International Journal of Thermophysics, Vol. 21, No. 5, 2000

Excess Molar Volumes of the Ternary Mixture (Cyclohexane + Tetrahydrofuran + Chlorocyclohexane) and the Binary Mixtures (Cyclohexane + Tetrahydrofuran and Cyclohexane + Chlorocyclohexane) at 298.15 and 313.15 K

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Received April 18, 2000

Densities of the ternary mixture (cyclohexane + tetrahydrofuran + chlorocyclohexane) and the binary mixtures (cyclohexane + tetrahydrofuran and cyclohexane + chlorocyclohexane) have been measured at 298.15 and 313.15 K. Excess molar volumes for the binary and ternary systems were fitted to the Redlich-Kister and Cibulka equations. Flory's theory has been used to predict excess molar volumes of binary and ternary mixtures at 298.15 K.

KEY WORDS: binary mixtures; chlorocyclohexane; cyclohexane; excess molar volumes; Flory theory; ternary mixture; tetrahydrofuran.

1. INTRODUCTION

In this paper we present experimental measurements of the density of the ternary mixture (cyclohexane + tetrahydrofuran + chlorocyclohexane) and for the binary mixtures (cyclohexane + tetrahydrofuran and cyclohexane + chlorocyclohexane) at 298.15 and 313.15 K. The density data have been used to calculate excess molar volumes of the mixtures. This work continues previous papers in which viscosities [1] and speeds of sound [2] of the same mixtures have been reported. The only literature data available for these systems were for the binary mixture cyclohexane + tetrahydrofuran [3].

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0195-928X/00/0900-1185$18.00/0

Flory's theory [4, 5] and the extension of this theory to multicomponent systems as outlined by Brostow and Sochanski [6] have been used to predict excess molar volumes of the binary and ternary mixtures at 298.15 K.

2. EXPERIMENT

The compounds used were cyclohexane (better than 99.9%), tetrahydrofuran (better than 99.5%), and chlorocyclohexane (better than 99%) obtained from Aldrich. The purities of these compounds were checked by a chromatographic method, comfirming the absence of other significant organic compounds. Thus, no further purification was necessary.

Densities, ρ, were measured with an Anton-Paar DMA-58 vibrating tube densimeter whose temeprature was controlled to within ± 0.01 K. The uncertainty of the density measurements was $\pm 1 \times 10^{-5}$ g · cm^{-3}. The calibration of the densimeter was carried out with deionized, doubly distilled water and dry air. The pure compound densities at 298.15 K are shown in Table I along with literature values [7–9].

The compositions (mole fraction) of binary and ternary mixtures were determined by mass using a Mettler H20T balance with a precision of ± 0.01 mg. The precision of the mole fraction is estimated to be better than $\pm 1 \times 10^{-4}$.

3. RESULTS AND DISCUSSION

Densities of the binary mixtures cyclohexane + tetrahydrofuran and cyclohexane + chlorocyclohexane at 298.15 and 313.15 K are shown in Table II. Densities of the ternary system (cyclohexane + tetrahydrofuran + cholorocyclohexane) at the same temperatures are given in Table III.

Table I. Densities, ρ, of Pure Compounds at 298.15 K and Comparisons with Literature Data

	ρ (g · cm^{-3})	
Compound	Exp.	Lit.
Cyclohexane	0.77382	0.77387 [7]
Tetrahydrofuran	0.88200	0.88197 [8]
Chlorocyclohexane	0.99329	0.99399 [9]

Table II. Experimental Densities, ρ, and Excess Molar Volumes, V^E, of Binary Mixtures Cyclohexane (1) + Tetrahydrofuran (2) and Cyclohexane (1) + Chlorocyclohexane (2) at 298.15 and 313.15 K

x_1	ρ ($g \cdot cm^{-3}$)	V^E ($cm^3 \cdot mol^{-1}$)	x_1	ρ ($g \cdot cm^{-3}$)	V^E ($cm^3 \cdot mol^{-1}$)
Cyclohexane (1) + tetrahydrofuran (2) at 298.15 K					
0.0506	0.87396	0.083	0.5067	0.81507	0.523
0.1003	0.86632	0.167	0.6062	0.80509	0.515
0.2004	0.85188	0.314	0.7047	0.79605	0.466
0.3017	0.83856	0.424	0.7880	0.78909	0.382
0.3992	0.82678	0.499	0.8844	0.78170	0.243
Cyclohexane (1) + tetrahydrofuran (2) at 313.15 K					
0.0986	0.85021	0.162	0.5975	0.79063	0.553
0.1960	0.83637	0.315	0.6996	0.78145	0.500
0.3019	0.82278	0.427	0.7997	0.77336	0.387
0.3970	0.81142	0.515	0.8992	0.76608	0.222
0.4989	0.80043	0.550			
Cyclohexane (1) + chlorocyclohexane (2) at 298.15 K					
0.1027	0.97269	−0.014	0.6034	0.86587	−0.008
0.2064	0.95142	−0.020	0.7013	0.84373	0.003
0.2966	0.93257	−0.022	0.7996	0.82109	0.012
0.3945	0.91172	−0.021	0.8984	0.79796	0.014
0.5021	0.88834	−0.016	0.9510	0.78550	0.010
Cyclohexane (1) + chlorocyclohexane (2) at 313.15 K					
0.0998	0.95851	−0.001	0.5978	0.85256	−0.026
0.2024	0.93753	−0.018	0.7011	0.82927	−0.017
0.2966	0.91788	−0.027	0.8001	0.80661	−0.018
0.4000	0.89591	−0.035	0.8947	0.78453	−0.014
0.4992	0.87437	−0.032			

Excess molar volumes, V^E, of the binary and ternary mixtures were calculated using the equation:

$$V^E = \sum_i x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{1}$$

where ρ and ρ_i are the densities of the mixture and of the pure component i, respectively, x_i is the mole fraction of component i, and M_i is the molar mass of the same component.

Excess molar volumes of the binary mixtures are shown in Table II and graphically represented in Fig. 1. Excess molar volumes of the binary

Table III. Experimental Densities, ρ, and Excess Molar Volumes, V^E, of the Ternary Mixture Cyclohexane (1) + Tetrahydrofuran (2) + Chlorocyclohexane (3) at 298.15 and 313.15 K

x_1	x_2	ρ ($g \cdot cm^{-3}$)	V^E ($cm^3 \cdot mol^{-1}$)	x_1	x_2	ρ ($g \cdot cm^{-3}$)	V^E ($cm^3 \cdot mol^{-1}$)
Cyclohexane (1) + tetrahydrofuran (2) + chlorocyclohexane (3) at 298.15 K							
0.0501	0.0515	0.97906	0.000	0.2987	0.3023	0.89793	0.131
0.0475	0.1003	0.97555	−0.004	0.2996	0.4031	0.88456	0.189
0.0493	0.8478	0.89043	0.061	0.3001	0.4983	0.87095	0.258
0.0492	0.9001	0.88242	0.067	0.3037	0.6026	0.85401	0.338
0.0948	0.0503	0.96921	−0.002	0.3974	0.1039	0.89907	0.058
0.0987	0.8508	0.87483	0.147	0.3958	0.2052	0.88694	0.129
0.1019	0.1046	0.96363	0.009	0.3958	0.3020	0.87412	0.203
0.0987	0.2136	0.95427	0.005	0.3641	0.3730	0.87216	0.239
0.1006	0.3011	0.94490	0.039	0.3838	0.4826	0.85076	0.346
0.0998	0.4013	0.93438	0.052	0.4992	0.1021	0.87618	0.076
0.0997	0.5030	0.92271	0.065	0.4991	0.2013	0.86285	0.173
0.1019	0.5970	0.91041	0.087	0.4965	0.3034	0.84866	0.285
0.1020	0.6957	0.89721	0.097	0.4936	0.4070	0.83335	0.386
0.0998	0.7969	0.88300	0.125	0.5935	0.1005	0.85448	0.107
0.1987	0.1053	0.94291	0.009	0.5952	0.2004	0.83957	0.227
0.2010	0.2007	0.93250	0.049	0.5918	0.3016	0.82457	0.361
0.2027	0.2992	0.92127	0.079	0.6931	0.1014	0.83078	0.143
0.1997	0.4038	0.90962	0.110	0.6942	0.2042	0.81434	0.296
0.2024	0.4930	0.89753	0.149	0.8139	0.0933	0.80292	0.170
0.2012	0.6035	0.88276	0.177	0.8483	0.0463	0.80245	0.077
0.2003	0.6989	0.86852	0.241	0.8317	0.0976	0.79791	0.177
0.3020	0.1006	0.92083	0.023	0.8942	0.0529	0.79021	0.109
0.3006	0.1978	0.91014	0.075				
Cyclohexane (1) + tetrahydrofuran (2) + chlorocyclohexane (3) at 313.15 K							
0.0514	0.0497	0.96420	0.001	0.2999	0.3030	0.88238	0.131
0.0481	0.1029	0.96033	0.002	0.2987	0.4040	0.86924	0.200
0.0509	0.8461	0.87382	0.068	0.3062	0.4928	0.85460	0.270
0.0487	0.8982	0.86631	0.077	0.2990	0.5980	0.84027	0.350
0.0992	0.0562	0.95376	0.000	0.3975	0.1013	0.88456	0.047
0.1008	0.8511	0.85776	0.161	0.3967	0.2056	0.87174	0.121
0.1015	0.1014	0.94916	0.009	0.3937	0.3028	0.85947	0.193
0.1017	0.2035	0.93949	0.012	0.3915	0.4050	0.84515	0.300
0.0994	0.3044	0.92978	0.021	0.4003	0.4992	0.82825	0.385
0.1007	0.4034	0.91861	0.044	0.4930	0.1055	0.86228	0.082
0.0997	0.5000	0.90754	0.058	0.4910	0.2075	0.84887	0.188
0.1004	0.6022	0.89455	0.076	0.4949	0.3023	0.83407	0.295
0.1016	0.6963	0.88118	0.105	0.4929	0.4030	0.81872	0.418
0.1007	0.8018	0.86565	0.143	0.5932	0.1031	0.83944	0.104
0.2031	0.1012	0.92747	0.012	0.5956	0.2008	0.82450	0.232
0.2005	0.2008	0.91761	0.044	0.5948	0.3033	0.80847	0.377
0.1988	0.3042	0.90650	0.068	0.6916	0.1038	0.81604	0.147
0.2013	0.4024	0.89405	0.107	0.6947	0.2016	0.79983	0.296
0.2004	0.5021	0.88135	0.145	0.7926	0.1027	0.79185	0.191
0.1997	0.5990	0.86786	0.200	0.7940	0.0526	0.79968	0.092
0.1994	0.7003	0.85254	0.255	0.8417	0.1037	0.77977	0.202
0.3013	0.0997	0.90619	0.024	0.8961	0.0515	0.77544	0.111
0.3015	0.2034	0.89432	0.069				

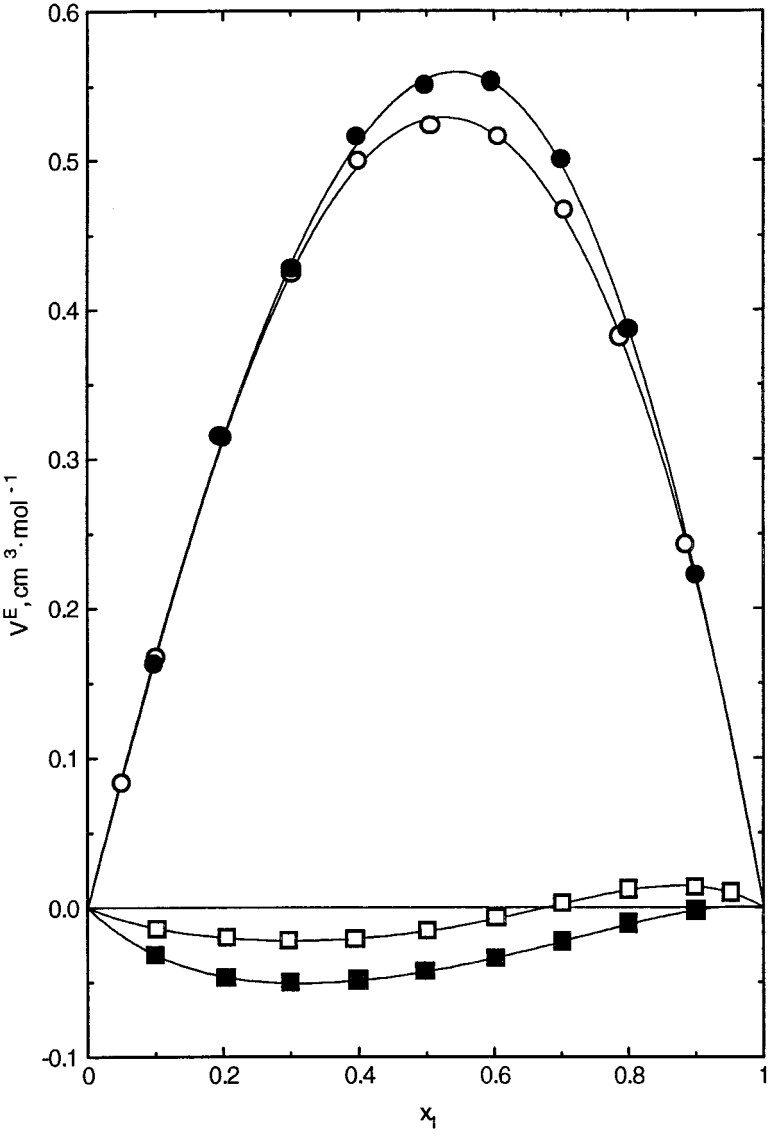

Fig. 1. Excess molar volumes of the mixtures cyclohexane (1) + tetrahydrofuran (2): (○) at 298.15 K; (●) at 313.15 K, and cyclohexane (1) + chlorocyclohexane (2): (□) at 298.15 K; (■) at 313.15 K as a function of mole fraction of cyclohexane, x_1.

mixture tetrahydrofuran + chlorocyclohexane have been given in a previous article [10].

Experimental results of excess molar volume of the binary mixtures were fitted to a Redlich–Kister equation:

$$V^{E} = x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p \tag{2}$$

where x_i denotes the mole fraction of component i and A_p's are adjustable parameters. These parameters along with the standard deviations, σ, obtained by least squares are presented in Table IV.

The excess molar volumes of the ternary mixture at 298.15 and 313.15 K are presented in Table III. We have fitted those results with the Cibulka equation [11]:

$$V^{E} = V^{E}_{bin} + x_1 x_2 (1 - x_1 - x_2)(B_1 + B_2 x_1 + B_3 x_2) \tag{3}$$

where

$$V^{E}_{bin} = V^{E}_{12} + V^{E}_{13} + V^{E}_{23} \tag{4}$$

and x_i is the mole fraction of component i in the ternary mixture. The adjustable coefficients, B_p, and standard deviations, σ, were calculated using least squares and are given in Table IV.

Table IV. Coefficients of the Redlich–Kister Eq. (3), A_p, Cibulka Eq. (4), B_p, and the Corresponding Standard Deviations, σ, for Excess Molar Volumes of the Binary and Ternary Systems at 298.15 and 313.15 K

System	T (K)	A_0	A_1	A_2	A_3	$\sigma(V^E)$
Cyclohexane (1) + tetrahydrofuran (2)	298.15	2.110	0.214	0.038	0.220	0.004
	313.15	2.220	0.410	−0.081	−0.072	0.005
Cyclohexane (1) + chlorocyclohexane (2)	298.15	−0.063	0.131	0.101	0.099	0.000
	313.15	−0.172	0.152	−0.024	0.088	0.000
Tetrahydrofuran (1) + chlorocyclohexane (2) [10]	298.15	0.024	−0.027	−0.017	−0.024	0.000
	313.15	−0.173	−0.103	0.096	−0.024	0.002
	T (K)	B_1	B_2	B_3		$\sigma(V^E)$
Cyclohexane (1) + tetrahydrofuran (2) + chlorocyclohexane (3)	298.15	−0.761	−0.565	−1.897		0.008
	313.15	0.551	−2.385	−1.258		0.008

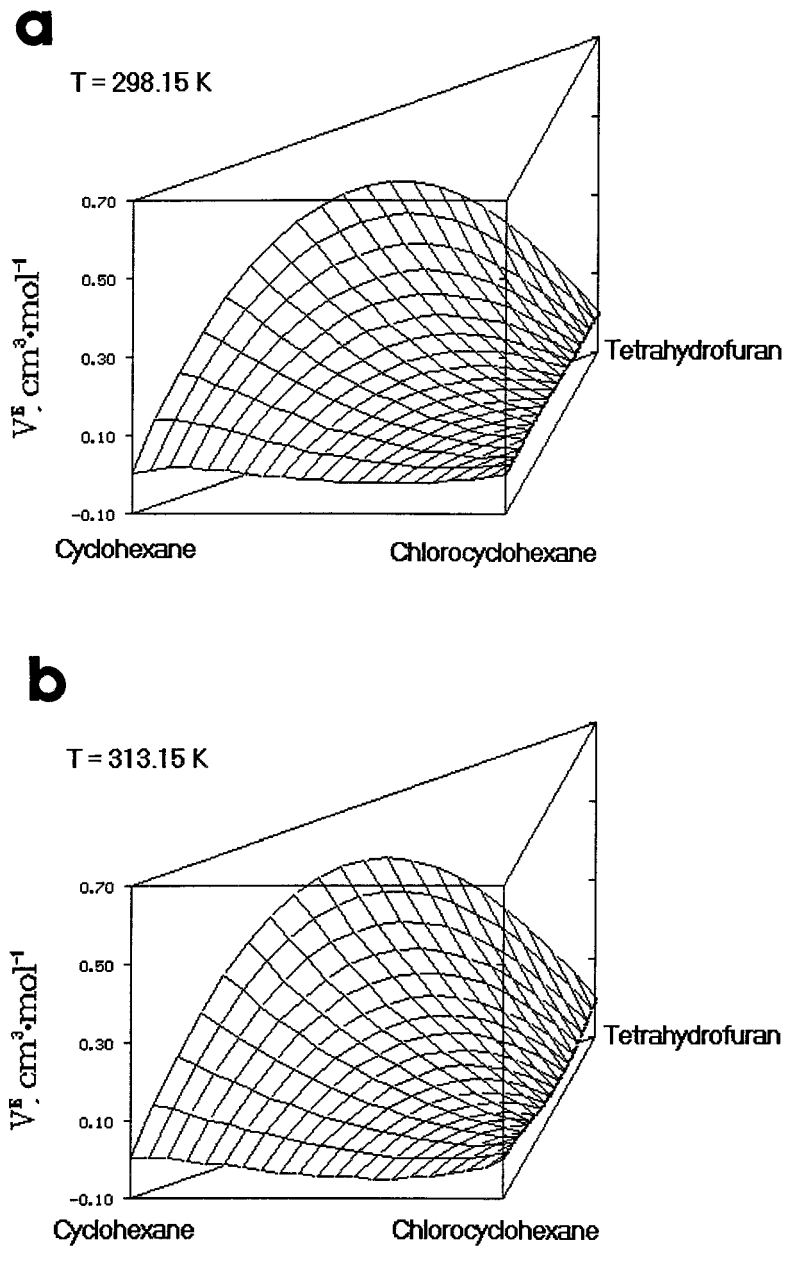

Fig. 2. Tri-dimensional surface of excess molar volumes of the ternary mixture cyclohexane (1) + tetrahydrofuran (2) + chlorocyclohexane (3) correlated with the Cibulka equation: (a) at 298.15 K; (b) at 313.15 K.

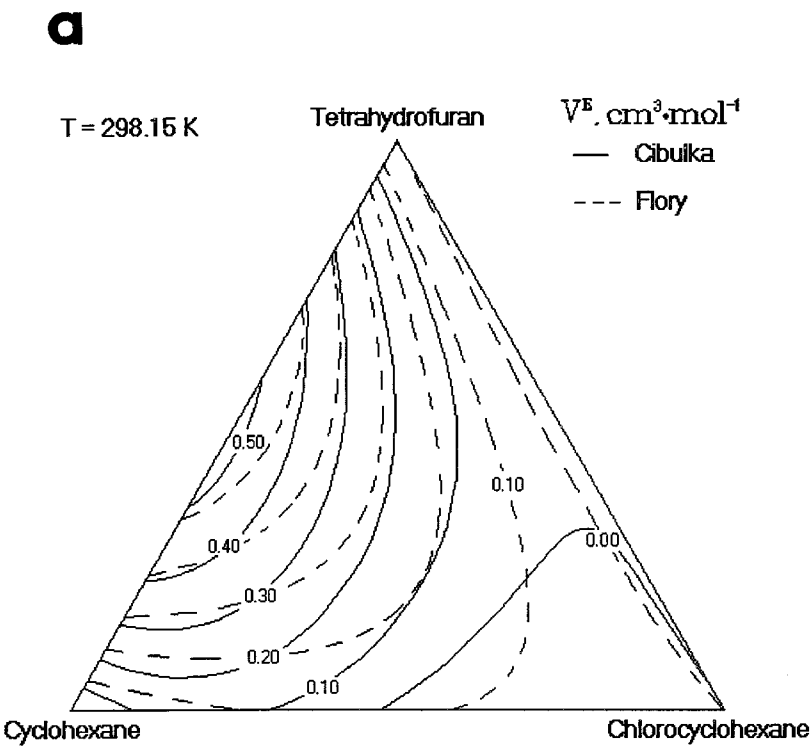

Fig. 3. Isolines of constant excess molar volumes of the ternary mixture cyclohexane (1) + tetrahydrofuran (2) + chlorocyclohexane (3): (a) correlated with the Cibulka equation (continuous lines) and Flory predictions (dashed lines) at 298.15 K; (b) correlated with the Cibulka equation at 313.15 K.

Tridmensional surfaces of V^E calculated from the Cibulka equation for the ternary system, at 298.15 and 313.15 K, have been plotted in Figs. 2a and b, respectively. The isolines at constant values of V^E have been presented in Figs. 3a and b.

The V^E values for the binary mixture cyclohexane + tetrahydrofuran are in good agreement with those reported in the literature by Arm and Bánkay [3]. These excess molar volumes are practically symmetrical and positive over the entire composition range at the two temperatures. Curves at 298.15 and 313.15 K are very similar, but the values increase with temperature, the maximum values are $V^E = 0.529\ \text{cm}^3 \cdot \text{mol}^{-1}$ at 298.15 K and $V^E = 0.543\ \text{cm}^3 \cdot \text{mol}^{-1}$ at 313.15 K.

For the binary mixture cyclohexane + chlorocyclohexane, the curves obtained are sigmoidal at both temperatures. Values at 298.15 K are

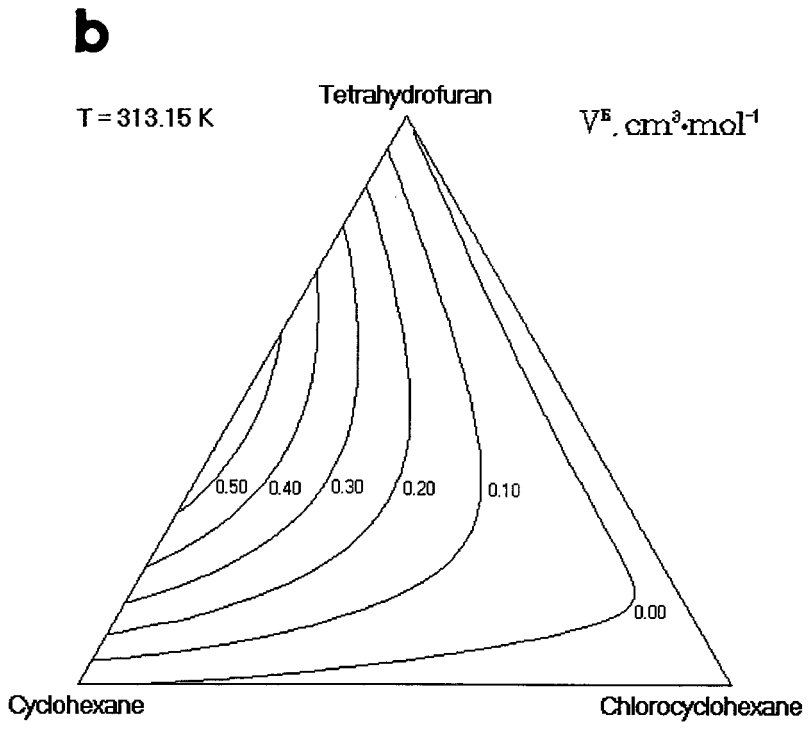

Fig. 3. *(Continued)*

negative for mole fractions of cyclohexane between 0.1 and 0.65 and slightly positive for larger mole fractions of cyclohexane. At 313.15 K the values are negative practically over the entire composition range. Excess molar volumes are small at both temperatures, with minimum values shifted towards higher concentrations of chlorocyclohexane: $V^E = -0.022$ $cm^3 \cdot mol^{-1}$ at 298.15 K and $V^E = -0.051$ $cm^3 \cdot mol^{-1}$ at 313.15 K.

The ternary excess molar volumes are positives practically over the entire composition range at both temperatures. There are only a few negative values for high mole fractions of chlorocyclohexane. The surfaces at the two temperatures are very similar but the values are slightly larger at the higher temperature.

4. THEORETICAL ANALYSIS

We have used Flory's theory and the extension of this theory to multicomponent systems by Brostow and Sochanski [6] to predict excess molar volumes of binary and ternary liquid mixtures from the properties of pure

components and from excess molar enthalpies of binary systems. In our study we have used excess molar enthalpies, H^E, of the binary mixtures at 298.15 K to determinate binary interaction parameters, X_{ij}, and then we have utilized those parameters to predict excess molar volumes of binary and ternary mixtures at the same temperature.

Here, only the equations needed for aplication to the present ternary system are summarized. V^E can be calculated from the equation:

$$V^E = (x_1 V_1^* + x_2 V_2^* + x_3 V_3^*)(\tilde{V} - \phi_1 \tilde{V}_1 - \phi_2 \tilde{V}_2 - \phi_3 \tilde{V}_3)$$

where the reduced volume of the mixture, $\tilde{V}$, can be obtained from the corresponding characteristic temperature, T^*, that is given by the equation:

$$T^* = \left(\frac{\sum_i \phi_i p_i^* - \Psi}{\sum_i \phi_i p_i^* / T_i^*} \right)$$

and

$$\Psi = \phi_1 \theta_2 X_{12} + \phi_2 \theta_3 X_{23} + \phi_3 \theta_1 X_{13}(s_3/s_1)$$

All of the other parameters in the above equations pertain to Flory's theory [4, 5].

Flory parameters of the pure components along with their physical properties are listed in Table V. Thermal expansion coefficients, α, were derived from the densities determined in the laboratory. Isothermal compressibilities, κ_T, were calculated from the experimental isentropic compressibilities, κ_s [2], the cubic expansion coefficients, α, and the molar heat capacities, C_P [12]. The number of contact sites per segment of a molecule i, s_i, were calculated with the Bondi's method [13].

Interaction parameters for the binary mixtures were calculated using equimolar H^E values [14–16]. These H^E values and interaction parameters

Table V. Physical Properties and Flory Parameters of the Pure Components at 298.15 K

Compound	α (mK^{-1})	κ_T (TPa^{-1})	s (nm^{-1})	$\tilde{V}$ ($cm^3 \cdot mol^{-1}$)	p ($J \cdot cm^{-3}$)
Cyclohexane	1.220	1140.0	13.51	1.2911	531.9
Tetrahydrofuran	1.243	997.9	12.38	1.2955	623.3
Chlorocyclohexane	0.994	994.0	13.72	1.2465	583.0

Table VI. Binary Interaction Parameters, X_{ij}, Along with Calculated, V^E_{cal} ($cm^3 \cdot mol^{-1}$), and Experimental, V^E_{exp} ($cm^3 \cdot mol^{-1}$), Equimolar Excess Molar Volumes of Binary Mixtures

System	H^E ($J \cdot mol^{-1}$)	X_{ij} ($J \cdot cm^{-3}$)	V^E_{cal} ($cm^3 \cdot mol^{-1}$)	V^E_{exp} ($cm^3 \cdot mol^{-1}$)
Cyclohexane (1) + tetrahydrofuran (2)	719.2 [14]	39.7	0.587	0.528
Cyclohexane (1) + chlorocyclohexane (3)	365.0 [15]	15.9	0.110	−0.016
Tetrahydrofuran (2) + chlorocyclohexane (3)	−51.3 [16]	−2.1	−0.031	0.006

are shown in Table VI along with calculated and experimental values of equimolar excess molar volumes of the binary mixtures. In this table it can be seen that predictions for the binary mixture cyclohexane + tetrahydrofuran are satisfactory, but predicted values of V^E for binary mixture cyclohexane + chlorocylohexane are not as good.

Isolines of constant value of V^E at 298.15 K predicted with Flory's theory for the ternary system are plotted in Fig. 3a along with experimental values obtained with the Cibulka equation. The predicted lines are in agreement with experimental lines, especially for larger values of excess molar volume.

ACKNOWLEDGMENTS

The authors are grateful for financial assistance from Universidad de Zaragoza (Proyecto UZ:96-232-47) and Diputación General de Aragón (PCB-0894).

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