The *infinite-line-charge* theory (*20*) gives the dependence of ϕ_v on ln *c* at extreme (but not infinite) dilution

$$(d\phi_v/d \ln c) = (\alpha z_p V_m/2 z_c \lambda)(d \ln \epsilon/d \ln P) = 0.429 \text{ mL mol}^{-1} \quad (11)$$

It can be demonstrated that eq 10 will approximate eq 11 in the limit of extremely small values of *c*. The value of $(d\phi_v/d \log c)$ for vinyl type strong polyelectrolytes ($\alpha = 1$, $z_p = z_c = 1$) with λ 2.832 is 0.429 mL mol^{-1}. The apparent molar volumes of NaPSS appear to approach the curve computed from eq 10 for concentrations at and below $c = 0.012$ monomolar. Deviations from cell theory predictions at and above these concentrations also have been observed in measurements of the heats of dilution of NaPSS (*5*, *21*) and presumably reflect polyion-polyion interactions. The theory shows the need for density measurements to at least 0.1 ppm, or better than ten times more sensitive than can be attained by the vibrating tube densitometer used in this research.

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Isobaric Binary Vapor–Liquid Equilibria Systems Acetonitrile–Ethylbenzene and Acetonitrile–*p*-Xylene

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Isobaric vapor–liquid equilibrium data for the wide boiling systems acetonitrile–ethylbenzene and acetonitrile–*p*-xylene were obtained at 760 mmHg pressure using a vapor recirculating type of equilibrium still. The *t–x–y* data for these systems were tested for thermodynamic consistency and correlated by the Wilson equation.

Isobaric vapor–liquid equilibrium data, which forms part of a program on the evaluation of nonideality characteristics for mixtures of C_8 aromatics and other types of compounds, were obtained for the systems acetonitrile–ethylbenzene and acetonitrile–*p*-xylene at 760 ± 2 mmHg pressure using a vapor recirculating type of equilibrium still. These systems have boiling ranges of 56.6 and 56.8 °C, respectively. Experimental data for these systems have not been reported in literature. The system acetonitrile–ethylbenzene did not form any azeotrope which confirms the observations made by Horsley (*4*). The system acetonitrile–*p*-xylene also did not form any azeotrope. Horsley has reported (*4*) the system acetonitrile–mixed xylenes as nonazeotropic.

Experimental Section

Analytical Techniques. Ethylbenzene from British Drug Houses, England, acetonitrile from British Drug Houses Ltd., India, and *p*-xylene from Riedel, Germany, were dried using suitable drying agents and then further purified by distillation in a glass column described elsewhere (*14*). Table I summarizes some of the physical properties of the compounds employed.

A modified version of the equilibrium still described by Rao and co-workers (*12*) was used for obtaining the vapor–liquid equilibrium data. The equilibrated mixtures were analyzed by the refractive index method using a Bausch and Lomb Abbe-3L refractometer. The apparatus, modifications, and analytical techniques have already been described (*14*). The estimated uncertainities in the measurements were composition, 0.002 mole fraction, temperature, 0.1 °C, and pressure, ±2.0 mmHg. Table II gives the refractive index–composition data. Figures 1 and 2 represent the boiling point–composition diagrams for the two systems acetonitrile–ethylbenzene and acetonitrile–*p*-xylene.

Results and Discussion

The liquid-phase activity coefficients were estimated from the experimental data taking into consideration the nonideality of the vapor phase employing the following equation (*1*, *6*)

$$\gamma_i = \pi y_i/P^0_i x_i \exp[(\pi - P^0_i)(B_i - V_i)/RT]$$

Table III gives the correlations used for the estimation of pure component vapor pressures, second virial coefficients, and liquid molar volumes. These correlations gave close fit (*8*) with the experimental pure component data from the literature.

Table I. Physical Properties of Pure Compounds

		Ethylbenzene	*p*-Xylene	Acetonitrile
Normal bp, °C	Exptl	136.20	138.40	81.60
	Lit. (*5*, *15*)	136.19	138.40	81.60
Refractive index	Exptl	$1.4910^{30°C}$	$1.4908^{30°C}$	$1.3385^{30°C}$
	Lit. (*15*)	$1.4905^{30°C}$	$1.4905^{30°C}$	$1.3415^{25°C}$
Density, $d_4{}^t$	Exptl	$0.8497^{35°C}$	$0.8433^{35°C}$	$0.7707^{30°C}$
	Lit. (*15*)	$0.8583^{30°C}$	$0.8523^{30°C}$	$0.7766^{25°C}$

Table II. Refractive Index-Composition Data at 30 ± 0.1 °C

Acetonitrile (1)-ethylbenzene (2) Mole fraction acetonitrile	Acetonitrile (1)-ethylbenzene (2) Refractive index	Acetonitrile (1)-*p*-xylene (2) Mole fraction acetonitrile	Acetonitrile (1)-*p*-xylene (2) Refractive index
0.0000	1.4910	0.0000	1.4908
0.0873	1.4855	0.0441	1.4880
0.1284	1.4820	0.0885	1.4850
0.1777	1.4790	0.0889	1.4860
0.2430	1.4740	0.1332	1.4825
0.3033	1.4690	0.2093	1.4753
0.3740	1.4620	0.2110	1.4750
0.4732	1.4491	0.2466	1.4725
0.5292	1.4425	0.2922	1.4688
0.5796	1.4350	0.3738	1.4600
0.6094	1.4300	0.4488	1.4530
0.6992	1.4145	0.5045	1.4455
0.7756	1.4000	0.6104	1.4300
10.8235	1.3890	0.6580	1.4238
0.8473	1.3840	0.6991	1.4149
0.8971	1.3705	0.7567	1.4045
0.9159	1.3655	0.7885	1.3965
0.9450	1.3570	0.8456	1.3832
0.9512	1.3555	0.8730	1.3771
0.9668	1.3505	0.9296	1.3606
0.9875	1.3435	0.9545	1.3529
1.0000	1.3385	0.9779	1.3460
		1.0000	1.3385

Table III. Correlations Used for the Estimation of Pure Component Properties

Component	Temp range, °C	Correlation	Constants
	For Vapor Pressures		
Acetonitrile	80–138	Erpenbeck-Miller EB2 (*7*)	$C_b = 0.66455^a$
			$B = 5.38525^a$
Ethylbenzene	80–138	EB2 (*7*)	$C_b = 0.68802^a$
			$B = 5.68734^a$
p-Xylene	80–138	EB2 (*7*)	$C_b = 0.68897^a$
			$B = 5.67737^a$
	For Second Virial Coefficients		
Acetonitrile	82–138	Black (*2*)	$A = 0.396$
			$B = 1.181$
			$C = 0.864$
			$D = 0.384$
			$E = 0.141$
			$m = 4.75$
Ethylbenzene	78–154	Pitzer and Curl (*10*)	
p-Xylene	78–154	Pitzer and Curl (*10*)	
	For Liquid Molar Volumes		
Acetonitrile	58–138	Surface tension (*3*)	
Ethylbenzene	78–154	Surface tension (*3*)	
p-Xylene	78–151	Surface tension (*3*)	

[a] Calculated.

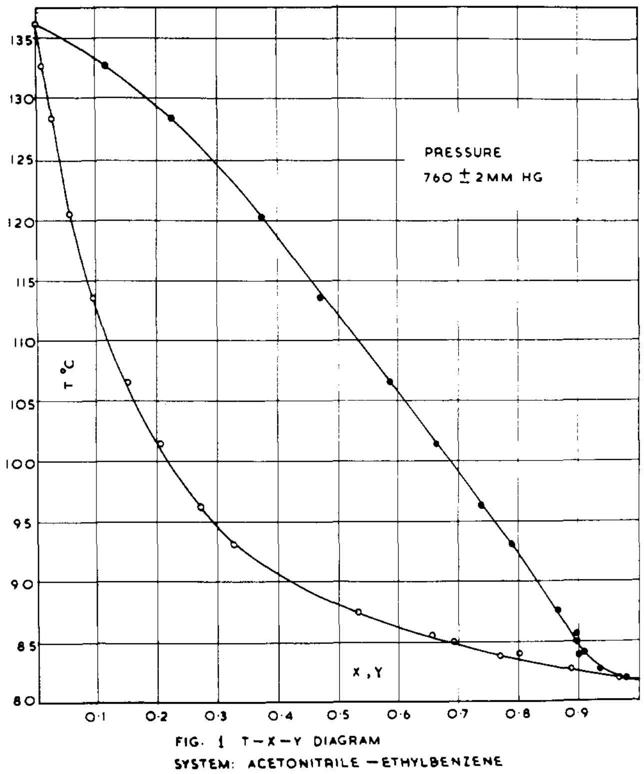

Figure 1. Boiling point-composition diagram for the acetonitrile–ethylbenzene system.

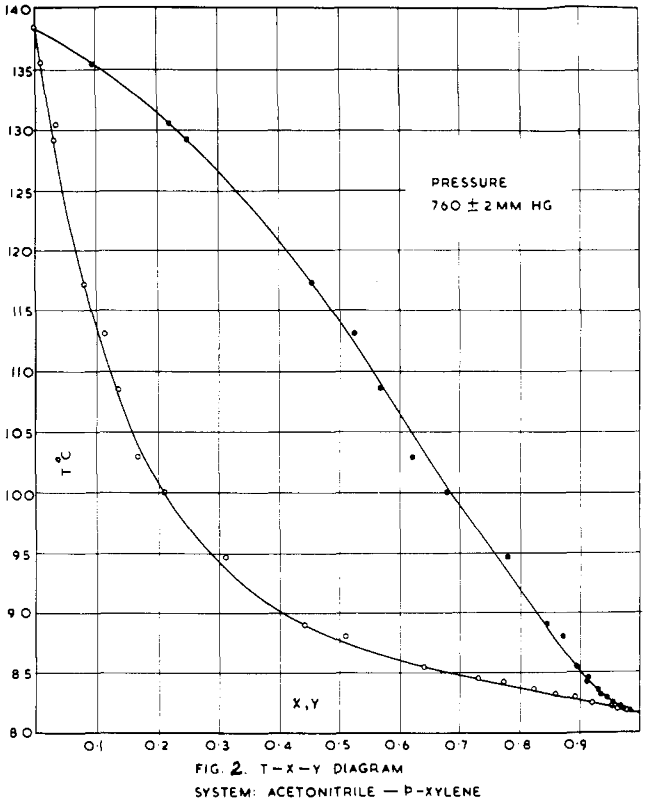

Figure 2. Boiling point-composition diagram for the acetonitrile–*p*-xylene system.

Table IV gives the experimental *t-x-y* data, vapor-phase imperfection coefficients, and activity coefficients.

The data for both the systems were assessed for thermodynamic consistency by applying the Redlich-Kister area test (*13*). The area difference in both systems was less than 4%. Moreover, the following criterion given by Prausnitz (*11*) was satisfied in both cases.

$$0.02 > \frac{(\text{area above } X \text{ axis}) - (\text{area below } X \text{ axis})}{(\text{area above } X \text{ axis}) + (\text{area below } X \text{ axis})}$$

The computed value of the right-hand side is 0.018 and 0.0018 for acetonitrile–ethylbenzene and acetonitrile–*p*-xylene systems, respectively. Considering the wide boiling range of the systems and the highly polar nature of acetonitrile, the data can be considered thermodynamically consistent.

The activity coefficient data were fitted into the Wilson correlation (*9*) which gave good fit of the data. The average deviations of the calculated compositions from the experimental

Table IV. Vapor-Liquid Equilibrium Data at 760 ± 1 mmHg Pressure

t, °C	x_1	y_1	y_1(calcd)[a]	Z_1	Z_2	γ_1	γ_2
		System Acetonitrile (1)-Ethylbenzene (2)					
132.75	0.0100	0.1150	0.096	1.108	0.996	3.741	0.978
128.50	0.0250	0.2250	0.215	1.101	0.991	3.158	0.973
120.53	0.0550	0.3725	0.383	1.087	0.982	2.761	1.014
113.62	0.0925	0.4700	0.522	1.073	0.975	2.380	1.091
106.50	0.1500	0.5850	0.654	1.058	0.967	2.127	1.135
101.50	0.2050	0.6600	0.726	1.047	0.962	1.965	1.167
96.25	0.2700	0.7350	0.761	1.035	0.956	1.879	1.179
93.08	0.3250	0.7850	0.781	1.028	0.953	1.800	1.152
87.50	0.5300	0.8650	0.848	1.015	0.947	1.399	1.265
85.59	0.6525	0.8950	0.876	1.010	0.945	1.235	1.425
85.00	0.6900	0.8950	0.883	1.008	0.945	1.186	1.632
83.77	0.7650	0.8975	0.916	1.005	0.943	1.108	2.199
84.00	0.7975	0.9050	0.892	1.006	0.944	1.066	2.345
82.70	0.8850	0.9325	0.935	1.003	0.942	1.024	3.078
81.75	0.9700	0.9780	0.975	1.000	0.941	1.005	3.984
		System Acetonitrile (1)-*p*-Xylene (2)					
135.50	0.0100	0.0950		1.113	0.996	2.948	0.985
129.25	0.0300	0.2500	0.225	1.102	0.989	2.884	0.981
130.50	0.0325	0.2175	0.248	1.104	0.990	2.265	0.992
117.50	0.0800	0.4550	0.446	1.081	0.975	2.461	1.044
113.10	0.1125	0.5250	0.548	1.072	0.970	2.210	1.075
108.64	0.1350	0.5700	0.579	1.063	0.964	2.198	1.144
102.95	0.1675	0.6200	0.606	1.051	0.958	2.185	1.258
100.00	0.2100	0.6800	0.671	1.044	0.955	2.046	1.229
94.59	0.3125	0.7780	0.771	1.032	0.949	1.788	1.175
88.90	0.4425	0.8450	0.813	1.018	0.942	1.580	1.233
88.00	0.5100	0.8720	0.851	1.016	0.941	1.447	1.197
85.50	0.6400	0.8950	0.879	1.010	0.938	1.262	1.462
84.50	0.7300	0.9150	0.903	1.007	0.937	1.162	1.637
84.24	0.7725	0.9125	0.918	1.007	0.937	1.102	2.019
83.50	0.8225	0.9300	0.926	1.005	0.936	1.076	2.127
83.08	0.8575	0.9350	0.934	1.004	0.936	1.049	2.499
82.82	0.8800	0.9440	0.941	1.003	0.935	1.039	2.581
82.43	0.9210	0.9550	0.957	1.002	0.935	1.015	3.196
82.11	0.9525	0.9675	0.971	1.001	0.935	1.003	3.885
81.91	0.9625	0.9725	0.973	1.001	0.934	1.003	4.195
81.81	0.9775	0.9825	0.984	1.000	0.934	1.000	4.466

[a] Calculated from the Wilson equation.

Table V. Average Deviations and Correlation Constants

System	Λ_{12}	Λ_{21}	Av abs error[a]		
			γ_1	γ_2	y_1
Acetonitrile-ethylbenzene	0.6212	0.3184	0.046	0.062	0.046
Acetonitrile-*p*-xylene	0.7823	0.2473	0.024	0.060	0.024

[a] Error = (exptl − calcd)/exptl.

values and the constants in this correlation are given in Table V.

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Glossary

B	gas-phase second virial coefficient, cm^3 mol^{-1}
P^0	pure component vapor pressure, mmHg
R	gas constant
T	absolute temperature, K
t	system temperature, °C
V	pure component liquid molar volume, cm^3 mol^{-1}
x	mole fraction in liquid phase
y	mole fraction in vapor phase
Z	vapor-phase imperfection coefficient
γ	activity coefficient
π	system pressure

Subscript

1	more volatile component
2	less volatile component
calcd	calculated
exptl	experimental

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