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Vapor-Liquid Equilibria for Fourteen Systems Consisting of Chlorinated Hydrocarbons and Alcohols

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Vapor-liquid equilibrium of 14 binary systems was determined with the help of a dynamic ebulliometer "Cathala," at the pressure of 760 mm Hg. Nine systems were constituted only with chlorinated solvents and the other five systems with chlorinated solvents and ethyl, methyl, or *n*-propyl alcohol. The tests of a thermodynamic consistency were carried out, and all the systems yielded smooth curves of $(y - x)$ plotted against x.

An ebulliometric study of nine binary systems composed of chlorinated solvents and five binary systems of chlorinated solvents with methyl, ethyl, and *n*-propyl alcohol was undertaken for the purpose of developing a method of predicting the distillation curves of the binary and ternary systems of these compounds. These data are of interest in the vinylic polymer industry. With regard to these 14 systems, only the following ones have already been studied (*1, 2, 9, 14*), at a pressure of 760 mm Hg: carbon tetrachloride and ethylene chloride, carbon tetrachloride and trichloroethene, and trichloroethene and tetrachloroethene. These 14 systems are quoted in Table I.

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Table I. Binary Systems

Carbon tetrachloride–ethylene chloride[a]	Trichloroethene–tetrachloroethene
Carbon tetrachloride–trichloroethene	Trichloroethene–*n*-propyl alcohol
Ethylene chloride–trichloroethene	Tetrachloroethene–methyl alcohol
Ethylene chloride–trichloroethene	Tetrachloroethene–*n*-propyl alcohol
Ethylene chloride–ethyl alcohol	1,2-*trans*-Dichloroethene–1,2-*cis*-dichloroethene
Ethylene chloride–*n*-propyl alcohol	1,1,1-Trichloroethane–1,2-*trans*-dichloroethene
Ethylene chloride–1,1,1-trichloroethane	1,2-*cis*-Dichloroethene–1,1,1-trichloroethane

[a] Ethylene chloride of Matheson, Coleman and Bell.

CHEMICALS

The boiling points, the refractive indices at 20° C, and the grades of each pure compound are given in Table II. Alcohols were distilled with sodium through a reflux column. The ethylene chloride of Matheson, Coleman and Bell used in various systems is not pure enough even after distillation. Therefore, the experiments were carried out using the reagent grade ethylene chloride of Merck, whose physical properties draw nearer to those which are in the tables.

The dichloroethenes 1,2-cis and -trans, and trichloroethane-1,1,1 were distilled before their use to obtain a grade material of 99.8%. The gas chromatographic analysis did not reveal impurities in the other compounds; therefore, they were used without further purifications.

Table II. Physical Properties of Chemicals

Materials	Grade	Boiling point, ° C		Refractive index, n_D^{20}	
		Exptl	Lit. (*7*)	Exptl	Lit. (*7*)
Carbon tetrachloride	Prolabo, Reagent Grade	76.7	76.7	1.4607	1.4604
Tetrachloroethene	Merck, Reagent Grade	120.9	121.0	1.5058	1.5044
Ethylene chloride	Matheson, Coleman and Bell	82.7	82.7	1.4450	1.4448 1.44476 (*5*)
Ethylene chloride	Merck, Reagent Grade	83.4	84.0 83.47 (*5*)	1.4450	1.4448 1.44476 (*5*)
Trichloroethene	Merck, Reagent Grade	86.7	87.0	1.4777	1.4784
1,2-*cis*-Dichloroethene	Pechiney Saint Gobain, 99.8%	60.0	60.3	1.4491	1.4490
1,2-*trans*-Dichloroethene	Pechiney Saint Gobain, 99.8%	47.4	47.5	1.4458	1.4454
1,1,1-Trichloroethane	Pechiney Saint Gobain, 99.8%	73.9	74.0 74.05 (*8*)	1.4381	1.43838 (*11*)
Methyl alcohol	Pure Grade	64.7	64.96	1.3290	1.3288
Ethyl alcohol	Pure Grade	78.3	78.5	1.3621	1.3611
n-Propyl alcohol	Prolabo, Pure Grade	97.1	97.1	1.3851	1.3850

Table III. Experimental Vapor-Liquid Equilibrium Data at 760 Mm of Hg Pressure

t	x_1	y_1	t	x_1	y_1	t	x_1	y_1	t	x_1	y_1
Carbon tetrachloride–ethylene chloride			Ethylene chloride–trichloroethene			Ethyl alcohol–ethylene chloride			1,1,1-Trichloroethane–ethylene chloride		
81.0	0.053	0.100	85.7	0.050	0.072	79.9	0.030	0.130	82.4	0.035	0.060
80.0	0.100	0.160	84.8	0.113	0.153	78.0	0.042	0.195	81.9	0.055	0.092
79.3	0.140	0.213	84.4	0.150	0.190	76.7	0.073	0.233	81.2	0.087	0.142
78.6	0.180	0.260	83.7	0.235	0.275	74.1	0.113	0.315	80.6	0.125	0.187
78.1	0.213	0.300	83.4	0.285	0.339	72.6	0.152	0.360	79.8	0.183	0.251
77.4	0.278	0.357	82.9	0.364	0.413	70.9	0.283	0.436	79.4	0.210	0.285
76.9	0.315	0.398	82.8	0.388	0.432	70.5	0.345	0.452	78.8	0.263	0.340
76.3	0.388	0.468	82.6	0.423	0.463	70.2	0.425	0.478	78.2	0.315	0.395
75.8	0.493	0.543	82.3	0.478	0.513	70.1	0.488	0.498	77.8	0.352	0.445
75.4	0.568	0.598	82.2	0.547	0.567	70.2	0.598	0.535	77.2	0.406	0.495
75.3	0.595	0.618	82.2	0.610	0.630	70.8	0.705	0.582	76.1	0.520	0.595
75.2	0.700	0.700	82.2	0.772	0.762	71.4	0.765	0.628	75.6	0.587	0.655
75.2	0.758	0.750	82.3	0.800	0.790	72.1	0.817	0.670	75.0	0.662	0.712
75.3	0.795	0.783	82.5	0.862	0.852	74.7	0.923	0.817	74.5	0.736	0.800
75.5	0.860	0.843	82.7	0.900	0.890	75.7	0.948	0.865	74.0	0.845	0.895
76.0	0.938	0.928	83.0	0.948	0.940	77.3	0.978	0.945	73.8	0.917	0.955
Combinations of feed			Combinations of feed			Combinations of feed			Combinations of feed		
78.6	0.188	0.268	83.4	0.280	0.312	71.6	0.210	0.295	81.4	0.080	0.120
76.8	0.325	0.405	82.2	0.731	0.725	70.1	0.528	0.513	76.6	0.465	0.552
75.3	0.805	0.787	82.4	0.850	0.840	72.9	0.862	0.715	74.3	0.795	0.835
Carbon tetrachloride–trichloroethene			Ethylene chloride–tetrachloroethene			Ethylene chloride–*n*-propyl alcohol			Trichloroethene–tetrachloroethene		
86.0	0.060	0.075	117.8	0.020	0.115	94.4	0.047	0.131	117.0	0.075	0.178
85.1	0.147	0.176	114.0	0.050	0.217	92.9	0.075	0.198	115.7	0.100	0.228
84.4	0.202	0.250	110.9	0.092	0.315	91.6	0.092	0.250	112.8	0.162	0.338
84.2	0.224	0.278	108.0	0.120	0.388	90.3	0.126	0.300	110.5	0.217	0.420
83.5	0.274	0.344	106.0	0.150	0.437	89.0	0.156	0.352	109.1	0.250	0.468
83.1	0.315	0.380	103.3	0.200	0.512	87.4	0.194	0.412	106.9	0.308	0.537
82.5	0.376	0.445	100.5	0.264	0.592	85.5	0.250	0.480	105.7	0.336	0.572
81.3	0.490	0.565	98.5	0.311	0.629	84.3	0.300	0.525	103.4	0.394	0.627
81.0	0.525	0.589	95.2	0.400	0.696	83.4	0.350	0.565	101.0	0.462	0.698
80.5	0.580	0.650	93.7	0.450	0.725	82.0	0.457	0.626	100.0	0.493	0.718
80.0	0.627	0.700	92.2	0.500	0.755	80.8	0.617	0.693	98.4	0.550	0.756
79.1	0.706	0.780	89.9	0.594	0.804	80.5	0.695	0.725	96.3	0.614	0.800
78.5	0.767	0.829	88.2	0.679	0.842	80.5	0.790	0.771	94.4	0.685	0.843
78.1	0.804	0.866	86.8	0.750	0.875	80.8	0.875	0.830	93.4	0.723	0.872
77.3	0.918	0.950	85.5	0.838	0.916	81.6	0.935	0.886	92.1	0.769	0.888
76.9	0.965	0.980	84.2	0.938	0.970	82.3	0.969	0.931	89.5	0.875	0.950
Combinations of feed			Combinations of feed			Combinations of feed			Combinations of feed		
85.1	0.148	0.180	102.3	0.222	0.535	81.0	0.587	0.680	113.8	0.142	0.297
81.7	0.451	0.525	98.9	0.300	0.620	80.4	0.732	0.741	104.4	0.364	0.609
78.1	0.808	0.873	88.8	0.632	0.822	81.8	0.944	0.899	91.0	0.809	0.919
Methyl alcohol–tetrachloroethene			1,2-*trans*-Dichloroethene–1,2-*cis*-dichloroethene			Trichloroethene–*n*-propyl alcohol			*n*-Propyl alcohol–tetrachloroethene		
117.2	0.001	0.074	58.7	0.064	0.100	95.3	0.030	0.089	116.0	0.015	0.150
113.2	0.003	0.210	57.9	0.110	0.169	93.5	0.059	0.175	113.0	0.024	0.229
107.7	0.003	0.335	57.0	0.160	0.237	91.8	0.092	0.230	109.1	0.050	0.335
102.7	0.003	0.445	56.1	0.224	0.320	90.8	0.112	0.292	104.4	0.082	0.430
97.6	0.008	0.530	55.4	0.252	0.356	89.3	0.147	0.351	102.8	0.100	0.460
93.0	0.011	0.588	54.3	0.325	0.432	87.8	0.188	0.412	99.9	0.150	0.516
87.0	0.017	0.660	53.0	0.411	0.524	86.7	0.222	0.457	98.1	0.200	0.560
80.5	0.024	0.724	52.3	0.465	0.574	85.0	0.300	0.523	97.1	0.240	0.577
70.2	0.066	0.800	51.5	0.542	0.639	84.0	0.360	0.560	95.7	0.336	0.618
65.3	0.215	0.837	50.7	0.602	0.687	83.0	0.434	0.605	95.0	0.400	0.630
64.4	0.533	0.848	50.1	0.655	0.734	82.4	0.507	0.641	94.7	0.476	0.638
63.9	0.776	0.859	49.3	0.747	0.804	82.0	0.577	0.671	94.2	0.600	0.665
63.5	0.883	0.883	48.5	0.838	0.872	81.7	0.742	0.729	94.0	0.703	0.702
63.6	0.937	0.913	48.2	0.877	0.911	82.9	0.916	0.833	94.3	0.827	0.773
63.8	0.950	0.927	48.0	0.900	0.919	83.3	0.930	0.852	95.0	0.900	0.845
64.2	0.979	0.958	47.7	0.944	0.957	84.6	0.964	0.907	95.9	0.949	0.910
Combinations of feed			Conbinations of feed			Combinations of feed			Combinations of feed		
116.5	0.001	0.110	57.4	0.137	0.206	86.8	0.221	0.452	110.6	0.037	0.291
64.2	0.656	0.852	51.6	0.535	0.636	81.8	0.636	0.689	94.5	0.504	0.646
63.6	0.931	0.910	48.0	0.901	0.923	82.1	0.861	0.782	94.8	0.873	0.818

(*Continued on next page*)

Table III. (*Continued*)

t	x_1	y_1	t	x_1	y_1
1,2-*trans*-Dichloroethene–1,1,1-trichloroethane			1,2-*cis*-Dichloroethene–1,1,1-trichloroethane		
72.4	0.038	0.079	73.1	0.048	0.074
71.0	0.075	0.158	72.3	0.100	0.143
70.1	0.094	0.188	70.9	0.186	0.256
69.1	0.122	0.239	70.3	0.221	0.302
66.3	0.200	0.371	69.4	0.282	0.372
63.2	0.291	0.485	68.0	0.367	0.467
61.9	0.338	0.544	67.4	0.408	0.513
60.7	0.372	0.591	66.6	0.464	0.568
58.9	0.446	0.660	65.8	0.522	0.625
56.1	0.560	0.745	65.0	0.584	0.681
53.2	0.681	0.828	64.1	0.662	0.748
52.3	0.734	0.867	63.5	0.697	0.776
51.3	0.787	0.901	63.0	0.737	0.808
50.0	0.843	0.930	62.2	0.807	0.861
49.2	0.890	0.947	61.6	0.856	0.901
48.6	0.926	0.966	61.2	0.899	0.929
Combinations of feed			Combinations of feed		
70.0	0.096	0.196	69.3	0.289	0.381
53.3	0.677	0.825	65.0	0.582	0.677
49.1	0.889	0.947	61.0	0.908	0.933

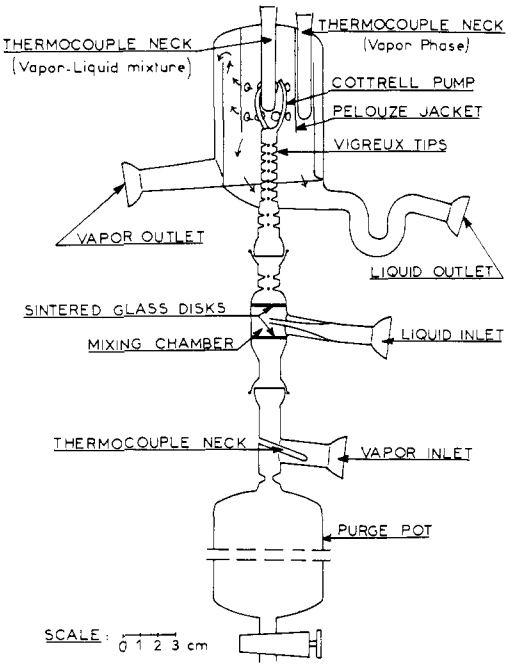

Figure 1. Cathala still

Table IV. Refractive Index–Composition Data at 20° C

x_1	n_D^{20}	x_1	n_D^{20}	x_1	n_D^{20}	x_1	n_D^{20}
Carbon tetrachloride–ethylene chloride		Ethylene chloride–tetrachloroethene		Ethylene chloride–1,1,1-trichloroethane		Tetrachloroethene–methyl alcohol	
0.092	1.4462	0.068	1.5020	0.061	1.4385	0.100	1.3630
0.199	1.4479	0.194	1.4949	0.141	1.4388	0.143	1.3766
0.302	1.4494	0.306	1.4886	0.228	1.4392	0.248	1.4062
0.420	1.4511	0.421	1.4817	0.348	1.4399	0.365	1.4329
0.450	1.4515	0.515	1.4761	0.455	1.4406	0.413	1.4429
0.552	1.4530	0.611	1.4702	0.584	1.4414	0.545	1.4658
0.666	1.4546	0.712	1.4636	0.702	1.4424	0.652	1.4797
0.723	1.4555	0.791	1.4586	0.818	1.4434	0.740	1.4883
0.801	1.4568	0.882	1.4527	0.907	1.4442	0.816	1.4948
0.892	1.4584	0.953	1.4482	0.949	1.4446	0.920	1.5011
Carbon tetrachloride–trichloroethene		Ethylene chloride–ethyl alcohol		Trichloroethene–tetrachloroethene		Tetrachloroethene–*n*-propyl alcohol	
0.089	1.4759	0.050	1.3648	0.057	1.5044	0.050	1.3929
0.155	1.4749	0.124	1.3749	0.125	1.5026	0.117	1.4033
0.277	1.4727	0.216	1.3837	0.224	1.5001	0.197	1.4151
0.365	1.4712	0.267	1.3883	0.329	1.4973	0.293	1.4284
0.433	1.4701	0.348	1.3956	0.431	1.4945	0.376	1.4394
0.539	1.4682	0.442	1.4035	0.534	1.4917	0.477	1.4513
0.611	1.4672	0.520	1.4099	0.631	1.4890	0.576	1.4630
0.691	1.4659	0.677	1.4222	0.728	1.4861	0.681	1.4752
0.801	1.4641	0.809	1.4326	0.819	1.4831	0.793	1.4866
0.872	1.4629	0.910	1.4394	0.912	1.4804	0.921	1.4990
Ethylene chloride–trichloroethene		Ethylene chloride–*n*-propyl alcohol		Trichloroethene–*n*-propyl alcohol			
0.102	1.4743	0.044	1.3873	0.047	1.3903		
0.187	1.4713	0.143	1.3925	0.124	1.3988		
0.280	1.4682	0.240	1.3984	0.219	1.4092		
0.362	1.4655	0.340	1.4045	0.310	1.4181		
0.487	1.4615	0.434	1.4102	0.404	1.4273		
0.590	1.4581	0.540	1.4165	0.500	1.4359		
0.695	1.4547	0.639	1.4225	0.608	1.4457		
0.763	1.4524	0.741	1.4286	0.708	1.4539		
0.848	1.4496	0.845	1.4349	0.823	1.4635		
0.913	1.4475	0.948	1.4415	0.938	1.4727		

APPARATUS

Vapor-liquid equilibria were determined in a dynamic ebulliometer after Cathala (*3, 4*) (Figure 1). Heated liquid and superheated vapor enter the mixing chamber at a constant rate where they equilibrate. The two phases remaining are then separated, collected, and analyzed.

Thermocouples are inserted in the exit of the Cottrell pump to measure the vapor-liquid temperature, and in the vapor jacket to measure the exiting vapor temperature. The difference between the two thermocouple readings controls the feed conditions and ensures that there is no radial temperature gradient in the separator.

Preliminary experiments, with both entering streams in liquid and vapor states, were run to ensure that the feeds used in the equilibrium determinations were in true equilibrium. These control experiments were made with each binary system, reversing the feeds on several occasions. Only three points are shown in Table III. Composition variations were less than 0.005 mole fraction, the limits of experimental accuracy possible with this apparatus. The results from this apparatus were compared with those from other types of equilibrium stills in the case of acetic acid–water binary systems (*6*). The thermocouples were iron-constantan calibrated against a platinum resistance thermometer. Temperatures were accurate to 0.1° C.

About 20 min were necessary to achieve equilibrium, after which samples were collected. The use of a peristaltic pump to feed the apparatus limited the amount of feed necessary for a determination to about 100 ml.

ANALYSIS OF SAMPLES

An immersion refractometer, with sodium-D line illumination, was used to measure refractive indices. All measurements were made at 20° ± 0.1° C. The maximum error possible was less than 0.003 mole fraction.

Refractive index–composition data were determined at 20° C for each of the 11 binary systems (Table IV). These data have not been previously published. However, refractometry is inadequate to determine composition of samples from the following systems:

1,2-*trans*-dichloroethene–1,2-*cis*-dichloroethene
1,1,1-trichloroethane–1,2-*trans*-dichloroethene
1,2-*cis*-dichloroethene–1,1,1-trichloroethane

Measurements on these systems are made with gas chromatography and are accurate to 0.02 mole fraction.

RESULTS AND DISCUSSION

Vapor-liquid equilibria were determined at 760 mm Hg for each system in Table I. Seven of these binary mixtures had a positive azeotrope. The azeotropic coordinates were determined in this work and in the previous works (*7, 10, 14*) as indicated in Table V.

The consistency of the data was examined for each system by plotting $(y - x)$ against x. In each case the curves were smooth, indicating no significant errors in the data. A stricter test for thermodynamic consistency is obtained by integrating the Gibbs-Duhem equation over the composition range at constant pressure. The appropriate equation is

$$\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = \int_0^1 \left(\frac{\Delta H_m}{RT^2}\right) (dT/dx_1) dx_1$$

where ΔH_m represents the heat of mixing per mole of mixture. The heats of mixing for these systems are not available in the literature. The thermodynamic consistency of the isobaric activity coefficient (γ_1, γ_2) at 760 mm Hg was tested by plotting log (γ_1/γ_2) against composition.

Table V. Azeotropic Coordinates

Systems	$(t° C)_{AZ}$ Exptl	$(t° C)_{AZ}$ Lit.	$(x_1)_{AZ}$ Exptl	$(x_1)_{AZ}$ Lit.
Ethylene chloride–trichloroethene	82.1	82.3 (*7*)	67.5	65.8 (*7*)
Ethylene chloride–*n*-propyl alcohol	80.4	80.5 (*10*)	75.0	73.5 (*10*)
Trichloroethene–*n*-propyl alcohol	81.6	81.75 (*10*) 81.8 (*7*)	71.8	69.0 (*10*) 69.0 (*7*)
n-Propyl alcohol–tetrachloroethene	94.0	94.0 (*10*) 94.05 (*7*)	70.5	72.3 (*10*) 71.7 (*7*)
Carbon tetrachloride–ethylene chloride	75.2	75.55 (*10*) 75.3 (*14*)	70.0	70.7 (*10*) 70.0 (*14*)
Ethylene chloride–ethyl alcohol	70.1	70.5 (*10*) 71.0 (*7*)	49.5	46.4 (*10*) 48.0 (*7*)
Methyl alcohol–tetrachloroethene	63.5	63.75 (*10*)	88.3	89.8 (*10*)

Except for the *n*-propyl alcohol–ethylene chloride system, where the difference in area was about 20%, the area difference in all systems was less than 10%. Since the heats of mixing are not negligible, the results are consistent.

CONCLUSION

The results obtained agree with other published results (*1, 2, 9, 14*). The data obtained in this work may be exploited to determine ternary vapor-liquid equilibrium data with the aid of such tools as van Laar, Margules, and Wilson's equations (*12, 13*).

ACKNOWLEDGMENT

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NOMENCLATURE

x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
t = temperature, ° C

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