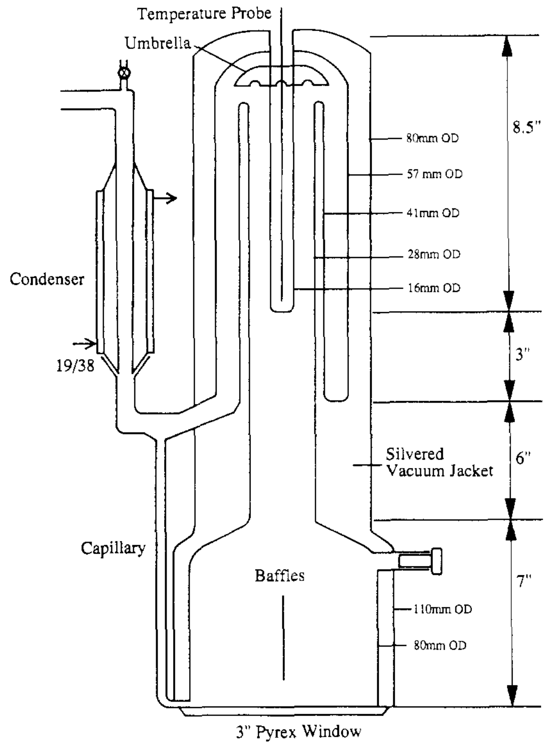

Figure 2. Modified boiler design.

stirring (Fisher Scientific stirring hotplate, 1500 rpm with 1.5-in. × 0.325-in. Teflon-coated stirring bar). The joint between the boiling flask and thermowell was also eliminated. A solvent charge opening was placed near the top of the boiling flask. Details of the design are given in Figure 2. Test runs showed that this design gave temperature stability equal to that of the Scott design. Results for the measurement of γ^∞ were also reproduced. Further modifications in the apparatus have also been made by Scott (*10*). These include the elimination of the "umbrella" at the top of the thermowell, allowing the temperature probe insert to be removable, thus eliminating the need for the solvent charge opening.

For measurement of limiting activity coefficients, the system used is that shown in Figure 3. Multiple boilers in series allow the simultaneous determination of γ^∞ for several different solutes in one solvent. Also, rather than the absolute boiling temperature being measured, a temperature difference is measured between a boiler containing pure solvent and one containing the mixture. Pressure fluctuations cause the temperature in each boiler to change, but by measuring a temperature difference, the effect of the pressure fluctuations is greatly reduced, but not eliminated, due largely to pressure drops in the lines.

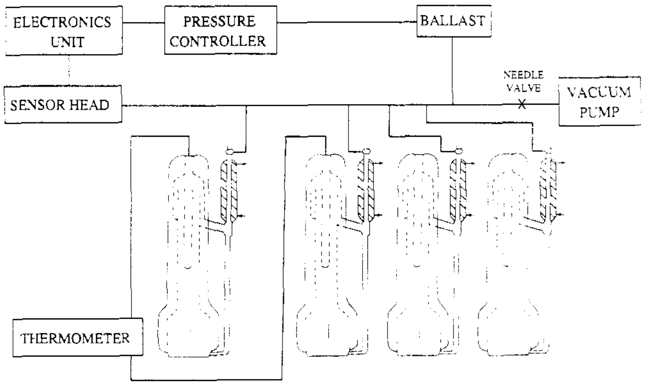

Figure 3. System used to measure limiting activity coefficients.

Constant pressure is maintained by an MKS Baratron system, consisting of type 170M-6B and 170M-44A electronics units and a type 310 BHS-1000 sensor head. A Granville-Phillips Series 216 automatic pressure controller allows dry air to bleed into the system. Interconnecting lines lead through a needle valve to a vacuum pump, and for better pressure control, a 25-L ballast tank is included. The system pressure is displayed on a digital pressure gauge with a resolution of 0.01 Torr. The system pressure is controlled to 0.04–0.15 Torr, depending on the magnitude of the total pressure and boiling characteristics of the solvent. Better pressure control would enhance the temperature stability even more. The temperature was measured with a Hewlett-Packard quartz thermometer (Model 2804A) and matching probes with a precision in the temperature difference measurement of 0.0001 °C.

Materials

The solvents used in this experiment should have a purity of 99.9+%. The solute purity is less critical, but it should be at least 99%. Purifications were performed as deemed necessary. Refractive index values are at 20 °C, measured with an Abbe Model refractometer. Stated accuracy is $\pm 0.0001 n_D$.

The following chemicals were used: acetone, Mallinckrodt Nanograde or Baker Analyzed Reagent, used as purchased; 1-butanol, Mallinckrodt Nanograde, n_D = 1.3995, or Baker Analyzed Reagent, fractionally distilled with middle 60% collected; butanone, Baker Analyzed Reagent, 99.6%, used as purchased; carbon disulfide, Mallinckrodt Reagent Grade, fractionally distilled with middle 60% collected; carbon tetrachloride, Baker Analyzed Reagent, 99.9+%, n_D = 1.4595, used as purchased; chloroform, Baker Analyzed Reagent, ethanol as stabilizer, or Mallinckrodt Spectrophotometric Grade, used as purchased; cyclohexane, Mallinckrodt Nanograde, n_D = 1.4268, or Burdick Jackson High-Purity Solvent, used as purchased. 1,4-dioxane, Baker Analyzed Reagent, 99.9+%, used as purchased; ethanol, Midwest Grain Products, n_D = 1.3625, dried over 3A molecular sieves; ethyl acetate, Baker Analyzed Reagent, 99.9+%, used as purchased; heptane, Aldrich, HPLC Grade, 99+%, n_D = 1.3879, used as purchased; hexane, Mallinckrodt ChromAR Grade, n_D = 1.3753, used as purchased; methanol, Mallinckrodt Nanograde, n_D = 1.3284, dried over 3A molecular sieves; methyl iodide, Aldrich Gold Label, fractionally distilled with middle 60% collected, stored over copper; methyl

Table I. Experimental Limiting Activity Coefficients

solute	solvent	T/K	γ_1^∞
butanone	acetone	298.3	1.06 ± 0.05
		308.2	1.10 ± 0.05
		318.3	1.05 ± 0.05
		328.5	1.10 ± 0.05
carbon disulfide	acetone	300.9	4.22 ± 0.1
		306.9	4.09 ± 0.1
		313.8	3.88 ± 0.1
		319.5	3.78 ± 0.1
		324.4	3.65 ± 0.1
		328.7	3.50 ± 0.1
carbon tetrachloride	acetone	300.9	2.09 ± 0.05
		306.9	2.07 ± 0.05
		313.8	2.07 ± 0.05
		319.5	2.07 ± 0.05
		324.4	2.03 ± 0.05
		328.4	2.04 ± 0.05
chloroform	acetone	307.1	0.503 ± 0.02
		313.9	0.510 ± 0.02
		319.5	0.509 ± 0.02
		324.3	0.524 ± 0.02
		328.5	0.530 ± 0.02
1,4-dioxane	acetone	298.3	1.35 ± 0.05
		308.2	1.39 ± 0.05
		318.3	1.36 ± 0.05
		328.5	1.37 ± 0.05
ethanol	acetone	298.3	2.44 ± 0.02
		308.2	2.24 ± 0.02
		318.3	2.07 ± 0.02
		328.5	1.92 ± 0.02
n-hexane	acetone	300.9	6.41 ± 0.1
		306.9	6.24 ± 0.1
		316.7	5.54 ± 0.1
		324.4	5.24 ± 0.1
		328.4	4.95 ± 0.1
nitromethane	acetone	298.3	1.10 ± 0.03
octane	acetone	298.3	11.04 ± 0.1
		308.2	9.75 ± 0.1
		318.3	7.83 ± 0.1
		328.5	7.06 ± 0.1
toluene	acetone	298.3	2.09 ± 0.05
		308.2	2.03 ± 0.05
		318.3	1.89 ± 0.05
		328.5	1.78 ± 0.05
carbon tetrachloride	1-butanol	359.6	2.58 ± 0.05
cyclohexane	1-butanol	349.5	3.85 ± 0.1
		359.9	3.70 ± 0.1
		370.0	3.61 ± 0.1
		381.0	3.48 ± 0.1
		389.9	3.08 ± 0.1
toluene	1-butanol	349.5	2.80 ± 0.1
		359.9	2.61 ± 0.1
		381.0	2.40 ± 0.1
		389.9	2.27 ± 0.1
acetone	carbon disulfide	298.3	8.34 ± 0.1
		308.4	7.52 ± 0.1
		318.6	7.19 ± 0.1
butanone	carbon disulfide	298.3	4.92 ± 0.1
		308.4	4.80 ± 0.1
		318.6	4.44 ± 0.1
1,4-dioxane	carbon disulfide	298.3	3.77 ± 0.1
		308.4	3.56 ± 0.1
		318.6	3.34 ± 0.1
ethanol	carbon disulfide	303.3	78.3 ± 2
		308.4	67.5 ± 2
		318.6	55.4 ± 2
nitromethane	carbon disulfide	298.3	41.3 ± 0.4
		308.4	34.5 ± 0.4
		318.6	30.6 ± 0.4
toluene	carbon disulfide	298.3	1.96 ± 0.03
		308.4	1.86 ± 0.03
		318.6	1.73 ± 0.03
acetone	carbon tetrachloride	328.8	2.82 ± 0.1
		338.6	2.68 ± 0.1
		344.3	2.58 ± 0.1
1-propanol	carbon tetrachloride	314.9	15.93 ± 0.3
		329.0	11.90 ± 0.2
1-propanol	carbon tetrachloride	338.8	9.82 ± 0.1
		344.2	8.78 ± 0.1
1-butanol	cyclohexane	312.8	28.13 ± 0.5
		322.9	21.46 ± 0.3
		333.0	16.47 ± 0.2
		343.0	13.31 ± 0.2
		352.9	11.05 ± 0.2
ethanol	cyclohexane	312.8	29.9 ± 2
		322.9	24.3 ± 1
		333.0	19.1 ± 1
		343.0	15.1 ± 0.5
		352.9	11.7 ± 0.5
n-hexane	cyclohexane	323.6	1.09 ± 0.01
		332.9	1.08 ± 0.01
		353.2	1.05 ± 0.01
1-pentanol	cyclohexane	312.8	22.11 ± 0.3
		322.9	16.73 ± 0.3
		333.0	12.77 ± 0.2
		343.0	10.48 ± 0.2
		352.9	8.12 ± 0.2
2-propanol	cyclohexane	312.8	23.40 ± 0.5
		322.9	18.34 ± 0.3
		333.0	15.72 ± 0.2
		343.0	12.74 ± 0.2
		352.9	10.45 ± 0.2
butanone	ethyl acetate	328.4	1.10 ± 0.01
chloroform	ethyl acetate	310.5	0.424 ± 0.01
		327.1	0.470 ± 0.01
		340.0	0.499 ± 0.01
		349.5	0.512 ± 0.01
1,4-dioxane	ethyl acetate	328.4	1.10 ± 0.03
ethanol	ethyl acetate	328.4	2.55 ± 0.03
		338.4	2.44 ± 0.03
		349.1	2.34 ± 0.03
nitromethane	ethyl acetate	328.4	1.29 ± 0.03
octane	ethyl acetate	328.4	3.59 ± 0.05
		338.4	3.34 ± 0.05
		349.1	3.06 ± 0.05
toluene	ethyl acetate	328.4	1.23 ± 0.02
		338.4	1.20 ± 0.02
		349.1	1.16 ± 0.02
acetone	*n*-hexane	301.9	6.12 ± 0.1
chloroform	*n*-hexane	301.9	1.577 ± 0.05
		317.6	1.538 ± 0.05
		334.7	1.462 ± 0.05
		340.6	1.418 ± 0.05
cyclohexane	*n*-hexane	341.0	1.054 ± 0.01
methanol	*n*-hexane	341.2	34.4 ± 2
2-propanol	*n*-hexane	318.3	18.80 ± 0.3
		328.3	14.88 ± 0.3
		341.3	11.35 ± 0.2
butanone	methanol	308.6	2.27 ± 0.05
		318.5	2.21 ± 0.05
		328.5	2.11 ± 0.05
		337.0	2.07 ± 0.05
cyclohexane	methanol	307.3	20.48 ± 0.2
		317.1	19.48 ± 0.2
		327.4	17.56 ± 0.2
		337.2	16.16 ± 0.2
1,4-dioxane	methanol	308.6	3.23 ± 0.05
		318.5	3.12 ± 0.05
		328.5	2.98 ± 0.05
		337.0	2.88 ± 0.05
ethanol	methanol	337.0	1.02 ± 0.02
nitromethane	methanol	308.6	5.05 ± 0.1
		318.5	4.70 ± 0.1
		328.5	4.24 ± 0.1
		337.0	3.83 ± 0.1
octane	methanol	308.6	43.2 ± 0.3
		318.5	39.7 ± 0.3
		328.5	35.9 ± 0.3
		337.0	32.3 ± 0.3
toluene	methanol	308.6	9.70 ± 0.1
		318.5	9.42 ± 0.1
		328.5	9.15 ± 0.1
		337.0	8.90 ± 0.1
n-hexane	methyl iodide	303.5	3.25 ± 0.1

Table I (Continued)

solute	solvent	T/K	γ_1^∞
n-hexane	methyl iodide	315.0	2.81 ± 0.1
octane	methyl iodide	303.5	12.1 ± 1
		315.0	10.3 ± 1
carbon tetrachloride	1-propanol	332.8	3.20 ± 0.1
		343.1	3.14 ± 0.1
		352.9	3.10 ± 0.1
		362.9	3.10 ± 0.1
		369.6	3.02 ± 0.1
carbon tetrachloride	2-propanol	354.7	3.41 ± 0.1
cyclohexane	2-propanol	313.1	5.15 ± 0.1
		320.9	5.07 ± 0.1
		331.6	4.74 ± 0.1
		343.2	4.73 ± 0.1
		354.8	4.55 ± 0.1
heptane	2-propanol	323.8	6.45 ± 0.1
heptane	2-propanol	332.7	6.28 ± 0.1
		343.7	5.90 ± 0.1
		354.6	5.70 ± 0.1
n-hexane	2-propanol	323.8	5.68 ± 0.1
		332.7	5.48 ± 0.1
		343.7	5.23 ± 0.1
		354.6	5.11 ± 0.1
methylcyclohexane	2-propanol	323.8	6.02 ± 0.1
		332.7	5.80 ± 0.1
		343.7	5.46 ± 0.1
		354.6	5.16 ± 0.1
toluene	2-propanol	313.2	4.97 ± 0.1
		321.0	4.66 ± 0.1
		331.6	4.34 ± 0.1
		343.1	4.08 ± 0.1
		354.7	3.63 ± 0.1

cyclohexane, Aldrich, anhydrous, 99+%, used as purchased; nitromethane, Aldrich, fractionally distilled with middle 60% collected; octane, Aldrich, anhydrous, 99+%, n_D = 1.3977, used as purchased; 1-pentanol, Aldrich, 99+%, used as purchased; 1-propanol, Baker Analyzed Reagent, 99.9+%, n_D = 1.3854, used as purchased; 2-propanol, Baker Analyzed Reagent, fractionally distilled with middle 60% collected; toluene, Baker Analyzed Reagent, 99.9+%, used as purchased.

Experimental Procedure

All boilers are first filled gravimetrically with about 40 mL of solvent. After the pressure is set, all boilers are heated to a steady-state refluxing condition. One temperature probe is placed in the reference boiler where it remains for the entire run. The other probe is placed in the first loading boiler. The temperature difference is taken until equilibrium is assured. This initial temperature offset is less than 0.01 °C and is due largely to uncertainties in the calibration of the thermometer probes. This initial difference is subtracted from all subsequent ΔT readings. The probe in the first loading boiler is placed in the second one and a 0.5–3.0-mL injection of either pure solute or a mixture of solute and solvent is made through a serum stopper into the first loading boiler. The temperature probe in the second loading boiler is allowed to equilibriate for about 10–15 min, and then the temperature difference between this boiler and the reference boiler is recorded. This probe in the second loading boiler is then moved to the third loading boiler, an injection is made to the second boiler, and the entire process is repeated until five injections have been made in each boiler. To measure γ^∞ for four solutes requires 8–10 h.

The apparatus has been operated successfully at pressures from 90 Torr to atmospheric pressure. Minor modifications of the pressure control system should allow the range to be extended down to possibly as low as 35 Torr, as reported by Scott (*1*). However, due to the shape of vapor pressure versus temperature curves, pressure fluctuations of the same order of magnitude cause much greater temperature fluctuations at low pressures. Operation above 1 atm would require the design of a completely new boiler, constructed out of metal. The applicable temperature range seems to be 3–4 °C above room temperature to 200 °C. At temperatures at or below room temperature, the vapors superheat and cause unstable and unreliable temperature readings. Solvents with freezing points below 0 °C are preferred, although Scott (*1*) has made measurements on solvents with freezing points up to 100 °C.

The method is best suited for binary systems whose relative volatilities are between 0.05 and 20. If the solvent is much more volatile than the solute, the value of γ^∞ is quite sensitive to the value of the limiting slope. If the solute is much more volatile than the solvent, then corrections for the amounts of solute in the vapor phase and liquid hold-up in the thermowell and condenser become quite important.

Data Reduction

The infinite dilution activity coefficient is determined with use of eq 1. The parameter determined from the experiment is $(\partial T/\partial x_1)_p^\infty$. The experimental T–x data are fit to various empirical equations:

$$\Delta T = Ax_1 + Bx_1^2 \quad \text{(quadratic)} \tag{2}$$

$$\Delta T = Ax_1 + Bx_1^2 + Cx_1^3 \quad \text{(cubic)} \tag{3}$$

$$1/\Delta T = A/x_1 + B/x_1x_2 \quad \text{(van Laar)} \tag{4}$$

For the first two expressions, $(\partial T/\partial x_1)_p^\infty = A$, and for the third expression, $(\partial T/\mathrm{d}x_1)_p^\infty = 1/B$. The fits are generally close to linear and usually differed by less than 3%. The value of $(\partial T/\partial x_1)_p^\infty$ chosen for use in eq 1 is that which comes from the expression having the smallest standard deviation, σ, in the data fitting:

$$\sigma = \left[\frac{\sum(\Delta T_{\text{calc}} - \Delta T_{\text{exp}})^2}{(\text{NDAT} - \text{NPAR})}\right]^{1/2} \tag{5}$$

where NDAT is the number of data points and NPAR is the number of adjustable parameters in the equation. With this criteria, the cubic equation usually fit the data best.

The value of γ^∞ initially calculated from eq 1 is not correct since no allowance has been made for the amount of solute and solvent in the vapor and in the liquid hold-up in the thermowell and condenser. Estimates of the vapor space and liquid hold-up volumes have been determined experimentally. The total vapor space was determined by simply finding the volume of water required to fill the thermowell and boiling flask and estimating the vapor space in the condenser up to the point where all of the vapor has been condensed. The actual vapor space during a run is found from subtracting the volume of the solvent in the boiling flask from the total vapor space estimate. Since the final value of γ^∞ is not very dependent on the vapor space, an estimate within 20 mL is more than sufficient. The liquid hold-up has a much larger effect. To measure it, the two-piece Scott design was used. First, the thermowell and stoppers were weighed. The weight of the air in the thermowell (determined from $pV = nRT$) was substracted to find the weight of the thermowell only. Next, approximately 400 mL of solvent were charged to the boiling flask, heated, and brought to a steady-state refluxing condition as during a normal run. The thermowell section was quickly removed from the boiling flask and condenser, restoppered, and reweighed. The weight of the solvent vapor in the thermowell (calculated from $pV = nRT$) was subtracted to give the weight of the thermowell plus liquid condensate only. The weight difference, then, gives the grams

Table II. Comparison to Literature Data

		this study		literature			
solute	solvent	T/K	γ^∞	T/K	γ^∞	technique[a]	ref
butanone	acetone	298.3	1.06	298.2	1.061	HC	12
CCl_4	acetone	319.5	2.07	318.2	2.15	EB	5
		328.4	2.04	327.6	2.13	EB	5
chloroform	acetone	307.1	0.50	308.3	0.53	EB	5
		328.5	0.53	327.4	0.58	EB	5
1,4-dioxane	acetone	298.3	1.35	298.2	1.289	HC	12
ethanol	acetone	308.2	2.24	306.8	2.24	EB	5
		328.5	1.92	327.4	1.92	EB	5
n-hexane	acetone	300.9	6.41	298.2	6.50	GLC	13
		300.9	6.41	298.2	6.07	HC	14
		306.9	6.24	308.2	6.44	EB	15
		316.8	5.54	318.2	5.85	EB	15
		328.4	4.95	328.2	5.35	EB	15
nitromethane	acetone	298.3	1.10	298.2	0.912	HC	12
octane	acetone	298.3	11.04	298.2	10.29	HC	12
toluene	acetone	298.3	2.09	298.2	1.889	HC	12
butanone	CS_2	298.3	4.92	298.2	5.14	HC	12
1,4-dioxane	CS_2	298.3	3.77	298.2	3.64	HC	12
nitromethane	CS_2	298.3	41.3	298.2	38.09	HC	12
toluene	CS_2	298.3	1.96	298.2	1.47	HC	12
acetone	CCl_4	344.3	2.58	346.8	2.59	EB	5
ethanol	cyclohexane	322.9	24.3	323.5	34.9	DIL	16
		343.0	15.1	342.8	21.3	DIL	16
chloroform	ethyl acetate	327.1	0.470	329.2	0.52	EB	5
		349.5	0.512	349.2	0.49	EB	5
ethanol	ethyl acetate	349.1	2.34	348.3	2.33	EB	5
nitromethane	ethyl acetate	328.4	1.29	330.5	1.47	EB	5
toluene	ethyl acetate	349.1	1.16	348.3	1.14	EB	5
chloroform	n-hexane	301.9	1.577	301.0	1.58	EB	5
		317.6	1.538	315.3	1.53	EB	5
		340.6	1.418	340.1	1.39	EB	5
cyclohexane	n-hexane	341.0	1.054	340.3	1.06	EB	5
butanone	methanol	298.2	2.36[b]	298.2	2.49	HC	12
cyclohexane	methanol	307.3	20.48	308.2	18.90	EB	5
		317.2	19.48	318.2	17.40	EB	5
1,4-dioxane	methanol	298.2	3.39[b]	298.2	3.39	HC	12
nitromethane	methanol	298.2	5.66[b]	298.2	5.59	HC	12
octane	methanol	298.2	48.7[b]	298.2	45.86	HC	12
toluene	methanol	298.2	10.0[b]	298.2	10.04	HC	12

[a] Techniques: DIL = dilutor; EB = differential ebulliometry; GLC = gas–liquid chromatography; HC = headspace chromatography. [b] Extrapolated using γ^∞ data at 308.6–337.0 K.

of liquid condensate that is converted to milliliters for use in the iteration scheme described below. Replicate trials using different solvents gave results within the estimated uncertainty (1.35 ± 0.1 mL). A 10% error in this value can introduce up to a 0.5% error in γ^∞, depending on the relative volatility of the system.

Now, with the initially calculated value of γ^∞ from eq 1, the vapor-phase composition in equilibrium with the liquid is calculated. The one-parameter Margules equation is used to find the finite concentration activity coefficient. The composition of the liquid hold-up is assumed to be the same as that of the vapor. With the proper stoichiometric relations, a new value of the liquid composition is calculated. The vapor-phase composition is then calculated anew and the process iterated until the liquid composition remains constant. This is done for all T–x points. Then, with the newly determined value of $(\partial T/\partial x_1)_p^\infty$, a new value of γ^∞ is calculated. This outer-loop iteration continues until there is no change in γ^∞ or in the liquid compositions. This vapor and liquid hold-up correction is very significant, particularly for systems of high relative volatility. For 2-propanol in cyclohexane at 312.8 K, the initially calculated value of γ^∞ is 22.24, but after accounting for the vapor and liquid hold-up, the final result is γ^∞ = 23.40. A sample plot of ΔT versus composition after completing the iterations is given in Figure 4.

Results

With use of the original Scott boiler design and the subsequent modified version, limiting activity coefficient data were measured, typically over 20–40 °C temperature intervals. The γ^∞ data are presented in Table I. The error estimates are based on replicate data, when taken, on standard deviations in the limiting slopes, and on the sensitivity of the γ^∞ values to the value of the slope and to the hold-up corrections.

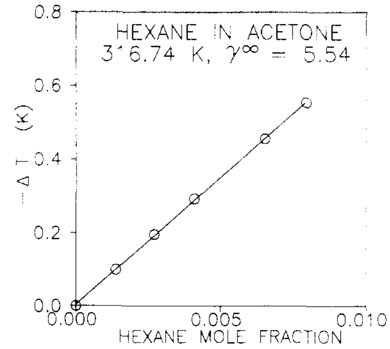

Figure 4. Sample ΔT versus x data.

Table II is a comparison of the γ^∞ values obtained in this study with those presented in the literature. Only actual measurements of γ^∞ are considered as there is a great deal of uncertainty (10–20% or more) with extrapolation of VLE data (*3*). A number of systems were studied for the purpose of comparison to previous ebulliometric results, such as those of Thomas et al. (*5*). The technique is the same, with the only difference being the radical change in the design of the boiler. As seen in Table II, agreement is quite good, usually within the

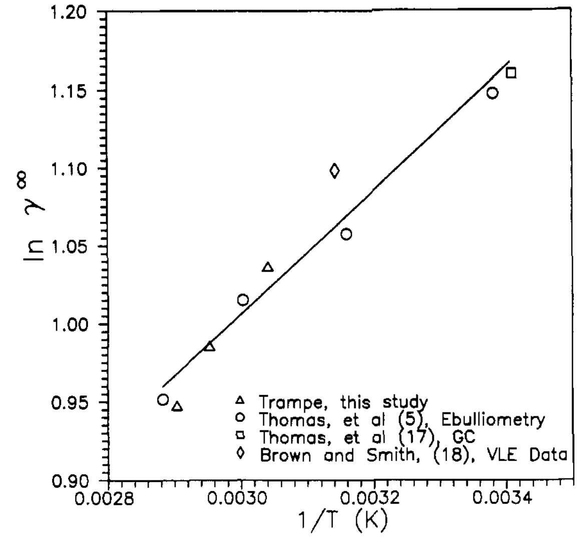

Figure 5. Comparison of experimental data to the literature for the solute acetone in the solvent carbon tetrachloride.

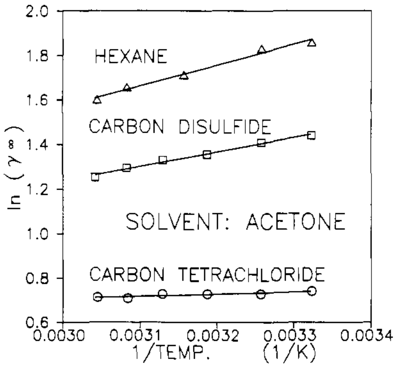

Figure 6. Temperature dependence of limiting activity coefficient data for several solutes in the solvent acetone.

stated error estimate. Comparison of the temperature dependence also showed that points on a plot of ln γ^∞ versus $1/T$ would typically fall within ±2% of the best fit line (Figure 5). Systems were also studied for comparison to a static technique incorporating gas chromatographic headspace analysis, as recently improved by Hussam and Carr (*11*). Except for one case, the results from the two techniques are within 10%. However, there seems to be a systematic bias where the values from the differential boiling point technique are consistently greater than the values from the headspace chromatographic technique, particularly for the solvents acetone and carbon disulfide.

Figure 6 is a plot of the temperature dependence of γ^∞ for several solutes in acetone. A value for the partial molar excess enthalpy at infinite dilution can be calculated from the slope of this curve as follows:

$$\frac{\partial \ln \gamma_1^\infty}{\partial 1/T} = \frac{\bar{h}_1^{E\infty}}{R} \qquad (6)$$

Except for highly solvated and associated solutions, $\bar{h}_1^{E\infty}$ should be constant over moderate temperature ranges. Thus, the plot of ln γ_1^∞ versus $1/T$ should be approximately linear.

Table III lists the values of $\bar{h}_1^{E\infty}$ as calculated from a linear fit and eq 6. However, due to the inherent loss of precision (1 order of magnitude or more) incurred in the differentiation procedure, the uncertainty in these values is estimated as follows: for $\bar{h}_1^{E\infty}$ = 10 000 J/mol or greater, the uncertainty is 10–20%; for $\bar{h}_1^{E\infty}$ = 2000–10 000 J/mol, the uncertainty is 20–40%; for $\bar{h}_1^{E\infty}$ = 2000 J/mol or less, the uncertainty is 40+%. For better determinations of $\bar{h}^{E\infty}$, an alternate technique has been developed incorporating asymmetric isothermal flow calorimetry (*19*).

Table III. Estimate of the Partial Molar Excess Enthalpy at Infinite Dilution

solute	solvent	$\bar{h}_1^{E\infty}$/(J/mol)	temp range/K
butanone	acetone	0	298–329
carbon disulfide	acetone	5 400	301–329
carbon tetrachloride	acetone	740	301–328
chloroform	acetone	−2 000	307–329
1,4-dioxane	acetone	0	298–329
ethanol	acetone	6 400	298–329
n-hexane	acetone	7 800	301–328
nitromethane	acetone		298
octane	acetone	12 600	298–329
toluene	acetone	4 400	298-329
carbon tetrachloride	1-butanol		360
cyclohexane	1-butanol	5 500	350–390
toluene	1-butanol	7 600	350–390
acetone	carbon disulfide	5 800	298–319
butanone	carbon disulfide	4 000	298–319
1,4-dioxane	carbon disulfide	4 700	298–319
ethanol	carbon disulfide	17 900	303–319
nitromethane	carbon disulfide	11 700	298–319
toluene	carbon disulfide	4 800	298–319
acetone	CCl_4	5 400	329–344
1-propanol	CCl_4	18 200	315–344
1-butanol	cyclohexane	21 500	313–353
ethanol	cyclohexane	21 500	313–353
n-hexane	cyclohexane	1 200	324–353
1-pentanol	cyclohexane	22 600	313–353
2-propanol	cyclohexane	18 100	313–353
butanone	ethyl acetate		328
chloroform	ethyl acetate	−4 400	311–350
1,4-dioxane	ethyl acetate		328
ethanol	ethyl acetate	4 000	328–349
nitromethane	ethyl acetate		328
octane	ethyl acetate	7 400	328–349
toluene	ethyl acetate	2 700	328–349
acetone	*n*-hexane		302
chloroform	*n*-hexane	2 300	302–341
cyclohexane	*n*-hexane		341
methanol	*n*-hexane		341
2-propanol	*n*-hexane	19 800	318–341
butanone	methanol	2 900	309–337
cyclohexane	methanol	7 000	307–337
1,4-dioxane	methanol	3 500	309–337
ethanol	methanol		337
nitromethane	methanol	8 400	309–337
octane	methanol	8 800	309–337
toluene	methanol	2 600	309–337
n-hexane	methyl iodide		304–315
octane	methyl iodide		304–315
carbon tetrachloride	1-propanol	1 400	333–370
carbon tetrachloride	2-propanol		355
cyclohexane	2-propanol	2 800	313–355
heptane	2-propanol	4 400	324–355
n-hexane	2-propanol	3 400	324–355
methylcyclohexane	2-propanol	4 800	324–355
toluene	2-propanol	6 700	313–355

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Glossary

γ_i^∞	limiting activity coefficient
$\bar{h}_i^{E\infty}$	partial molar excess enthalpy at infinite dilution
ϕ_i	vapor-phase fugacity coefficient
ϕ_i^s	fugacity coefficient at saturation pressure
P	total pressure
P_i^s	saturation pressure
R	gas constant
ΔT	temperature differential

v_i liquid molar volume
x_i liquid-phase mole fraction

Subscripts

1 solute
2 solvent

Registry No. CCl_4, 56-23-5; CS_2, 75-15-0; butanone, 78-93-3; chloroform, 67-66-3; 1,4-dioxane, 123-91-1; ethanol, 64-17-5; hexane, 110-54-3; nitromethane, 75-52-5; octane, 111-65-9; toluene, 108-88-3; cyclohexane, 110-82-7; acetone, 67-64-1; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 2-propanol, 67-63-0; methanol, 67-56-1; heptane, 142-82-5; methylcyclohexane, 108-87-2; ethyl acetate, 141-78-6; methyl iodide, 74-88-4.

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Bubble Pressures and Saturated Liquid Molar Volumes of Binary and Ternary Refrigerant Mixtures

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All measurements have been performed with a static apparatus using a variable volume cell described previously. The results are given at two temperatures for the dichlorotetrafluoroethane (1)–perfluoro-2-butyltetrahydrofuran (2) system [R114–FC75] and four temperatures for the three systems trifluoromethane (1)–trichlorofluoromethane (2) [R23–R11], trifluoromethane (1)–chlorodifluoromethane (2)–trichlorofluoromethane (3) [R23–R22–R11], and trifluoromethane (1)–chlorodifluoromethane (2)–dichlorotetrafluoroethane (3) [R23–R22–R114]. Experimental data of binaries are well represented by the one adjustable parameter Peng–Robinson equation of state involving a volume translation (simultaneous representation of vapor–liquid equilibria and saturated liquid molar volumes within 2%).

Introduction

This work is a continuing part of the development of a thermodynamic data base on refrigerant mixtures. Several systems have already been studied in the same laboratory (*1–4*).

The static method with a variable volume cell, which is very convenient for liquid-phase studies, was used here. Liquid composition is determined through accurate weighing on an analytical balance of 10^{-7}-kg sensitivity. The static cell used in this work is that described in Valtz et al. (*3*).

Experimental Section

Apparatus. Details about the equipment are given in Valtz et al. (*3*) and Fontalba et al. (*5*). The equipment was used as described in Valtz et al. (*3*).

Table I. Origin and Purity of Chemicals

component	origin	purity, % GLC
trichlorofluoromethane	Dehon	>99.9
chlorodifluoromethane	Prestogaz	>98
trifluoromethane	Dehon	>99
dichlorotetrafluoroethane	Dehon	>99.8
perfluoro-2-butyltetrahydrofuran	3M France	>95

Materials. The origin and purity of the chemicals are given in Table I. They were used without any further purification except for a careful degassing of the liquids.

Results

Two binary systems have been studied; results are reported in Tables II and III and displayed in Figures 1–4. The accuracies on data determination are either given inside the tables or in their legends. Figures 1 and 2 represent diphasic envelopes $P = f(x_1 \text{ or } y_1)$, respectively, for trifluoromethane (1)–trichlorofluoromethane (2) at four temperatures and dichlorotetrafluoroethane–perfluoro-2-butyltetrahydrofuran at two temperatures. Figures 3 and 4 represent saturated liquid molar volumes as a function of mole fractions for the same two binary systems. The results on the two ternary systems are given in Tables IV and V.

Data simulation was performed with use of Soave (*6*) and Peng–Robinson (P–R) (*7*) equations of state (see Appendix). Quite similar results are obtained for bubble curve modeling with each of these equations. However, saturated liquid molar volumes are best represented by the Peng–Robinson equation of state when a volume translation is used. Only our calculations with the Peng–Robinson equation of state are reported here.

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