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Diffusion and Viscosity in Water–Triethylamine Mixtures at 19 and 20 °C

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Diffusion and viscosity data have been collected for the system water–triethylamine at 19 and 20 °C, both in water-rich solutions and in triethylamine-rich solutions. The possibility of obtaining the spinodal composition by extrapolation of diffusion data is suggested.

The thermodynamics of a critical mixing region was first discussed by Gibbs[1] and several aspects of it were later clarified by various authors.[2-6] It can be shown that in an *n*-component system the stability with respect to diffusion is defined by

$$\sum_{i,k}\left(\frac{\partial\mu_i}{\partial n_k}\right)_{i\neq k}\delta n_i\delta n_k \geq 0 \qquad (1)$$

where μ_i and n_i are the chemical potential and the number of moles of component i.

Inequality 1 states that in a system stable with respect to diffusion any local concentration fluctuation regresses spontaneously. On the other hand, whenever inequality 1 does not hold, local fluctuations do not regress and the system undergoes a phase separation.

The equality sign in eq 1 is verified at the critical mixing point and along the so-called "spinodal" curve that separates the region of instable solutions from that of metastable ones.

The spinodal curve must of course be distinguished from the "binodal" curve that separates the region of stable from that of metastable solutions.[3]

In a two-component system, eq 1 reduces to

$$\partial\mu_1/\partial X_1 \geq 0 \qquad \partial\mu_2/\partial X_2 \geq 0 \qquad (2)$$

where X_1 and X_2 are the mole fractions of components 1 and 2.

Diffusion in a two-component system is described by Fick's law:

$$J_i = -D \text{ grad } C_i \qquad i = 1, 2 \qquad (3a)$$

or, in terms of mole fractions

$$J_i = -D(\partial C_i/\partial X_i) \text{ grad } X_i \qquad i = 1, 2 \qquad (3b)$$

where J_i and C_i are the flow and concentration of component i.

According to the thermodynamics of irreversible processes, eq 3 can be expressed in terms of the component i mobility and of its chemical potential gradient:

$$J_i = -L_i(\partial\mu_i/\partial X_i) \text{ grad } X_i \qquad (4)$$

the term $(\partial\mu_i/\partial X_i)$ is the "thermodynamic factor".

According to eq 2 the thermodynamic factor is null along the spinodal curve and at the critical mixing point, where, however, a further condition must be verified.

$$\partial^2\mu_i/\partial X_i^2 = 0 \qquad i = 1, 2 \qquad (5)$$

As a consequence of eq 4, the experimental diffusion coefficients must be zero along the spinodal curve. A wide number of literature data prove experimentally that $D = 0$ at a critical mixing point of a binary system. In a recent paper some of us[7] pointed out the possibility of obtaining the spinodal curve composition through the extrapolation of experimental diffusion data. Such a possibility seemed to us of some theoretical interest as a rare example of the possibility of obtaining thermodynamic data from the extrapolation of a typical "nonequilibrium" property.

Actually the extrapolation may be affected by some intrinsic uncertainty, but it is worth emphasizing that the result does not require any preliminary assumption on the couple component 1-component 2. Owing to this circumstance, such extrapolation seems to us to be similar to those generally used for extrapolating equilibrium properties, such as crioscopic or osmotic data.

We tried to verify the possibility of obtaining the spinodal curve composition through diffusion measurements in a two-component system which undergoes a phase separation.

We chose the system water–triethylamine (TEA), having a lower critical mixing temperature (see Figure 1). Such a system was widely studied at temperatures below the critical mixing point (18.33 °C), while no data are available at higher temperatures.[8-15]

In the following, we present a set of diffusion and viscosity measurements taken on the system H_2O–TEA at 19 and 20 °C in all ranges of composition of stable solutions.

Experimental Section

Material. Doubly distilled water was used. The triethylamine (TEA), reagent grade (C. Erba, Milan), was distilled and stored in the absence of carbon dioxide. However, freshly distilled material was always used for diffusion and viscosity runs.

Solutions. All solutions for diffusion and viscosity runs were made by weighing both components in a calibrated bottle filled in a thermostatic bath. This procedure allowed a reasonably accurate measurement of density. No correction for the weighing under vacuum was applied.

Diffusion. Diffusion experiments were carried out by using the Gouy interferometric technique that has been widely discussed in the literature.[16,17] The initial boundary was made by the syphoning technique.

The results are collected in Table I (19 ± 0.02 and 20 ± 0.02 °C). The density data given in Table I have been fitted with the following equations:

$$d_{19} = 0.7280 + 0.1009X_1 - 0.0761X_1^2 + 0.1889X_1^3 \pm 0.00054 \qquad X_1 \leq 0.79 \qquad (6)$$

$$d_{20} = 0.7270 + 0.1071X_1 - 0.0802X_1^2 + 0.1788X_1^3 \pm 0.00028 \qquad X_1 \leq 0.70 \qquad (7)$$

$$d_{19} = 0.9984 - 0.9776X_2 + 14.08X_2^2 - 454X_2^3 \pm 0.00015 \qquad X_2 \leq 0.0245 \qquad (8)$$

$$d_{20} = 0.9981 - 0.8534X_2 + 1.2657X_2^2 \pm 0.00018 \qquad X_2 \leq 0.0167 \qquad (9)$$

where indices 1 and 2 refer to water and TEA, respectively.

The refractive index of the system H_2O–TEA has a minimum at a H_2O mole fraction of $X_1 \simeq 0.4$. This fact hindered diffusion measurements in the composition range $0.3 \leq X_1 \leq 0.5$; furthermore, measurements at temperatures higher than 20 °C were useless for the purpose of this paper since the phase

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Table I. Diffusion Coefficients of the System Water (1)–Triethylamine (2)

19 ± 0.02 °C					20 ± 0.02 °C				
X_1[a]	ΔX_1[b]	d[c]	J_m[d]	$10^6 D$[e]	X_1[a]	ΔX_1[b]	d[c]	J_m[d]	$10^6 D$[e]
0.0300	0.0398	0.7294 0.7229	−29.3	22.48	0.0491	0.0392	0.7303 0.7341	−28.3	20.16
0.0699	0.0397	0.7330 0.7359	−28.8	16.61	0.0985	0.0393	0.7352 0.7385	−24.7	14.72
0.0992	0.0405	0.7352 0.7393	−26.9	14.12	0.1962	0.0587	0.7438 0.7490	−26.8	8.22
0.1974	0.0593	0.7437 0.7501	−28.8	8.06	0.5768	0.0383	0.7934 0.8002	29.0	1.622
0.2966	0.1025	0.7523 0.7635	−28.5	4.91	0.6120	0.0378	0.8000 0.8073	39.5	1.389
0.5626	0.0397	0.7912 0.7982	25.9	1.779	0.6309	0.0375	0.8034 0.8118	44.8	1.226
0.5898	0.0389	0.7955 0.8033	33.4	1.513	0.6504	0.0296	0.8083 0.8154	41.5	1.112
0.6292	0.0469	0.8046 0.8144	55.4	1.285	0.6712	0.0188	0.8143 0.8188	31.5	0.927
0.6743	0.0120	0.8163 0.8198	23.8	1.178	0.6899	0.0189	0.8190 0.8244	35.1	0.878
0.7200	0.0183	0.8298 0.8343	43.4	0.890	0.6939	0.0151	0.8209 0.8244	25.6	0.911
0.7486	0.0159	0.8384 0.8432	44.8	0.677	0.9843	0.0020	0.9843 0.9858	58.5	3.32
0.7784	0.0107	0.8480 0.8527	40.6	0.568	0.9882	0.0019	0.9877 0.9892	59.5	4.24
0.7840	0.0116	0.8486 0.8526	45.0	0.579	0.9900	0.0020	0.9893 0.9903	66.8	4.92
0.9803	0.0038	0.9784 0.9822	96.9	1.846	0.9921	0.0020	0.9906 0.9924	69.5	5.23
0.9843	0.0019	0.9839 0.9852	60.9	3.08	0.9960	0.0020	0.9941 0.9957	71.9	5.76
0.9902	0.0022	0.9890 0.9905	67.1	4.57					
0.9960	0.0020	0.9937 0.9958	71.7	5.68					

[a] X_1, water average mole fraction of each diffusion run. [b] ΔX_1, mole fraction difference between lower and upper solutions into the diffusion cell. [c] d, density of solutions used in each run, g/cm³. [d] J_m, Gouy fringe number. [e] D, diffusion coefficient, cm² s⁻¹.

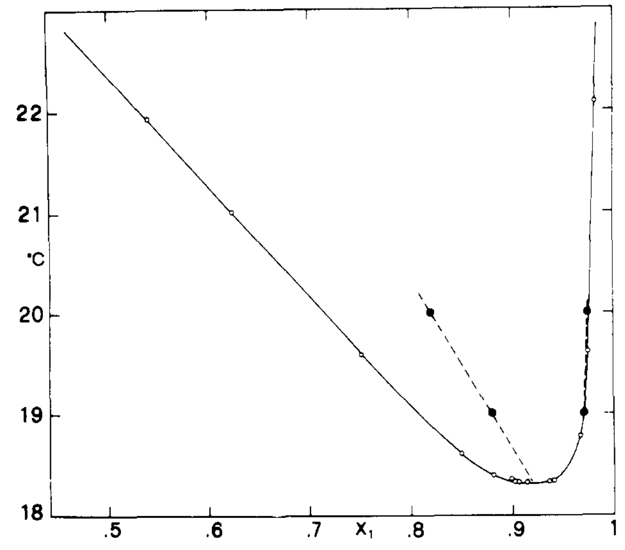

Figure 1. Triethylamine–water cosolute curve, from ref 10: (●) spinodal composition from extrapolation of diffusion data; X_1 = mole fraction of water.

separation curve approaches the range of composition $X_1 \simeq 0.5$ (see Figure 1).

From the experimental J_m given in Table I the following equation was obtained for the refractive index gradient:

$$dn/dX_1 \simeq \Delta n/\Delta X_1 = -0.0152 - 0.0326X_1 + 0.480X_1^2 - 1.172X_1^3 + 1.043X_1^4 \qquad X < 0.8 \quad (10)$$

In eq 10 $\Delta n = \lambda J_m/a = (2.184 \times 10^{-5})J_m$, where λ is the wavelength of the Hg green light (λ = 546.1 nm) and a is the thickness of the diffusion cell (a = 2.500 cm).

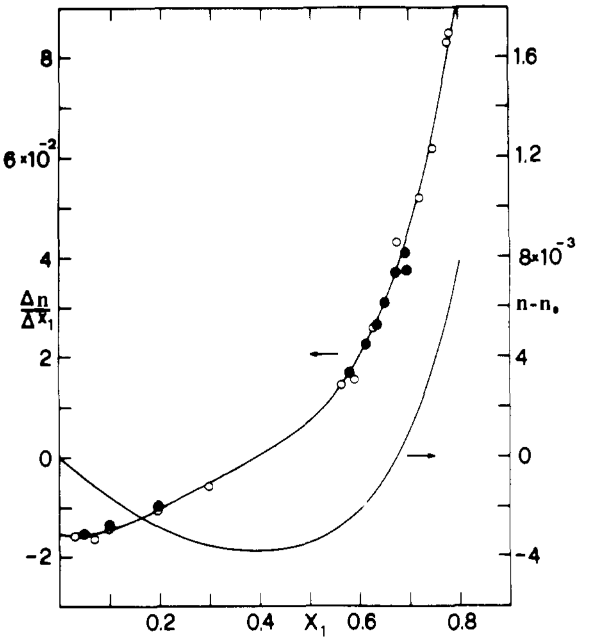

Figure 2. Refractive index increments and refractive indices of water–triethylamine solutions: experimental data from the values of J_m given in Table I; (○) 19 °C, (●) 20 °C; X_1, mole fraction of water; n_0 refractive index of pure triethylamine.

The experimental $\Delta n/\Delta X_1$ data and the graph of eq 10 are shown in Figure 2.

Table II. Cinematic and Dynamic Viscosities of the System Water-Triethylamine at 19 and 20 °C

	19 ± 0.02 °C		20 ± 0.02 °C	
X_1[a]	t/t_0[b]	η[c]	t/t_0[b]	η[c]
0.0000	0.4883	0.3667	0.4929	0.3608
0.1006	0.5602	0.4262	0.5674	0.4211
0.2040	0.6757	0.5207	0.6798	0.5113
0.2996	0.8295	0.6473	0.8367	0.6374
0.4007	1.0747	0.8519	1.0720	0.8296
0.4997	1.4455	1.1675	1.4395	1.1347
0.5997	2.0313	1.6803	2.0010	1.6137
0.7028	2.9435	2.5108	2.8721	2.3850
0.7996	3.9485	3.4890		
0.9800	1.7903	1.8115	1.7419	1.7217
0.9850	1.5782	1.6042	1.5663	1.5544
0.9905	1.3393	1.3677	1.3270	1.3230
0.9951	1.1622	1.1916	1.1747	1.1757
1.0000	1.0000	1.0299	1.0000	1.0050

[a] X_1, water mole fraction. [b] t/t_0, flow time relative to water. [c] η, viscosity in cP.

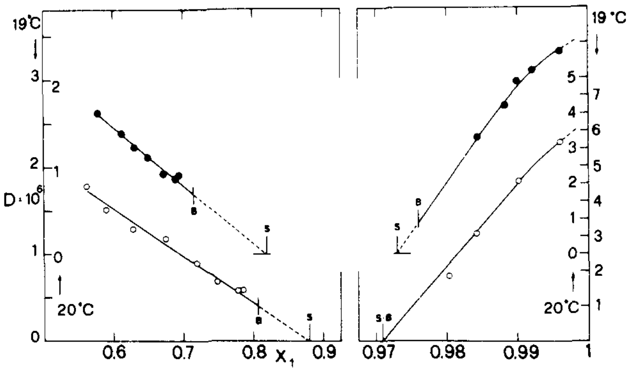

Figure 3. Water-triethylamine system, extrapolation of diffusion coefficients: X_1, H_2O mole fraction; B, binodal composition; S, spinodal composition; (○) 19 °C, (●) 20 °C.

Viscosity. Viscosity measurements were made by using an Ubbelhode viscometer, the experimental data are collected in Table II. The viscosity data were fitted by the following equations:

$$\eta_{19} = 0.359 + 1.309X_1 - 2.81X_1^2 + 8.02X_1^3 \pm 0.014 \text{ cP} \qquad X_1 < 0.8 \quad (11)$$

$$\eta_{20} = 0.351 + 1.075X_1 - 2.88X_1^2 + 7.75X_1^3 \pm 0.012 \text{ cP} \qquad X_1 < 0.7 \quad (12)$$

$$\eta_{19} = 1.030 + 28.06X_2 + 1043X_2^2 - (2.26 \times 10^4)X_2^3 \pm 0.014 \text{ cP} \qquad X_2 < 0.02 \quad (13)$$

$$\eta_{20} = 1.007 + 28.80X_2 + 848X_2^2 - (2.49 \times 10^4)X_2^3 \pm 0.008 \text{ cP} \qquad X_2 < 0.021 \quad (14)$$

Discussion

The diffusion coefficients in the neighborhood of the phase separation region are shown in Figure 3, both at 19 and 20 °C. A reasonably accurate extrapolation at $D = 0$ can be taken. The composition where $D = 0$ should correspond to the spinodal composition.

According to our results the spinodal curve lies very near to the binodal curve on the water-rich side of the composition diagram, while on the TEA-rich side the field of metastable solutions seems quite large. The spinodal compositions have also been reported on the Figure 1 graph.

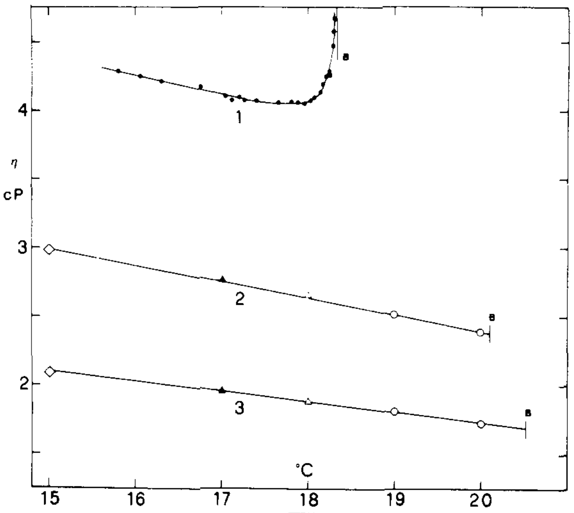

Figure 4. Viscosity of water-triethylamine solutions as a function of temperature: (1) water mole fraction $X_1 = 0.916$, from ref 19; (2) $X_1 = 0.703$; (3) $X_1 = 0.980$; (◇) from ref 14; (▲) from ref 15; (△) from ref 9; (○) our data; B, binodal composition.

Actually some uncertainty on the results is connected with our choice of a linear extrapolation. In fact there are not "a priori" reasons for preferring a linear extrapolation of diffusion data to a more sophisticated treatment of experimental data.

A check on the reliability of our extrapolated data could be done if we had good thermodynamic data on the H_2O-TEA system. Unfortunately the only available data are at lower temperatures,[8-11] and any attempt to extrapolate them at 19 and 20 °C was not satisfactory. A rough qualitative agreement was indeed obtained by extrapolating the thermodynamic factor data given by Haase and Siry;[12] however, the accuracy of the extrapolated thermodynamic factors is much lower than that of extrapolated diffusion data.

The viscous behavior of mixtures in a critical region is also anomalous, in fact a sharp increase in viscosity is generally observed.

This effect can be attributed to the growing of large composition fluctuations in the mixture.[18]

Literature data on the system water-TEA clearly show such an effect[19] in the composition range $0.05 \leq X_2 \leq 0.13$ by approaching the phase separation temperature (see Figure 4, graph 1).

Our experimental data are outside this range of composition, they are in good agreement with the results by some other authors taken at lower temperatures, but the anomalous growing of viscosity by approaching the phase separation temperature does not appear (see Figure 4, graphs 2 and 3).

A final remark may be given about viscosity data: they allowed a reasonable estimate of the limiting diffusion coefficient of water in TEA solutions by graphical extrapolation of the $D\eta$ products. The result at 19 °C was $D\eta = 1.03 \times 10^{-7}$ corresponding to $D° = 2.80 \times 10^{-5}$ cm^2 s^{-1}.

The Stokes radius of water molecule obtained from these data is 2.1×10^{-8} cm; the corresponding radius from self-diffusion data in pure water is about 1×10^{-8} cm.[20] The higher value found in TEA solution can be attributed to the strong solvation of H_2O in TEA solution. We may just mention that the same Stokes radius was found in the past for water molecules in acetic acid solution.[21]

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Vapor–Liquid Equilibria: Systems 2-Butanol–*p*-Xylene and 2-Butanol–*m*-Xylene

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Vapor–liquid equilibrium data have been measured for the binary systems 2-butanol–*p*-xylene and 2-butanol–*m*-xylene, at 685 mmHg pressure. The activity coefficients have been evaluated by taking into consideration the vapor phase nonideality. The *t*–*x*–*y* data have been subjected to a thermodynamic consistency test, and the activity coefficients have been correlated by Wilson's equation.

Introduction

The separation of the C_8 hydrocarbons, particularly *p*-xylene and *m*-xylene, is difficult. An attempt has been made here to separate the above mixtures by employing azeotropic distillation techniques. We have chosen 2-butanol as the entrainer. The vapor–liquid equilibria have been evaluated for the systems 2-butanol–*p*-xylene and 2-butanol–*m*-xylene.

Experimental Section

Materials. *p*-Xylene "Lab Chem" grade, obtained from E. Merck, West Germany, and *m*-xylene, "Lab Chem" grade, obtained from M/s. Pfizer, India, Ltd., were purified by the methods given by Riddick and Bunger (*9*). The 2-butanol supplied by Riedel-De-Haen AG, West Germany, was purified by the method suggested by Vogel (*12*). The *p*-xylene and *m*-xylene were dried over dry sodium, and 2-butanol was dried over anhydrous calcium chloride.

The liquids were distilled in a 30-mm glass column packed with 10-mm Raschig rings to a height of 1 m. The column was operated at total reflux for 30 min. The low boiling impurities were drawn off at a very low rate as rejects. When the desired boiling temperature was reached and remained constant for 15 min, the fraction was collected, while the column was operated at nearly total reflux. The physical properties of the materials used are listed in Table I.

Apparatus and Analytical Procedure. A vapor recirculation type equilibrium still described by Brown (*2*, *3*) was used to study the vapor–liquid equilibrium. The apparatus is shown in Figure 1.

The apparatus consists of a cylindrical-shaped boiler, one end of which is tapered gradually to a Cottrell pump which in turn is connected to a separation chamber. The inside wall of the boiler is coated with pulverized glass powder to avoid superheating and bumping. The boiler is heated with an external heater made of nichrome wire. Another heater is wound round the entire length of the Cottrell pump and the separating chamber. Plaster of paris is applied over the heater windings, and above this asbestos rope is wound. The other end of the boiler is fused to a B_{19} socket. An internal heater, made of nichrome wire fused to two tungsten leads which in turn are fused to a B_{19} cone, fits into this socket.

Table I. Physical Properties of Materials

	2-butanol	*p*-xylene	*m*-xylene
mole wt	74.12	106.16	106.16
density at 30 °C, g/cm^3			
exptl	0.7984	0.8524	0.8555
lit.	0.7983[a]	0.8525[b]	0.8557[b]
refractive index at 25 °C			
exptl	1.39492	1.49321	1.49462
lit.	1.39500[a]	1.49325[b]	1.49464[b]

[a] Reference 9. [b] Reference 10.

The sampling trap used is shown in Figure 2. The sample traps are provided with magnetically operated valves. Liquid and vapor samples could be withdrawn without disturbing the working of the still. At the time of sampling, the sample traps were cooled with freezing mixture and then the magnetic valves opened and the samples collected. The samples were analyzed by using a Pulfrich refractometer. All measurements were made at 30 ± 0.1 °C. A Colora ultrathermostat with a mercury to mercury thermoregulator was used to maintain the temperature during measurements to within ±0.1 °C. The samples were kept in the thermostatic bath for about 30 min, before being fed to the refractometer. The refractive index was measured with an accuracy of ±0.000 01. A mercury-in-glass thermometer calibrated against the vapor pressure measurements was used for temperature measurements. Several samples of known compositions were prepared, and their refractive index was measured. Thus a calibration chart was prepared. All the unknown compositions were obtained from this calibration chart and their refractive index.

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