Table II. Stability-Constant (log $\beta_{x'}$) Values of Metal Tartrates at $I = 0.1$ and 40 °C

pH	$10^3 U$, cm^2 V^{-1} min^{-1}	$10^3 \cdot$ [tart^{1-}], M	$10^3 \cdot$ [tart^{2-}], M	x'	log $\beta_{x'}$ this study	lit.
			Copper(II) Tartrate			
4.00	+1.00	2.80	1.93	1	3.40	
4.00	+0.50	2.80	1.93	1	3.41	
4.00	0	2.80	1.93	1	3.42	
					av = 3.41	
			Nickel(II) Tartrate			
4.26	+3.00	2.14	2.74	2	5.08	
4.75	0.00	0.98	4.03	2	5.57	
5.00	−2.80	0.63	4.36	2	6.32	
					av = 5.65	
			Cobalt(II) Tartrate			
5.00	+2.90	0.63	4.36	2	4.67	
5.15	0.00	0.44	4.53	2	4.99	
5.26	−2.30	0.35	4.64	2	4.88	
					av = 4.84	4.20[a]
			Thorium(IV) Tartrate			
4.20	−1.00	2.32	2.54	3	9.23	
4.40	−2.00	1.78	3.15	3	9.15	
4.60	−2.65	1.32	3.64	3	9.05	
					av = 9.14	

[a] At $I = 0.0$ and 25 °C.

Table III. Stability Constants of Copper(II) and Uranyl(II) Tartrates (Those of Binuclear and Hydroxo Complexes) at $I = 0.1$ and 40 °C

equilibrium considered	stability constant this study	lit.[a]
Copper(II) Tartrate		
$[Cu_2(tart)_2^0]/([Cu^{2+}]^2[tart^{2-}]^2)$	$10^{6.89}$	$10^{6.20}$
Uranyl(II) Tartrate		
$[UO_2(tart)^-][H^+]/[UO_2(tart)^0]$	$10^{-4.6}$	$10^{-5.60}$
$[(UO_2)_2(tart)_2^{2-}][H^+]^2/[UO_2(tart)^-]^2$	$10^{-9.4}$	
$[(UO_2)_2(tart)_2^{2-}][H^+]^2/([UO_2^{2+}]^2[tart^{2-}]^2)$	$10^{-8.8}$	$10^{-8.2}$

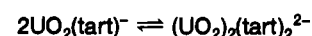[a] $I = 1.0$ and temp = 25 °C.

The first plateaus in all cases indicate individual mobilities of hydrated metal ions. In the case of copper the second plateau represents the protonated complex species and the third plateau represents a binuclear complex species. In the case of nickel and cobalt the second plateau represents a protonated or cationic complex species.

In the case of thorium the middle plateau is due to the formation of Th(tart)$_4^0$ neutral species as its mobility is near the zero mobility point. The uppermost plateau is due to the formation of an anionic complex species for all of the metal ions. In the case of uranyl the second plateau is due to the formation of UO$_2$(tart)$_1^0$ neutral species. This is due to the fact that this species finally forms a binuclear complex (1) which the final plateau represents.

It has been assumed that the neutral UO$_2$(tart)^0 first loses a proton from one of the hydroxyl groups of the ligand which subsequently forms a binuclear species, i.e.

$$UO_2{}^{2+} + tart^{2-} \rightleftharpoons UO_2(tart)^0$$

$$UO_2(tart)^0 \rightleftharpoons UO_2(tart)^- + H^+$$

$$2UO_2(tart)^- \rightleftharpoons (UO_2)_2(tart)_2{}^{2-}$$

All of these stability-constant values (log $\beta_{x'}$) have been given in Table II. Table III deals with the stability-constant values of binuclear and hydroxo complexes.

In the literature no mention is made of most of the complexes. For those having literature values, comparisons are too difficult because the literature values of I and temperature are quite different from the calculated values, although differences are very small wherever they are available. The precision of the method is comparable to that of paper chromatography. With future refinements in instrumentation, this new technique will be worth developing for it will enrich knowledge of the nature of charges and mobilities of complexes.

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Limiting Activity Coefficients from Differential Ebulliometry

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Infinite-dilution activity coefficients were measured for 147 systems using an improved differential ebulliometric technique. The results compare well with the limited literature data available. The observed temperature dependence of the data was also found to be reasonable.

Introduction

While the many advantages of limiting activity coefficients (γ^∞) in characterizing miscible solution behavior are well documented ($1-3$), their use has been primarily limited by the paucity of accurate data available. To help overcome this limitation, an improved differential ebulliometric technique was used to measure γ^∞'s for many industrially important systems.

The technique traces back to Swietoslawski in 1925, who, using the principle of the Cottrell pump, designed ebulliometers capable of measuring boiling points with extreme accuracy. Since 1925 the ebulliometer has been used very successfully (4) in the determination of boiling points, molecular weights, mutual solubilities, and sample purities and, most recently, in obtaining infinite-dilution activity coefficients (γ^∞'s). Eckert et al. (1) solved the major problems confronting previous researchers, namely, those of pressure fluctuations and loss of
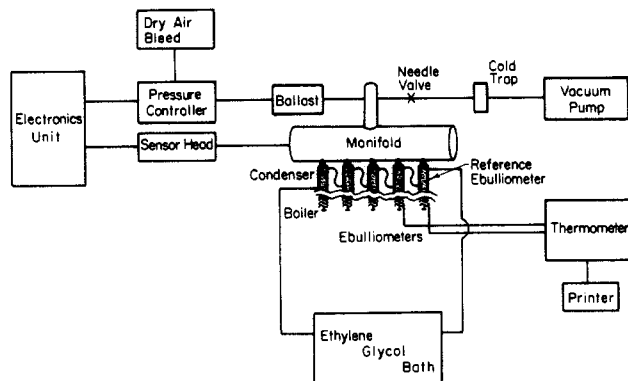
Figure 1. Overall design of system used to measure activity coefficients by differential ebulliometry.

volatile components. The technique has been further improved by redesigning both the pressure system and the ebulliometer itself. The pressure system has been modified to minimize any problems with leaks, to simplify the setting and measurement of the total pressure, and to permit the determination of four infinite-dilution activity coefficients simultaneously, three more than before. The ebulliometer has been improved to work better at low pressures, to facilitate ease of construction, and most importantly to extend the applicability of the technique to systems of greatly differing volatilities or with high limiting activity coefficients.

Following the development of Gatreaux and Coates (5) and adding terms to account for vapor-phase nonidealities, the expression used for γ^∞ is

$$\gamma_1^\infty = \phi^{(P_2^s)}[P_2^s - (1 - P_2^s V_2/RT + (P_2^s/\phi_2^s)(\partial\phi_2/\partial P) \times (dP_2^s/dT)(dT/dx_1)_P^\infty]/\{P_1^s\phi_1^s \exp[(P_2^s - P_1^s)V_1/RT]\} \quad (1)$$

A list of symbols is presented at the end of this paper. Fugacity coefficients were calculated by the method of Hadyn and O'-Connell (6). A list of the relevant pure-component information used in the calculation of γ^∞ may be found elsewhere (7).

Neglecting the fugacity coefficient and Poynting correction effects, generally of little significance, one may write the above equation as

$$\gamma_1^\infty = \frac{P_2^s - (dP_2^s/dT)(dT/dx_1)_P^\infty}{P_1^s} \quad (2)$$

The only term in either equation requiring binary data is $(dT/dx_1)_P^\infty$, i.e., the limiting composition derivative of the boiling temperature at constant total pressure. This quantity is measured through differential ebulliometry, as very accurate boiling temperatures are required to obtain the necessary slope.

An alternative to this method is fitting the $x-P-T$ data in the dilute region to an assumed solution of the Gibbs–Duhem equation to yield γ^∞. The details of this approach, a thorough treatment of the numerical considerations of the former method, and a comparison of the two approaches may be found elsewhere (1, 8).

Apparatus

The equipment used for the determination of γ^∞ is shown in Figures 1 and 2. Figure 1 shows the overall design of the system which is similar to that described by Null (9) and Wong and Eckert (10). The primary purpose of the experimental design was to develop a system which would most accurately measure the effect of concentration upon the boiling temperature of the solution. To this end it was necessary to minimize the effects of pressure fluctuations. As seen in Figure 1, the ebulliometers were connected through condensers to a common manifold, thus keeping the pressure in each ebulliometer the same. Rather than measure absolute boiling temperatures,
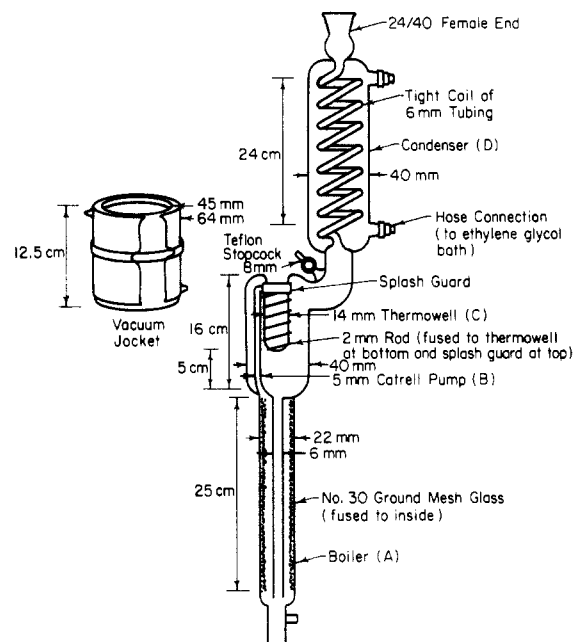

Figure 2. Ebulliometer design.

we measured the boiling difference between an ebulliometer containing the pure solvent and one containing the mixture. Even though pressure fluctuations caused the temperature in each ebulliometer to change, the temperature difference was not altered significantly.

Constant pressure was maintained by an MKS Baratrons system, capable of resolution to 10^{-3} kPa. It consisted of an MKS Baratron type 170M-6B electronics unit, a Granville-Phillips series 216 automatic pressure controller, and an MKS Baratron type 310 BHS-1000 sensor head. The pressure controller was connected to a 4-L ballast (to minimize pressure fluctuations) which in turn was connected to the manifold. The vacuum pump was connected to the manifold through a needle valve which regulated the conductance on the system. This system controlled the pressure to 0.01–0.05 kPa depending upon the boiling characteristics of the solvent and the magnitude of the total pressure.

The temperature difference between a loading ebulliometer and the reference ebulliometer was measured by a Hewlett-Packard quartz thermometer (2801A) with matching sensor probes capable of resolution to 10^{-4} °C. However, boiling characteristics frequently made the temperature difference accurate to only 10^{-3} °C. A DATAL Systems type DPP-7 thermal printer was connected to the thermometer to facilitate the tabulation of data.

The manifold has five ebulliometer connections which allow for four γ^∞'s to be determined simultaneously, three more than by the earlier design (1). Note that this entails four different solutes in the same solvent, as the solvent in the reference and loading ebulliometers must be the same. This greatly augmented the rate of data generation as four γ^∞'s could be measured in an 8-h period, about as long as it required to determine one γ^∞ with the older technique.

The present design of the ebulliometer as used by this research is given in Figure 2. It consists of a boiler (A), a 5-mm Cottrell tube (B), a thermowell (C), and a condenser (D). The boiler has 30-mesh ground-glass particles fused to the inner wall of the outer tube to promote better boiling. The liquid is heated by about 5 ft of nichrome wire wrapped in a helix around the boiler and connected to a Variac. As the solution is heated, bubbles of vapor and slugs of liquid jet up through the Cottrell pump and onto the thermowell. The thermowell is fitted with a tight glass spiral which breaks the runoff of the liquid; the liquid vaporizes at the expense of the sensible heat, and a true

vapor–liquid equilibrium is established on the outside of the thermowell. The temperature is measured by a thermometer probe immersed in mineral oil at the bottom of the thermowell. A condenser containing ethylene glycol at -20 °C was connected to the ebulliometer to avoid loss of volatile components through the top. The portion of the ebulliometer containing the thermowell was encased in a slit-silvered Dewar sleeve for insulation. The design has the following advantages over the earlier one (*1*): (1) the Teflon plug valve on the bottom of the ebulliometer facilitates cleaning and is significantly more airtight than the Teflon stopcock, (2) the internal Cottrell pump is easier to construct and makes the ebulliometer more compact, (3) the new model showed lower temperature fluctuations, especially at low pressures, and (4) most importantly, this design has a much lower vapor and liquid holdup correction, thus making the method much more applicable to highly nonideal systems and systems where the solute and solvent are of greatly differing volatilities (see below).

Materials

Reagent-grade or better solvents were used and were dried or further purified if deemed necessary. The purity of solute is not nearly as critical, but purifications were performed when thought necessary. Acetone was Fisher's reagent grade and was distilled before use, the middle 60% being collected. Benzene was Fisher's reagent grade and was used as purchased. Butanol was Mallinckrodt's reagent grade and was dried over 3A molecular sieves. Butanone was produced by Eastman and dried over 3A molecular sieves. *n*-Butyl chloride was produced by Eastman and used as purchased. *tert*-Butyl chloride was Aldrich's red lable and was used as purchased. Butyraldehyde was produced by Aldrich and used as purchased. Carbon tetrachloride was Mallinckrodt's spectrograde or Fisher's spectral grade and was used as purchased. Chloroform and cyclohexane were Mallinckrodt's spectrograde and were used as purchased. Cyclohexanone was Aldrich red label and was used as purchased. 1,2-Dichloroethane was Mallinckrodt's reagent grade and was dried over 4A molecular sieves. Ethanol was reagent grade produced by U.S. Industrial Chemicals and was used as purchased. Ethyl acetate was Mallinckrodt's reagent grade and was dried over 4A molecular sieves. Ethyl bromide was Mallinckrodt's reagent grade and was used as purchased. Ethyl iodide was Aldrich's red label and was distilled twice, dried over calcium hydride, and filtered twice. Heptane was spectral grade produced by Phillips Petroleum and was used as purchased. Hexane was spectral grade produced by Burdick and Jackson and was used as purchased. Methanol was produced by Fisher and used as purchased. Methylcyclohexane was produced by Eastman and used as purchased. Methylene chloride was Mallinckrodt's spectral grade and was used as purchased. Methyl propionate was produced by Aldrich and used as purchased. Nitrobenzene was Mallinckrodt's spectrograde and was used as purchased. Nitroethane was Aldrich's red lable and was used as purchased. Nitromethane was Mallinckrodt's reagent grade and was used as purchased. 1-Nitropropane was Aldrich's red label. It was distilled and dried over 4A molecular sieves. 2-Nitropropane was produced by Eastman, fractionally distilled, and dried over 4A molecular sieves. Propanol was Mallinckrodt's spectrograde and was used as purchased. Propionaldehyde was produced by Aldrich and used as purchased. Propionitrile was Aldrich's red label and was used as purchased. 2-Propyl iodide was produced by Aldrich and used as purchased. Pyridine was dried over 3A molecular sieves and fractionally distilled twice. Tetrahydrofuran was spectral grade produced by Burdick and Jackson and was used as purchased. Toluene was spectral grade produced by J. T. Baker and was used as purchased. Triethylamine was Aldrich's red label and was distilled, dried

over calcium hydride, filtered, and redistilled, the middle 60% being collected.

Experimental Procedure

The ebulliometers were cleaned by first flushing with distilled water, then rinsing twice with acetone, finally baking overnight in a drying oven. After cooling, the ebulliometers were filled gravimetrically with about 60 mL of solvent and connected to the manifold. Heating was initiated, the pressure set, and the system allowed to equilibrate with one temperature probe in a loading ebulliometer and the other in the reference ebulliometer. The temperature difference was then taken for about 3–5 min or until an equilibrium difference was assured. The probe in the first loading ebulliometer was then placed in a second one and a 0.2–1.0-mL injection of either pure solute or a mixture of solute and solvent was made through a serum stopper into the first ebulliometer. The temperature probe in the second ebulliometer was then allowed to equilibrate for about 5 min, and then 3–5 min of temperature difference was again recorded. The probe was placed in a third ebulliometer, an injection made to the second one, and the entire process repeated until either five or six injections had been made in each loading ebulliometer. Each series of four injections (one per loading ebulliometer) took 30–45 min, and an entire run lasted 6–8 h as it required 15–30 min for the temperature in an ebulliometer to equilibrate following an injection.

With this system the range of pressures for which reliable γ^{∞}'s may be obtained is 13 kPa to atmospheric pressure, although there is no reason why the system could not be easily modified to handle pressures above atmospheric. Unfavorable boiling characteristics seem to cause unsteady ΔT values for mixtures boiling much below 13 kPa. The applicable temperature range seems to be 28–200 °C. At temperatures below 28 °C, loss of volatile components out of the top causes problems. Although this system has not been tested above 100 °C, a similar ebulliometer (*11*) has been shown to work up to 200 °C.

Data Reduction

The infinite-dilution activity coefficients may be obtained from eq 1 or by a suitable solution of the Gibbs–Duhem equation for dilute $x–P–T$ data. A detailed discussion of the above methods along with the necessary computer programs are given by Nicolaides (*8*). A brief overview of the former procedure is reproduced here.

Equation 1 requires the calculations of $(dT/dx_1)_P$ at infinite dilution. This slope is obtained by fitting various analytic expressions to the $T–x$ data in the dilute region. All other terms in eq 1 were found from pure-component information. However, the γ^{∞} found in this manner is not entirely correct since no allowance has been made for the enrichment of the vapor phase or the liquid holdup with the more volatile component. Using this value of γ^{∞}, estimated values for the vapor-phase and liquid-holdup corrections, and the proper stoichiometric and thermodynamic relations, we obtain a new γ^{∞}. The ebulliometer has a vapor space of 100 cm³ and 0.6-cm³ liquid holdup. These corrections result in less than 10% error for relatively ideal systems with as much as a 50 °C boiling difference, or for systems of components of similar volatilities and values of γ^{∞} as high as 40.

Limiting slopes were determined by fitting the data to the following analytical equations:

$$\Delta T = ax \tag{3}$$

$$\Delta T = ax + bx^2 \tag{4}$$

$$\Delta T = ax + b \ln(1 + x) \tag{5}$$

$$\Delta T = ax + bx^2 + cx^3 \tag{6}$$

Table I. Ebulliometric Limiting Activity Coefficients

solute	solvent	T, K	γ^∞	uncertainty[a]	solute	solvent	T, K	γ^∞	uncertainty[a]
benzene	acetone	329.0	1.54	±0.03	acetonitrile	carbon tetrachloride	346.0	8.1	±0.03
		314.4	1.57	±0.03			340.2	8.7	±0.03
		304.0	1.59	±0.03			330.0	9.1	±0.03
carbon tetrachloride	acetone	327.6	2.13	±0.10			316.5	10.1	±0.03
		326.0	2.15	±0.10			314.9	10.7	±0.03
		310.9	2.13	±0.10	benzene	carbon tetrachloride	349.1	1.10	±0.03
		304.0	2.16	±0.10			328.3	1.10	±0.03
ethanol	acetone	327.4	1.92	±0.06	2-butanone	carbon tetrachloride	346.3	1.98	±0.03
		315.2	2.12	±0.06			340.2	2.02	±0.03
		306.8	2.24	±0.06			328.3	2.06	±0.03
ethyl iodide	acetone	326.4	2.04	±0.08			314.9	2.10	±0.03
		315.4	2.13	±0.06	cyclohexane	carbon tetrachloride	346.5	1.10	±0.02
		307.9	2.18	±0.05			341.2	1.09	±0.02
triethylamine	acetone	326.7	3.50	±0.15			330.4	1.10	±0.02
		315.5	3.73	±0.15			317.9	1.11	±0.02
		304.7	3.95	±0.25	heptane	carbon tetrachloride	349.1	1.15	±0.04
benzene	acetonitrile	318.2	2.95	±0.20			328.3	1.27	±0.04
carbon tetrachloride	acetonitrile	352.6	4.90	±0.40	nitromethane	carbon tetrachloride	349.1	8.4	±0.4
pyridine	acetonitrile	352.6	1.75	±0.08			340.2	9.1	±0.4
		334.6	1.81	±0.05			328.3	10.7	±0.4
		315.8	1.92	±0.08			314.9	11.7	±0.4
acetone	benzene	350.7	1.60	±0.03	2-nitropropane	carbon tetrachloride	346.3	3.96	±0.1
		349.8	1.62	±0.04			340.2	4.10	±0.1
		332.2	1.63	±0.05			333.0	4.24	±0.1
acetonitrile	benzene	318.2	3.08	±0.10			314.9	4.58	±0.1
cyclohexane	benzene	350.6	1.45	±0.05	triethylamine	carbon tetrachloride	347.1	0.81	±0.03
		335.2	1.52	±0.04			335.2	0.79	±0.03
		314.6	1.61	±0.05			321.7	0.75	±0.03
ethanol	benzene	349.0	7.60	±0.40	1-nitropropane	chlorobenzene	353.6	1.70	±0.06
		342.4	7.90	±0.40	acetone	chloroform	323.0	0.48	±0.03
heptane	benzene	349.4	1.59	±0.05			305.0	0.39	±0.05
		335.4	1.71	±0.04	acetonitrile	chloroform	331.9	1.35	±0.20
		318.0	1.92	±0.08			319.8	1.32	±0.05
nitromethane	benzene	318.2	3.48	±0.20			298.7	1.33	±0.10
pyridine	benzene	351.1	1.22	±0.06	benzene	chloroform	331.9	0.86	±0.04
		329.7	1.21	±0.06			319.8	0.83	±0.03
triethylamine	benzene	352.4	1.21	±0.05			298.7	0.75	±0.05
		336.7	1.24	±0.05	ethanol	chloroform	316.0	4.49	±0.10
tripropylamine	benzene	352.8	1.13	±0.05	ethyl bromide	chloroform	323.0	0.83	±0.02
acetone	n-butyl chloride	350.8	1.40	±0.03			305.0	0.82	±0.02
		343.2	1.42	±0.02	hexane	chloroform	331.9	1.66	±0.05
		326.7	1.53	±0.05			319.8	1.79	±0.05
		309.5	1.62	±0.04	methanol	chloroform	328.4	6.93	±0.10
pyridine	n-butyl chloride	349.3	1.38	±0.02			316.0	6.38	±0.20
triethylamine	n-butyl chloride	349.0	1.11	±0.03	nitromethane	chloroform	331.9	2.60	±0.20
		311.4	1.14	±0.03			319.8	2.90	±0.20
acetonitrile	2-butanone	333.3	1.25	±0.03	tetrahydrofuran	chloroform	323.0	0.25	±0.03
		314.7	1.25	±0.05			305.0	0.21	±0.02
1,2-dichloroethane	2-butanone	350.3	0.82	±0.03	triethylamine	chloroform	323.0	0.27	±0.05
		333.3	0.79	±0.01	benzene	cyclohexane	352.3	1.35	±0.03
		314.7	0.77	±0.01			333.0	1.41	±0.03
ethanol	2-butanone	348.6	1.74	±0.05			310.9	1.48	±0.08
		333.3	1.99	±0.04	2-butanone	cyclohexane	350.8	3.70	±0.10
		314.7	2.26	±0.05	n-butyl chloride	cyclohexane	350.8	1.43	±0.03
ethyl acetate	2-butanone	348.6	1.10	±0.08			340.7	1.46	±0.03
		333.3	1.10	±0.05			325.8	1.52	±0.03
		314.7	1.11	±0.05			315.1	1.56	±0.03
ethyl bromide	2-butanone	333.3	1.00	±0.03	1,2-dichloroethane	cyclohexane	351.2	2.29	±0.04
		314.7	1.05	±0.03			345.7	2.36	±0.04
methanol	2-butanone	333.3	2.09	±0.05			340.4	2.44	±0.04
		314.7	2.29	±0.08			334.2	2.52	±0.04
methylcyclohexane	2-butanone	348.6	3.08	±0.06	furfural	cyclohexane	349.2	13.9	±2
		333.3	3.35	±0.10			340.1	15.0	±2
		314.7	3.80	±0.05			337.6	15.7	±2
nitromethane	2-butanone	350.2	1.20	±0.03	2-nitropropane	cyclohexane	351.7	6.87	±0.3
		333.3	1.23	±0.03			346.1	7.40	±0.3
		314.7	1.25	±0.07			337.9	8.15	±0.4
pyridine	2-butanone	342.3	1.13	±0.02	acetone	1,2-dichloroethane	354.7	0.78	±0.02
triethylamine	2-butanone	352.0	2.12	±0.07			337.2	0.78	±0.02
		341.3	2.21	±0.07			318.5	0.76	±0.03
		316.0	2.48	±0.08	acetonitrile	1,2-dichloroethane	355.3	1.43	±0.06
acetone	carbon tetrachloride	346.8	2.59	±0.04			343.9	1.45	±0.07
		333.0	2.76	±0.04			318.5	1.47	±0.07
		316.5	2.88	±0.04	benzene	1,2-dichloroethane	355.0	1.04	±0.02
		295.7	3.15	±0.04			337.2	1.06	±0.02

Table I (*Continued*)

solute	solvent	T, K	γ^∞	uncertainty[a]	solute	solvent	T, K	γ^∞	uncertainty[a]
		318.4	1.08	±0.02			331.7	1.45	±0.05
2-butanone	1,2-dichloroethane	354.7	0.78	±0.02			307.2	1.50	±0.05
		318.5	0.73	±0.01	hexane	ethyl acetate	348.4	2.41	±0.08
carbon tetrachloride	1,2-dichloroethane	355.0	1.55	±0.02			324.4	2.77	±0.08
		337.2	1.65	±0.02			308.2	3.09	±0.12
		318.4	1.76	±0.02	methanol	ethyl acetate	350.4	2.65	±0.10
		306.9	1.86	±0.04	nitromethane	ethyl acetate	347.3	1.42	±0.07
ethanol	1,2-dichloroethane	337.2	7.2	±1.2			330.5	1.47	±0.07
		318.4	9.7	±0.3			311.7	1.62	±0.07
ethyl acetate	1,2-dichloroethane	318.4	0.83	±0.01	propionitrile	ethyl acetate	349.2	1.29	±0.05
heptane	1,2-dichloroethane	354.2	3.10	±0.10			329.2	1.35	±0.05
		337.2	3.86	±0.10			311.6	1.42	±0.05
		318.5	4.45	±0.15	tetrahydrofuran	ethyl acetate	348.3	1.03	±0.05
hexane	1,2-dichloroethane	354.2	3.01	±0.10			333.5	1.06	±0.05
		337.2	3.59	±0.10			313.0	1.10	±0.05
		318.5	3.99	±0.10	toluene	ethyl acetate	348.3	1.14	±0.04
isooctane	1,2-dichloroethane	343.5	3.43	±0.10			333.5	1.18	±0.04
methanol	1,2-dichloroethane	355.0	5.50	±0.10			313.0	1.27	±0.04
		337.2	6.93	±0.20	triethylamine	ethyl acetate	342.7	1.84	±0.05
		318.4	9.1	±0.4			321.2	1.94	±0.05
methylcyclohexane	1,2-dichloroethane	354.7	2.61	±0.04			306.2	2.04	±0.05
nitroethane	1,2-dichloroethane	354.2	1.39	±0.05	benzene	heptane	366.2	1.27	±0.03
		337.2	1.41	±0.05			350.6	1.33	±0.03
		318.5	1.49	±0.05			331.2	1.37	±0.06
nitromethane	1,2-dichloroethane	355.3	1.63	±0.05	furfural	heptane	369.1	9.6	±2
		343.9	1.73	±0.05			352.2	12.0	±2
		318.5	1.86	±0.05			332.0	14.4	±2
propionitrile	1,2-dichloroethane	355.3	1.11	±0.03	acetonitrile	hexane	340.9	12.4	±0.8
		343.9	1.11	±0.03			332.3	13.7	±0.8
		318.5	1.15	±0.03			322.9	16.8	±0.8
pyridine	1,2-dichloroethane	354.3	0.89	±0.01			295.0	27.6	±1.4
		330.0	0.90	±0.02	1-butanol	hexane	340.3	12.2	±0.5
triethylamine	1,2-dichloroethane	354.2	1.82	±0.05			331.8	15.1	±0.2
		329.0	1.96	±0.07			315.3	22.5	±1.5
		310.9	2.05	±0.07			301.0	33.0	±3.0
acetone	ethanol	348.3	1.92	±0.10	2-butanone	hexane	340.3	3.40	±0.1
		335.8	2.03	±0.10			332.0	3.60	±0.1
		322.5	2.17	±0.10			315.3	3.97	±0.1
benzene	ethanol	346.4	4.40	±0.20			298.0	4.38	±0.2
chlorobenzene	ethanol	348.0	4.90	±0.30	n-butyl chloride	hexane	340.3	1.40	±0.02
		335.8	5.10	±0.30			332.0	1.43	±0.02
		323.2	5.20	±0.30			315.3	1.50	±0.02
heptane	ethanol	347.8	10.3	±1.10			301.0	1.52	±0.02
		335.2	10.9	±1.0	*tert*-butyl chloride	hexane	340.1	1.27	±0.02
		319.4	11.8	±1.0			331.8	1.35	±0.02
hexane	ethanol	350.9	8.1	±0.5			315.3	1.40	±0.02
2-iodopropane	ethanol	350.9	5.19	±0.4			301.0	1.45	±0.02
		344.6	5.46	±0.4	carbon tetrachloride	hexane	340.3	1.16	±0.01
		325.1	6.56	±0.8			332.0	1.19	±0.01
pyridine	ethanol	350.6	0.94	±0.02			315.0	1.20	±0.02
		336.4	0.96	±0.02			301.0	1.20	±0.02
tripropylamine	ethanol	350.7	7.93	±0.5	chloroform	hexane	340.1	1.39	±0.03
		334.8	8.27	±0.5			331.8	1.48	±0.05
		323.4	8.68	±0.5			315.3	1.53	±0.02
toluene	ethanol	349.4	5.14	±0.2			301.0	1.58	±0.02
		330.0	5.34	±0.2	cyclohexane	hexane	340.3	1.06	±0.01
		318.5	5.60	±0.2			332.0	1.07	±0.01
acetonitrile	ethyl acetate	347.8	1.51	±0.05			315.3	1.09	±0.01
		330.5	1.58	±0.05			301.0	1.09	±0.01
		311.7	1.73	±0.05	cyclohexanone	hexane	332.0	4.7	±0.2
benzene	ethyl acetate	330.5	1.14	±0.02			315.1	5.3	±0.2
		311.7	1.14	±0.02			298.0	7.1	±0.5
2-butanone	ethyl acetate	348.3	1.04	±0.05	1,2-dichloroethane	hexane	339.4	2.32	±0.04
		333.5	1.08	±0.05			332.2	2.45	±0.05
		313.0	1.11	±0.05			316.0	2.73	±0.05
carbon tetrachloride	ethyl acetate	329.2	1.28	±0.03			298.0	3.17	±0.09
chloroform	ethyl acetate	349.2	0.49	±0.01	ethanol	hexane	322.6	23	±2
		329.2	0.52	±0.01			304.8	38	±3
1,2-dichloroethane	ethyl acetate	347.8	0.85	±0.02	ethyl acetate	hexane	339.4	2.39	±0.06
		330.5	0.83	±0.03			332.0	2.60	±0.06
		311.7	0.81	±0.02			316.0	2.95	±0.06
ethanol	ethyl acetate	348.3	2.33	±0.06			298.1	3.39	±0.06
		333.5	2.42	±0.06	ethyl bromide	hexane	340.3	1.26	±0.02
		313.0	2.84	±0.10			332.0	1.37	±0.02
ethyl iodide	ethyl acetate	343.9	1.41	±0.05			314.3	1.54	±0.03

Table I (*Continued*)

solute	solvent	T, K	γ^∞	uncertainty^a	solute	solvent	T, K	γ^∞	uncertainty^a
ethyl iodide	hexane	301.0	1.62	±0.1	pyridine	propionitrile	338.0	1.39	±0.04
		340.6	1.67	±0.04			323.3	1.36	±0.02
		329.1	1.83	±0.04	butyraldedyde	tetrahydrofuran	336.9	1.09	±0.08
		322.9	1.87	±0.04			328.4	1.10	±0.02
		298.0	2.07	±0.04			311.5	1.13	±0.02
nitroethane	hexane	339.4	10.0	±0.7			293.7	1.21	±0.02
		332.0	12.3	±1.0	chloroform	tetrahydrofuran	337.3	0.37	±0.02
		316.0	13.2	±1.3			327.7	0.35	±0.02
		298.1	20.7	±1.8	cyclohexane	tetrahydrofuran	337.3	1.59	±0.1
nitromethane	hexane	340.9	17.8	±1.0			327.7	1.69	±0.02
		332.3	19.9	±1.5	methylene chloride	tetrahydrofuran	336.9	0.50	±0.03
		322.9	23.9	±1.8			328.4	0.48	±0.01
1-nitropropane	hexane	340.3	8.5	±0.2			311.5	0.45	±0.01
		332.0	9.6	±0.4			293.7	0.41	±0.01
		315.3	11.5	±0.4	methyl propionate	tetrahydrofuran	327.7	1.32	±0.03
		301.0	14.1	±0.7			311.5	1.39	±0.03
propanol	hexane	340.1	13.7	±1.5	propionaldehyde	tetrahydrofuran	336.9	1.07	±0.04
		331.8	16.6	±1.5			328.4	1.08	±0.04
		315.3	26.1	±2.0			311.5	1.09	±0.04
		301.0	39.	±6.0			293.7	1.15	±0.06
propionitrile	hexane	340.9	10.0	±0.4	2-butanone	toluene	381.0	1.33	±0.04
		332.3	10.7	±0.4			362.7	1.35	±0.04
		322.9	13.6	±0.7			342.7	1.39	±0.03
		295.0	19.2	±1.0	1,2-dichloroethane	toluene	380.9	0.97	±0.05
2-propyl iodide	hexane	340.6	1.70	±0.08			342.7	0.95	±0.03
pyridine	hexane	340.6	4.04	±0.08	ethanol	toluene	381.0	4.39	±0.20
		330.1	4.22	±0.10			342.7	6.95	±0.20
		316.9	4.83	±0.10	ethyl acetate	toluene	380.9	1.20	±0.05
		296.6	5.90	±0.12			362.7	1.21	±0.06
tetrahydrofuran	hexane	340.2	1.51	±0.03			342.7	1.16	±0.02
		322.4	1.59	±0.03	methanol	toluene	381.0	5.00	±0.20
		304.8	1.65	±0.03	nitroethane	toluene	381.0	2.10	±0.04
triethylamine	hexane	340.7	1.06	±0.05			342.7	2.35	±0.05
		330.1	1.03	±0.08	1-nitropropane	toluene	362.7	1.73	±0.10
		322.9	1.10	±0.05	acetonitrile	triethylamine	348.7	5.50	±0.30
		298.0	1.10	±0.05	benzene	triethylamine	359.3	1.08	±0.02
toluene	hexane	322.8	1.46	±0.05			348.7	1.22	±0.08
		304.8	1.59	±0.05			323.5	1.28	±0.08
furfural	methylcyclohexane	372.9	8.4	±2	ethyl bromide	triethylamine	348.7	1.02	±0.04
		353.8	10.8	±2	1,2-dichloroethane	triethylamine	359.3	1.35	±0.05
		347.3	12.1	±2			348.7	1.40	±0.05
benzene	nitromethane	371.5	2.65	±0.20			323.5	1.44	±0.05
		358.9	3.06	±0.20	hexane	triethylamine	359.3	1.06	±0.03
chlorobenzene	1-nitropropane	353.5	1.35	±0.05			348.7	1.06	±0.03
cyclohexane	propionitrile	356.3	5.22	±0.4			323.5	1.06	±0.03
		336.7	6.00	±0.5	nitromethane	triethylamine	348.7	6.70	±0.50

^{a} Uncertainty based on the standard deviation of the fit to the $(dT/dx_1)_P^\infty$ expressions, on the sensitivity of the change in the value of γ^∞ to changes in the slope, and on the magnitude of the holdup correction.

The fits were generally close to linear and γ^∞'s obtained from the different functions usually differed by less than 5%. The limiting activity coefficients were chosen by fitting the values of the first four, the first five, and the first six injections with the equation which gave the lowest standard deviation in the limiting slope (usually about 1–2%).

Results

Using the ebulliometric technique, γ^∞ data were taken for 147 binary systems, generally over pressure intervals corresponding to 30–40 °C temperature ranges. The limiting activity coefficients are listed in Table I. These values were obtained from eq 1 and were averaged with those from a solution to the Gibbs–Duhem equation (Wilson or Van Laar equations) in the dilute region only when there was a large error in the calculation of $(dT/dx_1)_P^\infty$. The standard deviations in $(dT/dx_1)_P^\infty$ averaged 1–2% overall, excluding those systems for which the slope was too small to significantly affect the final values (e.g., benzene in carbon tetrachloride). The error estimates included in Table I account for the standard deviation in the limiting slope, the sensitivity of the system to changes in the slope, and the
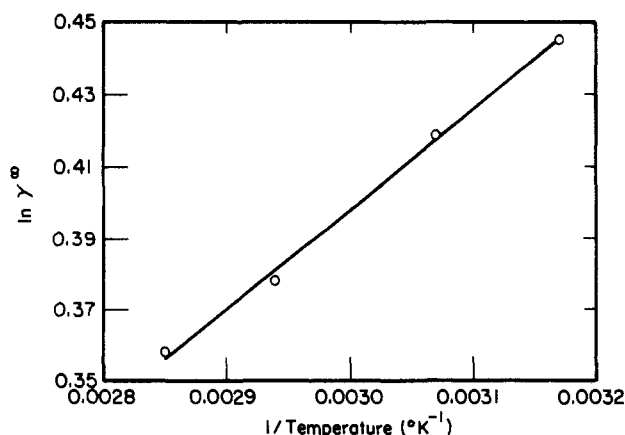

Figure 3. Limiting activity coefficient data for *n*-butyl chloride in cyclohexane.

magnitude of the holdup corrections.

Table II is a comparison of the γ^∞'s of this study with those obtained from extrapolation in the literature. Note that for

Table II. Comparison of Ebulliometric Limiting Activity Coefficients with Extrapolated Values from the Literature

solute	solvent	this study		lit.		
		T, K	γ^{∞}	T, K	γ^{∞}	ref
benzene	acetone	314.4	1.57	308.2	1.52	12
CCl$_4$	acetone	327.6	2.13	329.4	2.15	12
ethanol	acetone	327.4	1.92	329.4	1.78	12
benzene	acetonitrile	318.2	2.95	318.2	2.74	12
CCl$_4$	acetonitrile	352.6	4.90	318.2	5.66	2
acetone	benzene	350.7	1.60	353.3	1.65	12
acetonitrile	benzene	318.2	3.08	318.3	2.94	12
cyclohexane	benzene	350.6	1.45	353.2	1.45	12
ethanol	benzene	349.0	7.60	353.2	6.75	12
heptane	benzene	349.4	1.59	353.3	1.66	12
nitromethane	benzene	318.2	3.48	318.2	3.20	12
pyridine	benzene	351.1	1.22	353.3	1.29	12
triethylamine	benzene	336.7	1.24	333.2	1.22	12
ethanol	2-butanone	348.6	1.74	352.8	1.79	12
methanol	2-butanone	333.3	2.09	352.8	2.02	12
acetone	CCl$_4$	346.8	2.59	349.7	2.47	12
acetonitrile	CCl$_4$	316.5	10.1	318.2	9.30	2
benzene	CCl$_4$	349.1	1.10	349.9	1.10	12
2-butanone	CCl$_4$	346.3	1.98	349.7	1.78	12
cyclohexane	CCl$_4$	346.5	1.10	349.7	1.05	12
heptane	CCl$_4$	349.1	1.15	349.7	1.13	12
nitromethane	CCl$_4$	314.7	11.7	318.2	10.6	2
2-nitropropane	CCl$_4$	314.9	4.58	298.2	3.24	2
acetone	chloroform	323.0	0.48	323.0	0.44	2
benzene	chloroform	331.9	0.86	334.3	0.82	12
ethanol	chloroform	316.0	4.49	334.3	4.28	12
methanol	chloroform	328.4	6.93	334.3	6.96	12
benzene	cyclohexane	352.3	1.35	353.2	1.36	12
1,2-dichloroethane	cyclohexane	351.2	2.29	353.9	2.62	12
acetone	1,2-dichloroethane	354.7	0.78	356.6	0.81	12
benzene	1,2-dichloroethane	355.0	1.04	356.6	1.04	12
ethanol	1,2-dichloroethane	337.2	7.2	323.2	7.82	12
methanol	1,2-dichloroethane	337.2	6.93	333.2	7.41	12
acetone	ethanol	348.3	1.92	351.4	1.83	12
benzene	ethanol	346.4	4.40	351.4	3.96	12
chlorobenzene	ethanol	348.0	4.90	351.4	5.59	12
heptane	ethanol	347.8	10.3	351.4	10.9	12
hexane	ethanol	350.9	8.1	351.4	8.8	12
toluene	ethanol	349.4	5.14	351.4	5.14	12
ethanol	ethyl acetate	348.3	2.33	350.2	2.22	12
methanol	ethyl acetate	350.4	2.65	328.2	2.96	12
benzene	heptane	366.2	1.27	371.6	1.30	12
butanol	hexane	340.3	12.2	341.9	11.15	12
2-butanone	hexane	340.3	3.40	338.2	3.50	12
CCl$_4$	hexane	340.3	1.16	341.9	1.18	12
chloroform	hexane	340.1	1.39	341.9	1.38	12
cyclohexane	hexane	340.3	1.06	341.9	1.06	12
ethanol	hexane	322.6	23.0	341.9	21.3	12
ethyl iodide	hexane	329.1	1.83	333.2	1.91	12
triethylamine	hexane	340.7	1.06	333.2	1.03	12
toluene	hexane	322.8	1.46	341.9	1.36	12
benzene	nitromethane	371.5	2.65	318.2	3.39	12
2-butanone	toluene	342.7	1.39	323.2	1.47	12
1,2-dichloroethane	toluene	380.9	0.97	383.6	1.01	12
ethanol	toluene	381.0	4.39	383.6	5.28	12
methanol	toluene	381.0	5.00	383.6	6.85	12
nitroethane	toluene	342.7	2.35	318.2	2.44	12
benzene	triethylamine	348.7	1.22	333.2	1.17	12
hexane	triethylamine	323.5	1.06	333.2	1.03	12

relatively ideal systems (0.7 < γ^{∞} < 2.0) the values are in close agreement. For more highly nonideal systems the values can differ by 30% or more. This is thought to be due to the difficulty in extrapolating finite concentration data to infinite dilution for these highly nonideal systems.

Figures 3 and 4 are plots of the temperature dependence of limiting activity coefficients for two systems where the data were taken over at least a 30 °C temperature range. For real mixtures

$$[\partial(\ln \gamma_i)/\partial(1/T)]_{P,x} = \bar{h}_i^E/R \qquad (7)$$

where $\bar{h}_i^E$ is the component partial excess enthalpy. Regular

solutions will exhibit $\bar{h}_i^E$'s constant over moderate temperature ranges. Thus, a plot of ln γ^{∞} vs. 1/T should be approximately linear, and for the systems plotted this is shown to be true with the data falling within 1% of the best line through the points. Similar results were obtained with the other systems studied, although it would be expected that a straight line would not necessarily result for highly solvated and associated solutions.

These data are significant in that they characterize the dilute-solution behavior of many industrially important systems. They also should be useful in the development and evaluation of solution models and in providing insight into the nature of intermolecular forces in dilute solutions. Such a study is presented elsewhere (12).
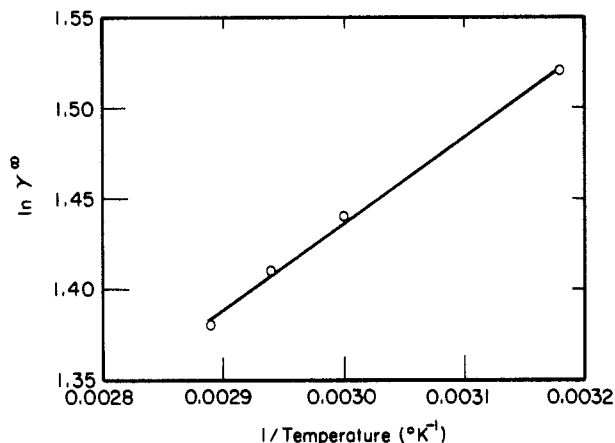
Figure 4. Limiting activity coefficient data for 2-nitropropane in carbon tetrachloride.

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Glossary

γ^{∞} limiting activity coefficient
$\bar{h}_i^E$ partial molar excess enthalpy

ϕ vapor-phase fugacity coefficient
ϕ^s fugacity coefficient at saturation pressure
P total pressure
P^s saturation pressure
R gas constant
V liquid molar volume
x liquid-phase mole fraction

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Measurements of the Viscosity of Saturated and Compressed Liquid Propane

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The shear viscosity coefficient of saturated and compressed liquid propane has been measured with a torsionally oscillating quartz crystal viscometer at temperatures between 90 and 300 K and at pressures up to 30 MPa (4350 psia). The estimated precision and accuracy of the measurements are about 1% and 2%, respectively. The measurements have been compared with an equation previously optimized to available data and proposed for calculating the viscosity of compressed gaseous and liquid propane at temperatures down to 140 K. Differences between the equation and the measurements reported here are within our experimental error at temperatures above 140 K. Differences between our measurements and the equation extrapolated to temperatures below 140 K increase with decreasing temperature (and increasing density) to about 30% at 90 K.

Introduction

This research is part of a long-range program on the thermophysical properties of compressed and liquefied hydrocarbon gases and their mixtures. The purpose of this report is to provide accurate wide-range viscosity measurements at low temperatures and liquid densities for testing and improving an equation previously proposed (1) for calculating the dependence of the shear viscosity coefficient of compressed gaseous and liquid propane on temperature and density.

The technical importance of propane is well-known: propane is an important constituent in both liquefied natural gas (LNG) and liquefield petroleum gases (LPG). Propane has an unusually long vapor pressure–reduced temperature curve, extending down to a reduced temperature of about 0.23 at low temperatures. Therefore, the thermophysical properties of propane are useful as the reference state in corresponding states calculations of the properties of higher molecular weight hydrocarbon fluids and their mixtures.

This report provides new absolute viscosity measurements for saturated and compressed liquid propane at temperatures between 90 and 300 K and at pressures to 30 MPa (4350 psia). The measurements have been compared with an equation previously proposed (1) for calculating the viscosity of propane at temperatures down to 140 K. The differences between the equation and the measurements reported here are discussed in detail.

Experimental Section

The measurement method, apparatus, and procedures are essentially the same as reported in our work on other fluids (2,