

Phase Equilibria of the Water–Sodium Chloride–Triethylamine System

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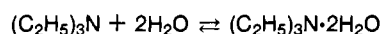
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Liquid–liquid equilibrium data for the water–sodium chloride–triethylamine system are reported at 20, 30, and 40 °C.

Strong molecular interactions create a thermodynamic behavior of the water–triethylamine (TEA) solution that is hard to interpret quantitatively (7).

The water–TEA system exhibits negative heats of mixing and negative excess entropies (2, 3, 12) and, as a consequence, a lower consolute temperature (1, 5, 13, 16, 17, 18).

These occurrences are strongly influenced by the following association equilibrium existing in solution (11, 15):



with the monohydrate appearing to be an ammonium hydroxide derivative and the second molecule of water to be hydrogen bonded.

These features, in conjunction with the sharp changes in solubility with temperature and the low solubility in water, indicated, in the past years, TEA to be one of the most suitable solvents for water desalination processes (4, 5, 6, 9, 10, 19).

Particular thermodynamic behavior and possible industrial relevance encouraged the present study on the determination of the liquid–liquid equilibrium of the water–sodium chloride–TEA system. Previous data on similar systems have been reported by Davison et al. (8).

Experimental Section

The determination of equilibrium was carried out at 20, 30, and 40 °C by 30-cm³ separator funnels with a thermostatic jacket (± 0.1 °C). The equilibrium vessels were loaded with equal quantities of amine and NaCl aqueous solution at concentrations up to the saturation value.

After an extended period of mixing and quantitative gravity separation, samples of each phase were withdrawn for analysis. Equilibrium compositions were determined by analyzing amine in the aqueous phase and sodium chloride in both phases. Water and TEA concentrations in organic phase resulted from mass balances based upon starting quantities and compositions. The concentration of TEA in the aqueous phase was determined by

Table I. Liquid–Liquid Equilibrium of the TEA–H₂O System

T (°C)	Wt % TEA in aqueous phase	Wt % TEA in amine phase
19.0	15.0	57.8
20.0	10.0	69.4
22.0	8.9	79.4
24.0	8.0	85.5
26.0	7.1	89.4
28.0	6.5	91.1
30.0	5.7	93.1
35.0	4.5	95.5
40.0	3.5	96.0

acid titration (14). Salt concentration was measured by weighing the fixed residue after slow evaporation, followed by complete drying in an oven at 110 °C. Larger samples of organic phase were prepared because of the low salt content; several determinations of each composition were carried out giving sufficient reproducibilities (± 0.005 as weight fraction). Occasional erratic results were discarded. TEA (Carlo Erba), 99.5 wt % pure, was distilled before using.

Results and Discussion

Determinations of H₂O–TEA solubility (Table I) give a sufficient agreement with very accurate data of other authors as shown in Figure 1.

Older data (16, 17, 18), obtained with a different experimental

Table II. Liquid–Liquid Equilibrium of the H₂O–NaCl–TEA System at 20 °C

Wt TEA/ wt salt solution	Organic phase		Aqueous phase		
	Wt % NaCl	Wt % TEA	Wt % NaCl	Wt % TEA	
1	—	69.4	—	10.0	
	0.040	83.6	1.1	7.5	
	0.060	88.9	2.0	6.3	
	0.070	90.9	3.0	5.0	
	0.085	91.6	4.0	4.6	
	0.080	92.0	5.0	4.4	
	0.085	92.6	5.9	3.6	
	0.085	92.8	6.9	3.3	
	0.085	93.4	7.8	2.9	
	0.080	94.0	9.7	2.3	
	0.075	94.4	11.4	2.0	
	0.070	94.3	13.2	2.3	
	0.065	95.5	15.0	1.3	
	1/3	—	69.4	—	10.0
		0.045	89.0	1.1	7.2
		0.055	91.9	2.0	6.8
0.075		92.0	3.0	4.9	
0.080		93.9	3.8	5.0	
0.085		93.9	5.2	4.4	
0.085		94.4	6.2	3.5	
0.080		94.7	7.2	3.4	
0.085		94.4	8.8	3.1	
0.075		95.4	10.0	2.4	
0.070		93.5	11.1	2.1	
0.070		95.3	13.4	1.9	
0.065		95.5	14.5	1.2	
3		0.050	86.9	1.2	7.0
		0.060	89.3	2.4	6.3
		0.080	89.9	3.6	5.0
	0.075	91.1	4.9	4.4	
	0.085	91.8	6.0	3.9	
	0.080	92.5	7.0	3.6	
	0.085	92.7	8.0	2.6	
	0.080	93.0	9.0	2.9	
	0.075	94.1	11.2	2.0	
	0.080	94.3	13.0	1.9	
	0.070	94.4	15.0	1.3	
	0.065	94.8	16.8	1.6	

procedure (synthetic method), slightly differ in the region of low temperatures for the amine phase.

The ternary equilibrium data are given in Tables II–IV; measurements for three weight ratios of TEA/aqueous salt solution are reported at 20 °C.

The noticeable salting-out effect induced by sodium chloride on the enlargement of the miscibility gap can be observed.

Special attention is given to the distribution curves of NaCl between the two phases (Figure 2). As temperature increases, the salt content is higher in the amine phase; these curves also show a maximum at about the same NaCl weight fraction in the aqueous phase.

Data were correlated with the following empirical equation:

$$\log \frac{x_0}{x} = k_s C_s (1 + kC) \quad (1)$$

where x_0 and x are the mole fractions of TEA in water and in salt

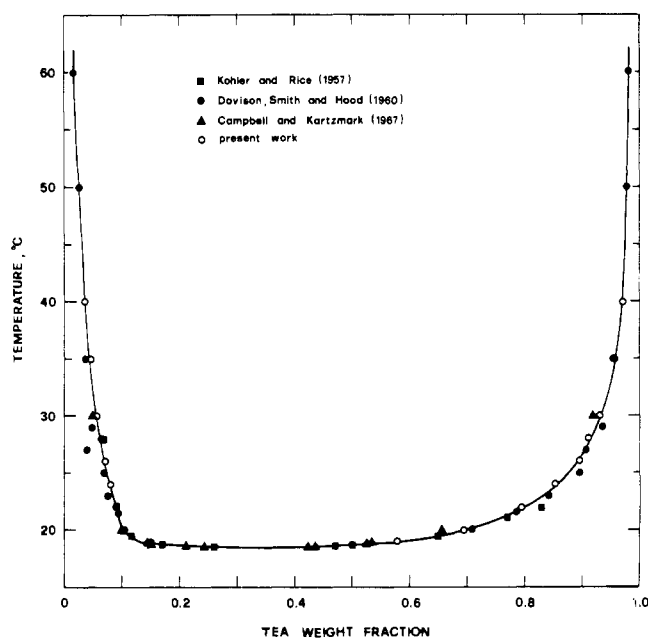


Figure 1. Miscibility gap of the H₂O–TEA system.

Table III. Liquid–Liquid Equilibrium of the H₂O–NaCl–TEA System at 30 °C

Organic phase		Aqueous phase	
Wt % NaCl	Wt % TEA	Wt % NaCl	Wt % TEA
—	93.1	—	5.7
0.155	93.7	1.0	5.0
0.170	94.5	1.8	4.1
0.200	95.0	2.8	3.3
0.225	95.0	3.7	3.2
0.230	95.2	4.6	3.0
0.230	95.5	5.7	2.5
0.240	95.4	6.5	2.4
0.230	95.7	7.4	2.1
0.240	95.6	9.4	1.8
0.225	95.7	11.0	1.5
0.220	95.7	12.9	1.2
0.210	95.7	14.8	1.0

aqueous solution, C_s and C the molarities of the salt and of the nonelectrolyte, and k_s and k two constants.

Values of k_s and k are reported in Table V. Equation 1 rep-

Table IV. Liquid–Liquid Equilibrium of the H₂O–NaCl–TEA System at 40 °C

Organic phase		Aqueous phase	
wt % NaCl	wt % TEA	wt % NaCl	wt % TEA
—	96.0	—	3.5
0.220	96.4	1.0	3.1
0.230	96.8	1.8	2.6
0.260	96.7	2.8	2.3
0.250	96.8	3.7	2.2
0.260	96.8	4.6	2.1
0.265	96.8	5.6	2.0
0.280	96.9	6.4	1.4
0.275	96.9	7.2	1.5
0.280	97.0	9.3	1.4
0.260	96.9	11.0	1.0
0.260	97.0	12.7	0.8
0.240	97.0	14.6	0.6

Table V. Values of Constants k_s and k in Equation 1

T (°C)	k_s	k
20	0.360	4.555
30	0.518	1.917
40	0.515	1.644

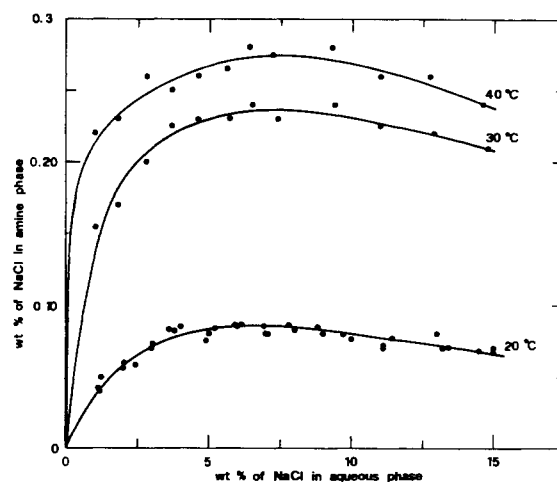


Figure 2. Distribution curves of NaCl between the amine and aqueous phase.

resents the experimental data with average deviation less than 10%.

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Phase-Equilibria Behavior of the System Carbon Dioxide–*n*-Butylbenzene–2-Methylnaphthalene

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The phase-equilibria behavior of the ternary system CO₂–*n*-butylbenzene–2-methylnaphthalene was studied in the liquid–vapor, solid–liquid–vapor, and liquid–liquid–vapor regions. Detailed pressure, temperature, molar volume and composition data for each region and also the selectivities of CO₂ in the ternary liquid–liquid–vapor region are presented. The liquid–liquid–vapor coexistence region for the ternary system was found to be bounded by a Q-point locus, a K-point locus, and a UCST locus. Also presented are the data on the depression in the melting point of 2-methylnaphthalene upon the addition of *n*-butylbenzene under atmospheric pressure.

Phase equilibria behavior of CO₂–hydrocarbon(s) systems have been studied by many investigators. Partial miscibility behavior has been observed for some of the systems (2, 5, 6, 7) and suggests the use of CO₂ as a selective solvent. Its potential use in this respect is supported by its availability, non-toxicity, and noncorrosiveness. The studies of CO₂ selectivity with respect to different hydrocarbons between liquid phases are needed to evaluate the use of CO₂ as a selective solvent.

Huie and co-workers (3) studied the ternary system CO₂–*n*-decane–*n*-eicosane and examined the selectivity of CO₂ for lower vs. higher alkanes. The results show that CO₂ selectively extracts the lower alkane from the higher alkane.

The Huie study was extended to systems of CO₂ with alkanes and aromatics by Kulkarni (4) and Zarah (9). Kulkarni studied the ternary system of CO₂–*n*-decane–2-methylnaphthalene, where the aromatic 2-methylnaphthalene has a similar melting point to that of *n*-eicosane. Zarah studied the system CO₂–*n*-butylbenzene–*n*-eicosane, where the aromatic *n*-butylbenzene has the same carbon number as *n*-decane. In both systems, CO₂ selectively extracts the compound with lower carbon number.

The systems of CO₂ with aromatic compounds have been studied only by Francis (7); all those studies were done at 25 °C. There has been no detailed work ever done on CO₂–aromatic systems. Therefore, our earlier work (3, 4, 9) was extended to a ternary system of CO₂–*n*-butylbenzene–2-methylnaphthalene. The relevant phase behavior for this system was studied. The selectivity of CO₂ in this ternary three-phase system, as well as the compositional and volumetric data, are reported. These data could be used for correlative purposes.

Experiments Performed

The following experiments were performed in this study: (a) The melting point depression of 2-methylnaphthalene upon the

addition of *n*-butylbenzene was measured at several compositions at atmospheric pressure. (b) The liquid–vapor isotherms of the ternary system CO₂–*n*-butylbenzene–2-methylnaphthalene were studied at different temperatures at certain mole ratios of the two hydrocarbons in the system. (c) The solid–liquid–vapor equilibria were studied for the same ternary system at certain mole ratios of the two hydrocarbons in the liquid phase. (d) The liquid–liquid–vapor region of the same ternary system was studied in detail, both by stoichiometric techniques and by sampling techniques.

Experimental Section

Most of the experiments involved in this study were done with a P-V-T apparatus which featured a glass equilibrium cell of about 10 cm³ in volume and a constant temperature bath. The detailed description of this apparatus and the experimental procedure is elsewhere (8). This apparatus was used for stoichiometric experiments.

The sampling study for the ternary liquid–liquid–vapor phase behavior was done by means of a Jerguson cell. There are two sampling ports on the cell, one being used to sample the upper liquid phase, the other used to sample the lower liquid phase.

For the stoichiometric experiments, the procedure is briefly described as follows: a measured amount of CO₂ is pressurized into the glass equilibrium cell which is initially loaded with a measured mass of the hydrocarbon components and the amount of CO₂ dissolved into the liquid solution is directly calculated by means of a material balance.

In the case of the two-phase liquid–vapor behavior study, the compositional and volumetric data are calculated straightforward. In the case of the solid–liquid–vapor system, the solid in the solution is kept in a trace amount during the experiment, so that the amount of solid is negligible (the solid phase can be assumed to be pure 2-methylnaphthalene). Therefore the composition and molar volume of the liquid phase can be calculated.

In the case of ternary three-phase liquid–liquid–vapor behavior, the composition and molar volume of the two liquid phases cannot be calculated with a single set of experimental data. Two separate runs were done to provide the data needed for property determination. In each run, the temperature and pressure were the same while one or the other of the liquid phases was kept in small amount.

The terminations (boundaries) for the ternary liquid–liquid–vapor loci with given mole ratios of the two hydrocarbons in the L1 phase are Q points (coexistence of the four phases V–L1–L2–S) at the lower temperature end, and K points (critical point