J. Chem. Eng. Data 1990, 35, 288–291

Densities and Viscosities of Binary and Ternary Liquid Systems Containing Xylenes

Lurdes Serrano,* J. Alves Silva, and Fátima Farelo

Department of Chemical Engineering, Technical University of Lisbon, 1096 Lisboa Codex, Portugal

Experimental measurements of density and viscosity of three binary systems, viz., *p*-xylene/*m*-xylene, *p*-xylene/*o*-xylene, and *m*-xylene/*o*-xylene, were performed over the complete concentration ranges, for temperatures between 273.15 and 303.15 K. For the same temperature interval, densities and viscosities of three ternary mixtures of the isomers were obtained. Experimental densities were compared with those predicted by the Hankinson–Brobst–Thomson method, showing average deviations of about 0.3%. The viscosity data were correlated by the McAllister equations, producing excellent representations of both binary and ternary data.

Introduction

The ability to accurately predict the viscosities of multicomponent organic mixtures over wide ranges of concentration and temperature is of the utmost importance when modeling and designing melt crystallizers. Due to the characteristics of their solid–liquid phase diagram, ternary xylene mixtures are specially suited to test the models developed. Nevertheless, to our knowledge, no viscosity data on these ternary mixtures were previously reported.

In this study, the viscosities and densities of binary and ternary mixtures of *p*-, *m*-, and *o*-xylenes were measured over the temperature range 273.15–303.15 K. Viscosity data were fitted to the semitheoretical relations proposed by McAllister (*1*) and by Kalidas and Laddha (*2*). Density data for the binary and ternary mixtures were compared with those predicted by the Hankinson–Brobst–Thomson method (HBT) extended to compressed liquids (*3*).

Experimental Section

Analytical grade xylenes were purchased from Fluka. *p*-Xylene was purified by continuous crystallization in a 2-in.-diameter column, Newton-Chambers (Sheffield, England) to 99.98%. *m*-Xylene and *o*-xylene were purified by standard methods (*4*) and subsequently analyzed by gas chromatography in a $^1/_8$-in.-diameter, 400-cm-length column ready packed with 4% Bentone 34, 3% silicone oil, and 10% dinonyl phthalate on Chromosorb W. The mole percentage of impurities in the purified *o*-xylene was 0.32 (mainly *m*-xylene) while in *m*-xylene it was 0.27 (0.13 and 0.14 of *o*- and *p*-xylene, respectively).

For each pure liquid, the measured density, the viscosity, and the refractive index at 298.15 K are listed in Table I. These values agree, within experimental error, with the literature values.

Solutions were prepared by weighing the chemicals directly into screw-capped Pyrex tubes, and the composition was checked by gas chromatography. The compositions are considered accurate to ±0.0004 in mole fraction.

For each binary system, the measurements were made at mole fraction intervals of about 0.1. Three ternary mixtures of X_1(*p*-xylene) + X_2(*o*-xylene) + X_3(*m*-xylene) were also studied, having the following compositions: $X_1 = 0.4890$, $X_2 = 0.2601$, $X_3 = 0.2509$; $X_1 = 0.2376$, $X_2 = 0.2391$, $X_3 = 0.5233$; $X_1 = 0.2297$, $X_2 = 0.5047$, $X_3 = 0.2656$.

Table I. Physical Properties[a] of Pure Chemicals at 298.15 K

	ρ, g cm^{-3}		η, cP		n_D	
chemical	exptl	lit.[b]	exptl	lit.[c]	exptl	lit.[b]
p-xylene	0.85663	0.85669	0.611	0.610	1.49323	1.49325
m-xylene	0.86006	0.85990	0.590	0.600	1.49466	1.49464
o-xylene	0.87538	0.87596	0.757	0.760	1.50268	1.50295
benzene	0.87365	0.87370	0.603	0.603[b]	1.49795	1.49796

[a] Symbols: ρ = density; η = viscosity; n_D = refractive index. [b] Reference 5. [c] Reference 6.

Density and viscosity measurements were carried out soon after the samples preparation in order to avoid preferential evaporation. All transfers of material between the screw-capped Pyrex tubes and the measuring apparatuses were made with syringes to reduce evaporation losses. Precautions were taken to prevent condensation of moisture into the samples during the temperature stabilization period.

Kinematic viscosities of the pure liquids and solutions were determined from flow times by using standard Ubbelohde viscometers (VHB-590, size I) recalibrated against distilled water (at each temperature studied) to check the manufacturer's calibration constant. Recalibration taking into account the kinetic end effects involved corrections lower than 0.5%. Measurements with benzene at 298.15 K were performed in order to ascertain the accuracy of our readings. The kinematic viscosities listed here represent the average values of at least five readings per sample and are estimated to be accurate to within ±0.002 cSt.

Densities of the pure and mixed fluids were obtained at the same temperatures used for viscosity measurements. Experiments were performed with a 20-mL pycnometer calibrated at each temperature with distilled water. Data reported in this study represent the average values of triplicate measurements with a reproducibility to ±0.000 05 g/cm^3.

Prior to any reading, the solutions contained in the viscometer and pycnometer were allowed a period of 30–45 min for temperature equilibration. The thermostated bath, Haake NB 22, equipped with an auxiliary cooler, EK11, was filled with ethanol and controlled to within ±0.01 K, near room temperature. For experiments below 283 K, temperature control was no better than ±0.03 K. The temperature was read with a Pt resistance thermometer coupled to a 6800 Comark microprocessor with a ±0.01 K resolution. The Pt resistance thermometer was calibrated to the IPTS-1968 scale over the temperature range 263–323 K and estimated to be accurate to ±0.08 K.

The viscosities and densities of samples made up of pure *p*-xylene or containing very high contents of this chemical could not be obtained for the lower temperatures investigated, due to their short crystallization induction period (melting point of pure *p*-xylene, 286.41 K).

Results and Discussion

Binary Systems. The experimental values of kinematic viscosities and densities for the three binaries, at different

0021-9568/90/1735-0288$02.50/0

Table II. Kinematic Viscosity Data for the Binary Mixtures at Various Temperatures

		viscosity, cSt						
system	X_1[a]	273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
p-xylene (1) + *m*-xylene	0.0000	0.916	0.857	0.809	0.760	0.719	0.686	0.650
	0.1059	0.922	0.863	0.812	0.762	0.722	0.688	0.653
	0.2110	0.928	0.869	0.815	0.766	0.727	0.690	0.656
	0.3111	0.932	0.871	0.818	0.771	0.731	0.693	0.658
	0.4004	0.936	0.875	0.822	0.777	0.733	0.696	0.661
	0.4942	0.941	0.877	0.825	0.779	0.738	0.698	0.663
	0.6121	0.949	0.886	0.830	0.782	0.741	0.700	0.666
	0.7004	0.953	0.890	0.834	0.786	0.743	0.705	0.668
	0.8132		0.893	0.839	0.791	0.748	0.709	0.672
	0.9097			0.842	0.793	0.751	0.710	0.674
	1.0000				0.798	0.752	0.713	0.676
p-xylene (1) + *o*-xylene	0.0000	1.225	1.136	1.054	0.980	0.920	0.865	0.814
	0.1022	1.192	1.105	1.027	0.958	0.899	0.845	0.799
	0.1927	1.160	1.076	1.000	0.933	0.882	0.826	0.781
	0.3017	1.125	1.047	0.976	0.912	0.859	0.807	0.766
	0.3961	1.097	1.025	0.956	0.892	0.840	0.793	0.751
	0.4960	1.073	0.995	0.935	0.875	0.825	0.777	0.738
	0.6119	1.046	0.969	0.912	0.857	0.810	0.761	0.722
	0.7034	1.026	0.949	0.896	0.842	0.795	0.749	0.710
	0.7900		0.934	0.881	0.826	0.780	0.738	0.699
	0.9031		0.922	0.863	0.810	0.767	0.723	0.687
	1.000				0.798	0.752	0.713	0.676
m-xylene (1) + *o*-xylene	0.0000	1.225	1.136	1.054	0.980	0.920	0.865	0.814
	0.1001	1.173	1.099	1.024	0.956	0.896	0.843	0.799
	0.2081	1.133	1.067	0.992	0.929	0.874	0.820	0.778
	0.2907	1.100	1.039	0.964	0.903	0.854	0.804	0.760
	0.4111	1.062	0.998	0.936	0.876	0.828	0.782	0.740
	0.5029	1.036	0.975	0.914	0.858	0.810	0.767	0.725
	0.6175	1.014	0.947	0.889	0.835	0.787	0.745	0.705
	0.7339	0.980	0.913	0.863	0.813	0.765	0.726	0.690
	0.8046	0.958	0.897	0.845	0.796	0.753	0.716	0.679
	0.9040	0.931	0.874	0.824	0.782	0.737	0.698	0.666
	1.0000	0.916	0.857	0.809	0.760	0.719	0.686	0.650

[a] X_1 = mole fraction of species 1.

Table III. Density Data for the Binary Mixtures at Various Temperatures

		density, g cm^{-3}						
system	X_1[a]	273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
p-xylene (1) + *m*-xylene	0.0000	0.880 36	0.876 62	0.872 54	0.868 09	0.863 78	0.860 06	0.855 87
	0.1059	0.880 02	0.876 18	0.872 25	0.867 55	0.863 53	0.859 77	0.855 31
	0.2110	0.882 19	0.875 87	0.871 83	0.867 27	0.863 32	0.859 59	0.855 02
	0.3111	0.879 71	0.875 58	0.871 43	0.866 97	0.863 12	0.859 42	0.854 84
	0.4004	0.879 49	0.875 30	0.871 24	0.866 73	0.862 84	0.859 13	0.854 70
	0.4942	0.879 25	0.875 00	0.871 03	0.866 47	0.862 55	0.858 81	0.854 49
	0.6121	0.878 82	0.874 64	0.870 58	0.866 14	0.862 06	0.858 40	0.854 14
	0.7004	0.878 50	0.874 40	0.870 24	0.865 91	0.861 63	0.858 06	0.853 66
	0.8132		0.874 08	0.870 03	0.865 51	0.861 33	0.857 62	0.853 24
	0.9097			0.869 89	0.865 16	0.861 06	0.857 20	0.852 91
	1.0000				0.864 88	0.860 73	0.856 72	0.852 39
p-xylene (1) + *o*-xylene	0.0000	0.894 37	0.891 37	0.887 39	0.882 88	0.879 46	0.875 58	0.871 36
	0.0969	0.892 41	0.889 37	0.885 41	0.881 26	0.877 11	0.873 44	0.869 28
	0.1927	0.890 99	0.887 68	0.883 87	0.879 65	0.875 40	0.871 50	0.867 41
	0.2790	0.889 76	0.886 16	0.882 53	0.878 21	0.873 88	0.869 75	0.865 73
	0.3961	0.887 65	0.884 08	0.880 24	0.876 02	0.871 75	0.867 67	0.863 65
	0.4898	0.885 99	0.882 45	0.878 42	0.874 28	0.870 07	0.866 05	0.862 03
	0.6119	0.883 77	0.880 19	0.876 14	0.872 10	0.867 85	0.863 82	0.859 78
	0.6921	0.882 35	0.878 73	0.874 66	0.870 73	0.866 44	0.862 40	0.858 33
	0.8273	0.880 19	0.876 13	0.872 41	0.868 24	0.863 87	0.859 87	0.855 68
	0.9031		0.874 69	0.870 98	0.866 80	0.862 43	0.858 42	0.854 23
	1.0000				0.864 88	0.860 73	0.856 72	0.852 39
m-xylene (1) + *o*-xylene	0.0000	0.894 37	0.891 37	0.887 39	0.882 88	0.879 46	0.875 58	0.871 36
	0.1001	0.892 86	0.889 80	0.885 77	0.881 51	0.877 27	0.873 64	0.869 59
	0.2081	0.891 52	0.888 09	0.884 12	0.879 77	0.875 71	0.872 17	0.868 31
	0.2907	0.890 58	0.886 77	0.882 86	0.878 43	0.874 47	0.870 70	0.866 39
	0.4111	0.888 65	0.885 01	0.881 14	0.876 81	0.872 53	0.868 96	0.864 97
	0.5029	0.887 16	0.883 70	0.879 86	0.875 64	0.871 31	0.867 77	0.863 53
	0.6175	0.885 57	0.882 04	0.878 15	0.873 97	0.869 52	0.865 89	0.861 15
	0.7339	0.883 97	0.880 36	0.876 41	0.872 28	0.867 93	0.864 02	0.860 14
	0.8046	0.882 93	0.879 19	0.875 34	0.871 13	0.867 01	0.862 87	0.859 06
	0.9040	0.881 46	0.877 59	0.873 90	0.869 55	0.865 31	0.861 42	0.857 51
	1.000	0.880 36	0.876 62	0.872 54	0.868 09	0.863 78	0.860 06	0.855 87

[a] X_1 = mole fraction of species 1.

Table IV. Kinematic Viscosity and Density Data for Ternary System *p*-Xylene (1) + *m*-Xylene (2) + *o*-Xylene (3) at Various Temperatures

system	mole fraction			273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
I	$x_1 = 0.4890$	ρ, g/cm^3	exptl	0.882 06	0.878 53	0.874 39	0.870 45	0.866 11	0.862 07	0.857 86
	$x_2 = 0.2601$		calcd	0.885 22	0.880 98	0.876 72	0.872 45	0.868 16	0.863 84	0.859 51
	$x_3 = 0.2509$	ν, cSt	exptl	0.994	0.933	0.874	0.821	0.776	0.734	0.698
			calcd	0.993	0.931	0.874	0.823	0.777	0.734	0.695
II	$x_1 = 0.2376$	ρ, g/cm^3	exptl	0.886 99	0.882 98	0.879 01	0.875 27	0.871 00	0.866 96	0.862 55
	$x_2 = 0.2391$		calcd	0.890 29	0.886 07	0.881 83	0.877 58	0.873 30	0.869 00	0.864 69
	$x_3 = 0.5233$	ν, cSt	exptl	1.052	0.989	0.927	0.870	0.822	0.779	0.738
			calcd	1.055	0.987	0.926	0.870	0.821	0.774	0.732
III	$x_1 = 0.2297$	ρ, g/cm^3	exptl	0.883 56	0.879 62	0.875 36	0.871 43	0.867 36	0.863 06	0.858 88
	$x_2 = 0.5047$		calcd	0.886 40	0.882 16	0.877 90	0.873 63	0.869 33	0.865 01	0.860 67
	$x_3 = 0.2656$	ν, cSt	exptl	0.990	0.924	0.866	0.815	0.768	0.725	0.690
			calcd	0.982	0.922	0.867	0.817	0.771	0.730	0.692

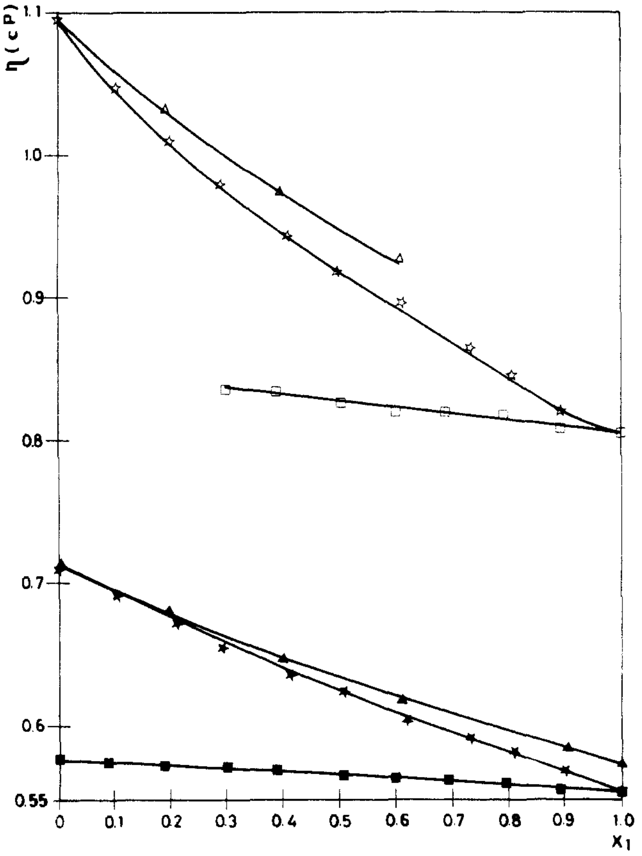

Figure 1. Dynamic viscosities vs composition of binary xylene systems. Experimental data at 273.15 K (open symbols) and 303.15 K (filled symbols): (△,▲) *p*-xylene (1)/*o*-xylene; (☆,★) *m*-xylene (1)/*o*-xylene; (□,■) *m*-xylene (1)/*p*-xylene. Calculated data: solid lines.

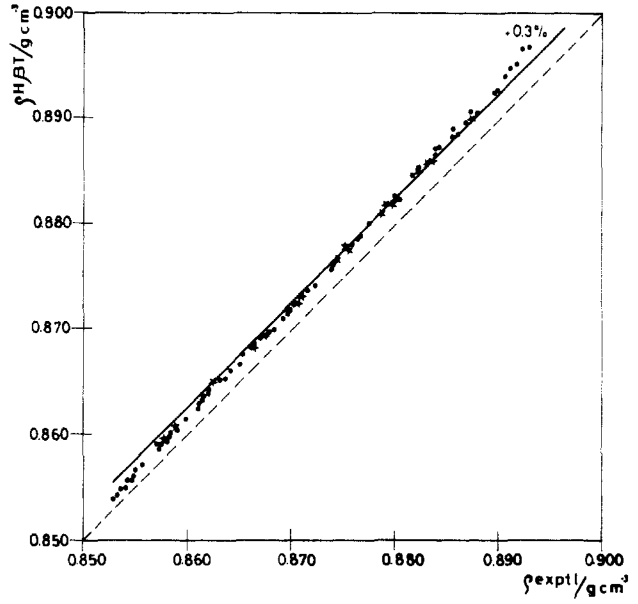

Figure 2. Parity plot of HBT vs experimental densities: (●) binary data; (★) ternary data.

temperatures and over the concentration range, are presented in Tables II and III, respectively.

Density data were also predicted as a function of temperature by the HBT method. Pure-components critical data required to estimate the liquid densities were obtained from the literature (*3*). For the three systems studied, the estimated densities are always higher than the experimental values with an average deviation of less than 0.3% and a maximum error of 0.47% for pure *o*-xylene at 273.15 K.

The binary kinematic viscosity data were correlated by using the cubic equation of McAllister (*1*)

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 + R^\circ \quad (1)$$

where R° was set equal to zero, since, for isomeric mixtures, the molecular weights ratio equals unity.

Pure-liquids viscosity data, ν_i, were first correlated with absolute temperature, using a two-constant Andrade-type equation, with correlation coefficients ranging from 0.9995 for *m*-xylene to 0.9999 for *p*-xylene. For both adjustable interaction parameters, ν_{ij} and ν_{ji}, a temperature dependence of the same form was adopted:

$$\nu_{ij} = A_{ij} \exp(B_{ij}/T) \quad (2)$$

Therefore, for each binary system the four Andrade parameters, A_{ij} and B_{ij} (i and j = 1,2; $i \neq j$), were estimated over the global set of data obtained at various temperatures and compositions, using the Nelder–Mead multivariable search method (*7*).

Comparison of experimental data with those obtained from the McAllister equation, after substitution of the values of the parameters, shows overall mean deviations of about 0.25% for the three systems. The largest percent deviations were found in general for 273.15 and 278.15 K (where the mean error is about 0.34%). In spite of the required extrapolation of the Andrade equation into the supercooled region for pure *p*-xylene, the deviation of the calculated viscosities of *p*-xylene binaries does not visibly depart from the average value.

In Figure 1 some experimental and calculated dynamic viscosities were plotted versus composition, for boundary temperatures 273.15 and 303.15 K. As expected, due to the similarity of the chemical species involved, very slight deviations from linearity were obtained.

Ternary Systems. Three ternary mixtures of xylenes were investigated in the temperature range 273.15–303.15 K. The experimental density and viscosity data are presented in Table IV, along with the corresponding estimated values.

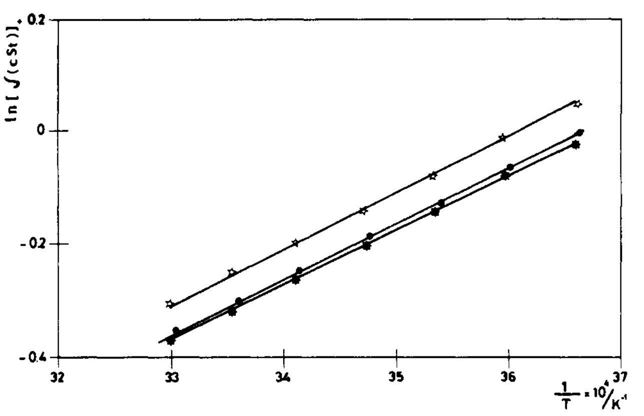

Figure 3. Kinematic viscosities of three ternary mixtures vs absolute reciprocal temperature. Experimental data: (●) (I); (☆) (II); (✱) (III). Calculated data: solid lines.

Table V. Andrade Constants for Kinematic Viscosity Correlation and Quality of Fit in the Temperature Range 273.15–303.15 K

system	A, cSt	B, K	$\delta(\nu)$, cSt	$(\Delta\nu\%)_{av}$
p-xylene, ν_1	0.028 21	962.83	0.0008	0.07
m-xylene, ν_2	0.028 37	948.50	0.0023	0.26
o-xylene, ν_3	0.019 54	1129.54	0.0031	0.25
p-xylene (1)/*m*-xylene (2)				
ν_{12}	0.025 65	987.21	0.0026	0.22
ν_{21}	0.028 78	948.62		
p-xylene (1)/*o*-xylene (3)				
ν_{13}	0.025 09	1013.77	0.0031	0.24
ν_{31}	0.023 75	1048.60		
m-xylene (2)/*o*-xylene (3)				
ν_{23}	0.029 16	962.67	0.0030	0.24
ν_{31}	0.029 17	986.10		
ternary mixtures				0.17 (I)
ν_{123}	0.031 23	941.67	0.0032	0.48 (II)
				0.45 (III)

Density predictions were carried out with the HBT method, the mean deviations between experimental and calculated values being always less than 0.3%. Figure 2 is a parity plot of measured and calculated binary and ternary densities for the xylene mixtures studied.

The correlation of the ternary kinematic viscosity data, over the temperature range 273.15–303.15 K, was performed with the Kalidas and Laddha expansion of the McAllister equation (*2*)

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + x_3^3 \ln \nu_3 + 3x_1^2x_2 \ln \nu_{12} + 3x_1^2x_3 \ln \nu_{13} + 3x_2^2x_1 \ln \nu_{21} + 3x_2^2x_3 \ln \nu_{23} + 3x_3^2x_1 \ln \nu_{31} + 3x_3^2x_2 \ln \nu_{32} + 6x_1x_2x_3 \ln \nu_{123} + R'^{\circ} \quad (3)$$

where once again R'° was set equal to zero for reasons identical with those given before for binary mixtures.

Equation 3 requires the knowledge of the binary interaction coefficient, ν_{123}, which must be assessed from experimental data. Therefore, assuming for this coefficient a temperature dependence as described by eq 2 and using pure-component and binary parameters, the two ternary Andrade constants, A_{123} and B_{123}, were calculated over the experimental data gathered for system I (Table IV). Mixtures II and III were used to evaluate the effectiveness of the McAllister method in the prediction of the viscosities of ternary systems. The average deviation found was about 0.37%. Figure 3 shows the experimental and calculated ternary viscosity data plotted as a function of the absolute temperature reciprocal.

The Andrade parameters required to estimate the kinematic viscosities of the ternary system, in the temperature range previously referred to, are shown in Table V along with the standard deviations, $s(\nu)$, and average percent deviations $(\Delta\nu\%)_{av}$. The accuracy with which the McAllister equation fits the viscosity data for binary mixtures of xylenes supports the use of this equation in the range of temperature studied. For liquid ternary mixtures, it also allows the estimation of viscosity data, over the whole concentration range, within acceptable margins of accuracy.

Registry No. *o*-Xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3.

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Received for review April 18, 1989. Accepted March 16, 1990. This work was sponsored by the Instituto Nacional de Investigação Científica, Portugal (Grant No. TLE/6-1F88).

Heat of Mixing of 1,3-Dioxolane + Trichloroethylene

Romolo Francesconi*

Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, 40126 Bologna, Italy

Fabio Comelli

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, 40126 Bologna, Italy

The excess molar enthalpy H^E of 1,3-dioxolane + trichloroethylene was measured in a flow microcalorimeter as a function of mole fraction x_1 of 1,3-dioxolane at 288.15, 298.15, and 313.15 K under atmospheric pressure. The H^E vs x_1 curves are S-shaped, with $H^E < 0$ over nearly the entire x_1 range, except at $x_1 \simeq 1$, and with positive molar excess heat capacity, $C_p^E = dH^E/dT$. This suggests complex formation in the liquid mixture.

Introduction

The present work is an extension of a series of previous investigations (*1*) on binary mixtures of a common solvent, 1,3-dioxolane. The main purpose of these studies is to obtain thermodynamic information as to the dependence of the molar excess enthalpy H^E on the nature of the groups of the second component. The group investigated in this paper is the chlorine of trichloroethylene.

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