no liquid phase was observed when $C_0 < 10^{-6}$ mole fraction.

Acknowledgment

I am grateful to Prof. Bjørn Pedersen, Department of Chemistry, University of Oslo, and to Dr. Dag Slotfeldt-Ellingsen, Senter for Industriforskning (Oslo), for their valuable suggestions and support in the preparation of this manuscript.

Registry No. HCl, 7647-01-0.

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Received for review October 1, 1986. Accepted August 10, 1987.

Thermodynamic Properties of Binary Acid–Base Mixtures

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Densities and viscosities at 308.15 K were determined for the systems propionic acid (PA) + aniline (A), + *N*-methylaniline (MA), and + *N*-ethylaniline (EA). From the experimental results, the excess molar volumes, excess viscosities, and excess molar free energy of activation of flow were calculated. The results are discussed in terms of theories of nonelectrolyte solutions. Deviations from ideal behavior are more pronounced for the system PA + A than for the systems PA + MA and PA + EA. The results suggest complex formation between the components in all the systems in the mole ratio 2:1 (PA:anilines) approximately.

Very few studies (*1–3*) on properties such as viscosities, densities, and refractive indices of nonelectrolyte acid–base binary liquid mixtures have been reported. We have therefore taken up such studies as a continuation of our studies (*4*, *5*) on properties of nonelectrolytes.

The results obtained for the systems propionic acid (PA) + aniline (A), + *N*-methylaniline (MA), and + *N*-ethylaniline (EA) are reported in this paper.

Densities and viscosities of the systems mentioned were measured at 308.15 K. Excess functions V^E (excess molar volume), η^E (excess viscosity), and G^{*E} (excess molar free energy of activation of flow) were calculated from the experimental results at different mole fractions. The values obtained are discussed in terms of nonelectrolytic interactions.

Experimental Section

Densities were measured with a 18-mL bicapillary pycnometer having a capillary diameter of 0.85 mm. The pycnometer was calibrated by using double distilled water (density 994.06 kg m^{-3} at 308.15 K). All weighings were done on a Mettler balance (±0.05 mg). The necessary buoyancy correction was applied. The density values were reproducible within ±0.2 kg m^{-3}. A thermostatically controlled water bath, capable of maintaining the temperature constant to ±0.02 K, was used in the studies.

Table I. Physical Properties of the Liquids Investigated at 308.15 K

liquid	density, kg m^{-3} this work	density, kg m^{-3} lit.[a]	viscosity, kg m^{-1} s^{-1} × 10^4 this work	viscosity, kg m^{-1} s^{-1} × 10^4 lit.[a]
propionic acid	978.2	978.0	8.894	8.885
aniline	1008.8	1008.9	26.153	26.630
N-methylaniline	973.9	973.6	15.146	15.470
N-ethylaniline	948.5	948.4	14.999	15.490

[a] Reference 7.

Viscosities of the pure liquids and the liquid mixtures were detd. with a modified Ostwald viscometer. The time of efflux of a constant volume of liquid through the capillary was measured with the help of a precalibrated ROCAR stop watch capable of recording ±0.1 s. The viscometer was always kept in a vertical position in a water thermostat at 308.15 ± 0.02 K. The efflux time for water at 308.15 K was about 302 s. The flow time was maintained at deliberately high value to minimize the kinetic energy corrections.

The viscosity was calculated from the average efflux time, t, and density, ρ, according to

$$\eta/\rho = at - b/t \qquad (1)$$

where a and b are the characteristic constants of the viscometer. The constants were determined by taking water and benzene as the calibrating liquids and used to calculate the kinetic energy correction. The corrections were found to be negligible. The viscosity measurements were accurate to ±0.5 × 10^{-4} kg m^{-1} s^{-1}.

Propionic acid (from Fluka, puriss grade, purity ≫ 99 mol % $C_2H_5CO_2H$) was dried over anhydrous sodium sulfate and fractionally distilled. The fraction distilling at 412.15–415.15 K was collected and refractionated over potassium permanganate. The middle fraction distilling at 413.85 K and 760 mm was collected.

Each of aniline, *N*-methylaniline, and *N*-ethylaniline was distilled twice over zinc dust and over anhydrous Na_2SO_4 at reduced pressure. The middle half of each of two distillations (*6*) (colorless liquid) was recovered. Water distilled twice in the presence of alkaline permanganate was used in the studies.

Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

Results

The measured densities and viscosities of the pure liquids are presented in Table I together with the literature (*7*) values. The measured and reported values are in reasonable agreement.

The molar volume (V) of the solution was obtained from the equation

$$V = (X_1M_1 + X_2M_2)/\rho \qquad (2)$$

where M_1 and M_2 are molecular masses of the pure components 1 and 2 and X_1 and X_2 are their mole fractions.

Excess properties (*8*) Y^E are calculated by using the equation

$$Y^E = Y - (X_1Y_1 + X_2Y_2) \qquad (3)$$

where Y, Y_1, and Y_2 are the specific properties of the mixture and of the pure components 1 and 2, respectively.

Excess molar free energy of activation of flow, G^{*E}, was calculated from the equation

$$G^{*E} = RT \ln \eta V - (X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2) \qquad (4)$$

where η and V are viscosity and molar volume, respectively, of the mixtures; η_1, η_2 and V_1, V_2 are the viscosities and molar volumes of the pure components 1 and 2, respectively, R is the gas constant, and T is the absolute temperature.

Discussion

In most theories of the behavior of nonelectrolyte solutions the major contribution to the deviation from ideal mixing is attributed to the dispersion forces (*9*). In such theories the deviations are expected to be positive. Negative deviations from ideal behavior in mixtures of molecules differing in size are accounted by geometric considerations (*10*).

The systems under study exhibited a positive maximum in excess viscosities. This behavior is therefore traced to the formation of a complex (*11*) between the components through intermolecular hydrogen bonding. According to Fialkov (*12*), the composition of the complex formed can be fixed, at least to a first approximation, from the mole ratio at the maximum. The results in the present studies indicate complex formation in all the systems in the mole ratio 2:1 approximately (2 propionic acid:1 anilines). The shift in maximum in the different systems bears a parallelism to the relative strength of the intermolecular hydrogen bonding between the components concerned.

A negative value of V^E indicates strong interactions between the components of the mixture. V^E becomes increasingly negative as the strength of interaction between the components increases. The minimum in V^E can be explained by the strength of the base (*13*) involved and the stability of the complex.

The basicity of the anilines decreases in the order EA > MA > A. The results in Table II indicate that the V^E values at minima follow the order A < MA < EA. The observed order for V^E can be therefore explained on the basis of the strength of acid–base interaction.

Table II. Experimental Values of Density (ρ) and Viscosity (η) and the Calculated Values of Excess Viscosity (η^E), Excess Molar Volume (V^E), and Excess Molar Free Energy of Activation of Flow (G^{*E}) for the Binary Mixtures at 308.15 K

X_1[a]	ρ, kg m^{-3}	$10^4\eta$, kg m^{-1} s^{-1}	$10^4\eta^E$, kg m^{-1} s^{-1}	V^E, cm^3 mol^{-1}	G^{*E}, cal mol^{-1}
		Propionic Acid + Aniline			
0.0000	1008.8	26.153	0.000	0.0000	0.00
0.1243	1011.3	29.124	5.116	−0.5125	145.75
0.2382	1014.1	32.031	9.990	−1.0133	276.58
0.3507	1016.9	35.900	15.801	−1.5019	417.66
0.4545	1019.8	39.710	21.402	−1.9694	544.60
0.5568	1022.2	44.675	28.133	−2.3785	680.97
0.6544	1022.9	47.623	32.765	−2.6403	781.92
0.7452	1019.4	41.687	28.396	−2.5648	760.20
0.7903	1015.4	34.023	21.511	−2.3590	666.75
0.8345	1010.8	27.923	16.174	−2.1112	576.43
0.8774	1003.5	20.084	9.074	−1.6674	405.97
0.9180	996.0	15.607	5.299	−1.1977	281.65
0.9595	987.2	11.676	2.083	−0.6316	135.35
1.0000	978.2	8.894	0.000	0.0000	0.00
		Propionic Acid + Methylaniline			
0.0000	973.9	15.146	0.000	0.0000	0.00
0.1405	977.9	16.889	2.621	−0.3874	115.10
0.2649	981.6	18.169	4.679	−0.7171	201.26
0.3831	985.5	19.585	6.834	−1.0329	285.51
0.4886	989.2	20.580	8.489	−1.3116	348.98
0.5912	992.2	21.430	9.981	−1.4899	405.57
0.6846	994.3	21.150	10.285	−1.5899	426.00
0.7714	994.4	19.312	8.989	−1.5136	397.17
0.8525	992.3	16.309	6.493	−1.2672	319.45
0.8913	989.9	14.497	4.923	−1.0390	260.28
0.9291	986.7	12.264	2.926	−0.7606	170.78
0.9645	982.6	10.527	1.411	−0.4138	90.00
1.0000	978.2	8.894	0.000	0.0000	0.00
		Propionic Acid + Ethylaniline			
0.0000	948.5	14.999	0.000	0.0000	0.00
0.1567	955.1	17.056	3.014	−0.4609	136.50
0.2906	960.5	18.971	5.746	−0.7456	249.06
0.4142	968.5	21.672	9.201	−1.2555	370.58
0.5224	974.3	23.015	11.204	−1.4960	441.45
0.6217	981.1	25.331	14.127	−1.7897	529.04
0.7121	986.6	25.750	15.098	−1.9267	564.42
0.7933	989.6	23.786	13.630	−1.8380	545.00
0.8687	989.9	19.156	9.460	−1.5296	427.44
0.9032	988.8	16.906	7.421	−1.2889	361.14
0.9363	986.4	14.119	4.837	−0.9563	261.17
0.9694	982.8	11.130	2.049	−0.5331	126.31
1.0000	978.2	8.894	0.000	0.0000	0.00

[a] Mole fraction of propionic acid.

The values of excess free energy of activation of flow are positive and increase with increase in propionic acid concentration. Reed and Taylor (*15*) and Mayer et al. (*14*) reported that G^{*E} can be considered a reliable criterion to detect or exclude the presence of interaction between unlike molecules. According to these authors, the magnitude of the positive values is an excellent indicator of the strength of specific interactions. G^{*E} values for the systems under study are in the order PA + A > PA + MA > PA + EA.

The properties studied thus indicate that the strength of interaction follows the order PA + A > PA + MA > PA + EA. This trend suggests that intermolecular hydrogen bonding and acid–base interactions play a significant role in the systems investigated.

Glossary

V^E	excess volume, cm^3 mol^{-1}
η^E	excess viscosity, kg m^{-1} s^{-1}
G^{*E}	excess molar free energy of activation of flow, cal mol^{-1}
ρ	density, kg m^{-3}
η	viscosity, kg m^{-1} s^{-1}
V	molar volume of solution
M	molecular mass

X	mole fraction
R	gas constant

Subscripts

1,2	component number in mixtures

Superscript

E	excess

Registry No. PA, 79-09-4; A, 62-53-3; MA, 26915-12-8; EA, 103-69-5.

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Received for review October 15, 1986. Revised July 13, 1987. Accepted November 23, 1987.

Vapor–Liquid Equilibria at 760 mmHg in the Systems Propyl Bromide–*tert*-Butyl Alcohol and Propyl Bromide–*p*-Xylene

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Vapor–liquid equilibria for the title systems have been determined at 760 mmHg. The propyl bromide–*tert*-butyl alcohol system shows positive deviations from ideal behavior and presents a minimum boiling point azeotrope at 68.55 °C with 23.5 mol % propyl bromide. The system propyl bromide–*p*-xylene behaves ideally. The boiling points were well correlated with the composition of the liquid phase.

The present work is part of our program for determining VLE data for organic systems in which one of the components is a bromide.

Experimental Section

Purity of Materials. Propyl bromide (99.6+%) was supplied by Bromine Compounds Ltd., Beer-Sheva, and analytical grade *tert*-butyl alcohol (99.5%+) and *p*-xylene (99.3%+) were purchased from Merck. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities. Properties of the components appear in Table I.

Table I. Physical Properties of Pure Components

propyl bromide	refract. index (25 °C)	normal bp, °C
propyl bromide	1.4300[a]	70.55[a]
	1.4302[b]	70.80[c]
tert-butyl alcohol	1.3853[a]	82.50[a]
	1.3851[b]	82.42[b]
p-xylene	1.4935[a]	138.20[a]
	1.4933[b]	138.36[b]

[a] This work. [b] Reference *3*. [c] Reference *4*.

Table II. Experimental Vapor–Liquid Equilibria Data for *tert*-Butyl Alcohol (1)–Propyl Bromide (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
69.00	0.080	0.125	2.6586	1.0105
68.65	0.140	0.170	2.0978	1.0363
68.66	0.170	0.185	1.8795	1.0540
68.54	0.204	0.205	1.7447	1.0760
68.55	0.230	0.220	1.6602	1.0909
68.43	0.280	0.245	1.5268	1.1334
68.52	0.290	0.243	1.4565	1.1493
69.03	0.405	0.305	1.2819	1.2393
69.60	0.515	0.370	1.2031	1.3612
70.40	0.610	0.430	1.1421	1.4944
71.15	0.650	0.465	1.1158	1.5199
71.35	0.665	0.455	1.0583	1.6081
71.50	0.680	0.470	1.0474	1.6127
71.80	0.695	0.500	1.0660	1.5700
71.90	0.700	0.510	1.1157	1.6020
75.80	0.870	0.700	1.0333	1.9884
76.91	0.900	0.755	1.0377	2.0553
77.80	0.925	0.805	1.0395	2.1231
78.39	0.933	0.820	1.0259	2.1570
78.30	0.941	0.835	1.0394	2.2508
79.10	0.957	0.870	1.0323	2.3780
79.65	0.970	0.905	1.0371	2.4517
80.50	0.980	0.935	1.0339	2.4694

Apparatus and Procedure. An all-glass modified Dvorak–Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental details have been described previously (*2*). All analyses were carried out by gas chromatography on a Packard-Becker 417 apparatus provided with thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with OV-17 and operated isothermally at 80 °C for separating *tert*-butyl alcohol and 100 °C for separating *p*-xylene. Injector and detector temperatures were (220, 240 °C) and (220, 230 °C), respectively. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried to convert the peak area ratio to composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C.

0021-9568/88/1733-0106$01.50/0