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Excess Volumes for Ternary Mixtures Containing 1,1,1-Trichloroethane + *n*-Hexane with 1-Propanol, 1-Butanol, and 1-Pentanol, at 303.15 K

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Excess volumes of three ternary mixtures were measured at 303.15 K. The mixtures included 1,1,1-trichloroethane and *n*-hexane as common components. 1-Propanol, 1-butanol, and 1-pentanol were noncommon components. Excess volumes are positive over the entire range of composition in the three mixtures. The positive excess volume has been attributed to the dominant nature of the structure-breaking effect of the components. The experimental results were also compared with those predicted by empirical equations (*1*).

Introduction

It is observed from a survey of the literature that excess thermodynamic properties of ternary mixtures have been measured to a limited extent. Further, it is found that no data have been collected for ternary mixtures that include halogenated hydrocarbons and hydrocarbons as common components. Hence, we report here new experimental data, at 303.15 K, for excess volumes of three ternary mixtures. The mixtures included 1,1,1-trichloroethane and hexane as common components and 1-propanol, 1-butanol, and 1-pentanol as noncommon components. The measured excess volumes have been compared with those predicted from binary data with use of semiempirical equations (*1*).

Experimental Section

The ternary excess volumes were measured by a single component per loading dilatometer described by Naidu and Naidu (*2*). The mixing cell contained three bulbs of different capacities. Mercury was used in the bottom to separate three components. One of the three bulbs was fitted with a capillary (i.d., 1.0 mm), and the other two were fitted with ground-glass stoppers. The excess volumes measured were accurate to ±0.003 $cm^3\ mol^{-1}$.

Table I. Densities of Pure Components at 303.15 K

compound	densities, g/cm³ experimental	literature[5]
1,1,1-trichloroethane	1.321 02	1.320 96
1-propanol	0.795 71	0.795 67
1-butanol	0.801 94	0.802 06
1-pentanol	0.807 52	0.807 64
n-hexane	0.650 63	0.650 70

All the chemicals used were of analytical grade. The alcohols were further purified by the methods described by Rao and Naidu (*3*). 1,1,1-Trichloroethane and *n*-hexane were purified by the methods described by Riddick and Bunger (*4*). The dried samples were distilled through a fractionating column. The purity of the samples was checked by comparing the measured densities with those reported in the literature (*5*) (Table I). The densities were measured by a bicapillary pycnometer that offered an accuracy of 3 parts in 10^5.

Results

The excess volume data for three ternary systems are given in Table II. The binary data for 1,1,1-trichloroethane with 1-alkanols and 1,1,1-trichloroethane with *n*-hexane were taken from the literature (*6*, *7*). The measured excess volume data for the binary systems of *n*-hexane with the three 1-alkanols are graphicly represented in Figure 1. The least-squares parameters for all these binary systems are given in Table III. The ternary excess volume data predicted on the basis of empirical equations proposed by Redlich-Kister, Kohler, and Tsao-Smith, are given in columns 3-5 of Table II.

The dependence of experimental ternary excess volumes $V^E_{123}(\mathrm{exp})$ on composition is expressed by the polynomial

$$V^E_{123}(\mathrm{exp}) = V^E_{123}(\mathrm{b}) + X_1X_2X_3[A + BX_1(X_2 - X_3) + CX_1^2(X_2 - X_3)^2] \quad (1)$$

Table II. Excess Volumes of Ternary Systems, 1,1,1-Trichloroethane (1) + *n*-Hexane (2) + 1-Alkanol (3) at 303.15 K

			V^E_{123}				
X_1	X_3	V^E(exp)	Redlich and Kister	Kohler	Tsao-Smith	ΔV^E_{123}[a]	δ^E[b]
		1,1,1-Trichloroethane + *n*-Hexane + 1-Propanol					
0.1300	0.5807	0.165	0.103	0.095	0.098	0.062	0.002
0.1753	0.4175	0.276	0.181	0.172	0.182	0.095	0.001
0.2034	0.6805	0.063	0.033	0.034	0.038	0.030	0.003
0.3205	0.3814	0.265	0.153	0.165	0.171	0.112	0.002
0.3253	0.2649	0.351	0.239	0.253	0.271	0.112	0.000
0.4062	0.3782	0.236	0.151	0.114	0.146	0.085	0.000
0.5108	0.2560	0.296	0.200	0.207	0.213	0.096	0.001
0.5710	0.2033	0.295	0.209	0.222	0.234	0.084	0.000
0.7142	0.2217	0.134	0.118	0.148	0.153	0.016	0.002
		1,1,1-Trichloroethane + *n*-Hexane + 1-Butanol					
0.1083	0.7588	0.004	-0.046	-0.058	-0.068	0.050	0.003
0.2344	0.6509	-0.005	-0.026	-0.044	-0.061	0.021	0.008
0.3058	0.5428	0.046	0.019	-0.002	-0.023	0.027	0.001
0.3985	0.4457	0.099	0.064	0.043	0.023	0.035	0.004
0.4147	0.4295	0.108	0.071	0.053	0.031	0.037	0.006
0.5973	0.2734	0.185	0.124	0.117	0.102	0.061	0.007
0.6392	0.2616	0.153	0.117	0.109	0.094	0.036	0.000
0.6970	0.1672	0.216	0.114	0.145	0.146	0.102	0.003
0.8248	0.0472	0.162	0.112	0.116	0.138	0.050	0.000
		1,1,1-Trichloroethane + *n*-Hexane + 1-Pentanol					
0.1875	0.5338	0.070	0.002	-0.009	-0.041	0.068	0.001
0.2360	0.6240	0.079	0.018	0.010	-0.016	0.061	0.003
0.3198	0.5136	0.145	0.065	0.055	0.017	0.080	0.004
0.4440	0.4293	0.201	0.120	0.110	0.073	0.081	0.009
0.4620	0.1903	0.287	0.198	0.218	0.179	0.089	0.006
0.5381	0.3425	0.203	0.155	0.148	0.155	0.048	0.008
0.6082	0.2666	0.226	0.175	0.172	0.131	0.051	0.003
0.6962	0.1541	0.214	0.180	0.185	0.152	0.034	0.005
0.7592	0.1779	0.185	0.164	0.163	0.137	0.021	0.001

[a] $\Delta V^E_{123} = V^E_{123}(\text{exp}) - V^E_{123}(\text{b})$, where $V^E_{123}(\text{b})$ is the excess volume predicted by the Redlich and Kister relation. [b] δ^E is the deviation of the experimental value, $\Delta V^E_{123}(\text{exp})$, from that calculated according to eq 1.

Table III. Equations Fitting the Experimental Data of the Excess Volumes for the Binary Systems and the Standard Deviation, $\sigma(V^E)$, at 303.15 K

	a_0, cm^3 mol^{-1}	a_1, cm^3 mol^{-1}	a_2, cm^3 mol^{-1}	$\sigma(V^E)$, cm^3 mol^{-1}
1,1,1-trichloroethane + *n*-hexane (6)	0.9490	0.0250	-0.4200	0.003
1,1,1-trichloroethane + 1-propanol (7)	0.1250	0.8420	0.4939	0.001
1,1,1-trichloroethane + 1-butanol (7)	0.0461	0.7403	0.1736	0.002
1,1,1-trichloroethane + 1-pentanol (7)	0.5027	0.6742	0.2673	0.006
n-hexane + 1-propanol	0.7124	1.1297	1.1301	0.004
n-hexane + 1-butanol	0.3690	1.1143	0.0706	0.004
n-hexane + 1-pentanol	-0.3629	0.7091	0.3912	0.005

where $V^E_{123}(\text{b}) = V^E_{12} + V^E_{23} + V^E_{13}$ and X_1, X_2, and X_3 are mole fractions of 1,1,1-trichloroethane, *n*-hexane, and an alcohol. *A*–*C* are constants, and their values, obtained by a least-squares method, are given in Table IV.

Discussion

The experimental ternary excess volumes are positive over the entire range of composition in the three ternary mixtures. The positive excess volumes suggest that the structure-breaking effect of the components is dominant in all three mixtures. This contention is in line with that used to explain excess volumes of the binaries present in each ternary mixture. The results show that there is no simple correlation between the excess volume of ternary mixtures and the chain length of the alcohols that are noncommon components in the mixtures.

A close examination of experimental data and those predicted by empirical equations shows that all the equations predict V^E_{123} values that are in qualitative agreement with the

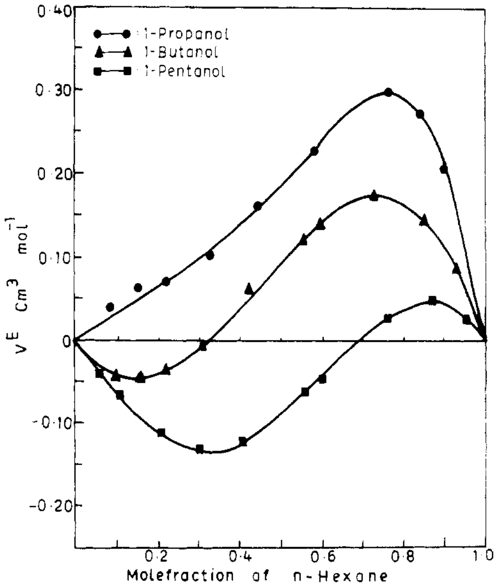

Figure 1. Mole fraction versus excess volume.

Table IV. Values of Ternary Constants, *A*–*C* and σ at 303.15 K

systems	*A*, cm^3 mol^{-1}	*B*, cm^3 mol^{-1}	*C*, cm^3 mol^{-1}	σ, cm^3 mol^{-1}
1,1,1-trichloroethane + *n*-hexane + 1-propanol	3.17	3.78	-78.3800	0.002
1,1,1-trichloroethane + *n*-hexane + 1-butanol	7.58	42.05	-99.50	0.005
1,1,1-trichloroethane + *n*-hexane + 1-pentanol	2.45	0.99	36.85	0.005

measured V^E_{123} data. Finally, it may be stated that none of the relations is capable of predicting the ternary data exactly.

Registry No. 1,1,1-Trichloroethane, 71-55-6; *n*-hexane, 110-54-3; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0.

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Compressibility Isotherms of Simulated Natural Gases

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The compressibility isotherms of two samples of simulated natural gases containing, respectively, 88% and 80% methane have been measured at 298.15 and 323.15 K and pressures up to 160 bar by using a Burnett apparatus. The experimental data for the compressibility factor are compared with values calculated by the recently developed truncated virial equation of state for multicomponent gas mixtures for which the appropriate parameters were previously evaluated from experimental *pVT* data of pure gases and binary and ternary gas mixtures. It is found that the virial equation of state is capable of predicting the compressibilities of natural gases within 0.1% of the experimental values, provided the density and the composition are within the applicability range of the fitted parameters.

Introduction

A study of the compressibility isotherms of natural gases is useful both from a practical and a theoretical point of view. On the practical side, a knowledge of the compressibility isotherms of natural gases is essential in the gas industry for performing custody-transfer calculations. The theoretical interest in this subject arises from the fact that natural gases are multicomponent mixtures and the development of an equation of state of such mixtures needs proper evaluation of the interaction of dissimilar molecules. Therefore, a number of investigations is currently being carried out at several gas research laboratories as well as at some academic institutions to develop accurate equations of state of natural gases in order to compute the compressibility factor for given values of pressure, temperature, and composition. However, in order to test the validity of these equations, accurate compressibility data for natural gases of different compositions are necessary. Measurements on simulated natural gases have the advantage that an equation of state can be examined for any desired composition. It is, therefore, considered worthwhile to measure the compressibility isotherms of two samples of simulated natural gas of different compositions and to examine how well a truncated form of the virial equation of state for multicomponent mixtures, developed recently in this laboratory (*1*, *2*), agrees with the experimental results. The experimental data reported in this paper should also be useful in evaluating the performance of other existing equations of state as well as in the development of new equations of state for multicomponent gas mixtures.

Table I. Composition of the Simulated Natural Gases

compounds	composition, mol % sample A	sample B	applicability range of GERG eq
methane	88.269	80.078	>50
ethane	6.115	11.641	<10
propane	0.998	6.530	<5
butane	0.989	1.750	<1.5
nitrogen	2.693	0	<50
carbon dioxide	0.936	0	<30

Experimental Section

The compressibility isotherms were measured in a Burnett apparatus based on repeated expansions of the measuring gas from a principal vessel to an expansion vessel. Since the apparatus, shown schematically in Figure 1, has been described in detail in a previous publication (*3*), only important features will be outlined here. The principal vessel, a steel cylinder A of 12-mm i.d., 30-mm o.d., and 27-cm^3 inner volume, is connected via an expansion valve V1 to a Ruska differential pressure meter B that together with the connecting capillaries form the expansion volume. The chambers can be evacuated or filled with the measuring gas by a filling–evacuation system attached to the apparatus via valve V2. The oil side of the differential pressure meter is connected to a hydraulic oil pump that in turn is connected to a Michels pressure balance and to a specially designed 3-m mercury column. The complete assembly including the valves is placed in an oil thermostat C, the temperature of which can be maintained constant to within 1 mK of any desired temperature by means of a proportional–integral temperature regulating system.

The measurements were carried out on two samples of simulated natural gas received from the Royal Dutch Shell Laboratory, Amsterdam. The compositions of the samples, as specified by the laboratory, are given in Table I. The experimental data were taken at 298.15 and 323.15 K and at pressures ranging from 1.5 to 160 bar. In each Burnett run, the chambers are filled with the sample gas to a desired initial pressure that is measured by the pressure balance after bringing the differential pressure meter to its null position. The accuracy of pressure measurements by the pressure balance is better than 0.01%. The expansion valve V1 is then closed, and the expansion volume is evacuated to 10^{-4} mmHg by

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