

Phase Diagram of Butyronitrile–Chloroethane Determined by Differential Thermal Analysis

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The temperature–composition phase diagram of the butyronitrile–chloroethane system was determined by differential thermal analysis. The butyronitrile–chloroethane system is a simple eutectic, the eutectic point being $-185\text{ }^{\circ}\text{C}$ (88 K) and 48 mol % butyronitrile. The thermodynamics of the liquid phase were tested against a number of solution models and were found to be best represented by the associated solution model with the solution consisting of free butyronitrile, free chloroethane, and dimolecular complexes composed of one butyronitrile and one chloroethane. This model was also used to estimate the vapor pressure of butyronitrile–chloroethane solutions.

Introduction

The liquid range of the butyronitrile (BN)–chloroethane (CE) system extends from room temperature to below the superconducting transition temperature of $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$. For this reason, solutions of BN and CE have served as solvents for subambient-temperature electrolytes. Furthermore, on the basis of estimates of the vapor pressure above these solutions, they merit consideration as working fluids in a cryogenic refrigeration system. In the present investigation the phase diagram of BN and CE was determined by differential thermal analysis (DTA). This system presented some atypical experimental challenges: at room temperature BN is a liquid while CE is a gas; BN has an affinity for water—to avoid contamination special procedures had to be adopted; the temperature range of interest, *i.e.*, -195 to $-100\text{ }^{\circ}\text{C}$ (78–173 K), extended beyond that of commercially available DTA instrumentation. This paper reports the measured phase diagram, presents a thermodynamic model to explain the liquidus behavior, and estimates the vapor pressure of BN–CE solutions.

Literature

The BN–CE eutectic was first mentioned as a low-temperature liquid by McDevitt *et al.*¹ However, limited attention has been given to the systematic determination of the phase diagram. Ching *et al.* report values for the liquidus based upon viscosity measurements.² However, BN is prone to supercooling. This makes it difficult to obtain an accurate determination of the liquidus and, furthermore, makes it virtually impossible to distinguish the solidus from the liquidus.

Experimental Section

Apparatus. The DTA apparatus used in this research was designed in accordance with the guidelines of Vassallo and Harden³ and is shown in Figure 1. The chill block was made of copper rod, $\frac{3}{4}$ in. in diameter, and consisted of two parts. In the lower part, there were three small wells, 10 mm deep \times 4 mm in diameter, one for the specimen and two for the reference materials. Redundant references were used for several reasons. The eutectic temperature had been reported to be $-185\text{ }^{\circ}\text{C}$ (88 K), which is beyond the range of commercially available DTA instrumentation. Construction of an apparatus that would

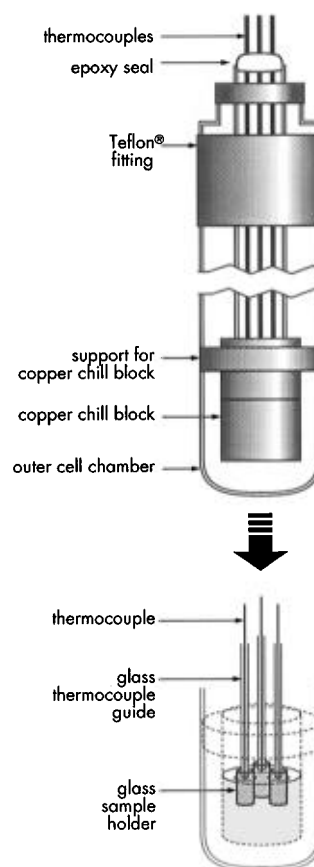


Figure 1. Cell for DTA measurements.

operate over a temperature range extending down to $-196\text{ }^{\circ}\text{C}$ (77 K) required the use of a temperature control technique incapable of assuring that there were no temperature gradients in the chill block. In addition, temperature differences during thermal events were expected to be small. Under these circumstances, the presence of a second reference allowed the data to be validated. Glass sample holders were inserted in the wells. These sample holders were made of Pyrex tubing, 12 mm long \times 3 mm i.d., one-end-sealed and ground flat. The holders contained approximately 0.1 mL of liquid. Alumina powder was used as the reference material as it has a negligible vapor pressure and does not undergo a phase change on the temperature interval traversed in this investigation. Alumina

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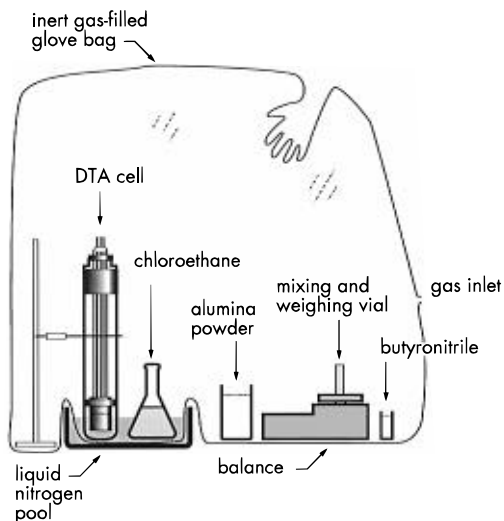


Figure 2. Station for solution preparation and cell assembly.

powder was mixed with the specimen so that the thermal characteristics of the specimen and reference were more nearly matched.

The upper half of the chill block served as both a cover and a positioning device for the three thermocouples. There were three feed-throughs, each lined with glass tubing that extended into the glass sample holders when the two halves of the chill block were assembled. The glass tubes prevented the tips of the thermocouples from bending and assured that the tip positions were reproducible and centered in the wells. At the top of the cell, the thermocouple wires exited through a glass tube and were sealed in place with epoxy. Temperature was monitored using ASTM type T thermocouples (copper-constantan) which were calibrated at five temperatures between room temperature and $-196\text{ }^{\circ}\text{C}$ (77 K). The total error in the absolute temperature was computed to be $\pm 0.3\text{ }^{\circ}\text{C}$.

Drying of the Chemical Components. Both the CE and BN were dried prior to mixing. The CE was dried by condensing the gas over 3A molecular sieves. The liquid was stored at $-37\text{ }^{\circ}\text{C}$, below its normal boiling point. The BN was dried by successive decanting: the liquid was poured over 3A molecular sieves, left a minimum of 12 h on the drying agent, and then decanted again over fresh drying agent. The liquid was dried twice over 3A sieves and twice over activated alumina. The liquid was stored over activated alumina.

Procedure. A typical experiment began by placing the tools required to charge the cell, clean glass sample holders, and the DTA apparatus in a glovebag filled with dried argon or nitrogen. The glovebag was placed in an external liquid nitrogen pool as shown in Figure 2.

The glass sample holders for the two references were filled with alumina powder. Then, the sample holder for the test solution was half-filled, by volume, with alumina powder. All three sample holders were placed in their respective positions in the lower half of the copper chill block which in turn was placed in the liquid nitrogen cooling pool. At this time, the upper half of the copper chill block was also cooled in the liquid nitrogen. Some of the alumina powder was then placed at the bottom of the outer cell chamber to enhance thermal transport during cooling and warming cycles.

The solutions under test were prepared by pouring BN into a vial which was then covered. The vial was placed in the external liquid nitrogen pool until the BN had solidified. The BN was weighed, and CE, which had been stored in the same liquid nitrogen pool, was thawed and added. When the solution reached the desired composition as determined by weighing and

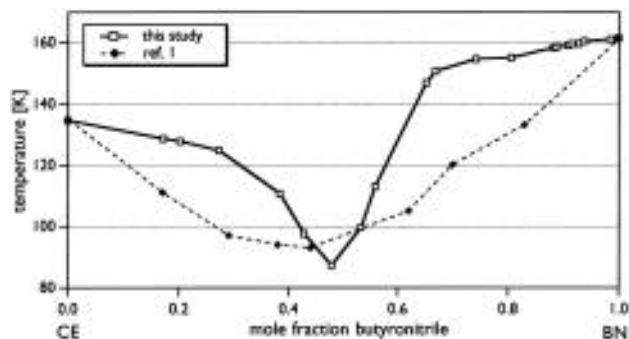


Figure 3. Phase diagram of butyronitrile–chloroethane.

all of the BN had melted, a sample of the solution was withdrawn with a eye dropper and added to the alumina powder in the sample holder. The top of the copper chill block with the thermocouples was fit onto the bottom section of the copper chill block, and the top and bottom were screwed together. The entire assembly was placed in the glass chamber and sealed with a Teflon compression fitting.

Once sealed, the cell was wrapped in aluminum foil which served as a Faraday shield. The voltages of the thermocouples were measured with a multichannel digital voltmeter (Keithley, Model 199, Cleveland, OH) and were recorded by a computer running in-house software. The three thermocouples in the DTA cell were referenced to a fourth ASTM type T thermocouple immersed in an ice-water bath. The cell was cooled and warmed at various rates in the temperature gradient above a liquid nitrogen pool. Linear cooling was more difficult to attain than linear warming.

Data Analysis. The measured voltages from the three thermocouples were first referenced to the zero of the ice-water bath. Then, using calibration curves measured for each thermocouple, the voltages were converted to temperature. From these temperatures the differential curves were computed. Generally, the temperature of the liquidus is determined in a cooling experiment and is taken to be the onset of the differential peak.⁴ However, BN has a strong tendency to supercool even when heavily seeded with alumina powder as a nucleating agent. Indeed, in the present study there was wide scatter in the results obtained from cooling curves. Consequently, only warming curves were used in developing the phase diagram. This proved to be satisfactory except in the determination of the solidus at the low-temperature extremes of the investigation where precise control of temperature was not attainable. The liquidus was determined from the peak in the warming curve, justified by the fact that peak temperature was invariant with heating rate.⁵ The values of heating rate employed in this study ranged from 4 to 40 K min^{-1} . The estimated errors were ± 0.02 in mole fraction and $\pm 0.3\text{ }^{\circ}\text{C}$ in temperature.

Results and Discussion

The measured phase diagram is shown in Figure 3 along with the data of Ching et al.² The BN–CE system is a simple eutectic, the eutectic being $-185\text{ }^{\circ}\text{C}$ (88 K) and 48 mol % BN.

For dilute solutions, Raoultian behavior is exhibited by the solvent. In the absence of solid solubility, the enthalpy of fusion of the pure solvent can be evaluated from the slope of the liquidus by

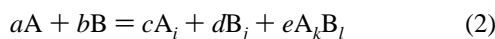
$$x_i = \frac{\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (1)$$

where x_i is the mole fraction of the solute, R is the gas constant, T_m is the melting point of the pure solvent, and T is the liquidus

temperature. The value of the melting point of each component was taken from the literature.^{6,7} From the measured phase diagram the values of the enthalpy of fusion were determined to be 5.03 kJ mol⁻¹ for BN and 4.74 kJ mol⁻¹ for CE. These compare with the values of 5.02 kJ mol⁻¹ for BN determined by phase diagram measurements⁶ and 4.45 kJ mol⁻¹ for CE determined calorimetrically.⁷

Thermodynamic Modeling. The measured liquidus exhibits a pronounced change in slope near 30 and 60 mol % BN. This is indicative of nonideal behavior, in particular, nonrandom entropy of mixing. The shape of the liquidus is highly suggestive of compound formation. A number of models were tested for their ability to represent the thermodynamic behavior of the liquid, and the associated solution model was found to best simulate the measured phase diagram.

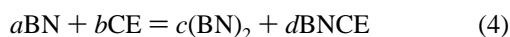
In the associated solution model, a binary solution of A and B contains polyatomic aggregates of the principal components: these include A_i and B_j, the polyatomic homonuclear species, sometimes termed "self associates," and A_kB_l, the polyatomic heteronuclear species, sometimes termed "complexes." The formation of the binary solution can be written as



for which the equilibrium constant is

$$K = \frac{x_{A_i}^c x_{B_j}^d x_{A_kB_l}^e}{x_A^a x_B^b} \quad (3)$$

On the basis of observations in related systems,^{8,9} the formation of the following two associated species is anticipated: (BN)₂, *i.e.*, dimolecular self-associates of BN, and BNCE, *i.e.*, dimolecular complexes consisting of one BN and one CE. The formation of such solutions can be represented by a reaction having the form of eq 2:



However, on the strength of recent measurements made in this laboratory of the variation in dielectric constant with composition and temperature in solutions of BN–CE,¹⁰ one can justify the approximation that the extent of self-association in BN is negligibly small, *i.e.*, $c = 0$ in eq 4. This reduces the formation reaction to



for which the equilibrium constant is

$$K = \frac{x_{BNCE}}{x_{BN}x_{CE}} \quad (6)$$

According to the associated solution model, the mole fraction of free BN, *i.e.*, the amount that has not reacted with CE to form BNCE, can be expressed in terms of the relative amounts of the principal components, BN and CE, x_{BN} and x_{CE} , by¹¹

$$x_{BN_1} = \frac{x_{BN} - x_{CE} + \sqrt{x_{BN}^2 + x_{CE}^2 - 2x_{BN}x_{CE}\left(\frac{K-1}{K+1}\right)}}{1 + \sqrt{x_{BN}^2 + x_{CE}^2 - 2x_{BN}x_{CE}\left(\frac{K-1}{K+1}\right)}} \quad (7)$$

where the subscript BN₁ denotes unassociated BN. As anticipated, the limit of $K = 0$ predicts no complex formation, *i.e.*, $x_{BN_1} = x_{BN}$.

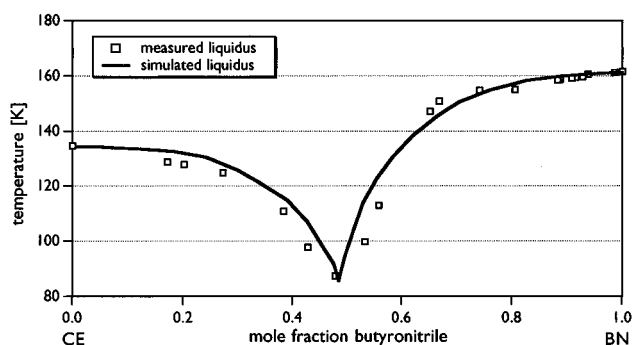


Figure 4. Comparison of measured liquidus and simulated liquidus. Measurements were performed by DTA. Simulation was with the associated solution model.

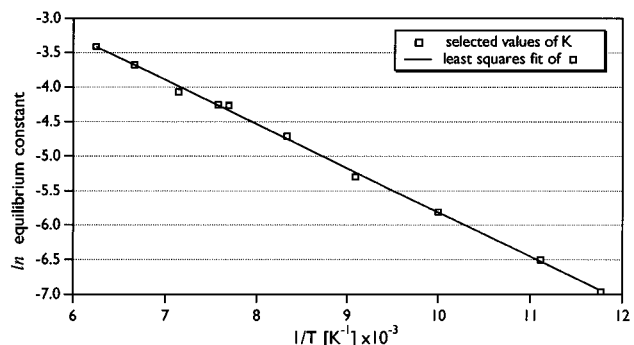


Figure 5. Temperature dependence of the equilibrium constant. K was chosen on the basis of the best fit of the liquidus data to the associated solution model.

The phase diagram of BN–CE was simulated by using eq 4 to generate free energy isotherms for the liquid and followed by determination of the tangent common to the free energy isotherm of the solid. It was assumed that there is no solid–solid solubility, *i.e.*, all solid phases are present as pure components. The use of the associated solution requires setting the value of only one adjustable parameter: the equilibrium constant, K , as defined in eq 6. At each temperature, the value of K was selected on the basis of the agreement between the simulated and measured liquidus. Figure 4 shows the results of the simulation as well as the measured phase diagram.

Figure 5 shows the temperature dependence of the selected values of the equilibrium constant. Gibbs–Helmholtz behavior is evident. The results can be represented by

$$K = 1.61 \exp\left(\frac{5350}{RT}\right) \quad (8)$$

The values of the enthalpy and entropy of association are -643.6 J mol⁻¹ and 3.97 J mol⁻¹ K⁻¹, respectively. At 125 K eq 8 gives a value of $K = 277$, which means that the concentration of unreacted BN is $x_{BN} = 0.0012$. Clearly, this indicates that the reaction between BN and CE to form the complex, BNCE, effectively goes to completion.

Estimation of Vapor Pressure of BN–CE Solutions. With this model it is possible to estimate the vapor pressure of BN–CE solutions

$$P_{\text{total}} = a_{BN}p_{BN}^{\circ} + a_{CE}p_{CE}^{\circ} \quad (9)$$

where a_i is the activity of i in solution and p_i° is vapor pressure of pure component i . The vapor pressures of BN and CE were extrapolated from higher temperatures,¹² and the activity coefficients were computed using the relationship

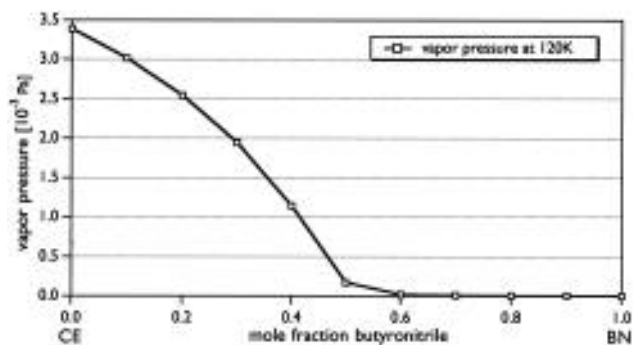


Figure 6. Computed vapor pressure over butyronitrile–chloroethane solutions at 120 K.

$$\gamma_i = \frac{1}{x_i^0} \frac{x_i}{x_i} \quad (10)$$

where x_i^0 is the mole fraction of uncomplexed i in the pure liquid, here assumed to be 1 for both BN and CE.

An example of how vapor pressure varies with composition is given in Figure 6, which shows the isotherm at 120 K. The CE dominates the vapor pressure, and at the eutectic composition the computed vapor pressure is significantly lower than that given by Raoult's Law.

One can speculate as to the utility of the eutectic liquid as a candidate working fluid in a cryogenic refrigeration system. At -153 °C (120 K) the eutectic has a vapor pressure of 0.0005 Pa. The extrapolated enthalpies of evaporation at -153 °C (120 K) are 48.9 and 28.89 kJ mol $^{-1}$ for BN and CE, respectively.¹²

Summary

The phase diagram of the BN–CE system has been determined by DTA to be a simple eutectic, the eutectic point being

-185 °C (88 K) and 48 mol % BN. BN–CE is well modeled as an associated solution. Three species are speculated to exist in the liquid phase: free BN, free CE, and dimolecular complexes of one BN and one CE. The presence of these species is consistent with the interpretation of the measured relative dielectric constants of these solutions.¹⁰

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References and Notes

- (1) McDevitt, J. T.; Ching, S.; Sullivan, M.; Murray, R. W. *J. Am. Chem. Soc.* **1989**, *111*, 4528.
- (2) Ching, S.; McDevitt, J. T.; Peck, S. R.; Murray, R. W. *J. Electrochem. Soc.* **1991**, *138*, 2308.
- (3) Vassallo, D. A.; Harden, J. C. *Anal. Chem.* **1962**, *34*, 132.
- (4) Mackenzie, R. C., Ed. *Differential Thermal Analysis*; Academic Press: London, 1970.
- (5) Wunderlich, B. *Thermal Analysis*; Academic Press: Boston, MA, 1990.
- (6) Timmermanns, J. *Bull. Soc. Chim. Belg.* **1935**, *44*, 17.
- (7) Gordon, J.; Giauque, W. F. *J. Am. Chem. Soc.* **1948**, *70*, 1506.
- (8) Murray, F. E.; Schneider, W. G. *Can. J. Chem.* **1955**, *33*, 797.
- (9) Nickerson, J. D.; McIntosh, R. *Can. J. Chem.* **1957**, *35*, 1325.
- (10) Michnick, R. B.; Rhoads, K. G.; Sadoway, D. R. Submitted for publication in *J. Electrochem. Soc.*
- (11) Prigogine, I.; Defay, R. *Chemical Thermodynamics*; John Wiley and Sons: New York, 1954.
- (12) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Taylor and Francis: Washington, DC, 1989.

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