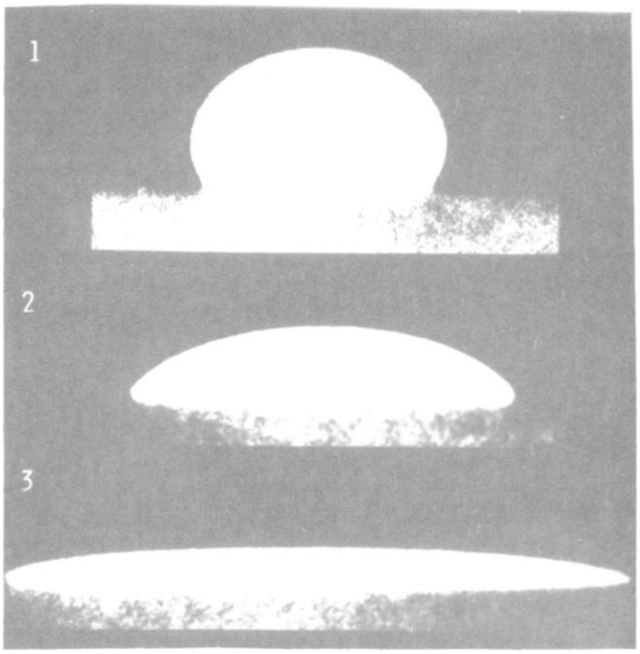

Figure 3. Sessile drop of a $PbCl_2$–KCl–NaCl mixture (4/3/3 molar ratio) on graphite at 793 K under (1) argon atmosphere, (2 and 3) dry air.

interfacial tensions of salt mixtures on BN substrate.

Conclusions

1. The molten chloride mixtures studied under an argon atmosphere formed contact angles less than 40° on substrates made of polycrystalline alumina (Al_2O_3), quartz (SiO_2), and Inconel. The contact angle formed on ZrO_2 varied between 27 and 81°, and the contact angle formed on BN varied between 73 and 130°.
2. Graphite and amorphous carbon substrates were the least wetted and under an argon atmosphere the contact angles varied between 90 and 150°.
3. The contact angles formed on graphite substrates did not change when the argon atmosphere was replaced with chlorine gas. However, when air or dry air was introduced, the contact angle decreased rapidly and complete wetting was observed after about 5 min. This effect was not observed when the graphite substrate was replaced with BN.

Acknowledgment

We are grateful to Dr. J. E. Dutrizac for many helpful discussions.

Registry No. $PbCl_2$, 7758-95-4; KCl, 7447-40-7; NaCl, 7647-14-5; LiCl, 7447-41-8; Al_2O_3, 1344-28-1; C, 7440-44-0; BN, 10043-11-5; ZrO_2, 1314-23-4; quartz, 14808-60-7; Inconel, 12606-02-9; graphite, 7782-42-5.

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Physicochemical Properties of Mono- and Diisocyanates

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Liquid density, viscosity, specific heat, and vapor pressure data are reported for a new class of mono- and diisocyanates.

Introduction

Isocyanates are well established for use in the production of foams, elastomers, coatings, adhesives, and fibers. A new series of isocyanates, shown in Table I, is commercially available. The materials are 1,3-bis(1-isocyanato-1-methylethyl)benzene [*m*-TMXDI], 1,4-bis(1-isocyanato-1-methylethyl)benzene [*p*-TMXDI], 1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene [*m*-TMI], and 1-(1-isocyanato-1-methylethyl)-4-(1-methylethenyl)benzene [*p*-TMI]. Chemically these compounds contain the isopropylidene $(CH)_2C<$ group which separates the isocyanate function from the aromatic ring. In this paper we report physicochemical data for these compounds.

Experimental Section

Materials. All compounds are liquids at room temperature except *p*-TMXDI which is a solid (mp 80 °C). Purity of the compounds was not established rigorously. Estimation by gas chromatographic analysis gave contents of the desired isomers of 99%, 99%, 98%, and 91% for *m*-TMXDI, *p*-TMXDI, *m*-TMI, and *p*-TMI, respectively. For isotenescope vapor pressure measurements, materials were further purified by freeze–pump–thaw cycles to remove volatiles. All materials are American Cyanamid Research samples.

Liquid Density. A PAAR DMA-10 density meter (*1*) was used to measure densities every 5 deg from 25 to 80 °C. Temperature was regulated to ±0.1 °C. No liquid densities were determined for *p*-TMXDI as it is solid in this temperature range.

Viscosity. Cannon-Fenske capillary viscometers were used to measure kinematic viscosities from 25 to 180 °C. Flow times were repeatable within 1%. Temperatures were accurate to ±2 °C. For *p*-TMXDI, viscosities were measured from

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Table I. Chemical Structures

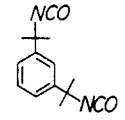
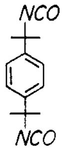
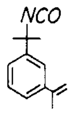
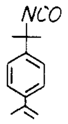
abbreviation	*m*-TMXDI	*p*-TMXDI	*m*-TMI	*p*-TMI
formula				
chemical formula	$C_{14}H_{16}N_2O_2$	$C_{14}H_{16}N_2O_2$	$C_{13}H_{15}NO$	$C_{13}H_{15}NO$
chemical name	1,3-bis(1-isocyanato-1-methylethyl)benzene	1,4-bis(1-isocyanato-1-methylethyl)benzene	1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene	1-(1-isocyanato-1-methylethyl)-4-(1-methylethenyl)benzene

Table II. Physicochemical Properties of *m*-TMXDI

property	*t*, °C	equation
ρ, g/cm^3	25–80	$\rho = 1.0940 - 9.2 \times 10^{-4}t$
V_m, cm^3/mol	25–80	$V_m = 223.95 + 0.16122t + 4.3926 \times 10^{-4}t^2$
η, cSt	25–180	$\ln \eta = -4.480 + \frac{1838}{t + 273.1} + 6.7 \times 10^5 \left[\frac{1}{t + 273.1} - \frac{1}{380}\right]^2$
C_p, J/(g °C)	60	1.9
	160	2.0
p, Torr	25–153	$\log p = 8.914 - \frac{3405}{t + 273.1}$

Table III. Physicochemical Properties of *p*-TMXDI

property	*t*, °C	equation
η, cSt	80–180	$\ln \eta = -4.512 + \frac{1943}{t + 273.1} + 2.8 \times 10^5 \left[\frac{1}{t + 273.1} - \frac{1}{380}\right]^2$
C_p, J/(g °C)	60	1.7 (solid)
	160	1.9
p, Torr	100–155	$\log p = 9.8463 - \frac{3866}{t + 273.1}$

80 to 180 °C, that is, above its melting point.

Specific Heat. Specific heats were measured at 60 and 160 °C by using a Perkin-Elmer DSC2 differential scanning calorimeter and the technique of O'Neil (*2*) with sapphire (*3*) as the reference material. Accuracy of the measurements was estimated by determining the specific heat of dodecane.

Vapor Pressure. A number of techniques was used to measure vapor pressures. Reduced pressure boiling points were measured by differential thermal analysis above 105 °C. Isotenescope (*4*) measurements were made for *m*- and *p*-TMXDI above 90 °C. Gas chromatographic head-space analysis was used at room temperature. No measurements were made for *m*-TMI.

Results

Tables II–V summarize our results. Density data are fitted by regression analysis to an equation linear in temperature. Molar volumes determined from densities are fitted to a quadratic equation. Estimated error, based on the precision of the PAAR DMA-10 instrument as reported by the manufacturer, is ±0.001 g cm^{-3}.

Kinematic viscosity data show pronounced curvature with temperature. However, the quadratic equation models the data within ±2%.

Measured specific heats for dodecane are within ±3% of literature values (*6*). We believe our isocyanate values are of equal accuracy.

Vapor pressures are fitted to the equation

$$\log p = A - B/(t + 273.1)$$

Because we included the data from all three experimental techniques, each with its own experimental uncertainty, statistical treatment of the data is not justified. Eighty-five percent of our experimental data fit the indicated equations within ±15% or ±0.1 Torr, whichever is greater.

Table IV. Physicochemical Properties of *m*-TMI[a]

property	*t*, °C	equation
ρ, g/cm^3	25–80	$\rho = 1.0269 - 8.7 \times 10^{-4}t$
V_m, cm^3/mol	25–80	$V_m = 196.10 + 0.16102t + 1.9303 \times 10^{-4}t^2$
η, cSt	25–180	$\ln \eta = -3.813 + \frac{1419}{t + 273.1} + 3.6 \times 10^5 \left[\frac{1}{t + 273.1} - \frac{1}{380}\right]^2$
C_p, J/(g °C)	60	1.9
	160	2.1

[a] See ref 5 for comparable density, molar volume, and viscosity data from 10 to 60 °C; also a boiling point of 84 °C at 1 Torr is reported.

Table V. Physicochemical Properties of *p*-TMI

property	*t*, °C	equation
ρ, g/cm^3	25–80	$\rho = 1.0363 - 8.4 \times 10^{-4}t$
V_m, cm^3/mol	25–80	$V_m = 194.59 + 0.14089t + 2.9517 \times 10^{-4}t^2$
η, cSt	25–180	$\ln \eta = -4.150 + \frac{1605}{t + 273.1} + 2.2 \times 10^5 \left[\frac{1}{t + 273.1} - \frac{1}{380}\right]^2$
C_p, J/(g °C)	60	1.8
	160	1.9
p, Torr	25–190	$\log p = 9.643 - \frac{3570}{t + 273.1}$

Acknowledgment

We thank W. E. Mealmaker and E. H. Stene for their experimental assistance and S. Greenhouse for his statistical curve fit of the viscosity data.

Glossary

C_p	specific heat, J g^{-1} °C^{-1}
ρ	liquid density, g cm^{-3}
η	kinematic viscosity, cSt
t	temperature, °C
p	pressure, Torr

Conversion

1 cal g^{-1} °C^{-1} = 4.18 J g^{-1} °C^{-1}
1 g cm^{-3} = 10^3 kg m^{-3}
1 cSt = 10^{-6} m^2 s^{-1}

Registry No. 1,3-Bis(1-isocyanato-1-methylethyl)benzene, 2778-42-9; 1,4-bis(1-isocyanato-1-methylethyl)benzene, 2778-41-8; 1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene, 2094-99-7; 1-(1-isocyanato-1-methylethyl)-4-(1-methylethenyl)benzene, 2889-58-9.

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Supplementary Material Available: All of our experimental density, viscosity, and vapor pressure data (2 pages). Ordering information is given on any current masthead.

Vapor–Liquid Equilibria of the System Trimethyl Borate (1)–*n*-Cyclohexane (2)

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Vapor–liquid equilibria for the binary system trimethyl borate (1)–*n*-cyclohexane (2) have been measured at 101.325 kPa. The data have been checked for thermodynamic consistency and also correlated by the Wilson equations.

Isobaric vapor–liquid equilibrium data for the system trimethyl borate (1)–*n*-cyclohexane (2) were measured at 101.325 kPa ± 0.3 (760 ± 2 mmHg) in an Altsheler circulation-type still. Details of the Altsheler still can be found in the reference by Hala et al. (*1*). The still contained two thermocouples, one submerged in the boiling liquid and one in the vapor space directly above the boiling liquid. The two thermocouples were calibrated; however, they did not always give the same value during still operation. Maximum variation was ±0.3 K. When variations occurred, the liquid temperature was reported. Temperatures are believed to be accurate to ±0.1 K.

Materials Used

The trimethyl borate was manufactured by the Aldrich Chemical Co. and was received with a nominal purity of 99%. This purity was not sufficient, so the chemical was further purified by simple distillation. The *n*-cyclohexane was manufactured by Burdick & Jackson and was received with a purity of 99.9%. The purity was acceptable and the *n*-cyclohexane was used as received. Properties of these materials compared with literature values are shown in Table I.

Methods of Analysis

A Bausch & Lomb precision refractometer along with a carefully prepared calibration curve was used to determine composition of the liquid phase and the vapor phase. The refractometer used a sodium D-line as the light source and provided a precision of ±0.000 03 RI units. The prism in the refractometer was maintained at a temperature of 298.15 ± 0.1 K.

Table I. Physical Properties of the Pure Components

Trimethyl Borate	
boiling point, K	
lit.	341.85 (*2*)
measd	341.62
refractive index (temp, K)	
lit.	1.35422 (300.15) (*3*) 1.35503 (298.15) (*3*) 1.3550 (298.15) (*4*) 1.35517 (298.15) (*5*)
measd	1.35441 (298.15)
***n*-Cyclohexane**	
boiling point, K	
lit.	353.87 (*6*) 353.85 (*7*)
measd	353.88
refractive index (temp, K)	
lit.	1.4262 (293.15) (*6*) 1.4266 (293.15) (*7*)
measd	1.4275 (298.15) 1.4264 (293.15)

Vapor Pressure Equations

trimethyl borate (*8*)

$$\ln P^0 = 13.1756 - 1357.14/(T - 134.33)$$

n-cyclohexane (*9*)

$$\ln P^0 = 15.7527 - 2766.63/(T - 50.50)$$

Discussion of Results

The experimental results are shown in Table II and Figure 1. Data show that the system exhibits positive deviations from Raoult's law and does not possess an azeotrope. The activity coefficients range between 1.000 and the estimated infinitely dilute values of $\gamma_1^\infty = 1.563$ and $\gamma_2^\infty = 1.408$. All of the activity coefficients except for the infinite dilution values were calculated by the equation

$$\gamma_i = y_1\pi/\Phi x_i P^0$$

where

$$\Phi = \phi_i \exp\left[\frac{1}{RT}\int_{P^0}^{\pi} V_i \, d\pi\right] \Big/ \hat{\phi}_i$$

and is the ratio of the fugacity coefficient of the pure component at its vapor pressure to the component in the vapor mixture at the total pressure multiplied by the exponential term called the Poynting correction. Fugacity coefficients were calculated by using the Redlich and Kwong equation of state. Values of Φ ranged from 0.98 to 1.02.

The data were subjected to a thermodynamic consistency test as suggested by Fredenslund et al. (*10*). In this procedure the excess Gibbs function is expressed as a Legendre polyno-

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