Isothermal Vapor−Liquid Equilibria and Excess Volumes of Propanenitrile or Butanenitrile + Heptane or + Benzene Mixtures

Manuela Artal, José Muñoz Embid, Gabriele Marras,[†] Inmaculada Velasco, and Santos Otín*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, 50009-Zaragoza, Spain

Isothermal vapor−liquid equilibria (VLE) at 318.15 K and molar excess volume V^E at 298.15 K have been measured for liquid propanenitrile or butanenitrile + heptane or + benzene mixtures. The VLE data were reduced using the Redlich−Kister equation, taking into consideration the vapor phase imperfection in terms of the second molar virial coefficients.

Introduction

The thermodynamic behavior of mixtures containing nitriles is of considerable interest because of the high polarity of these compounds. However, the thermodynamic properties of mixtures containing less volatile nitriles than acetonitrile are lacking. In this paper we report molar excess volumes, at 298.15 K, and isothermal vapor−liquid equilibrium data, at 318.15 K, for propanenitrile (C_3H_5N) and butanenitrile (C_4H_7N) + heptane (C_7H_{16}) and + benzene (C_6H_6). As far as we know, the only volumetric measurements on these mixtures are by Wang et al. (1993) on V^E of $C_3H_5N + C_6H_6$. Vapor−liquid equilibria of $C_3H_5N + C_7H_{16}$ at 298.15 and 308.15 K or $C_4H_7N + C_7H_{16}$ at 298.15 K have been measured by Kikic et al. (1980). No vapor−liquid equilibrium measurements have been published for C_3H_5N or $C_4H_7N + C_6H_6$.

Experimental Section

Materials. Propanenitrile was from Aldrich Chemie (better than 99 mol % pure), butanenitrile was from Fluka AG Buchs (better than 99 mol % pure), and heptane and benzene were from Fluka AG Buchs (better than 99.5 mol % pure). In Table 1, we compare the measured densities and vapor pressures of the products with literature values.

Apparatus and Procedure. Vapor−liquid equilibrium data were taken at constant temperature in a dynamic still designed by Berro et al. (1982). The temperature T inside the equilibrium cell was measured with a precision of 0.01 K by means of a Digitec digital thermometer (Digitec Corp. Model 5831). The pressure P was measured by means of a Digiquartz Transmitter of Paroscientific Inc. Model 1015A calibrated in the pressure range 0−0.1 MPa. The accuracy of the pressure measurements is 0.01%. Liquid and vapor mole fractions, x_1 and y_1, respectively, were determined by densimetric analysis using an Anton Paar Model DMA 60 densimeter equipped with a DMA 602 cell in a flow system as described by Muñoz Embid et al. (1991). The densimeter calibration was performed, at atmospheric pressure, by using doubly distilled and degassed water, benzene, and dried air. The vibrating-tube temperature was measured by means of a Anton Paar DM 100-30 digital thermometer and was regulated to better than 0.01 K using a Neslab RTE-210 thermostat. The uncertainty of the composition measurements was estimated to be ±0.001 mole fraction. Molar excess volumes were calculated from density measurements, carried out in the same densimeter. Mixtures were prepared by mass, the mole fraction error estimated to be less than 1×10^{-4}. Duplicate densities of pure liquids and mixtures studied agreed to within 2×10^{-5} g cm^{-3}.

Table 1. Densities $\varrho_i°$ and Vapor Pressures $P_i°$ of the Pure Components

	$\varrho_i°$(298.15 K)/(g cm^{-3})		$P_i°$(318.15 K)/kPa	
	this work	lit.[a]	this work	lit.
propanenitrile	0.776 82	0.779 82	15.786	15.585[a]
butanenitrile	0.785 97	0.786 5	7.287	7.239[b]
heptane	0.679 08	0.679 46	15.354	15.32[b]
benzene	0.873 14	0.873 60	29.871	29.81[b]

[a] Riddick et al. (1986). [b] *TRC Thermodynamic Tables* (1994).

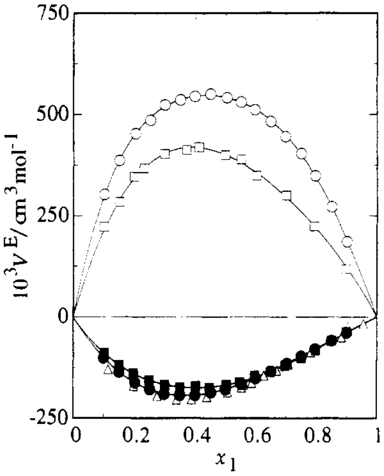

Figure 1. Excess molar volumes V^E (298.15 K) as a function of mole fraction x_1. Continuous curves, smoothed values, eq 1; points, direct experimental values: ○, propanenitrile (1) + heptane (2); □, butanenitrile (1) + heptane (2); ●, propanenitrile (1) + benzene (2); ■, butanenitrile (1) + benzene (2); △, propanenitrile (1) + benzene (2) (Wang et al., 1993).

Experimental Results and Discussion

Molar excess Gibbs energies G^E were calculated by reduction of the experimental $P-x_1$ data with the Redlich−Kister equation. Vapor phase nonideality and the variation of the Gibbs energy of the pure liquid components with pressure were accounted for in terms of the molar second virial coefficients B_{ij}, estimated by the method of Tsonopoulos (1974, 1975), and the liquid molar volumes. The critical volume for butanenitrile (V_c = 286 cm^3 mol^{-1}) was estimated according to the Joback method (modification of Lydersen's method) (Reid et al., 1986).

[†] On leave of absence from the Dipartimento di Scienze Chimiche, Università di Cagliari, Via Ospedale 72, 09124 Cagliari, Italy.

0021-9568/95/1740-1154$09.00/0

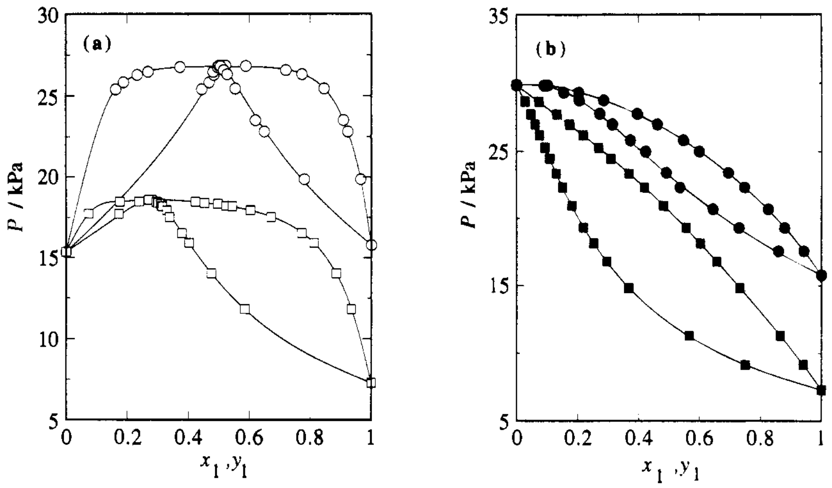

Figure 2. Vapor–liquid equilibrium diagrams at 318.15 K. Pressure, P, as a function of mole fraction in the liquid, x_1, or vapor, y_1, phase. Continuous curves, smoothed values, eq 2; points, direct experimental values: (a) ○, propanenitrile (1) + heptane (2); □, butanenitrile (1) + heptane (2); (b) ●, propanenitrile (1) + benzene (2); ■, butanenitrile (1) + benzene (2).

Table 2. Excess Molar volumes V^E at 298.15 K as a Function of Mole Fraction x_1, Coefficients A_j, Eq 1, and Standard Deviations $\sigma(V^E)$, Eq 3

x_1	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x_1	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x_1	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x_1	$V^E/(\mathrm{cm^3\ mol^{-1}})$
Propanenitrile (1) + Heptane (2)							
0.1012	0.303	0.3510	0.536	0.5500	0.531	0.7493	0.404
0.1500	0.387	0.3986	0.545	0.5964	0.512	0.7962	0.349
0.2039	0.453	0.4495	0.551	0.6486	0.483	0.8493	0.273
0.2525	0.486	0.5034	0.541	0.6968	0.446	0.9007	0.187
0.3001	0.524						
$V^E/\{x_1(1-x_1)\ \mathrm{cm^3\ mol^{-1}}\} = 2.168 - 0.322(2x_1 - 1) + 0.844(2x_1 - 1)^2 - 0.661(2x_1 - 1)^3$							
$\sigma(V^E)/(\mathrm{cm^3\ mol^{-1}}) = 0.0034$							
Butanenitrile (1) + Heptane (2)							
0.1004	0.223	0.2990	0.403	0.4987	0.400	0.7009	0.300
0.1515	0.284	0.3711	0.412	0.5508	0.389	0.7930	0.224
0.2004	0.346	0.4120	0.419	0.6023	0.349	0.8981	0.119
0.2324	0.367						
$V^E/\{x_1(1-x_1)\ \mathrm{cm^3\ mol^{-1}}\} = 1.599 - 0.644(2x_1 - 1) + 0.420(2x_1 - 1)^2$							
$\sigma(V^E)/(\mathrm{cm^3\ mol^{-1}}) = 0.0056$							
Propanenitrile (1) + Benzene (2)							
0.0993	−0.101	0.3495	−0.193	0.5520	−0.165	0.7500	−0.097
0.1505	−0.136	0.4002	−0.193	0.6010	−0.151	0.7953	−0.079
0.2024	−0.162	0.4522	−0.186	0.6515	−0.134	0.8498	−0.058
0.2509	−0.179	0.4999	−0.179	0.7024	−0.115	0.8994	−0.038
0.2985	−0.190						
$V^E/\{x_1(1-x_1)\ \mathrm{cm^3\ mol^{-1}}\} = -0.712 + 0.436(2x_1 - 1) - 0.093(2x_1 - 1)^2$							
$\sigma(V^E)/(\mathrm{cm^3\ mol^{-1}}) = 0.0005$							
Butanenitrile (1) + Benzene (2)							
0.1015	−0.089	0.3502	−0.174	0.5481	−0.161	0.7516	−0.102
0.1517	−0.119	0.4027	−0.171	0.5970	−0.145	0.7974	−0.083
0.1986	−0.140	0.4477	−0.175	0.6496	−0.136	0.8495	−0.058
0.2497	−0.157	0.5036	−0.168	0.6975	−0.121	0.8993	−0.036
0.3013	−0.168						
$V^E/\{x_1(1-x_1)\ \mathrm{cm^3\ mol^{-1}}\} = -0.672 + 0.258(2x_1 - 1) - 0.051(2x_1 - 1)^2 + 0.155(2x_1 - 1)^3$							
$\sigma(V^E)/(\mathrm{cm^3\ mol^{-1}}) = 0.0021$							

The V^E values at 298.15 K and G^E values at 318.15 K are collected in Tables 2 and 3. Smoothing equations of the types

$$V^E_{calc}/\{x_1(1 - x_1)\} = \sum A_j(2x_1 - 1)^{j-1} \qquad (1)$$

and

$$G^E_{calc}/\{x_1(1 - x_1)RT\} = \sum A_j(2x_1 - 1)^{j-1} \qquad (2)$$

were fitted by the method of least squares. The A_j parameters are given in Tables 2 and 3 together with the standard deviations $\sigma(Q)$ calculated as

$$\sigma(Q) = [\sum(Q - Q_{calcd})^2/N]^{1/2} \qquad (3)$$

where N is the number of experimental values and $Q = V^E$, P, or y_1.

Figures 1 and 3 compare our experimental results of V^E and VLE with those of Wang et al. (1993) and Kikic et al. (1980), respectively.

The thermodynamic consistency of the experimental data was checked by means of the test of Van Ness et al. (1973) in the version of Fredenslund et al. (1977). According to this test, the data are considered consistent if the mean absolute deviation in y, $\delta(y)$, is less than 0.01. In this work,

Table 3. Experimental Vapor–Liquid Equilibrium Pressure P and Vapor Mole Fraction y_1 at 318.15 K as a Function of Liquid Mole Fraction x_1, Coefficients A_j, Eq 2, Standard Deviations $\sigma(P)$ and $\sigma(y_1)$, Eq 3, Molar Second Virial Coefficients B_{ij}, and Liquid Molar Volumes of Pure Components $V_i°$

Propanenitrile (1) + Heptane (2)

x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.1619	0.4435	25.404	0.5217	0.5003	26.854	0.8445	0.5533	25.450
0.1874	0.4682	25.833	0.5887	0.5055	26.832	0.9079	0.6203	23.526
0.2321	0.4836	26.285	0.7197	0.5161	26.577	0.9226	0.6497	22.832
0.2676	0.4813	26.482	0.7727	0.5272	26.326	0.9645	0.7798	19.882
0.3725	0.4954	26.774						

$$G^E/\{x_1(1-x_1)RT\} = 2.1384 + 0.0105(2x_1-1) + 0.1767(2x_1-1)^2$$

$$\sigma(P)/\mathrm{Pa} = 29;\ \sigma(y_1) = 0.0076$$

$$B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -3199;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -2316;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -1931$$

$$V_1°/(\mathrm{cm^3\ mol^{-1}}) = 70;\ V_2°/(\mathrm{cm^3\ mol^{-1}}) = 147$$

Butanenitrile (1) + Heptane (2)

x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0739	0.1725	17.738	0.4975	0.3089	18.344	0.7720	0.3785	16.528
0.1755	0.2389	18.486	0.5239	0.3113	18.218	0.8126	0.4025	15.925
0.2816	0.2695	18.585	0.5445	0.3149	18.190	0.8849	0.4754	14.028
0.4231	0.2942	18.465	0.6036	0.3290	17.944	0.9344	0.5854	11.832
0.4530	0.3002	18.398	0.6722	0.3377	17.524			

$$G^E/\{x_1(1-x_1)RT\} = 1.8500 - 0.1437(2x_1-1) + 0.2189(2x_1-1)^2 - 0.0752(2x_1-1)^3$$

$$\sigma(P)/\mathrm{Pa} = 23;\ \sigma(y_1) = 0.0044$$

$$B_{11}/(\mathrm{cm^3\ mol^{-1}}) = -4036;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -2316;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -2251$$

$$V_1°/(\mathrm{cm^3\ mol^{-1}}) = 87;\ V_2°/(\mathrm{cm^3\ mol^{-1}}) = 147$$

Propanenitrile (1) + Benzene (2)

x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.1012	0.0901	29.839	0.4609	0.3128	27.000	0.7473	0.5354	22.322
0.2024	0.1540	29.324	0.5462	0.3716	25.846	0.8250	0.6440	20.696
0.2845	0.2046	28.760	0.5986	0.4220	25.000	0.8788	0.7294	19.304
0.3949	0.2718	27.773	0.6939	0.4904	23.421	0.9421	0.8585	17.585

$$G^E/\{x_1(1-x_1)RT\} = 0.5585 - 0.1129(2x_1-1) + 0.0543(2x_1-1)^2$$

$$\sigma(P)/\mathrm{Pa} = 27;\ \sigma(y_1) = 0.0065$$

$$B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -3199;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -1274;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -1473$$

$$V_1°/(\mathrm{cm^3\ mol^{-1}}) = 70;\ V_2°/(\mathrm{cm^3\ mol^{-1}}) = 89$$

Butanenitrile (1) + Benzene (2)

x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0734	0.0276	28.650	0.3089	0.1082	24.464	0.6026	0.2523	18.151
0.1318	0.0469	27.711	0.3683	0.1301	23.340	0.6569	0.2957	16.799
0.1731	0.0604	26.968	0.4193	0.1510	22.306	0.7327	0.3674	14.835
0.2176	0.0750	26.188	0.4819	0.1813	20.941	0.8647	0.5668	11.317
0.2675	0.0921	25.275	0.5563	0.2189	19.315	0.9403	0.7506	9.160

$$G^E/\{x_1(1-x_1)RT\} = 0.3359 - 0.1250(2x_1-1) + 0.0846(2x_1-1)^2$$

$$\sigma(P)/\mathrm{Pa} = 34;\ \sigma(y_1) = 0.0018$$

$$B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -4036;\ B_{22}/(\mathrm{cm^3\ mol^{-1}}) = -1274;\ B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -1691$$

$$V_1°/(\mathrm{cm^3\ mol^{-1}}) = 87;\ V_2°/(\mathrm{cm^3\ mol^{-1}}) = 89$$

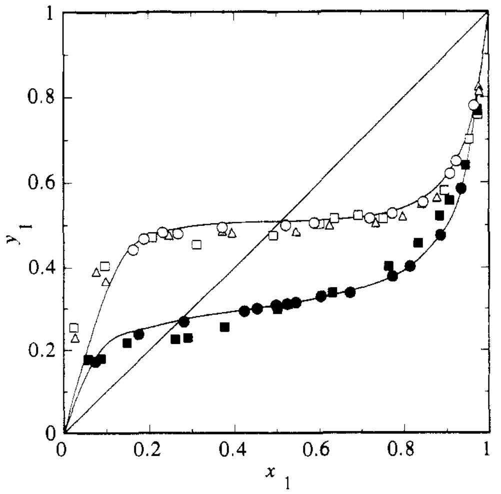

Figure 3. Vapor–liquid equilibrium diagrams for the propanenitrile (1) + heptane (2) system [□, 298.15 K (Kikic et al., 1980); △, 308.15 K (Kikic et al., 1980); ○, 318.15 K (this work)] and for the butanenitrile (1) + heptane (2) system [■, 298.15 K (Kikic et al., 1980); ●, 318.15 K (this work)]. Continuous curves, smoothed values.

the $\delta(y)$ values obtained are $\delta(y) = 0.0068$ for propanenitrile + heptane, $\delta(y) = 0.0031$ for butanenitrile, $\delta(y) = 0.0047$ for propanenitrile + benzene and $\delta(y) = 0.0014$ for butanenitrile + benzene, showing them to be thermodynamically consistent. The propanenitrile + heptane system shows an azeotrope at nearly equimolar composition, $x_1 = 0.5092$, and $P = 26788$. The butanenitrile + heptane system shows azeotrope formation at $x_1 = 0.2735$ and $P = 18593$. The propanenitrile + benzene system presents an azeotrope in the range of dilute nitrile solutions ($x_1 = 0.0397$ and $P = 29923$) (Figure 2).

The calculated molar excess Gibbs energies of all the mixtures are positive but considerably larger in the case of nitrile + alkane than in the case of the corresponding nitrile + benzene, suggesting the existence of strong specific nitrile–aromatic π system interactions. This is further supported by the V^E values (Figure 1) which are positive for nitrile + alkane mixtures and negative for nitrile + benzene mixtures.

Literature Cited

Berro, C.; Rogalski, M.; Peneloux, A. A new ebulliometric technique vapour-liquid equilibria in the binary systems ethanol – n-heptane and ethanol – n-nonane. *Fluid Phase Equilib.* **1982**, *8*, 55–73.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor - liquid equilibria using UNIFAC*; Elsevier: Amsterdam, 1977.

Kikic, I.; Alessi, P.; Gozzi, P.; Lapasin, R. L.; De Santis, R. Excess Free Energy for Mixtures Containing Nitriles. *J. Chem. Eng. Data* **1980**, *25*, 33–36.

Muñoz Embid, J.; Artal, M.; Fernández, J.; Velasco, I.; Otín, S. Excess Enthalpies of α,ω-Dibromoalkane + *n*-Hexane Mixtures at 298.15 K and Isothermal Vapor–Liquid Equilibrium of 1,3-Dibromopropane to *n*-Nonane at 348.15 K. *J. Chem. Eng. Data* **1991**, *36*, 428–430.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1986.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; John Wiley & Sons: New York, 1986.

TRC Thermodynamic Tables. Non-Hydrocarbons; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1994.

Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J.* **1974**, *20*, 263–272.

Tsonopoulos, C. Second Virial Coefficients of Polar Chloroalkanes. *AIChE J.* **1975**, *21*, 827–829.

Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor - liquid equilibrium. I. Appraisal of data reduction methods. *AIChE J.* **1973**, *19*, 238.

Wang, H.; Zheng, G.; Chen, M. Excess molar volumes of (an aliphatic nitrile + an aromatic hydrocarbon) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1993**, *25*, 949–956.

Received for review April 5, 1995. Accepted June 5, 1995.[⊗]

JE950085X

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.