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Excess Free Energy for Mixtures Containing Nitriles†

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Vapor-liquid equilibrium compositions of binary systems containing propionitrile or butyronitrile and a hydrocarbon were determined at 298.15 and 308.15 K. The excess free energies obtained through data reduction were correlated by means of semiempirical equations.

Introduction

Although measurements of thermodynamic properties of mixtures containing less volatile nitriles than acetonitrile have so far received little attention from experimentalists, the study of the effects of the high dipole moments of nitriles on the equilibrium behavior of these solutions seems to be of considerable interest.

Our group has already been concerned with the determination of excess enthalpy[1] and activity coefficients at infinite dilution[2] in the systems hydrocarbon-nitrile. The purpose of the present paper is to determine the excess free energy of binary systems containing a hydrocarbon (toluene, *n*-heptane, or methylcyclohexane) and a nitrile (propionitrile or butyronitrile) from isothermal vapor-liquid equilibrium measurements.

These data are also expected to be useful for reliably extending the tables of group-interaction parameters used in group-contribution methods for the calculation of activity coefficients such as the UNIFAC model.[3]

Experimental Section

Liquid-Vapor Equilibrium Apparatus. The experimental procedure was based on a gas-stripping apparatus first employed by Leroi et al.[4] to obtain activity coefficients at infinite dilution. The apparatus was later adapted by Kikic and Alessi[5] for the determination of liquid-vapor equilibrium data at finite concentrations.

Figure 1 shows the equilibrium cell and the apparatus employed. The mixture to be investigated was placed in the cell (C) kept at constant temperature (T_1) (298.15 or 308.15 K (±0.01 K)).

The cell differs from that proposed by Leroi et al.[4] in having, at its inlet, a spiral (I) for the preheating of the gas and, at the outlet, a series of bulbs (II) which prevent the entrainment of liquid droplets. The entrance of the gas from the bottom of the cell through a porous disk (E) provides the necessary turbulence for the stirring of the liquid.

The direct injection of vapor phase into the gas-liquid chromatographic apparatus allows the compositions of the vapor phase (y) to be obtained; the analysis of liquid phase in the cell gives the composition of the liquid phase at equilibrium (x). The only problem is the correct evaluation of chromatographic correction factors for the liquid and vapor phases.

For the gas-liquid chromatographic analysis, a Carlo Erba chromatograph (Model B) with thermal conductivity detector was employed. The chromatographic column (2 m long, 4 mm i.d.) was filled with silanized Chromosorb W 60/80 covered with PEG 1500 (10%). The temperature of the oven varied in the range 318-343 K according to the systems investigated.

Table I. Vapor-Liquid Equilibrium Data at 298.15 and 308.15 K for the System *n*-Heptane-Propionitrile

298.15 K		308.15 K	
x_1	y_1	x_1	y_1
0.026	0.241	0.023	0.186
0.027	0.229	0.024	0.175
0.046	0.299	0.073	0.348
0.105	0.420	0.123	0.436
0.248	0.485	0.159	0.450
0.307	0.478	0.203	0.480
0.363	0.485	0.266	0.495
0.398	0.498	0.375	0.500
0.509	0.524	0.455	0.514
0.689	0.545	0.606	0.517
0.793	0.528	0.629	0.513
0.904	0.595	0.754	0.523
0.976	0.745	0.902	0.632
		0.924	0.609
		0.973	0.769

Table II. Vapor-Liquid Equilibrium Data at 298.15 and 308.15 K for the System Toluene-Propionitrile

298.15 K		308.15 K	
x_1	y_1	x_1	y_1
0.047	0.065	0.026	0.041
0.107	0.125	0.117	0.130
0.159	0.162	0.209	0.200
0.212	0.203	0.254	0.220
0.267	0.235	0.327	0.267
0.338	0.284	0.425	0.330
0.437	0.347	0.547	0.424
0.533	0.402	0.739	0.574
0.726	0.559	0.826	0.662
0.824	0.627	0.878	0.720
0.913	0.759	0.951	0.845
0.972	0.893	0.960	0.849

Table III. Vapor-Liquid Equilibrium Data at 298.15 K for the System *n*-Heptane-Butyronitrile

x_1	y_1	x_1	y_1
0.026	0.232	0.499	0.701
0.055	0.360	0.623	0.744
0.093	0.443	0.709	0.769
0.116	0.479	0.739	0.773
0.168	0.543	0.852	0.781
0.237	0.597	0.912	0.820
0.369	0.662	0.943	0.822
0.475	0.689		

Materials. The hydrocarbons obtained from Fluka were 99.0 mol % purity. These were used as such without any further purification.

Propionitrile and butyronitrile, obtained from Fluka, were purified in a laboratory distillation column by discarding the first 10% distillate and the last 10% residue. After this treatment the nitriles were maintained dried with anhydrous magnesium sulfate.

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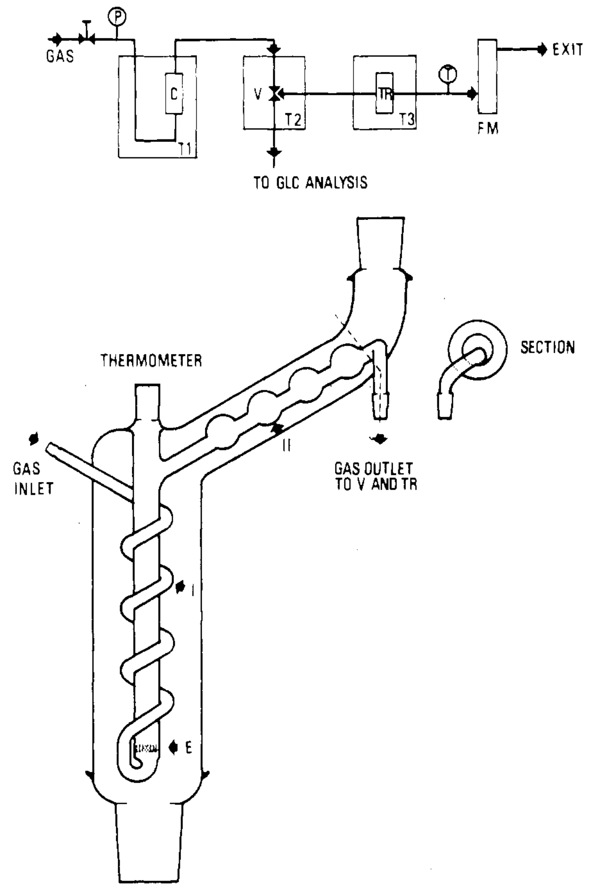

Figure 1. Experimental apparatus.

Table IV. Vapor-Liquid Equilibrium Data at 298.15 K for the System Toluene-Butyronitrile

x_1	y_1	x_1	y_1
0.029	0.072	0.670	0.729
0.075	0.164	0.728	0.772
0.147	0.278	0.756	0.792
0.260	0.412	0.848	0.857
0.375	0.498	0.914	0.902
0.527	0.626	0.956	0.937
0.608	0.691		

Table V. Vapor-Liquid Equilibrium Data for the System Methylcyclohexane-Propionitrile at 298.15 K

x_1	y_1	x_1	y_1
0.083	0.145	0.577	0.309
0.176	0.210	0.668	0.323
0.281	0.262	0.772	0.373
0.370	0.285	0.961	0.715
0.474	0.306		

For both solvents and hydrocarbons, no impurity was detected by gas-liquid chromatographic analysis.

Experimental Results and Discussion

Tables I-VI report the experimental vapor-liquid equilibrium data obtained at 298.15 and 308.15 K for two systems (*n*-heptane-propionitrile and toluene-propionitrile) and at 298.15 K for four other systems (*n*-heptane-butyronitrile, toluene-butyronitrile, methylcyclohexane-propionitrile, and methylcyclohexane-butyronitrile).

The reproducibility of vapor-phase composition measurements was generally lower than 1% and that of liquid-phase composition measurements lower than 0.5%.

All the systems showed the presence of an azeotrope; the behavior of the system hydrocarbon-propionitrile at 298.15 K is reported, as an example, in Figure 2.

Table VI. Vapor-Liquid Equilibrium Data at 298.15 K for the System Methylcyclohexane-Butyronitrile

x_1	y_1	x_1	y_1
0.099	0.271	0.486	0.458
0.193	0.350	0.699	0.615
0.287	0.351	0.841	0.753
0.406	0.381		

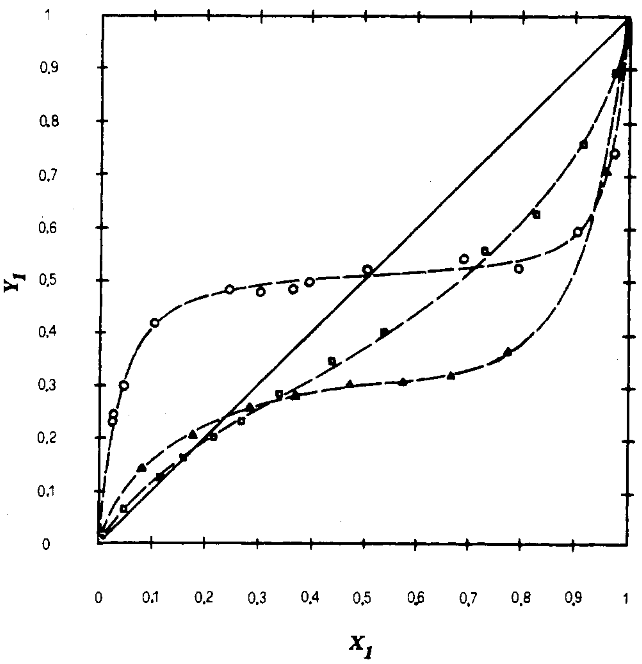

Figure 2. Equilibrium data at 298.15 K: (○) *n*-heptane-propionitrile, (△) methylcyclohexane-propionitrile, (□) toluene-propionitrile.

Data Reduction

Vapor-liquid data reduction allows estimating the excess free energy of solution. The equilibrium equations are

$$Py_1 = \gamma_1 x_1 P_{s1} \qquad (1)$$

$$Py_2 = \gamma_2 x_2 P_{s2} \qquad (2)$$

In these relationships, the pressure dependence of the pure liquid reference fugacity was neglected and the fugacity coefficients in the vapor phase were assumed to be unitary. These simplifications are justified by the low pressures of the systems.

The semiempirical models of Wilson[6] and Abrams-Prausnitz[7] (UNIQUAC) were used to calculate activity coefficients which are the partial molar quantities of the excess free energy. To this end, the two adjustable parameters of the Wilson and UNIQUAC equations were obtained by minimizing, with the simplex method, the objective function

$$\sum_i (y_{i(\text{exptl})} - y_{i(\text{calcd})})^2 \qquad (3)$$

where

$$y_{i(\text{calcd})} = \frac{\gamma_i x_i P_s}{\gamma_1 x_1 P_{s1} + \gamma_2 x_2 P_{s2}} \qquad (4)$$

Vapor pressures of pure components were calculated by the Antoine equation, whose constants were taken from the compilation of Reid et al.[8]

The numerical values of the constants, the absolute average deviations, and mean standard deviations of vapor-phase compositions for all the systems studied are reported in Table VII.

The agreement between the two models is quite good; both equations correlate data with similar deviations.

It is possible to calculate the excess free energies according to the Wilson and UNIQUAC models with the parameters given in Table VII.

Table VII. Parameters of Wilson and UNIQUAC Equations for the Systems Investigated[a]

		Wilson model				UNIQUAC model			
system[b]	T, K	Λ_{12}	Λ_{21}	$10^{-2}\lvert\overline{\Delta y}\rvert$	$10^{-6}\sigma$	τ_{12}	τ_{21}	$10^{-2}\lvert\overline{\Delta y}\rvert$	$10^{-6}\sigma$
nC$_7$-PPN	298.15	0.033	0.139	1.020	179.65	0.293	1.097	2.902	1458.09
nC$_7$-PPN	308.15	0.041	0.174	1.249	260.36	0.277	1.158	1.801	535.33
Me-c-C$_6$-PPN	298.15	0.164	0.306	3.112	1621.14	0.538	0.897	0.825	122.71
T-PPN	298.15	0.468	0.645	1.235	245.13	0.456	1.416	0.702	98.93
T-PPN	308.15	0.525	0.669	1.175	286.88	0.413	1.534	1.119	194.35
nC$_7$-BTN	298.15	0.116	0.200	2.004	565.19	0.344	1.344	2.413	838.64
Me-c-C$_6$-BTN	298.15	0.385	0.337	5.823	6211.21	1.594	0.291	1.085	246.82
T-BTN	298.15	0.577	0.828	0.967	180.36	0.405	1.644	1.189	207.77

[a] The absolute average deviations and the mean standard deviations are relative to vapor-phase compositions. [b] Key: nC$_7$ = n-heptane, Me-c-C$_6$ = methylcyclohexane, T = toluene, PPN = propionitrile, BTN = butyronitrile.

Table VIII. Free Energy Average Deviations

		av dev	
system[a]	T, K	Wilson model	UNIQUAC model
nC$_7$-PPN	298.15	0.048 516 7	0.016 077 5
nC$_7$-PPN	308.15	0.036 114 8	0.011 419
Me-c-C$_6$-PPN	298.15	0.103 448	0.051 204 6
T-PPN	298.15	0.024 098 5	0.025 126
T-PPN	308.15	0.017 718 8	0.028 663 7
nC$_7$-BTN	298.15	0.093 851 7	0.016 501 2
Me-c-C$_6$-BTN	298.15	0.078 297 5	0.008 855 63
T-BTN	298.15	0.013 340 6	0.008 001 06

[a] See footnote b on Table VII for key to abbreviations.

Figure 3 reports the free energies at 298.15 K for the system methylcyclohexane–butyronitrile which showed the best agreement between experimental (obtained by fitting the experimental ln γ_1/γ_2 data through a polynomial of the fourth degree) and UNIQUAC data.

Table VIII gives the average deviations for all the systems studied.

The UNIQUAC equation, in this case, correlates the data better than the Wilson equation; in almost all cases there are more than 50% differences.

With regard to the comparison with the heat of mixing data, the agreement is only qualitative, as was to be expected because of the very slight difference between the two temperatures studied.

The activity coefficients at infinite dilution predicted through the UNIQUAC equation are closer to those obtained by liquid–liquid chromatography.[2]

The comparison is shown in Table IX.

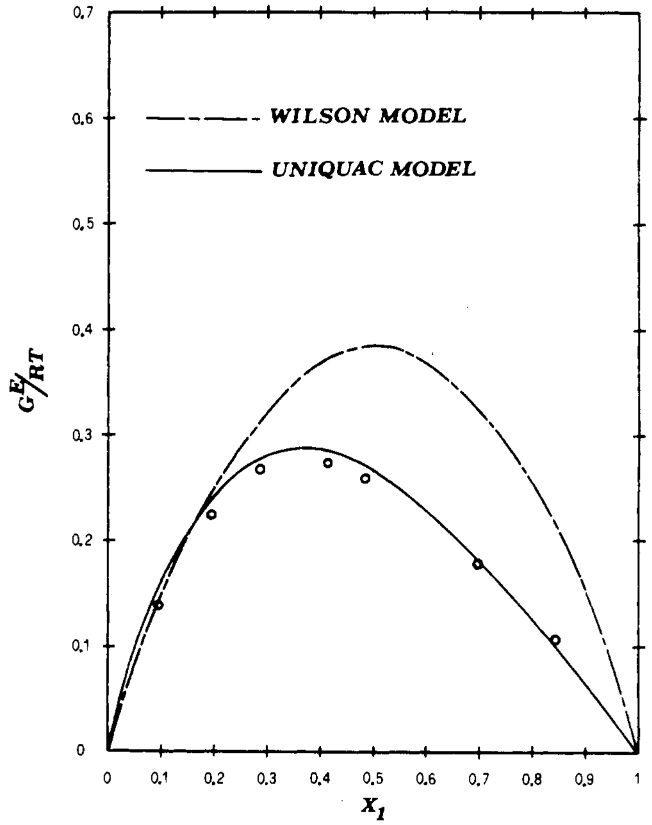

Figure 3. Excess free energy vs. liquid molar fraction at 298.15 K for the system methylcyclohexane–butyronitrile (O, experimental values).

Table IX. Comparison between Activity Coefficients at Infinite Dilution Determined by Liquid–Liquid Chromatography[2] and Those Evaluated with Wilson and UNIQUAC Models

			ln γ_1^∞	
system[a]	T, K	(ln $\gamma_1^\infty)_{\text{exptl}}$[b]	Wilson	UNIQUAC
nC$_7$-PPN	298.15	2.50	4.272	2.401
MC$_y$C$_6$-PPN	298.15	2.30	2.502	1.909
T-PPN	298.15	0.51	1.114	0.679
nC$_7$-BTN	298.15	1.95	2.954	1.458
MC$_y$C$_6$-BTN	298.15	1.78	1.618	2.165
T-BTN	298.15	0.42	0.722	0.424

[a] See footnote b on Table VII for key to abbreviations. [b] From ref 2.

Appendix

The Wilson equation for the excess free energy of binary mixtures is

$$G^E/RT = -x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (x_2 + \Lambda_{21}x_1) \quad (5)$$

where Λ_{12} and Λ_{21} are adjustable parameters.

The UNIQUAC equation is

$$G^E/RT = x_1 \ln (\phi_1/x_1) + x_2 \ln (\phi_2/x_2) + (z/2)\left(q_1x_1 \ln \frac{\theta_1}{\phi_1} + q_2x_2 \ln \frac{\theta_2}{\phi_2}\right) - q_1x_1 \ln (\theta_1 + \theta_2\tau_{21}) - q_2x_2 \ln (\theta_2 + \theta_1\tau_{12}) \quad (6)$$

$$\phi_1 = \frac{x_1r_1}{x_1r_1 + x_2r_2} \qquad \phi_2 = 1 - \phi_1 \quad (7)$$

$$\theta_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2} \qquad \theta_2 = 1 - \theta_1 \quad (8)$$

where τ_{12} and τ_{21} are adjustable parameters. Pure component parameters "r" and "q" have the following values: n-heptane r = 5.1742, q = 4.396; methylcyclohexane r = 4.0464, q = 3.24; toluene r = 3.9228, q = 2.968; propionitrile r = 2.5445, q = 2.264; butyronitrile r = 3.2189, q = 2.804. The coordination number "z" was assumed equal to 10.

Glossary

G^E	excess free energy
P	pressure

P_s	vapor pressure
q	pure-component area parameter
r	pure-component volume parameter
R	gas constant
T	temperature in Kelvin degrees
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
$\lvert\overline{\Delta y}\rvert$	absolute average deviation of vapor-phase composition
z	coordination number

Greek Letters

γ	activity coefficient
ϕ	segment fraction
Λ	parameter of Wilson equation
σ	mean standard deviation
τ	parameter of UNIQUAC equation
θ	area fraction

Subscripts

1	hydrocarbons
2	nitriles
i	index
exptl	experimental values
calcd	calculated values
W	value calculated with Wilson equation
U	value calculated with UNIQUAC equation

Exponent

∞	infinite dilution

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Density, Viscosity, and Surface Tension of Mixed Molten Hydrates.
2. Mixtures of Zinc Nitrate and Nickel Nitrate Hexahydrates

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Densities, viscosities, and surface tensions of mixtures containing $Zn(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ have been measured as a function of temperature and composition. The equivalent volume–composition and fluidity–composition isotherms were linear but the surface tension–composition isotherms exhibited appreciable negative deviations from the additive values, the deviations being the maximum around equimolar composition. The fluidity data were fitted to the equations $\phi = A_\phi T^{-1/2} \exp[-B_\phi/(T - T_{0,\phi})]$ and $\phi = A_\phi' \exp[-B_\phi'/(V - V_{0,\phi})]$ based upon the free volume model; A_ϕ, B_ϕ, $T_{0,\phi}$, A_ϕ', B_ϕ', and $V_{0,\phi}$ are empirical parameters. Composition dependences of these parameters have been discussed.

Introduction

Recently, quite a few reports concerning the physicochemical studies of hydrated melts in pure and mixed states have been published (*3*, *14*, *16–19*). Moynihan et al. (*21*) has shown that the system containing the molten tetrahydrates of calcium and cadmium nitrates behaves nearly ideal above 60 °C but considerable negative deviations in conductance and fluidity isotherms are observed at lower temperatures. A nonideal character of mixing the molten hydrates is also apparent from the studies of the system $Cr(NO_3)_3{\cdot}9H_2O + (Ca,Cd)(NO_3)_2{\cdot}4H_2O$ (*19*).

In order to examine whether such nonideal behavior is related to the polarizability, charge type, and/or the nature of the hydration sphere of the two constituent cations, we selected the present system containing the cations of the same charge to radius ratio and having a similar hydration sphere. The present paper thus presents some of the observations on the system containing the molten hydrates of zinc and nickel nitrate hexahydrate.

Experimental Section

Hexahydrates of nickel nitrate (BDH) and zinc nitrate (S. Merck) were of LR grade purity. The melting temperatures of these salts as determined by the cooling curve method were 56.8 and 36.8 °C for the nickel and zinc salt, respectively, with corresponding literature (*26*) values being 56.7 and 37 °C. An agreement between the measured melting temperatures and the literature melting temperatures leads one to believe that the salts were of the stoichiometry as given by the manufacturers. This was verified for zinc nitrate hexahydrate by an EDTA titration (*24*) and for nickel nitrate hexahydrate by a gravimetric (*24*) method by precipitating Ni^{2+} as dimethylglyoxime. Repeated cross checks gave the water content to be within ±0.02 of the stoichiometric value of six.

Mixtures were prepared by melting the requisite amounts of the salts in Pyrex glass flasks (ca. 100 cm^3) fitted with a airtight ground glass joint at the top and filtered in situ through glass filters (porosity G-3) under a slight positive pressure of dry, CO_2-free air. Filtered melts were then maintained at about 60–70 °C for about 1 h, for maturing.

Densities were measured by measuring the volumes of a certain amount of melt in a precalibrated densitometer capable of reading up to 0.01 cm^3. The details regarding the design and calibration of the densitometer and the measuring technique have been described earlier (*16*, *17*). Estimated accuracy of experimental densities is ±0.1%.

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