J. Chem. Eng. Data 1991, *36*, 473–474

Excess Volumes of Binary Mixtures of Methylcyclohexane with Substituted Benzenes and Cyclohexanone

D. Venkatesulu, B. Busa Goud, and M. V. Prabhakara Rao*

Chemical Laboratories, Sri Venkateswara University, Tirupati 517 502, India

Volume changes on mixing of binary liquid mixtures of methylcyclohexane with chlorobenzene, nitrobenzene, benzonitrile, and cyclohexanone have been measured as a function of composition at 303.15 and 313.15 K with use of a dilatometer. The excess volumes are positive over the entire range of composition for chlorobenzene and change sign from negative to positive, with increasing methylcyclohexane concentration, for the remaining systems.

Introduction

In the frame of a systematic study of the volumetric properties of liquid mixtures, we report in this paper experimental molar excess volumes V^E for methylcyclohexane + chlorobenzene, nitrobenzene, benzonitrile, or cyclohexanone. No literature V^E data are available for these mixtures.

Experimental Section

Apparatus and Procedure. Excess volumes were measured by using a single composition per loading type dilatometer described by Rao and Naidu (*1*). The dilatometer was made of two bulbs of different capacities connected through a U tube. Mercury in the U tube separates the liquids in the two bulbs. One end of the first bulb was fitted with a capillary outlet, and the opposite end of the second bulb was closed with a ground-glass stopper. Four dilatometers of the aforementioned type were used to cover the entire range of composition. The composition of each mixture was determined directly by weighing with an accuracy of 0.0002 in mole fraction. All weights were corrected for buoyancy. Measurements were made at 303.15 and 313.15 K by employing a thermostatic bath maintained constant to within 0.01 K. Values of V^E were reproducible to ±0.003 cm^3 mol^{-1}.

Materials. Methylcyclohexane (BDH) was purified as described by Rao and Naidu (*1*). Chlorobenzene (E. Merck), nitrobenzene (BDH), and benzonitrile (Riedel) were purified as described by Reddy et al. (*2*). Cyclohexanone (BDH) was dried over anhydrous sodium sulfate for 2 days and then fractionally distilled.

The purities of the chemicals were checked by comparing the densities ρ measured with a bicapillary pycnometer (*3*) with literature data (*4*) (Table I). The purity of the liquids was further confirmed by gas–liquid chromatography.

Table I. Densities, ρ, of Pure Components at 303.15 K

component	ρ/(gm cm^{-3}) present work	lit. (*4*)
methylcyclohexane	0.760 25	0.760 31
chlorobenzene	1.095 46	1.095 50
nitrobenzene	1.193 37	1.193 41
benzonitrile	0.996 22	0.996 28
cyclohexanone	0.937 57	0.937 61

Table II. Experimental Excess Molar Volumes, V^E, as a Function of x_1, the Mole Fraction of Methylcyclohexane, Coefficients a_i, Equation 1, and Standard Deviations, $\sigma(V^E)$ (cm^3 mol^{-1}), Equation 2

	303.15 K		313.15 K	
	x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
	Methylcyclohexane (1) + Chlorobenzene (2)			
	0.1197	0.042	0.1228	0.035
	0.2895	0.090	0.2770	0.076
	0.3242	0.095	0.3277	0.089
	0.4604	0.134	0.4412	0.116
	0.5703	0.150	0.5495	0.134
	0.6342	0.158	0.6091	0.141
	0.7716	0.147	0.7960	0.135
	0.8433	0.117	0.8554	0.114
a_0	0.5589		0.5065	
a_1	0.3685		0.4083	
a_2	0.1949		0.2400	
$\sigma(V^E)$	0.003		0.002	
	Methylcyclohexane (1) + Nitrobenzene (2)			
	0.1272	−0.010	0.1076	−0.068
	0.2810	−0.017	0.2919	−0.076
	0.3110	−0.014	0.3257	−0.071
	0.4596	0.019	0.4421	−0.028
	0.5674	0.056	0.5831	0.037
	0.6350	0.075	0.5831	0.066
	0.7756	0.113	0.7860	0.092
	0.8460	0.103	0.8477	0.079
a_0	0.1222		0.0030	
a_1	0.6538		0.9084	
a_2	0.4767		−0.0021	
$\sigma(V^E)$	0.003		0.003	
	Methylcyclohexane (1) + Benzonitrile (2)			
	0.1175	−0.023	0.1102	−0.036
	0.2451	−0.035	0.2582	−0.048
	0.3259	−0.015	0.3137	−0.040
	0.4460	0.021	0.4601	0.019
	0.5648	0.062	0.5252	0.045
	0.6317	0.088	0.6507	0.102
	0.7782	0.121	0.7854	0.136
	0.8373	0.110	0.8493	0.118
a_0	0.1505		0.1350	
a_1	0.7710		0.9292	
a_2	0.3398		0.3349	
$\sigma(V^E)$	0.004		0.004	
	Methylcyclohexane (1) + Cyclohexanone (2)			
	0.1223	−0.012	0.1153	−0.009
	0.2278	0.001	0.2202	0.005
	0.3356	0.020	0.3163	0.043
	0.4482	0.045	0.4808	0.108
	0.5893	0.090	0.5703	0.132
	0.6271	0.098	0.6274	0.145
	0.7814	0.115	0.7830	0.132
	0.8339	0.108	0.8284	0.116
a_0	0.2579		0.4508	
a_1	0.6269		0.6379	
a_2	0.2140		−0.1098	
$\sigma(V^E)$	0.003		0.003	

0021-9568/91/1736-0473$02.50/0

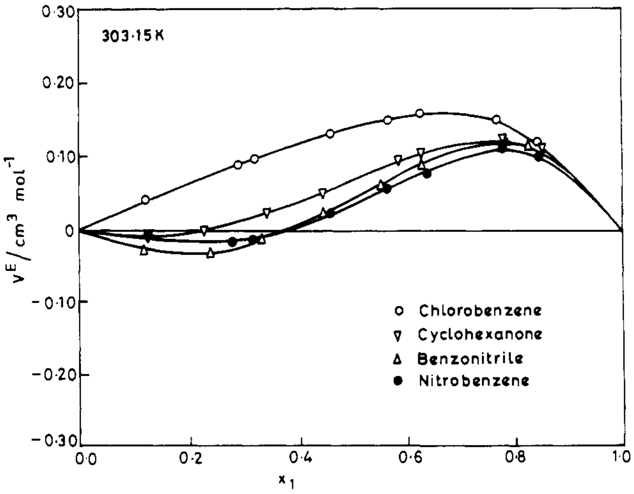

Figure 1. Excess molar volumes V^E as a function of the mole fraction x_1 of methylcyclohexane: points, experimental results; curves, results calculated with eq 1.

Results and Discussion

The V^E data of methylcyclohexane (1) + chlorobenzene (2), + nitrobenzene (2), + benzonitrile (2), or + cyclohexanone (2) are presented as a function of mole fraction x_1 in Table II and Figure 1. The experimental V^E_{exp} data were fitted to an empirical equation of the form

$$V^E/(cm^3\ mol^{-1}) = x_1(1 - x_1)[a_0 + a_1(2x_1 - 1) + a_2(2x_1 - 1)^2] \quad (1)$$

The parameters a_i along with the standard deviations $\sigma(V^E)$

$$\sigma(V^E) = [\sum(V^E_{exp} - V^E)^2/(n - p)]^{1/2} \quad (2)$$

where n is the number of experimental points and p the number of parameters a_i, were evaluated by the least-squares technique and are given in Table II.

The observed V^E values result from the balance of dipole-dipole interactional contributions, leading to expansion in volume, and geometrical packing or free volume effects, leading to contraction in volume.

The curves in Figure 1 show that the excess volumes are positive for chlorobenzene, over the whole range of composition, and change sign for the remaining three systems.

The comparison of V^E data at 303.15 and 313.15 K reveal that the effect of temperature is almost negligible for the investigated mixtures.

Registry No. Methylcyclohexane, 108-87-2; cyclohexanone, 108-94-1; chlorobenzene, 108-90-7; nitrobenzene, 98-95-3; benzonitrile, 100-47-0.

Literature Cited

(1) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(2) Reddy, S. S.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 173.
(3) Rao, M. V. P. Ph.D. Thesis, Sri Venkateswara University, Tirupati, India, 1974.
(4) Riddick, J. A.; Bunger, W. S.; Sakano, T. K. *Techniques of Chemistry*, 4th ed.; Wiley: New York, 1986; Vol. II, p 1325.

Received for review July 17, 1990. Accepted May 29, 1991.

Isothermal Vapor–Liquid Equilibria and Excess Volumes for the Systems *n*-Hexane + Ethylbenzene, 2-Methylpentane + *n*-Heptane, and 2-Methylpentane + *n*-Octane

C. Berro,* F. Laïchoubi, and E. Rauzy

Laboratoire de Chimie-Physique, Faculté des Sciences de Luminy, 13288 Marseille Cedex 9, France

Vapor–liquid equilibria (VLE) and molar excess volumes have been obtained for *n*-hexane + ethylbenzene, 2-methylpentane + *n*-heptane, and 2-methylpentane + *n*-octane. The VLE data were reduced according to the maximum-likelihood principle. The thermodynamical consistency was verified. The parameters of NRTL, Wilson, and UNIQUAC equations were fitted, and the VLE data were compared with Abdoul group contribution predictions.

Introduction

We recently developed in our laboratory a group contribution model for predicting the thermodynamic properties of mixtures present in petroleum fluids (*1*, *2*). The application of this method to literature vapor–liquid equilibrium (VLE) data showed poor agreement for 2-methylpentane + *n*-octane (*3*), while the 2-methylpentane + *n*-hexane system (*4*) was in good agreement. Our aim was to know whether the discrepancy is due to the inadequacy of the model or to the inaccuracy of experiments. Therefore, we measured isothermal vapor–liquid equilibria for 2-methylpentane + *n*-octane at 328.15 K. We report also VLE data for 2-methylpentane + *n*-heptane at 318.15 and 328.15 K (*5*) and for *n*-hexane + ethylbenzene at 338.15 K. The experimental molar excess volumes of all mixtures at 298.15 K, used to determine the vapor- and liquid-phase compositions, are also reported.

Experimental Section

Materials. *n*-Hexane and *n*-heptane were "Uvasol" reagents from Merck with stated minimum purities of 97 and 99%, respectively. *n*-Octane and ethylbenzene were Fluka "puriss" products with respectively 99.5 and 99% purity. 2-Methylpentane was a 98% "prosynthesis" grade reagent from Merk.

These materials were purified by fractional distillations on a 60 real plates Oldershaw type column. The *n*-hexane was subjected to distillation three times.

The densities of the purified substances were measured with an Anton Paar (DMA-60) densimeter at 298.15 K (Table I). They are in excellent agreement with literature values (*6*).

Apparatus and Procedure. Vapor–liquid equilibrium data were determined at constant temperature in a dynamic still designed by Berro et al. (*7*).

The temperature inside the equilibrium cell was measured by means of a Lauda R42 digital thermometer with a platinum sensor which has a precision of $\sigma_e(T) = 0.01$ K. The pressure was measured by means of a Digiquartz pressure transducer of Paroscientific Inc., Model 215A, calibrated in the pressure range 0–10 MPa. The estimated precision of the pressure measurements is $\sigma_e(P) = 0.01$ KPa.