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Note

EXCESS MOLAR VOLUMES OF TRICHLOROETHYLENE WITH CYCLOHEXANONE, METHYLISOBUTYLKETONE, AND 1,4-DIOXANE AT 308.15 AND 318.15 K

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As part of a study of thermodynamic properties of binary liquid mixtures involving complex formation [1–3], we report in this paper excess molar volumes for trichloroethylene + cyclohexanone, + methylisobutylketone, and + 1,4-dioxane, measured at 308.15 and 318.15 K.

EXPERIMENTAL

Methylisobutylketone (B.D.H.) was purified by the method described earlier [4], trichloroethylene (B.D.H.), cyclohexanone (B.D.H.), and 1,4-dioxane (B.D.H.) were purified by the standard methods described in the literature [5]. The purity of the chemicals was ascertained by comparing the measured density and refractive index data with the literature values [6].

Excess molar volumes were measured using the continuous-dilution dilatometer of Dickinson et al. The procedure for filling and use of the dilatometer [7], and the calibration of the capillaries and glass tube used in the fabrication of the dilatometer [7,8], were described earlier. V_m^E values were accurate to ± 0.002 cm^3 mol^{-1}.

RESULTS AND DISCUSSION

Excess molar volumes for the three binary mixtures measured at 308.15 and 318.15 K are reported in Table 1 and plotted in Fig. 1. The composition dependence of excess molar volumes are represented by an equation of the type:

$$V_m^E(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\sum_{i=0}^{3} v_i(1-2x)^i \quad (1)$$

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TABLE 1

Experimental excess molar volumes

T (K)	x	V_m^E ($cm^3\ mol^{-1}$)	δV_m^E ($cm^3\ mol^{-1}$)	x	V_m^E ($cm^3\ mol^{-1}$)	δV_m^E ($cm^3\ mol^{-1}$)
x Trichloroethylene + (1 − x) cyclohexanone						
308.15	0.0882	−0.022	0.003	0.4168	−0.122	−0.001
	0.1429	−0.038	0.002	0.4994	−0.142	0.002
	0.1569	−0.042	0.002	0.5634	−0.155	0.005
	0.1811	−0.052	−0.001	0.6124	−0.165	0.004
	0.2015	−0.058	−0.001	0.6616	−0.174	0.000
	0.2311	−0.066	−0.001	0.7264	−0.178	−0.005
	0.2618	−0.075	−0.001	0.7786	−0.169	−0.005
	0.2975	−0.085	−0.001	0.8319	−0.148	−0.003
	0.3455	−0.101	−0.002	0.9270	−0.076	0.006
	0.3849	−0.112	−0.001			
318.15	0.1305	−0.061	0.000	0.4783	−0.201	−0.007
	0.1521	−0.072	−0.002	0.5194	−0.202	0.005
	0.1843	−0.085	−0.003	0.6111	−0.228	0.001
	0.2172	−0.091	−0.004	0.6607	−0.231	0.002
	0.2401	−0.102	0.002	0.7606	−0.223	−0.003
	0.3016	−0.125	0.002	0.8492	−0.182	−0.006
	0.3730	−0.159	−0.004	0.8907	−0.132	0.007
	0.4233	−0.171	0.003			
x Trichloroethylene + (1 − x) methylisobutylketone						
308.15	0.1435	−0.052	−0.004	0.4331	−0.157	−0.004
	0.1867	−0.071	−0.003	0.4942	−0.172	−0.005
	0.2334	−0.086	0.002	0.5594	−0.183	−0.004
	0.2549	−0.093	0.004	0.6262	−0.191	−0.001
	0.2695	−0.099	0.004	0.6581	−0.194	0.001
	0.3059	−0.113	0.004	0.7243	−0.196	0.005
	0.3784	−0.138	0.001	0.8206	−0.187	0.005
	0.4137	−0.148	0.001	0.8974	−0.157	−0.007
318.15	0.1042	−0.062	−0.002	0.4655	−0.209	−0.002
	0.1777	−0.105	−0.005	0.5386	−0.223	−0.006
	0.2057	−0.112	0.002	0.6510	−0.211	0.004
	0.2486	−0.134	0.000	0.7208	−0.198	0.002
	0.2653	−0.139	0.003	0.7792	−0.178	0.000
	0.2959	−0.151	0.004	0.8189	−0.158	0.000
	0.3371	−0.169	0.001	0.8665	−0.124	0.004
	0.4006	−0.192	−0.001	0.9184	−0.092	−0.006
x Trichloroethylene + (1 − x) 1,4-dioxane						
308.15	0.1093	0.026	−0.003	0.5889	0.027	−0.002
	0.1854	0.041	−0.003	0.6286	0.017	−0.001
	0.2303	0.054	0.003	0.6809	0.007	0.006
	0.2618	0.057	0.002	0.7229	−0.013	0.001
	0.3202	0.063	0.004	0.7632	−0.024	0.002

TABLE 1 (continued)

T (K)	x	V_m^E ($cm^3\ mol^{-1}$)	δV_m^E ($cm^3\ mol^{-1}$)	x	V_m^E ($cm^3\ mol^{-1}$)	δV_m^E ($cm^3\ mol^{-1}$)
	0.3896	0.061	0.001	0.8222	−0.042	−0.001
	0.4197	0.056	−0.003	0.8669	−0.048	−0.001
	0.4869	0.048	−0.003	0.8958	−0.048	−0.002
	0.5526	0.036	−0.002	0.9249	−0.041	−0.001
318.15	0.1088	0.026	0.000	0.5042	−0.020	0.001
	0.1304	0.029	0.000	0.5527	−0.032	−0.001
	0.1595	0.030	−0.001	0.6335	−0.045	0.002
	0.2040	0.031	0.000	0.7003	−0.054	0.001
	0.2415	0.029	0.000	0.7541	−0.059	−0.002
	0.2861	0.025	0.001	0.7849	−0.058	−0.001
	0.3456	0.014	−0.001	0.8381	−0.052	0.000
	0.3667	0.013	0.002	0.9125	−0.034	0.001
	0.4587	−0.012	−0.002			

where x is the mole fraction of trichloroethylene. The values of the parameters v_i are obtained by the method of least squares and are given in Table 2, along with the standard deviations $\sigma(V_m^E)$. The difference between experimental V_m^E and that obtained on the basis of eqn. (1), for the same mole fraction, are given in Table 1 as δV_m^E.

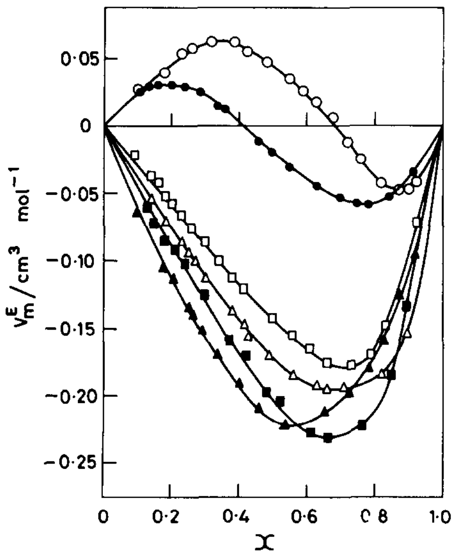

Fig. 1. Excess molar volumes: x trichloroethylene + $(1-x)$ cyclohexanone at (□) 308.15 K, (■) 318.15 K; x trichloroethylene + $(1-x)$ methylisobutylketone at (△) 308.15 K, (▲) 318.15 K; and x trichloroethylene + $(1-x)$ 1,4-dioxane at (○) 308.15 K, (●) 318.15 K.

TABLE 2

The least-square parameters and standard deviation of V_m^E

x Trichloroethylene +	T (K)	v_0	v_1	v_2	v_3	$\sigma(V_m^E)$ ($cm^3\ mol^{-1}$)
$(1-x)$ Cyclohexanone	308.15	−0.5788	−0.5317	−0.2471	0.0044	0.003
	318.15	−0.8069	−0.6491	−0.2993	0.1238	0.005
$(1-x)$ Methyliso-	308.15	−0.6711	−0.3982	−0.4849	−0.6770	0.004
butylketone	318.15	−0.8510	−0.2877	−0.0625	−0.0284	0.003
$(1-x)$ 1,4-Dioxane	308.15	0.1973	−0.3394	−0.4626	−0.2567	0.003
	318.15	−0.0780	−0.4671	0.0003	0.0386	0.001

Excess molar volumes are negative in the mixtures of trichloroethylene + cyclohexanone, and + methylisobutylketone, over the whole composition range, at both temperatures. V_m^E values are skewed towards higher x values in the two systems. In the system of trichloroethylene + 1,4-dioxane, V_m^E values change sign from positive to negative with increase in x. The change in sign of V_m^E is observed at $x \approx 0.7$ and 0.4, at 308.15 and 318.15 K, respectively. Negative V_m^E may be attributed to the presence of strong dipolar interactions and is probably due to formation of hydrogen bonds between unlike molecules. Positive V_m^E values, in the lower range of x for the trichloroethylene + 1,4-dioxane, may be due to the existance of weak dipolar interactions between unlike molecules. The magnitude of the observed V_m^E in the three systems, is in order with the polarizabilities of the non-common components. The negative temperature coefficient of V_m^E indicates the formation of complex in the three systems.

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